A comprehensive review of hazards identification and risk assessment in ammonia plants

As part of our ongoing efforts to improve safety and reliability in ammonia plants, we develop an extensive risks database using a HAZID type exercise. Based on our own experience, researching a collection of industry case studies and experience from other plants, we built a collection of over 300 potential and past causes of incidents that already happened or might occur in ammonia plants. We want to share part of these risks with the participants at this symposium and include other risks in the Fertilizer Academy online training platform as part of the industry training program developed by the authors of this paper.

Dan Cojocaru
Fertilizer Industrial Services Ltd, United Kingdom

Venkat Pattabathula
SVP Chemical Plant Services, Australia

Introduction: "Organizations have no memory" – Trevor Kletz

During their career, the authors of this paper witnessed that the same process safety incidents were repeatedly occurring. Discussions with our extensive network of peers and colleagues allow us to understand that what happens in an ammonia or urea plant somewhere in Asia can happen again in Europe, Africa, or North America. We saw how new people are making the same mistakes that the old-timers made years ago.

Trevor Kletz observed that "Organizations have no memory". It seems that each person was learning from their own mistakes but had not learned from mistakes made by their predecessors. The memory issue occurs because operating and maintenance personnel are promoted, retired, take a vacation, are absent for one reason or another, or their job duties are reallocated.

The problem is that history is repeating itself and the main question is what we are going to do about it?

Our view is as follows:

1) identify those hazards associated with the operation and maintenance of ammonia or urea plants,
2) categorize them based on plant units,
3) assess the risks and identify the associated safeguards and
4) develop an online training program where new operators and engineers can

learn about the risks associated with operating and maintaining these plants, and more experienced personnel can refresh their memory to maintain their awareness and keep their skills sharp. For this purpose, we developed Fertilizer Academy.

This paper describes at a high level the first 3 steps listed above.

What is HAZID? HAZardous IDentification (Studies)

HAZID studies are systematic critical examinations of facilities to identify any potential hazards and the consequential effects on the facility. A HAZID would often address both process and non-process hazards.

Sometimes operators and engineers are more familiar with HAZOP (Hazard and Operability Study).

Both HAZID and HAZOP are risk analysis tools used in workplace settings. They are, however, separate procedures with distinct purposes:

- HAZID (Hazard Identification) is a general risk analysis tool designed to alert management of any threats and hazards on the job site.
- HAZOP (Hazard and Operability Study) is used to identify potential abnormalities in the plant operation and pinpoint their causes.

A HAZOP study is a well-documented qualitative review of process systems, where hazards can be addressed. The study can lead to a follow-up semi-quantitative or analysis such as Layer of Protection Analysis (LOPA) or a more detailed analysis such as Fault Tree Analysis or Quantitative Risk Analysis (QRA) to ensure risks are reduced to an acceptable level while examining more cost effective options.

HAZID, on the other hand, can be carried out at a process unit level and does not necessarily require much documentation.

HAZID and Hazard and Operability (HAZOP) studies are different, however complimentary, and are carried out at different points in developing a design. HAZID is conducted in the early phases of the design, during FEED, where HAZOP requires a more mature level of detail in the project documentation; typically when P&IDs are about 85% completion.

They are complementary and not interchangeable. HAZOP is cause-driven and accepts the conclusion that a hazard's likelihood is acceptably low. HAZID is consequence-driven and assumes that the hazard can occur.

HAZID studies are comprehensive in their scope, looking at all possible sources of hazards to a site examining a model at a time and postulating on mechanisms by which chosen hazardous events could occur.

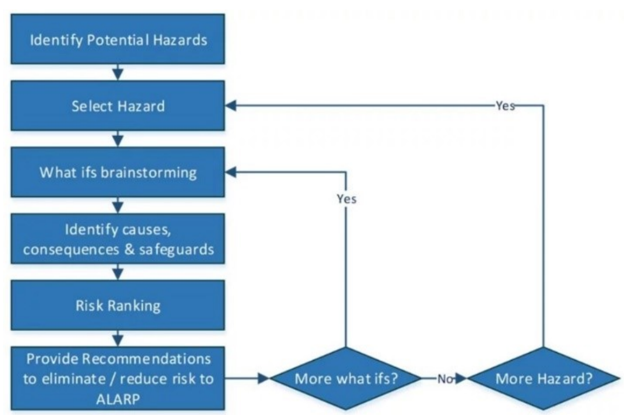


Figure 1. HAZID Study Activity Diagram.

Presentation of findings

In the following chapters, some of our key findings are listed for each of the following ammonia plant units:

Ammonia Plant (ISBL):
- Feed gas Preparation and Reforming Section
- Shift Converters Section

- CO2 Removal Section
- Methanation Section
- Ammonia Synthesis Loop Section
- Ammonia Refrigeration / Purge Gas Recovery Sections

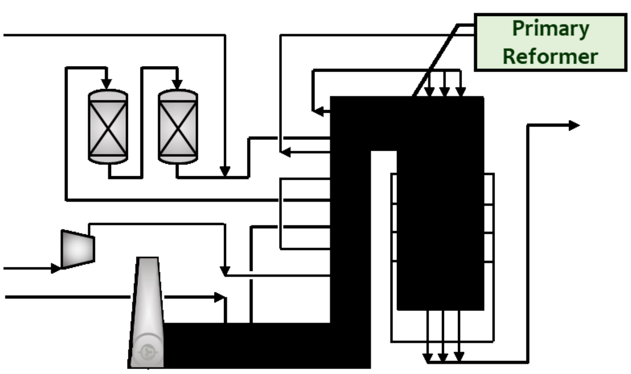
Ammonia Plant (OSBL):
- Ammonia Storage Tanks and Pumps
- Ammonia Storage Tank Flare

Utilities
- Steam and Condensate Systems
- Other Systems

General Sitewide Issues

Each finding is categorized as follows:
- Critical event
- Potential Cause(s)
- Potential Consequence(s)
- Prevention Measures
- Mitigation Measures

Ammonia Plant - Feed gas Preparation and Reforming Section



Critical Event	Loss of containment of natural gas due to piping, flange leaks, etc.
Potential Cause(s)	Corrosion, impact, third-party activity, gasket leak, valve passing or left open, thermal overpressure, mechanical failure, weld defect.
Potential Consequence(s)	Fire with associated equipment damage, business interruption, the reportable release of flammable materials
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the mechanical integrity (MI) program Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc. Pressure relief devices installed on the piping system The compressor unit has high discharge pressure cut-out
Mitigation Measures	The area is electrically rated as Class 1 div. 2 Operator rounds would detect leaks based on sound All equipment is outdoors with little if any potential for confinement

Critical Event	Loss of containment of natural gas in the convection coils
Potential Cause(s)	Overheating, fatigue, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Release of natural gas from the flue stack reportable release of flammable materials, and business interruption
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Pressure relief devices installed on the piping system

	The compressor unit has high discharge pressure cut-out
Mitigation Measures	Reformer flue gas stack elevated and designed to prevent personnel exposure or ignition (material will dissipate)

Critical Event	Loss of containment of natural gas in the reformer tubes
Potential Cause(s)	Overheating, fatigue, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Fire inside the box with the potential for fire to propagate outside if the reformer wall fails or travels outside the bottom. Fire with associated equipment damage, business interruption, the reportable release of flammable materials
Prevention Measures	Tubes constructed of high alloy chrome nickel steel QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines
Mitigation Measures	Spare tubes kept in inventory Temperature control system with high-temperature alarms and shutdown

Critical Event	Incorrect handling of spent catalyst in desulfurisers - pyrophoric Zinc Oxide
Potential Cause(s)	The incorrect procedure, handling error
Potential Consequence(s)	Equipment damage
Prevention Measures	Procedures for handling spent catalyst
Mitigation Measures	Spare vessel installed (A/B)

Figure 2. Catalyst loading process.

Critical Event	Loss of containment of syngas in the secondary reformer
Potential Cause(s)	Mechanical failure of the liner collapse/damage
Potential Consequence(s)	Fire inside the box with the potential for fire to propagate outside if the reformer wall fails. Fire with associated equipment damage, business interruption, the reportable release of flammable materials (state issue)

Prevention Measures	The vessel is ceramic lined, and the lining is rated to withstand maximum heating potential (inherently safe) QA/QC process for confirming correct design, manufacturing and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines and vessels Thermal indicating paint on the outside of the vessel Vessel inspections Start-up procedures to prevent damage to the liner
Mitigation Measures	Temperature control system with high-temperature alarms and shutdown

Critical Event	Loss of containment of quench water
Potential Cause(s)	Corrosion, impact, third party activity, flange/gasket leak, valve passing or left open, thermal overpressure, mechanical failure, weld defect
Potential Consequence(s)	Loss of quench water could increase the potential for convection coils failure due to excessive heat leading to the release of superheated HP steam from the flue stack and business interruption
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Temperature indication system on the steam system
Mitigation Measures	Reformer flue stack elevated and designed to prevent personnel exposure

Critical Event	Loss of containment of the HP steam line
Potential Cause(s)	Corrosion, impact, third party activity, flange/gasket leak, valve passing or left open, thermal overpressure, mechanical failure, weld defect
Potential Consequence(s)	Personnel injury for exposure to 1600 psig. Steam; business interruption - plant downtime (1 week)
Prevention Measures	QA/QC process for confirming correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Temperature indication system on the steam system
Mitigation Measures	Some backup steam is available from the existing plant for use on some sections of the process

Critical Event	Incorrect ignition of the Reformer burners, flameout/re-ignition
Potential Cause(s)	Operator error, valve passing or left open, mechanical failure
Potential Consequence(s)	Personnel injury from fire/explosion or falling from the platform - business interruption - plant downtime (2 weeks)
Prevention Measures	Standard operating procedure and training
Mitigation Measures	See above

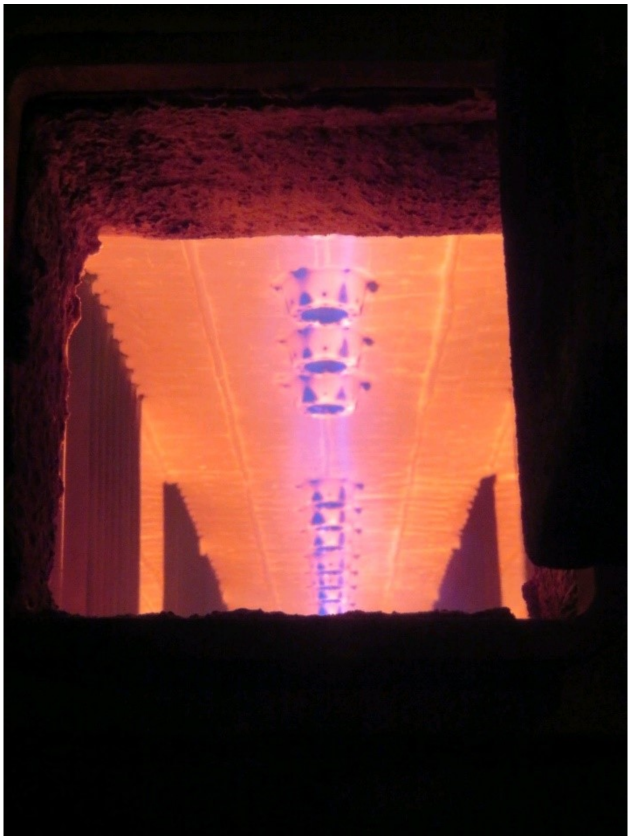
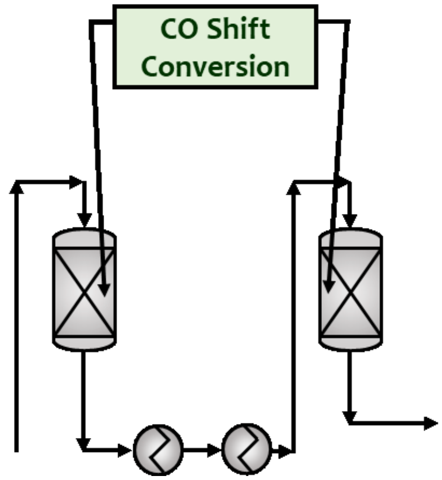


Figure 3. Reformer burners

Critical Event	Incorrect steam/carbon ratio at start-up or shutdown
Potential Cause(s)	Human error (not following the procedure, procedure or training incomplete or inaccurate)
Potential Consequence(s)	Extended downtime and/or catalyst damage
Prevention Measures	Standard operating procedure and training Implementation of an Advanced Process Control system to reduce the probability of human error by automation.
Mitigation Measures	See above

Ammonia Plant – Shift Converters Section



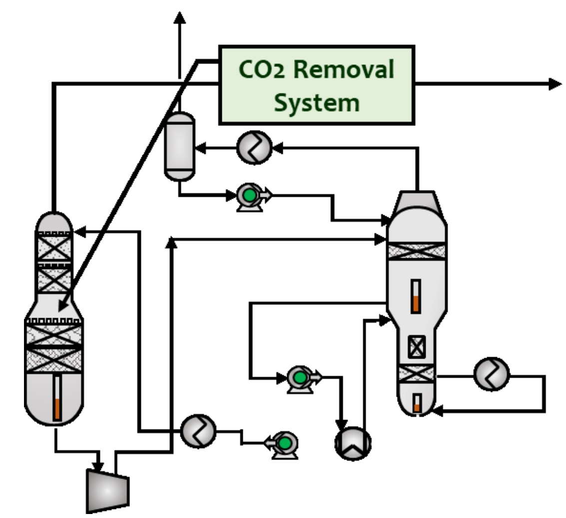
Critical Event	Loss of containment of process gas due to piping, flange, etc.
Potential Cause(s)	Corrosion, impact, third party activity, gasket leak, valve passing or left open, thermal overpressure, mechanical failure, weld defect
Potential Consequence(s)	Fire with associated equipment damage, business interruption, the reportable release of flammable materials (state issue) with entrained CO
Prevention Measures	QA/QC process for confirming correct design, manufacturing and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Lines run in pipeway and not close to vehicles etc. Pressure relief devices installed on piping system/vessels where required Compressor unit has high discharge pressure cut-out

Mitigation Measures	The area is electrically rated as Class 1 div. 2 Operator rounds would detect leaks based on sound All equipment is outdoors with little if any potential for confinement

Critical Event	Loss of containment of process gas due to piping, flange, etc.
Potential Cause(s)	Corrosion, impact, third party activity, gasket leak, valve passing or left open, thermal overpressure, mechanical failure, weld defect
Potential Consequence(s)	Potential personnel exposure to CO
Prevention Measures	QA/QC process for confirming correct design, manufacturing and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc. Pressure relief devices installed on piping system/vessels where required The compressor unit has high discharge pressure cut-out
Mitigation Measures	All equipment is outdoors

Critical Event	Tubing leak/failure in E-208 or E-209
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Steam enters the process gas system leading to reverse flow back through upstream equipment leading to catalyst bed upset, potential overpressure of the equipment with the release of flammable gas and fire
Prevention Measures	Relief valves were installed and designed to handle the API (520/521) tube rupture case for the heat exchanger tubes
Mitigation Measures	The area is electrically rated as Class 1 div. 2 Operator rounds would detect leaks based on sound All equipment is outdoors with little if any potential for confinement

Ammonia Plant – CO2 Removal Section



Critical Event	Loss of containment of process gas due to piping, flange, etc.
Potential Cause(s)	Corrosion, impact, third-party activity, gasket leak, valve passing or left open, thermal overpressure, mechanical failure, weld defect.
Potential Consequence(s)	Fire with associated equipment damage, business interruption, the reportable release of flammable materials with entrained CO

Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program with an RBI program in place Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc. Pressure relief devices installed on piping system/vessels were required
Mitigation Measures	The area is electrically rated as Class 1 div. 2, gas detectors Operator rounds would detect leaks based on sound All equipment is outdoors with little if any potential for confinement

Critical Event	Tubing leak / failure in reboilers
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Potential overpressure from high-pressure process gas entering the CO_2 stripper. Fire with associated equipment damage, business interruption, and reportable release of flammable materials (Loss of containment is a state regulatory issue). Hydrogen contamination of the CO_2 system leads to upsets and business interruption
Prevention Measures	Relief valves were installed and designed to handle the API (520/521) tube rupture case for the heat exchanger tubes
Mitigation Measures	Overpressure protection for the vessels/piping routed to a safe release of containment.

	The area is electrically rated as Class 1 div. 2 Equipment is included in the Maintenance and inspection program Gas detectors, operator rounds would detect leaks based on sound All equipment is outdoors with little if any potential for confinement

Figure 4. aMDEA Solution Storage Tank

Critical Event	Tubing leak/failure in heat exchangers
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Potential overpressure deaerator from high-pressure process gas entering the system. Fire with associated equipment damage, business interruption, the report-

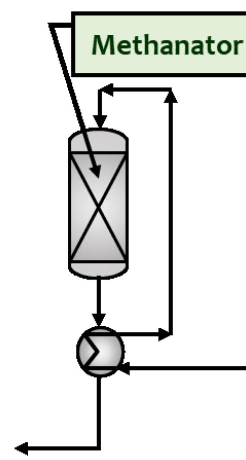
	able release of flammable materials (Loss of containment is a state regulatory issue).
Prevention Measures	Relief valves were installed and designed to handle the API (520/521) tube rupture case for the heat exchanger tubes The discharge point is elevated away from personnel
Mitigation Measures	Overpressure protection for the vessels/piping routed to a safe release of containment. Area is electrically rated as Class 1 div. 2 Equipment is included in the Maintenance and inspection program gas detectors, operator rounds would detect leaks based on sound All equipment is outdoors with little if any potential for confinement

Critical Event	Loss of containment from the lean solution system piping, pump leak / failure, etc.
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Release of solvent to containment; potential for fire from dissolved gas in the solution, personnel exposure to toxic solvent (toxic hazard) - C=3
Prevention Measures	QA/QC process for confirming correct design, manufacturing and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc.

	Pressure relief devices installed on piping system/vessels where required
Mitigation Measures	Concrete containment for solvent containing equipment

Critical Event	Vessel entry (CSE procedures not followed completely)
Potential Cause(s)	Inaccurate or incomplete procedures or training for CSE, LO/TO, etc., causing incomplete venting, gas testing, etc.
Potential Consequence(s)	Potential for fire/explosion from hot work, personnel exposure to toxins
Prevention Measures	CSE program with procedures LO/TO program with procedures
Mitigation Measures	PPE available for authorized activities

Ammonia Plant – Methanation Section



Critical Event	Loss of containment at Methanator due to high temperature
Potential Cause(s)	Excessive exothermic reaction due to incorrect composition from upstream upset
Potential Consequence(s)	Release of flammable gas from the failed vessel with potential for fire with associated equipment damage, business interruption, and the reportable release of

	flammable materials (Loss of containment is a state issue). Possible personnel exposure
Prevention Measures	Temperature monitoring and trip system for the Methanator
Mitigation Measures	The area is electrically rated as Class 1 div. 2 Equipment is included in the Maintenance and inspection program

Critical Event	Personnel exposure to Nickel Carbonyl, Ni(CO)4 formed during the shutdown. Note: not present during operation
Potential Cause(s)	Line or equipment leaks, incorrect blowdown of the Methanator, incorrect purging with nitrogen, etc.
Potential Consequence(s)	Personnel exposure to Ni(CO)4
Prevention Measures	PPE is required for maintenance activities where the potential for Ni(CO)4 exposure (IDLH 1ppb) is possible
Mitigation Measures	Methanator blowdown routed to a safe release of containment

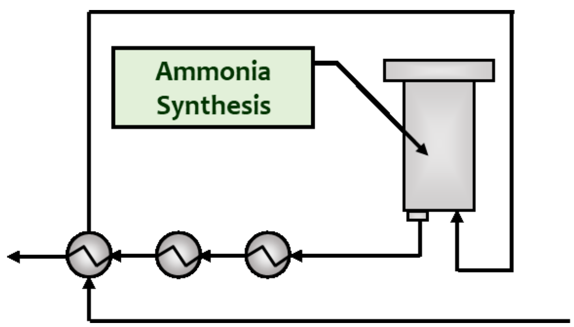
Critical Event	Tubing leak/failure in the exchanger
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Possible high temperature in a vessel leading to release of flammable gas from the failed vessel with potential for fire with associated equipment damage, business interruption, the reportable release of flammable materials (loss of containment is a state regulatory issue). Possible personnel exposure. Potential fire at the PSV discharge point.
Prevention Measures	Relief valves were installed and designed to handle the API (520/521) tube rupture case for the heat exchanger the discharge point is elevated away from personnel
Mitigation Measures	Inherently safer design of heat exchanger with robust materials and fabrication.

Critical Event	Tubing leak / failure in CW exchanger
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Potential for release of flammable gas and fire at the cooling tower with associated equipment damage, business interruption, and reportable release of flammable materials (loss of containment is a state regulatory issue).
Prevention Measures	Relief valves were installed and designed on the cooling water system to handle the API (520/521) tube rupture case for the heat exchanger tubes The discharge point is elevated away from personnel
Mitigation Measures	The cooling water system is open to the atmosphere limiting overpressure consequences

Critical Event	The vent header contains liquid leading to excessive back pressure
Potential Cause(s)	Incorrect vent header design causing places for liquid build-up

Potential Consequence(s)	Potential for relief system to not function as designed due to high back pressure causing overpressure of equipment, the release of flammables, with potential for fire with associated equipment damage, business interruption, the reportable release of flammable materials (loss of containment is a state regulatory issue). Possible personnel exposure.
Prevention Measures	Improved design practices
Mitigation Measures	Follow inherently safer design practices

Ammonia Plant – Ammonia Synthesis Loop and Ammonia Refrigeration Section



Critical Event	Loss of containment at syngas compressor from piping, seals, flanges, etc.
Potential Cause(s)	Corrosion, overpressure, surging, mechanical failure, weld defect
Potential Consequence(s)	Release of flammable gas from failed equipment with the potential for fire with associated equipment damage, business interruption, and reportable release of flammable materials (loss of containment is a state regulatory issue). Potential for lube oil fire. Possible personnel exposure
Prevention Measures	Relief valves were installed to prevent overpressure Standard safety protection package for compressors
Mitigation Measures	Compressors are located outside, not inside of a structure with improved ventilation Gas detection system Fire suppression system

Figure 5. Compressor house after a fire

Critical Event	Tubing leak/failure in the heat exchanger
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect

Potential Conse-quence(s)	Potential for release of ammonia and flammable gas and fire at the cooling tower with associated equipment damage, business interruption, and reportable release of flammable materials (state issue).
Prevention Measures	Relief valves were installed and designed on the cooling water system to handle the API (520/521) tube rupture case for the heat exchanger tubes The discharge point is elevated away from personnel
Mitigation Measures	The cooling water system is open to the atmosphere limiting overpressure consequences Water may mitigate some of the ammonia vapour

Critical Event	Loss of containment from piping or vessel failure
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect, overheating vessel / failed cooling system, etc.
Potential Conse-quence(s)	Fire and personnel exposure to ammonia
Prevention Measures	QA/QC process for confirming correct design, manufacturing and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc. Pressure relief devices installed on piping system/vessels where required
Mitigation Measures	Equipment is included in the Maintenance and inspection program

Figure 6. Synthesis loop fire aftermath due to pipe rupture.

Critical Event	Loss of containment from piping or vessel failure, cryogenic concerns, etc.
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Conse-quence(s)	Personnel exposure to ammonia
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures

	Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc. Pressure relief devices installed on piping system/vessels where required
Mitigation Measures	Equipment is located outdoors, which provides ventilation and limits the potential for confinement

Critical Event	Loss of containment - pump seal failure
Potential Cause(s)	Overpressure, normal wear, and tear
Potential Consequence(s)	Personnel exposure to ammonia
Prevention Measures	Pump included in the Preventive Maintenance program
Mitigation Measures	Equipment is located outdoors which provides ventilation and limits the potential for confinement

Ammonia Plant – Purge Gas Recovery Section

Critical Event	Loss of containment from piping or vessel failure – Low-pressure side
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Personnel exposure to ammonia
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc. Pressure relief devices installed on piping systems/vessels were required.
Mitigation Measures	Equipment is located outdoors, which provides ventilation and limits the potential for confinement

Critical Event	Loss of containment of purge gas due to piping, flange, etc. – High-pressure side
Potential Cause(s)	Corrosion, impact, third party activity, gasket leak, valve passing or left open, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Fire with associated equipment damage, business interruption, the reportable release of flammable materials
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the MI program Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc.

	Pressure relief devices installed on piping systems/vessels were required The compressor unit has high discharge pressure cut-out
Mitigation Measures	The area is electrically rated as Class 1 div. 2 Operator rounds would detect leaks based on abnormal sound All equipment is outdoors with little if any potential for confinement

Ammonia Storage Tanks and Pumps

Figure 7. Cryogenic pumps

Critical Event	Storage tanks failure due to overpressure from an inability to relieve excess pressure
Potential Cause(s)	Hot ammonia vapour from ISBL enters the storage tank
Potential Consequence(s)	Potential to roll the ammonia storage tank causing overpressure, tank failure and release of ammonia to the containment dike. Potential personnel exposure, offsite impact and reportable release
Prevention Measures	Pumps have discharge check valves
Mitigation Measures	Tanks are located inside a containment dike designed to hold loss of containment from 1 or the 2 tanks. Tanks have pressure relief installed and pressure control directed to a flare.

Critical Event	Pipeline to bullet failure due to overpressure from the inability to relieve excess pressure
Potential Cause(s)	Hot ammonia vapor from ISBL enters the bullet faster than it is removed
Potential Consequence(s)	Potential to overpressure and cause vessel failure and release of ammonia to the containment area. Potential personnel exposure, offsite impact, and reportable release
Prevention Measures	
Mitigation Measures	Pressure protection device on the vessel

Critical Event	Release of ammonia from unloading system piping, loading arms, connections, etc.
Potential Cause(s)	Loss of containment of ammonia from the pipe system, e.g. corrosion, gasket failure, impact to pipe, valve open or leaking, railcar movement, etc.
Potential Consequence(s)	Release of ammonia to the unloading area. Potential personnel exposure, offsite impact, and reportable release.
Prevention Measures	Breakaway fittings QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures

	Equipment is included in the maintenance and inspection program. Commissioning includes pressure testing lines Lines run in pipe way and not close to vehicles etc.
Mitigation Measures	Pressure protection device on railcar Excess flow valves installed in the system

Critical Event	Oxygen infiltration into the ammonia storage tanks leads to stress corrosion cracking and tank failure
Potential Cause(s)	Loss of containment of ammonia from the tank
Potential Consequence(s)	Release of ammonia to the unloading area. Potential personnel exposure, offsite impact, and reportable release
Prevention Measures	The design prevented its return of ammonia vapour to the storage tank - routed to the flare. Equipment included in the Maintenance and inspection program
Mitigation Measures	Equipment is located outdoors Water curtains/deluge sprinklers

Critical Event	Vacuum in the ammonia tank.
Potential Cause(s)	During a shutdown, demin water is added to a tank that contains only ammonia vapour.
Potential Consequence(s)	Tank damage, the release of ammonia vapour, potential offsite odour complaints; business interruption
Prevention Measures	Vacuum breaker on tanks Tank refrigeration system provides pressure control
Mitigation Measures	Two storage tanks allow for operating flexibility

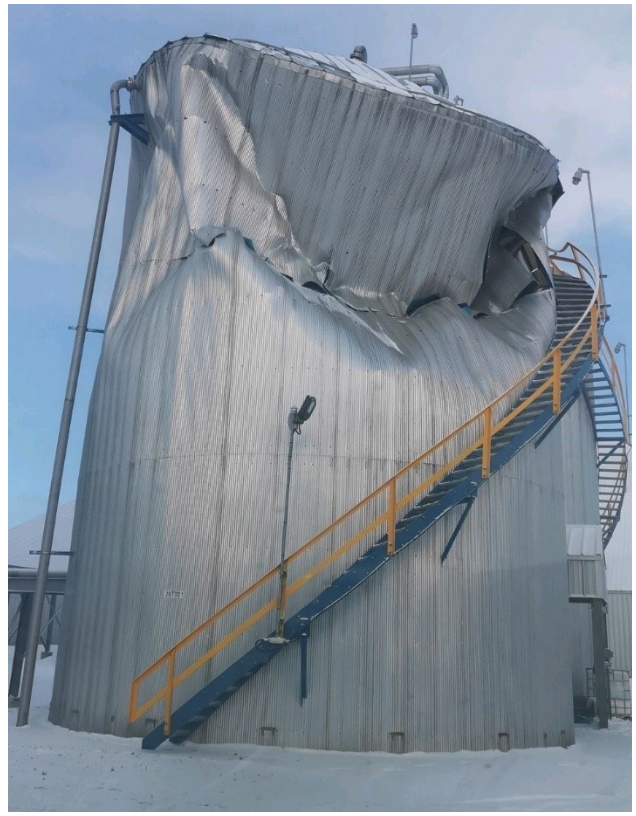


Figure 8. Destruction of a storage tank due to vacuum conditions

Critical Event	Ammonia release is followed by fire and explosion.
Potential Cause(s)	Release of ammonia causing vapour build-up under the tank (elevated tank design) or just a large release. If ignited, significant overpressures can be generated due to partial confinement.
Potential Consequence(s)	Tank damage, the release of ammonia vapor, business interruption.
Prevention Measures	Limited ignition sources in the area. Not credible for ignition

Mitigation Measures	Tanks are inside a containment sized to hold 1 or the 2 tanks

Critical Event	Release of ammonia from process equipment
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Release of ammonia vapour, potential offsite odour complaints, business interruption.
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing equipment
Mitigation Measures	Equipment is located outdoors, and the potential for concentration build-up to cause personnel injury is remote Limited personnel in the area Gas detection system

Critical Event	Liquid carryover to the flare
Potential Cause(s)	Malfunction of the level control system on the KO drum.
Potential Consequence(s)	Potential flame out, possible personnel exposure to liquids released from the flare, business impacts.
Prevention Measures	Dual KO drums installed on the ammonia flare system Site glass is used for manual draining of any liquids.
Mitigation Measures	Inherently safer design

Ammonia Storage Tank Flare

Figure 9. Storage tank flare

Critical Event	Internal explosion in the flare system.
Potential Cause(s)	Air ingress through an open valve or other openings mixes natural gas with subsequent ignition.
Potential Consequence(s)	Explosion with internal fire, potential personnel impact, possible offsite issues (flare is near roadway); business interruption
Prevention Measures	Continuous sweep gas supplied to flares
Mitigation Measures	Inherently safer design

Critical Event	Flashback from the flare through the feed pipes.
Potential Cause(s)	Shutdown scenario with air ingress mixing with ammonia to form a flammable atmosphere ignited by the flare burner.
Potential Consequence(s)	Explosion with internal fire, potential personnel impact, possible offsite issues (flare is near roadway); business interruption
Prevention Measures	Continuous sweep gas supplied to flares

Mitigation Measures	Inherently safer design

Critical Event	Ammonia is released into the atmosphere from a flare.
Potential Cause(s)	Flameout
Potential Consequence(s)	Potential reportable release of ammonia with possible offsite impacts, media attention
Prevention Measures	Inspection and testing program for flare pilots
Mitigation Measures	The flare discharge point is elevated, which reduces the potential for offsite impacts due to natural dispersion

Critical Event	Fuel gas fire
Potential Cause(s)	Loss of containment of fuel gas from the gas piping (corrosion, gasket failure, impact to pipe, valve open or leaking).
Potential Consequence(s)	Equipment damage and business interruption
Prevention Measures	QA/QC process for confirming the correct design, manufacturing, and installation standards and procedures Equipment included in the Maintenance and inspection program Commissioning includes pressure testing equipment.
Mitigation Measures	Equipment is located outdoors with limited personnel access in the area.

Critical Event	Exposure of personnel to ammonia.
Potential Cause(s)	Draining of the flare knockout drum.
Potential Consequence(s)	Potential worker exposure to ammonia
Prevention Measures	Procedures and training
Mitigation Measures	Equipment is located outdoors, which provides for the dissipation of ammonia released.

Steam and Condensate Systems

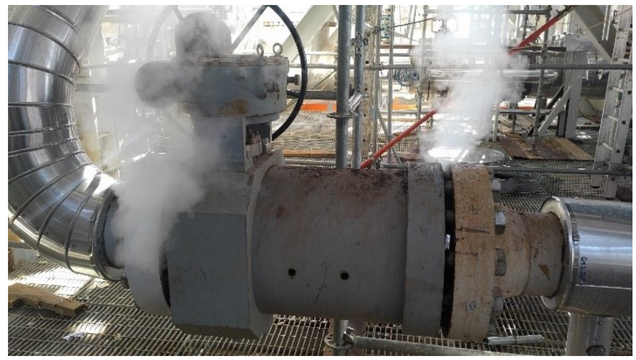


Figure 10. High-pressure steam valve leaking

Critical Event	Liquid carryover from stripper
Potential Cause(s)	Malfunction of the level control system.
Potential Consequence(s)	Damage to the primary reformer catalyst causing reduced production or shutdown and business interruption.
Prevention Measures	Potential plant outage
Mitigation Measures	Inherently safer design

Critical Event	Gas blowby to BFW system
Potential Cause(s)	Malfunction of the level control system.
Potential Consequence(s)	Upset to the steam system causing reduced production or shutdown and business interruption
Prevention Measures	Potential plant outage

Mitigation Measures	Inherently safer design

Critical Event	Loss of containment lines or vessel
Potential Cause(s)	Corrosion, overpressure, mechanical failure, weld defect
Potential Consequence(s)	Personnel exposure to HP steam
Prevention Measures	QA/QC process for confirming correct design, manufacturing and installation standards and procedures Equipment included in the Maintenance and Inspection program Commissioning includes pressure testing lines. Lines run in pipe way and not close to vehicles etc. Pressure relief devices installed on piping system/vessels as required.
Mitigation Measures	Isolation valves available

Critical Event	Compressor Overspeed with associated damage
Potential Cause(s)	Leaking check valve from reverse flow of MP steam into steam turbine when the unit is down
Potential Consequence(s)	Internal damage to compressor causing business interruption
Prevention Measures	Check valve installed
Mitigation Measures	The compressor has Overspeed protection.

Critical Event	Low-pressure damage to the deaerator.
Potential Cause(s)	Thermal changes
Potential Consequence(s)	Release of steam and condensate, business interruption
Prevention Measures	Pressure/vacuum protection device on a vessel
Mitigation Measures	BFW quality issues in the long term

Critical Event	Loss of Demineralization water supply.
Potential Cause(s)	Pump failure, line rupture, demineralization unit malfunction, etc.
Potential Consequence(s)	Loss of ability to generate process steam leading to process shutdown, business impacts
Prevention Measures	Maintenance and inspection program in place
Mitigation Measures	Dual pumps provided

Cooling Water and Nitrogen System

Figure 11. Cooling water towers

Critical Event	Loss of containment of chemicals used as part of the system

Potential Cause(s)	Piping failure due to corrosion, erosion, poor fabrication or installation, etc.
Potential Consequence(s)	Limited personnel injury due to the nature of the materials used
Prevention Measures	QA/QC process associated with commissioning
Mitigation Measures	Chlorine is not a chemical being used in the process

Critical Event	Over-pressuring of the nitrogen header or system equipment
Potential Cause(s)	Reverse flow occurring at nitrogen users
Potential Consequence(s)	Potential to overpressure the nitrogen header resulting in catastrophic failure and release of nitrogen
Prevention Measures	Overpressure protection from PSVs
Mitigation Measures	Site emergency response protocol Limited potential for personnel hazardous exposure.

General Site-wide Issues

Figure 12. Ammonia plant site

Critical Event	Vehicle impact with plant equipment.
Potential Cause(s)	Driver error, poor visibility, excess speed. Also, lifting over live processing plants and dropped equipment occurs or fallen cranes.
Potential Consequence(s)	Potential for release of hazardous materials, e.g. resulting in fires.
Prevention Measures	Traffic speed control onsite already established, route design, etc.
Mitigation Measures	Site Emergency Plan Operator Capability Fire Protection: Ring main, Fogging etc Personnel and Visitor Inductions Established chemical plant facility

Critical Event	Sampling throughout the plant
Potential Cause(s)	Procedures call for sampling under select conditions
Potential Consequence(s)	Potential for exposure to the following: Toxic gases (NOx, NH_3); High temperatures; Flammable gases; Asphyxiants.
Prevention Measures	Procedures
Mitigation Measures	PPE: mono-goggles Safety Shower Fire Protection First Aid Station Established chemical plant facility

Critical Event	Operator struck by air/nitrogen hose.

Potential Cause(s)	Connector failure
Potential Consequence(s)	Potential for injury
Prevention Measures	Annual hose inspection program
Mitigation Measures	PPE First Aid Established chemical plant facility.

Critical Event	Hazardous situations rotating/moving equipment
Potential Cause(s)	Pumps, compressors, fan blades.
Potential Consequence(s)	Potential for injury to people, e.g. clothing caught in moving parts.
Prevention Measures	Signage Protective Shielding etc Guarding
Mitigation Measures	PPE First Aid Established chemical plant facility

Critical Event	Site-wide traffic incidents
Potential Cause(s)	A leak from a road tanker due to collisions with a vehicle
Potential Consequence(s)	Release of materials on the site roads. Environmental impact.
Prevention Measures	Traffic Management System on site, route design etc.
Mitigation Measures	Site Storm Water Treatment

Critical Event	Plant Wide. People coming in contact with hot surfaces (above 60 deg C)
Potential Cause(s)	No / damaged insulation on hot pipework
Potential Consequence(s)	Burn injury to people
Prevention Measures	Maintenance Design / Barriers
Mitigation Measures	First Aid PPE Established chemical plant facility

Critical Event	Hazards of cold ammonia and nitrogen.
Potential Cause(s)	Release of cryogenic nitrogen or cold ammonia throughout the plant.
Potential Consequence(s)	Potential for cold burn injuries.
Prevention Measures	Maintenance: Regular inspection, NDT Alarms and Trips
Mitigation Measures	PPE First Aid Established chemical plant facility

Critical Event	Flooding / Earthquakes / Strong Winds
Potential Cause(s)	Adverse natural events
Potential Consequence(s)	Potential for releases e.g. Ammonia, natural gas
Prevention Measures	The flood study is done in the FEED phase, and the results are included in the Basis of the Design

	Earthquakes and historic meteorological data used in the Basis of Design
Mitigation Measures	Structural and drainage systems designed to withstand the flooding, earthquakes, and strong winds

Critical Event	Contaminated Soil / Groundwater
Potential Cause(s)	Accidental release
Potential Consequence(s)	Exposure to personnel during excavation for construction/operations
Prevention Measures	Procedures/dial before you dig Established chemical plant facility with all underground piping known and marked
Mitigation Measures	Spillage control and environmental cleaning procedures in place

Critical Event	Electrocution
Potential Cause(s)	Contact with any voltage
Potential Consequence(s)	Fatality / serious injury
Prevention Measures	Trained personnel / authorized electrician Isolation procedures are in place.
Mitigation Measures	

Critical Event	Confined Space Entry
Potential Cause(s)	Work inside vessels, tanks, underground, excavation
Potential Consequence(s)	Fatality / serious injury
Prevention Measures	CSE procedures
Mitigation Measures	

Conclusions

The purpose of this review of hazards identification for ammonia plants is to trigger the brainstorming when performing a risk assessment or HAZID studies for existing and future facilities. This paper will not offer a full identification of all potential hazards associated with ammonia plants operation. Its purpose is to help the readers to further identify additional risks and safeguards based on their own and their colleague's experience when performing job safety analysis, risk assessment, and hazard identification workshops. Once the risks and safeguards are identified, these should be further analyzed during the HAZOP studies based on existing site conditions or project specifications.

Catastrophic failure of Primary Reformer due to Mixed Feed Crossover piping rupture

Catastrophic failure of an ammonia plant primary reformer occurred due to a mixed feed crossover piping longitudinal weld seam failure. This weld seam failure was the direct cause of an initial loss of primary containment that induced a reverse flow condition which resulted in the complete failure of other major components throughout the reformer. This paper presents the sequence of events and associated root causes that resulted in the failure of the mixed feed crossover piping. Learnings are being shared as the potential exists for other operators to have a similar type of failure.

Zaheer Ramdath, Graig Davis
Proman, Trinidad and Tobago

Introduction

The primary reformer mixed feed crossover piping and other reformer components ruptured on an ammonia plant resulting in multiple fires on November 10, 2017. The failure occurred in a 1 850 MTPD (2 040 STPD) plant located in Trinidad and Tobago. This incident was classified as a Tier 1 process safety incident. There were no injuries resulting from this event.

The initiating event of this Tier 1 process safety incident was the longitudinal rupture of the mixed feed crossover piping which resulted in a reverse flow condition. The reverse flow condition caused major transfer line damage within the radiant section. It also caused riser tube and outlet header failures. There were also accompanying fires and explosions within and under the primary reformer radiant box.

The causal factors, root cause, successful repair approach and recommendations to prevent a reoccurrence are discussed within this paper. Several areas of process safety management are engaged in the discussion relative to this incident inclusive of plant operating parameters and mechanical integrity.

Process Description

The primary reformer is a top fired furnace containing radiant and convection sections. Reforming occurs in catalyst packed tubes contained in the radiant box. Desulfurized natural gas feed is mixed with medium pressure (MP) steam. The gas and steam mixture then flows through the mixed feed preheat coil of the convection section of the primary reformer where it is heated to 1150°F (621°C). The mixed feed then flows to the top of the radiant section, via the mixed feed crossover piping. It then splits into five equal and parallel sub headers. The 5 five sub headers distribute the flow to 280 catalyst tubes. There are five tube outlet collection headers that returns the flow upward through the radiant fire box via riser tubes that discharge into a transfer line and is then sent to the secondary reformer. See Figure 1 for a process flow diagram for the ammonia plant primary reformer with mixed feed, MP steam and natural gas flows highlighted.

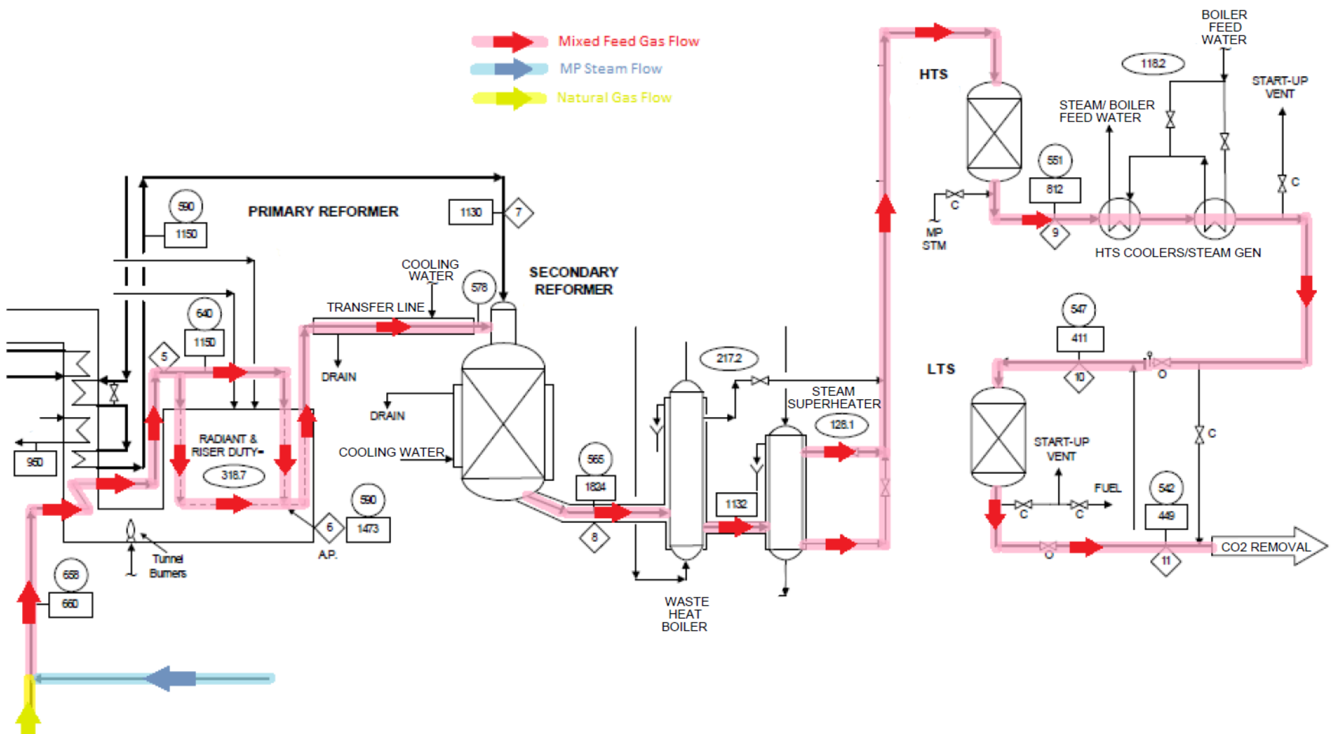


Figure 1: Process flow diagram for the ammonia plant Primary reformer

During secondary reforming, process gas mixes with preheated process air to provide the nitrogen required for the ammonia synthesis reaction. The oxygen in the air combusts a portion of the process gas from the primary reformer, leading to a temperature of about 2395°F (1313 °C). This reaction occurs in a special mixing and combustion chamber known as an air stream nozzle. The hot gas from this combustion passes down through a bed of nickel reforming catalyst where it reacts to produce more hydrogen in an analogous manner to the Primary reformer.

The secondary reformer effluent passes directly to the secondary reformer waste heat boiler where high pressure steam is generated. The effluent then passes to the high-pressure steam superheater and then it enters the high temperature shift converter (HTS) at 700 °F (371 °C).

Incident Description

Immediately prior to the incident that occurred on November 10, 2017, the ammonia plant was in steady operation at 93% plant rate and there were no personnel in the process area of the plant at the time of the incident.

On November 10, 2017, at 23:53:03 plant operations personnel in the ammonia plant heard a very loud noise while they were inside the control building. At that same point in time, natural gas flow to the primary reformer increased from 74 klb/hr to 100.9 klb/hr (note that the range of the transmitter was 0-100 klb/hr) and steam flow to the primary reformer increased from 298 klb/hr to 355 klb/hr (range of the transmitter was 0 - 350 klb/hr).

At 23:53:16 the primary reformer harp temperatures began to increase from their normal temperature of approximately 1400 ºF (760 °C) to approximately 2400 ºF (1316 °C) with the highest recorded temperature being 2588 ºF (1420 °C). The primary reformer outlet temperature also increased to a peak temperature of 2441 ºF (1338 °C).

At 23:53:26 the primary reformer box pressure increased from -0.31 inH2O (-77 Pascals) to 0.78 inH2O (194 Pascals) and the primary reformer was shut down by a radiant section firebox high pressure interlock. Feed gas flow to the reformer then decreased from 88 klb/hr to 0 klb/hr after the shutdown of the reformer.

Field operators investigated the loud noise but were unable to communicate with the control room via radio due to the intensity of the noise.

At 23:53:35 air to the secondary reformer began to decrease from 205 klb/hr to 0 klb/hr. The Primary reformer harp temperatures then began to decrease.

At 23:53:55 steam flow to the primary reformer was 345 klb/hr and had started to decrease.

Field operators observed fire emanating from the underside of the radiant box of the primary reformer during this event. A pressure wave was also felt by operators as they approached the primary reformer. Field operators advanced to the primary reformer, activating fire hydrant monitors along the way. The fire had already subsided upon their arrival at the Primary reformer, but the reformer outlet header boxes were found to be glowing orange.

At 23:55:26 the primary reformer harp temperatures and outlet temperatures decreased to 500 ºF (260 °C). The operators then secured the plant per the Standard Operating Procedure (SOP).

Inspection Findings

Mixed Feed Cross Over Piping

Initial visual inspection revealed a large rupture on the longitudinal weld seam on the first straight run of piping exiting the mixed feed coil. (Figures 2 and 3) The rupture was measured to be 85 in (216 cm) in length and 16 in (40.6 cm) wide at the widest point. The fracture centerline was observed to be positioned at the center of the longitudinal weld seam of the pipe. Two distinct zones were present on the fracture surface of the pipe with a more oxidized surface noted to be from the outer diameter towards the inside of the pipe with an average depth of 0.750 in (1.91 cm). The thickness of the pipe was 1 in (2.54 cm). At certain locations along the ruptured section, the fracture surface showed about 96% of the total piping thickness to be more oxidized.

Figure 2: Photo of ruptured mixed feed piping

Figure 3: Photo of ruptured mixed feed piping

Subsequent inspection on the remainder of the 16 in (40.6 cm) diameter pipe and pipe fittings revealed cracks along the longitudinal weld seam and on the intrados (inner bend) of an elbow within the piping system.

Primary Reformer Inlet Manifold and Pigtails

Liquid Penetrant Testing (PT) and Radiographic Testing (RT) were performed on 100% of inlet pigtails on all rows with no relevant indications found. Manual diametrical measurements were also collected, and less than 3% expansion was noted.

Primary Reformer Catalyst Tubes

Visual inspection performed on all catalyst tubes revealed no considerable damage to tubes except for one tube which had a bend at the inlet pigtail. Eddy current testing was performed on all 280 tubes with no relevant indications noted. Replica metallography was also performed on a sample tube within the radiant section. Microstructural analysis showed the tube was fit for service. The tube's catalyst support mesh was found severely fouled with molten debris.

Primary Reformer Outlet Headers

100% penetrant testing was performed on the primary reformer outlet headers' welds. No indications related to the incident were found. Replica metallography was also performed on random external areas of the pigtails and headers revealing no abnormalities. Manual outer diametrical measurements on every third pigtail revealed no significant deviations. 100% RT was also performed on all outlet header to outlet header welds and no defects were found. PT was performed on outlet header to weld-o-let welds with no defects found.

Severe failures were noted on all five riser outlet manifold tees. The failure was caused by a significant temperature excursion which resulted in the burn through of the parent metal of these tees during the reverse flow event, see Figure 4. This occurred within a 5 in (12.7 cm) diameter circular area consistent with the inner diameter of a riser.

Figure 4: Photo of outlet header tee showing burn through due to reverse flow

Primary Reformer Risers

Visual inspection conducted revealed risers B, D & E failed directly under the transfer line insulation can, with riser E being completely dislocated and resting on the radiant box wall. The extent of riser failures was varied, with large gaping fractures with jagged edges, see Figure 5. Significant bowing was also observed on all risers including risers A and C.

Figure 5: Photo of risers that were ruptured and dislocated

Primary Reformer Transfer Line

Internal inspection of the transfer line revealed refractory material and solidified molten metal deposited at the flanged end of the transfer line, See Figure 6. The internal liners of the riser transition assemblies were also damaged. Subsequent inspection of the transfer line showed severe damage to the internal liner components.

Figure 6: Photo showing refractory material and solidified molten metal deposited at the flanged end of the transfer line

Primary Reformer Tunnels

The ammonia plant primary reformer has six tunnels (A to F). Inspection of tunnel B found that 85% of the wall and tunnel covers were either dislodge, fallen or broken. The tunnel was noted to have collapsed in the middle, with approximately 6 feet of tunnel on either end remaining intact, see Figure 7. Inspections of the other five tunnels found that these tunnels were in good condition with deflections not exceeding 2 in.

Figure 7: Photo showing significant damage to tunnel B walls and covers

Process Findings

Loss of Primary Containment

On November 10, 2017, between 23:53:00 and 23:53:05, the natural gas flow to the primary reformer increased by 36%. Medium pressure steam flow to the primary reformer increased by 19% between 23:53:03 and 23:53:05 There was no operator action to initiate these flow increases. These increases over-ranged the respective transmitters which resulted in the controllers exiting automatic control.

At 23:53:05, the process pressures downstream the HP Steam Super-heater, and High Temperature Shift Converter, began declining from the normal operating values of 531 psig (36.6 bar) and 520 psig (35.9 bar) respectively.

The combination of the significantly increased flow upstream the primary reformer mixed feed coil and falling pressures downstream the primary reformer (with no process vents open) suggested a loss of primary containment from one or more components at 23:53:03. This also aligned with the observation by the process operators of a very loud noise like that of a relief valve lifting. The incident inspection findings of failed primary reformer components also supported this.

Reverse Flow

During the period 23:53:06 to 23:53:16, the differential pressures between the High Temperature Shift Converter and Low Temperature Shift Converter (LTS) declined to zero with the pressure between them being recorded at 480 psig (33.1 bar). The differential pressure transmitters for the HTS and LTS normally read zero if the pressure differential is negative. The pressure just upstream of the HTS and LTS was 458 psig (31.6 bar) at that time but in the normal process flow it should have been a higher pressure.

The reverse order of the pressures above coupled with the zero differential pressure recorded across the HTS and LTS suggests that reverse flow was taking place.

Reverse flow was also inferred since a reduction in temperatures at the outlet of the waste heat boiler and steam superheater was observed at 23:53:15. This is because the process gas downstream the waste heat boiler is at a lower temperature during normal operation. At 23:53:15 combustibles in Flue Gas increased to 350 ppm which was the upper limit of this instrument.

In the process stream from the primary reformer onward, the first protection against reverse flow was a check valve at the inlet to the CO_2 absorber. Reverse flow occurred from upstream the CO_2 absorber toward the primary reformer. When the pressure upstream the HTS and LTS decreased, reverse flow occurred from upstream the CO_2 absorber at a pressure of 511 psig (35.2 bar) to atmospheric pressure at the mixed feed piping rupture point. This occurred between 23:53:06 and 23:59:00

Temperature Excursions

The outlet headers discharge to the transfer line and the transfer line then sends the combined gas from all outlet headers to the secondary reformer. Each outlet header has temperature measurement. At 23:53:16, the temperatures at the Primary reformer outlet headers A, B and E had increased by approximately 50°F (28°C). By 23:53:26, the temperatures on all eleven indicators on the outlet headers were in the range of 1531°F (833°C) to 2182°F (1194°C). By 23:53:36, these temperatures peaked to a maximum of 2588°F (1420°C).

During normal operation of the secondary reformer, a portion of the partially reformed gas from the primary reformer is burnt auto thermally in air to provide the heat necessary for secondary reforming. This reaction normally produces temperatures in the ignition chamber of the secondary reformer in the order of 2400°F (1316°C).

The composition of reformed gas was lower in methane and higher in hydrogen during the reverse flow event since this gas had already been reformed by both the primary and secondary reformers. The combustion reaction in reverse flow was between air and hydrogen as opposed to air, hydrogen and methane in normal operation. This change in gas composition had a higher heat of combustion and temperature in the reverse flow scenario when compared to normal operation. This aligned with the peak temperatures observed in the primary reformer outlet headers and transfer line.

High Radiant Box Pressure

At 23:53:26, the Hi-Hi Box Pressure interlock activated. This interlock initiated a trip of the fuel, natural gas, and air feeds, leaving the process steam flow which then extinguished the fires caused by the loss of containment.

At 23:53:26, the Induced Draft (ID) fan of the primary reformer was in operation and only came offline at 23:56:45 The Forced Draft (FD) fan also showed a healthy value until 23:53:26 and combustion air pressure was also healthy. The fuel systems, ID fan and FD fan operated normally up to 23:53:26. The Hi-Hi Box Pressure trip at 23:53:26 was then attributed to the failure of one or more riser tubes. Inspection findings support this theory and coincides with the increase in flue gas combustibles to 350 ppm (overrange limit).

Other Findings

Failure Sequence

Failure of the mixed feed crossover piping as the initiating event aligned with the high flows, declining pressure and elevated temperatures associated with the reverse flow that was observed.

The reformer differential pressure transmitter high-side pressure measurement tapping point was found to be severed from the pipe. This tapping point is located directly downstream of the location of the mixed feed crossover piping failure. This exposed it to atmospheric pressure and coincides with the reading of 0 psig (0 bar) at 23:53:06.

From the inspection findings of this piping, approximately 96% of the total fracture surface was found to be more oxidized than the rest of it which suggested that it was compromised prior to the November 10, 2017 event. Calculation of the system pressure required to rupture the remaining thickness was found to be 461.6 psig (31.82 bar) which was lower than the operating pressure of the system and confirmed that once the piping thickness reduced to this point, it was no longer able to contain the operating pressure. The calculations were done at the normal operating temperature of the system, which was 1130°F (610°C).

Before the piping failure there were no signs of a leak on the mixed feed cross over piping. Common indications of a leak on this piping system are condensate leaking through the insulation or unusual noise from any section of the piping. These observations were not made during routine plant checks suggesting that a leak did not exist before the piping rupture.

Based on this information, the following was the sequence of failures on the primary reformer:

1. Between 23:53:03 to 23:53:05, failure of the longitudinal weld seam of the mixed feed crossover piping occurred initiating a high flow of natural gas and steam in forward flow to the open piping. The pressure containing equipment between the point of failure on the mixed feed piping and the check valve at the inlet of the CO_2 absorber started to de-pressure causing reverse flow. Hot gases travelled from the combustion chamber of the secondary reformer in reverse flow through the transfer line, down the riser tubes toward the outlet collection header.
2. This hot gas and molten metal impinging on the collection header melted the header tees and caused failure of these tees. Failure of the tees then resulted in the hot hydrogen rich gas exiting the bottom of the primary reformer and auto igniting. This caused the fires that were later observed by the process operators while they made their way to the primary reformer.
3. Elevated temperature gas in reverse flow led to failures of the riser tubes immediately below the riser insulation can. It was concluded that risers B, C, D & E failed due to pressure because of a reduced tensile strength influenced by the increased temperatures of the reverse flow. The increase in flue gas combustibles to 350 ppm (overrange limit) occurred at this point.

The mixed feed crossover piping downstream the point of failure did not experience a temperature increase throughout this incident. Had reverse flow of hot gas to the ruptured mixed feed piping occurred for an extended period, damage to the primary reformer tubes would have resulted and high temperatures would have been recorded by instrumentation in this area. The failure of the outlet header tees occurred shortly after the mixed feed crossover piping failure which limited the exposure of the catalyst tubes to elevated temperature.

Mixed Feed Cross Over Piping Specification and Material

The ammonia plant designer specified ASME B31.3 (2002) as the design code for process piping at the time of construction of the plant.

Post-incident inspection across the mixed feed crossover piping revealed that the piping was within the permitted thickness. Positive Material Identification (PMI) on the parent material and the longitudinal welds found the chemical composition to be within specification and there was no visible defect on the root or cap of the weld at the time of construction of the piping components and systems.

Mixed Feed Cross Over Piping Operating Conditions

The operating condition of the ammonia plant were reviewed from the time of commissioning of the plant in 2009 to the time of failure. Focus was placed on the operating pressure and temperatures that the mixed feed crossover piping was subjected to.

Operating pressure was found to be within the design limits, however, excursions in temperature were found mostly during transient conditions at plant shutdown and start-up.

To avoid temperature increases under normal operating conditions, mixed feed flow was normally correlated to the primary reformer firing to ensure there was adequate flow for the reformer flue gas heat to be removed. During plant shutdowns where steam availability was reduced, there may have been insufficient flow to avoid temporary temperature excursions.

Historical Failures

Similar failures on sister plants

There were two other ammonia plants of similar design located in Point Lisas, Trinidad that also experienced similar longitudinal weld seam failures on the mixed feed piping.

One of these plants had to be taken offline in February 2014 due to a small longitudinal weld seam failure on an elbow on the mixed feed cross over piping. PT and Ultrasonic Testing for flaw detection (UT Flaw) were performed on all similar elbows revealing cracks along both inner and outer radius longitudinal weld seams. PT and UT Flaw were also performed on random longitudinal seam welds on the straight piping sections. No relevant indications were found. All elbows were replaced with seam welded elbows. In January 2017, the entire mixed feed crossover piping system was replaced with seamless piping. At the time of changeout, the seamed piping had been in service for approximately fifteen years.

The other sister ammonia plant was taken offline for maintenance on February 2014 and defects were found on the longitudinal seam welds of three elbows using PT and UT Flaw. These elbows were subsequently replaced in kind. In October 2014, the entire mixed feed crossover piping system was upgraded to seamless piping. In this case, the seamed piping had operated for approximately ten years.

Critical failure of mixed feed piping

Based on the defects noted on the two sister plants, a decision was made to proactively replace the piping on the ammonia plant discussed within this paper. Replacement of the entire piping system was scheduled for the next turnaround in February 2018 and the seamless piping was procured in 2015. Unfortunately, the piping failed before its planned replacement. At the time of failure, the mixed feed cross over piping was in service for approximately nine years.

Discussion

Use of Seamed piping

The plant designer specified ASTM A403 GR. WPS304H (seamless) piping for the mixed feed crossover piping. The technical specification for furnace tubes was applicable to the section of piping that failed and states that "Wrought pipe and tube materials shall be seamless unless noted otherwise in the purchase order or on the drawings." It also states that "Rolled and welded (non-seamless) pipe or tube when specified, shall have the entire weld length radiographed."

On all three plants mentioned in this paper, piping of the thickness required by ASME B31.3

(2002) was installed but seam welded piping and fittings were used. The installation met the ASME B31.3 (2002) requirements but was not in accordance with the plant designer furnace specification for seamless piping and fittings

Causal Factor and Root Cause

The causal factor was identified as hot/solidification cracking of longitudinal weld seam during manufacture. The root cause was found to be improper weld geometry resulting in uneven thermal gradients during welding/cooling causing the creation of hot/solidification cracks.

Process Hazard Analysis

Process Hazard Analyses (PHAs) were done on the ammonia plant in 2007 and 2015 respectively with the former one being the original PHA. These PHAs did not consider reverse flow as a scenario and there were no direct safeguards against reverse flow.

Analysis and Cause

Metallurgical examination

Quantitative metallurgical examination was conducted on the failed section of the mixed feed crossover piping. This examination found that failure was attributed to defects caused by improper longitudinal seam welding during manufacture. These weld defects, in combination with creep, may have significantly reduced the design life of the piping.

Creep is a phenomenon related to a combination of stress and temperature over time. In 300 series stainless steel, creep occurs at temperatures greater than 950°F. Under normal plant conditions (approx. 1150°F), the mixed feed piping operated within the creep region. Creep degradation was therefore expected and considered in the piping design for a minimum plant design lifetime of fifteen years. Weld manufacturing defects (solidification cracking) combined with creep will significantly reduce design life. This may have been the reason that the piping failed after nine years in service.

Creep rupture testing was conducted by the manufacturers of the riser tubes and outlet headers. They indicated that 80-90% of outlet header life was already consumed. These were then recommended to be replaced as part of the repair.

Failure Analysis

Failure analysis determined that hot/solidification cracking was the defect present in the longitudinal weld seam. Hot/solidification cracking is a phenomenon related to actual welding parameters during fabrication. This cracking was found to be because of improper welding geometry such as excessive weld width-to-depth ratio. With improper weld geometry, welding and cooling occurs with uneven thermal gradients leading to the formation of cracks. In this case, the crack orientation was in line with the weld bead making detection using RT difficult. The mixed feed cross over piping was subjected to 100% RT across the longitudinal weld and no defects were found during manufacture.

Crack propagation within the weld progressed over time until failure occurred because of a combination of pressure and thermal cycles during normal and transient plant conditions. Failure occurred once these subcritical cracks grew to a critical point where there was insufficient remaining wall thickness to withstand the internal pressure with ductile overload occurring.

Figure 8 shows a specimen taken along the fracture surface on the longitudinal weld seam.
Figures 9 shows a metallographic cross section of the fracture surface running through the weld.
Figure 10 shows metallographic cross sections that are polished and etched with subcritical cracks extending from the outer surface through the microstructure of the weld bead.

Figure 8, Specimen taken along fracture surface on the longitudinal weld seam

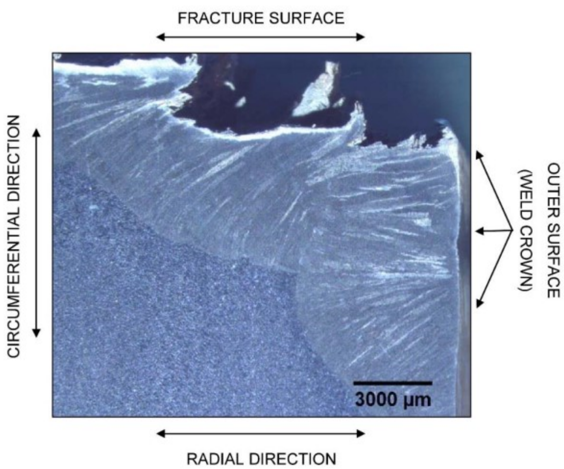


Figure 9, Metallographic cross section of fracture surface running through the weld

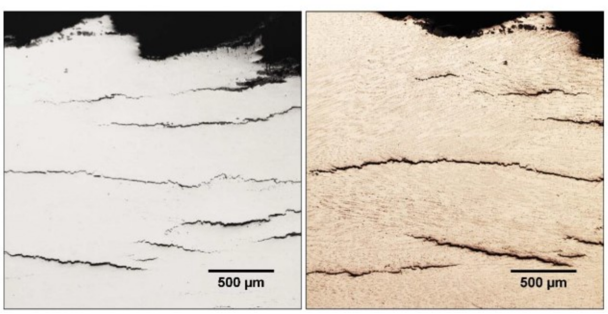


Figure 10, Metallographic cross sections showing as polished (left) and etched (right) with subcritical cracks extending from the outer surface through the microstructure of the weld bead.

The root cause of this incident was improper weld geometry resulting in uneven thermal gradients during welding and cooling of the welds, causing the creation of hot/solidification cracks. Had seamless piping been used, this phenomenon will not have occurred.

Recommendations

The following actions were recommended following this incident:

1. Implement additional NDE requirements for new pipe procurement to improve inspection confidence.
2. Perform NDE on existing plant piping operating within the creep region, to ensure serviceability.
3. Conduct an engineering review of the reforming section to determine the need to enhance the safeguards in this section of the plant, including mitigation against reverse flow.
4. Conduct a review of all piping in elevated temperature and pressure service to identify use of similar material in similar service and evaluate on a case-by-case basis.

Conclusion

Failure of the primary reformer mixed feed crossover piping was the direct cause of the first loss of primary containment on November 10, 2017. This induced a reverse flow condition which exposed the reformer components to temperatures above their design limits to the point of failure. The failure mechanism for the mixed feed crossover piping was determined to be hot/solidification cracking during fabrication due to incorrect weld geometry. This in additional to the piping creep expected for this piping system resulted in significant reduction in the expected life of the piping which resulted in premature failure.

Fitness-For-Service Assessment and Material Properties for Alloy 20Cr32Ni1Nb in Outlet Manifolds

Cast Alloy 20Cr32Ni1Nb is a common material in steam-methane reformer outlets because of its excellent creep-rupture properties at operating conditions. The welds in headers, tees, and fittings between the manifolds and transfer headers are made using filler metals or electrodes with high-nickel or "matching" compositions. Unfortunately, unplanned shut-downs can occur because of component failures. This paper provides an overview of currently available fitness-for-service (FFS) assessment and remaining-life prediction methodologies for these components and a summary of available material properties for the as-cast, as-welded, ex-service, and laboratory-aged materials from which they are fabricated. Gaps in methodologies and properties are identified, and tests to fill those gaps are recommended.

Michiel P. Brongers, Jeong K. Hong
Self employed

Carl E. Jaske
HSI Group, Inc.

Jeremy B. Nelson
Koch Ag & Energy Solutions, LLC

Jose E. Ramirez
Air Products and Chemicals, Inc.

Introduction

Primary reformers are an essential component of traditional ammonia and methanol plants, and reformer furnaces are also used to produce hydrogen in refineries. Reformer units need to operate reliably under relatively constant conditions and with planned shut-downs to keep plants online and running effectively. Unplanned shut-downs can often be caused by failures of components and/or headers in the outlet manifold system. Therefore, industrial users are interested in improved approaches for remaining-life (RL) predictions of the plant equipment that is made with high-temperature alloys. Cast Alloy 20Cr32Ni1Nb is of particular interest in this paper. Specifically, there is a strong interest in using high-temperature and low-temperature fracture toughness testing to develop data needed for use in fitness-for-service (FFS) calculations for Steam Methane Reformer (SMR) outlet manifolds and for the application of weld repairs.

Objectives

The objectives of this research were to determine material property data are needed for FFS and remaining life analysis, document currently available data, and identify data gaps for a test plan.

Background

Reformer furnace outlet manifolds can be made from austenitic stainless steels, such as those listed in Table 1. The principal difference between this cast alloy and the wrought alloys is niobium is used in the cast composition rather than titanium and aluminum.

Element	Material and Unified Numbering System (UNS) Designation			
	ASTM A351 [1] Grade CT15C (UNS N08151)	Alloy 800 [2] (UNS N08800)	Alloy 800H [2] (UNS N08810)	Alloy 800HT [2] (UNS N08811)
Carbon (C)	0.05-0.15	0.10 max	0.05-0.10	0.06-0.10
Chromium (Cr)	19.0-21.0	19.0-23.0	19.0-23.0	19.0-23.0
Nickel (Ni)	31.0-34.0	30.0-35.0	30.0-35.0	30.0-35.0
Manganese (Mn)	0.15-1.50	1.5 max	1.5 max	1.5 max
Silicon (Si)	0.50-1.50	1.0 max	1.0 max	1.0 max
Copper (Cu)	-	0.75 max	0.75 max	0.75 max
Aluminum (Al)	-	0.15-0.60	0.15-0.60	0.15-0.60(*)
Titanium (Ti)	-	0.15-0.60	0.15-0.60	0.15-0.60(*)
Niobium (Nb)	0.50-1.50	-	-	-
Phosphorous (P)	0.03 max	0.045 max	0.045 max	0.045 max
Sulfur (S)	0.03 max	0.015 max	0.015 max	0.015 max
Iron (Fe)	Remainder	Remainder	Remainder	39.5 min
Other: Al + Ti				0.85-1.20(*)

(*) Apparent discrepancy: Al or Ti cannot be less than 0.25 for Al+Ti specified as 0.85-1.20.

Table 1 Chemical compositions of ASTM A351 Grade CT15C and Alloys 800, 800H, and 800HT.

This paper is based on Materials Technology Institute (MTI) Project 356 of 2021 [3]. MTI prior work includes Final Report 227 in 2018 [4] on the high-temperature behavior of 20Cr32Ni1Nb, and an Atlas of Microstructures in 2014 [5] that relates the metallographically observed area fraction % of different metallurgical phases in 20Cr32Ni1Nb samples to their historic exposure temperature, time, and stress level.

Outlet manifold systems typically operate at temperatures of 750°C (1382°F) to 900°C (1652°F) and internal pressures of 2,000 to 3,500 kPag (290 to 508 psig) [6, 7]. Diameters are from 15.2 to 25.4 cm (6 to 10 inches) and wall thicknesses from 1.9 to 3.8 cm (0.75 to 1.5 inches). Welds connecting headers and pigtails are made using filler metals or electrodes of high-nickel alloys or matching materials. Traditionally, manifold components have been manufactured from wrought Alloy 800/800H/800HT. Alloying with niobium has been shown beneficial for creep resistance [8], As systems have increased in size, cast Alloy 20Cr32Ni1Nb has become an industry standard as a result of its better performance and lower cost [9]. Alloy 20Cr32Ni1Nb has been selected for SMR outlet manifolds because of both its weldability and strength at temperature [10], [7] and weldments made of Inconel 617 are as strong as or even stronger than Alloy 20Cr32Ni1Nb base metal and Alloy 800H [6]. However, generic stress-rupture (time to failure) and creep-rupture (strain rates) properties for cast Alloy 20Cr32Ni1Nb have not been developed.

The base material of welded cast Alloy 20Cr32Ni1Nb is used in applications requiring good corrosion resistance and moderate strength at elevated temperatures. However, the repair weldability typically becomes worse with prolonged service exposure. This is related to the loss of ductility due to the formation of nickel silicide, known as G-phase [11]. To avoid the formation of G-phase, micro-alloyed versions of Alloy 20Cr32Ni1Nb have been developed, with controlled carbon and low-silicon content [12].

Cracking during shut-down or repair welding as a result of the service-induced embrittlement of these heat-resistant castings is of great practical concern in the refining and petrochemical industries. Service-exposed cast Alloy 20Cr32Ni1Nb is considered difficult to repair because it can show severe susceptibility to liquation cracking[1] as well as significant loss in on-cooling ductility. Therefore, a high-temperature solution annealing heat treatment is usually performed before repair welding [13]. An example of a successful repair procedure included the application of solution annealing, removal of damage, repair welding, and inspection [14].

Fitness For Service

A typical FFS situation arises when inspection of an aged reformer manifold reveals indications of creep cracking or other damage, and a remaining-life estimate of the uninspected portions of the manifold is required. However, other situations may benefit from fracture mechanics-based FFS assessment. These include, but are not limited to:

- Example Scenario 1 - Assessment of fabrication issues (e.g., inspection indications at welds),
- Example Scenario 2 - Possibility of increased start-up rate for SMRs – After first start-up,
- Example Scenario 3 - Making repair decisions during turn-around,
- Example Scenario 4 - Assessment of the need for solution annealing and post-weld heat treatment,
- Example Scenario 5 - Assessing effects of thermal history of SMR headers.

In all these scenarios, the integrity assessment requires operational history data (number of start-ups/shut-down cycles, and time of operation at different temperatures and pressures) the basic geometry of the component, its configuration within the system (supports, restraints), size and shape of the flaw indication or defect, and knowledge of the material properties at ambient and elevated temperatures.

The material properties are the most challenging to obtain, because they depend on many factors, including the original metal chemistry, the number of start-up/shut-down cycles, and the history of exposure times at different temperatures and pressures. Furthermore, temperature-dependent properties are essential when finite element analysis (FEA) is employed to model the behavior of complex geometries [15].

Literature Search

The material conditions of interest in this study included:

- As-cast (manufacturer),
- Ex-service (stress, time, temperature, start-up/shut-down cycles),
- As-welded (welding consumable, heat treatment if any), and
- Laboratory-aged (time, temperature).

Future research could include:

- Distinguish between alloy chemistry variations, or micro-alloying additions,
- Distinguish between static casting versus centrifugal casting, or
- Distinguish between materials of different grain sizes, grain shapes.

Fracture Mechanics in the SMR Life Cycle

The three major life cycle stages of an SMR are: new design and construction, turn-around maintenance, and end-of-life management. Catalyst tubes are used as reference, but these discussions also apply to outlet systems.

1 Liquation cracking is a form of hot cracking, and refers to the formation of defects in the heat affected zone (HAZ), base metal, or previously deposited weld metal that is reheated by a subsequent weld. Another form of hot cracking is solidification cracking, which refers to the formation of shrinkage cracks during the solidification of weld metal.

New Design and Construction

SMRs are pressure equipment of which the tubes are commonly designed in accordance with API Standard 530 [16]. It is noted that API 530 does not strictly apply because it does not have data for the HP alloys. Other internals can be designed in accordance with ANSI/API Standard 560 [17]. Component fittings can be manufactured in accordance with ASME B16.9 [18]. Non-fired piping can be designed per ASME B31.3 [19]. API is in the process of developing API Standard 561 [20]. API 561 will provide design guidelines for reformers, but currently most SMRs are designed using proprietary guidelines of the specific fabricator, and these may or may not apply the approach of API 530.

A design life of 100,000 hours (11.4 years) is typically used for "normal operation". In manufacturer's literature, average or minimum time-to-rupture for alloys is often reported for 100,000 hours. By considering the actual past and anticipated future operating conditions as well as the absence or presence of flaws, the calculated RL can come out to be either greater or less than 100,000 hours.

Turn-Around Maintenance

When an SMR is operating as desired, the owner/operator can adhere to a schedule of periodic turn-arounds (TARs) to perform inspections and maintenance. A period of 3 to 5 years between TARs is typical, so there are only two or three shut-down/start-ups per tubing lifecycle. Alternatively, re-tubing can be based on a retirement-for-cause philosophy or in some cases to improve the productivity of the SMR. An RL assessment can be performed to estimate how many future start-up cycles and/or how many years of operation may be remaining.

Similarly, if a process upset occurs, an unplanned outage may be needed, and the TAR schedule can then be adjusted accordingly. A shut-down/start-up cycle puts the materials through a period of primary creep, which reduces the remaining life more than secondary creep would have if normal operations would have been maintained.

Deviations from Normal Operation, and End-Of-Life Management

The original design of SMRs provides one temperature and pressure to achieve a minimum of 100,000 hours of life with "normal operation", but reality is that actual operations use slightly lower or higher temperatures to adjust for the required production rates. Temperatures are not constant but fluctuate over time, and temperatures are not the same across the entire height, width, and depth of the furnace. Process upsets including thermal excursions and planned and unplanned shut-down/start-up cycles are not included in the design calculations.

Fracture mechanics analysis is essential for crack-like flaws because it allows one to calculate how close to failure flaws of different sizes and shapes may be for different operating conditions. When damage is more widely distributed, as is often the case for creep damage, continuum damage models are employed. A widely used FFS standard is API 579-1/ASME FFS-1 [21].

Material Property Data Needed for FFS Assessments

The following material properties are needed over a range of temperatures, including ambient temperature, start-up/cool-down transients, typical and maximum operating temperature, as well as for upset (overheating) conditions. Each property should be measured on material that, as far as reasonably possible, is matching the thermal history of the component being assessed. These properties are:

- Stress-strain curves [yield strength (YS), ultimate tensile strength (UTS), elastic modulus (E)],
    - Distinct values of YS, UTS, E are less desirable than full curves.

- Charpy V-notch (CVN) impact data correlations have been used to estimate fracture toughness, in the absence of other data.
- Fracture Toughness (J, K, CTOD),
    - CVN impact values are less desirable than measured fractured toughness.
- Stress-rupture data (stress, temperature, rupture time),
- Creep-rupture data (isochronous stress-strain curves). A review of this method was given by Marriot in 2011 [22],
    - At high temperatures test to failure, and
    - At lower temperatures test until a stable rate is measured.
- Creep regime fatigue curves, for crack initiation,
- Static creep crack growth rate data (crack extension with time, da/dt), and
- Cyclic crack growth rate data (crack extension with cycles, da/dN).

Material Property Data for Alloys Similar to Alloy 20Cr32Ni1Nb

For reference, this section presents creep rupture data for wrought Alloys 800 800H, and 800HT. These data were later used to compare with Alloy 20Cr32Ni1Nb. Figure 1 shows a graph that was constructed from the minimum design stress, Min. S(r), data for Alloy 800H, which is included in ASME Section III Division 5 Subsection HB Subpart B [23]. The authors of this review performed curve fitting of this *"ASME reference Larson Miller Parameter (LMP) data",* and found that an LMP constant $C_{LMP} = 16.12$ provided a best-fit, and was further used.

In 1998, the National Research Institute for Metals (NRIM), Japan, published [24] data for 21Cr-32Ni-Ti-Al alloy tubes, which is Alloy 800H; see Figure 2.

Figure 3 shows LMP curves constructed from the minimum properties of Alloy 800, Alloy 800H, Alloy 800HT, as listed in API 530, 6th Ed. [25], API 530, 7th Ed. [16] and ASME Sec III Div 5 Subsection HB Subpart B [23].

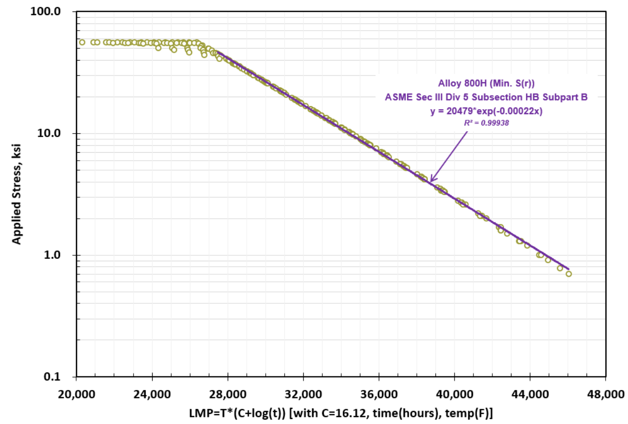


Figure 1 LMP curve for minimum design stress data for Alloy 800H, per ASME Section III.

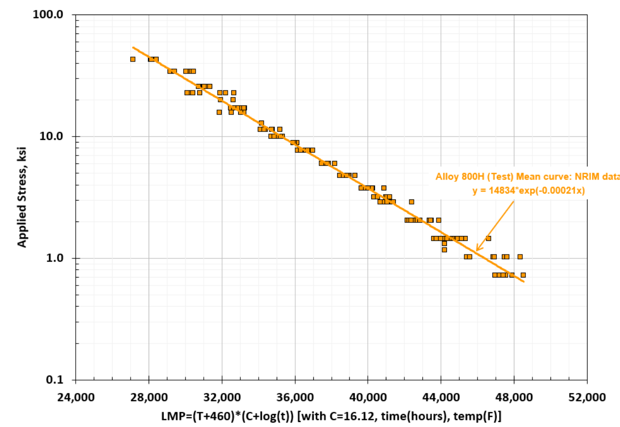


Figure 2. LMP curve constructed from stress-rupture test data for Alloy 800H from NRIM.

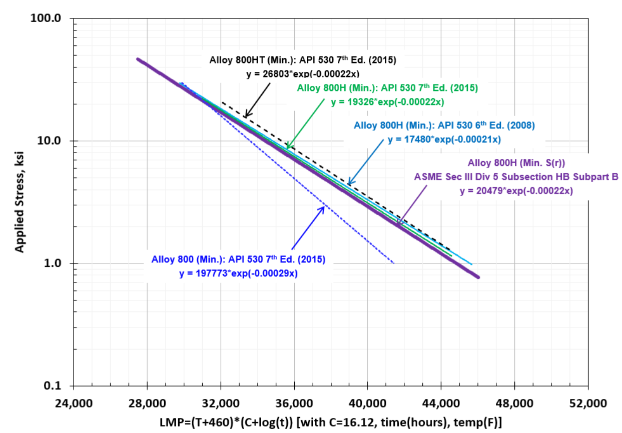


Figure 3. LMP curves constructed for MININUM properties of Alloy 800, Alloy 800H, Alloy 800HT, using data from API 530, and ASME Section III.

Figure 4 shows LMP curves constructed from the average properties of Alloy 800, Alloy 800H, Alloy 800HT, as listed in Table 10B.2 and Table 10B.4 of API 579-1/ASME FFS-1 (2021) [21] and NRIM Data Sheet 26B (1998) [10]. The underlying information for the equations in API 579-1/ASME FFS-1 (2021) are API 530, 6th Ed. [10] and WRC Bulletin 541, 2nd Ed. [27]. API 530, 7th Ed. [10] does not provide equations, but minimum properties in a tabulated format.

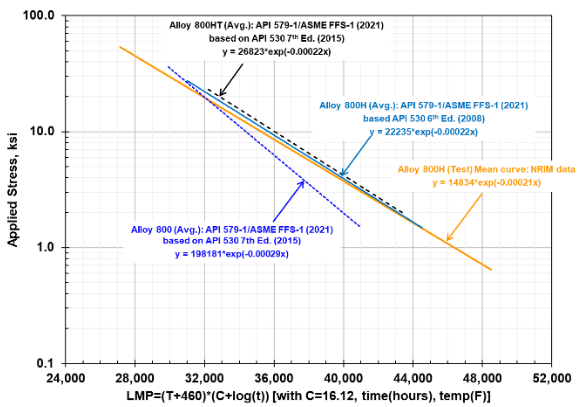


Figure 4. LMP curves constructed for average properties of Alloy 800, Alloy 800H, Alloy 800HT, using data from API 530 and NRIM.

Material Property Data Available from Literature

There is relatively little published about material property data for cast Alloy 20Cr32Ni1Nb, as will be discussed in more detail later. Available data concentrates on tensile properties and creep performance.

Tensile Properties – Base Metal

Figure 5 and Figure 6 show tensile data as a function of temperature, and percent elongation as a function of temperature, for materials from eight (8) different manufacturers.

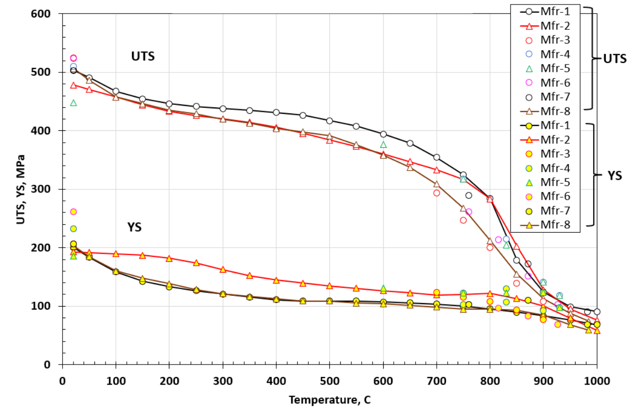


Figure 5. Yield Strength and Ultimate Tensile Strength as function of temperature for as-cast Alloy 20Cr32Ni1Nb for different manufacturers. Mfr-4 and Mfr-5 are minimum values, Mfr-2, Mfr-5, and Mfr-8 are micro-alloyed versions.

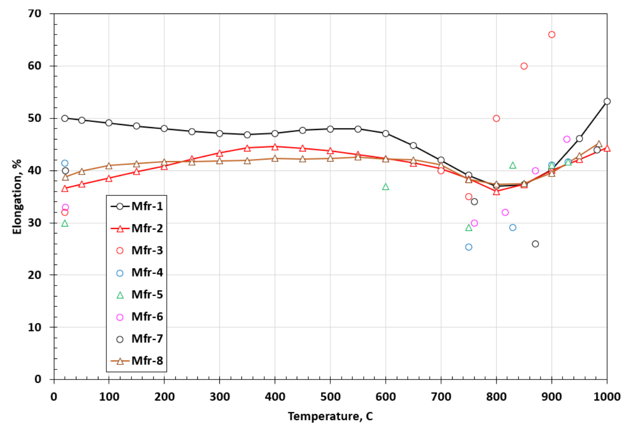


Figure 6. Elongation as function of temperature, for as-cast Alloy 20Cr32Ni1Nb from different manufacturers. Mfr-4 and Mfr-5 data are minimum values, Mfr-2, Mfr-5, and Mfr-8 are micro-alloyed versions.

Creep Rupture Properties – Base Metal

The literature review identified 50 data-points from stress-rupture tests of Alloy 20Cr32Ni1Nb in the as-cast condition, and the data are shown in Figure 7. The hatched line in the figure is the mean curve through the data, and the solid lines indicate the 95%-confidence interval of the data (mean ± 2 standard deviations [SD]). Four data-points are located below the mean – 2 SD curve.

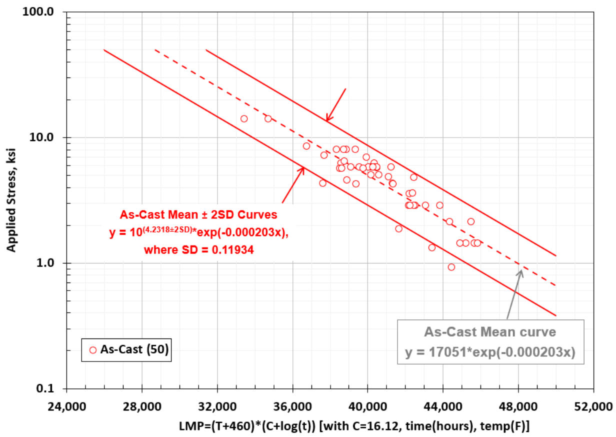


Figure 7. Mean LMP curve (hatched) and mean ± 2 standard deviation curves, for as-cast Alloy 20Cr32Ni1Nb, constructed from 50 data points. Slope C=16.12; refer to Figure 1.

Creep Rupture Properties – Weld Metal

Figure 8 shows LMP data for Alloy 20Cr32Ni1Nb in the as-cast, as-welded, and welded + aged conditions for cross-weld specimens. The laboratory aging was done prior to creep testing. The as-welded data are located predominantly in the lower range of as-cast values. This is concerning, because the minimum properties of the as-welded material are lower than the minimum properties expected for as-cast material, which follow the ASME minimum design stress curve for Alloy 800H.

In contrast, the welded + aged material data are located around the mean curve of the as-cast values. These data are from three different batches of steels and were part of different studies, so they cannot be directly compared. None of the material plotted in the welded + aged condition was also tested in the as-welded condition. More research is needed, using the same heat of weld and base metal, to investigate the effects of aging heat treatment of welded material on creep resistance.

The literature review identified 38 data-points from stress-rupture tests of Alloy 20Cr32Ni1Nb in the ex-service conditions to which solution annealing (SA) was applied (15 data-points), and in the laboratory-aged condition with or without SA heat treatment (23 data-points).

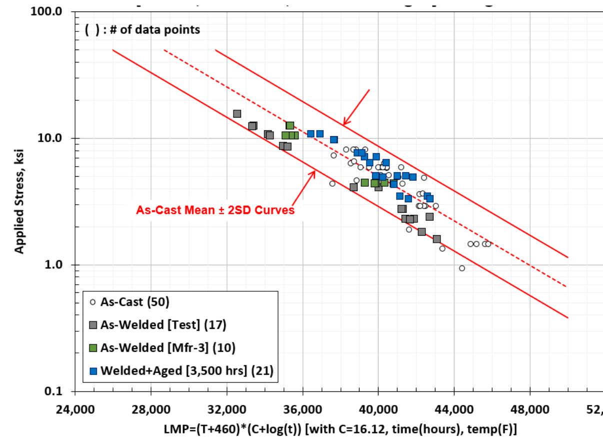


Figure 8. LMP data for Alloy 20Cr32Ni1Nb in as-cast, as-welded and in as-welded + aged conditions, constructed from 48 data points. Slope C=16.12; refer to Figure 1.

Figure 9 shows the ex-service data together with the LMP data for Alloy 20Cr32Ni1Nb in ex-service + SA, lab-aged, and lab-aged + SA conditions. With the exception of one data-point for 16 years of exposure + SA, all the data sets for ex-service + SA, lab-aged, and aged + SA are within mean ± 2 SD of as-cast data.

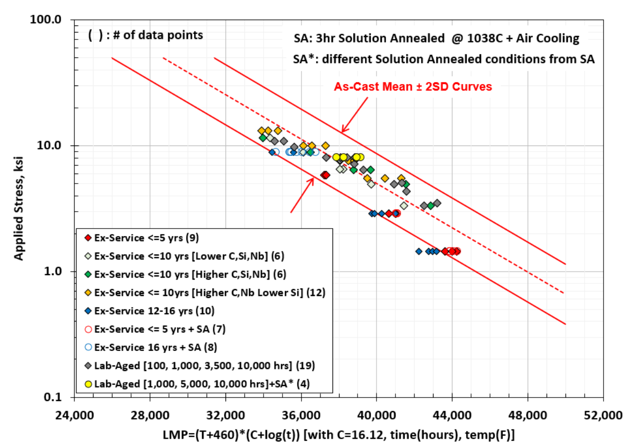


Figure 9. LMP data for Alloy 20Cr32Ni1Nb after laboratory aging (lab-aged) and/or solution annealing (SA), constructed from 38 data points. Slope C=16.12; refer to Figure 1.

Increased creep-rupture properties (shift to the right on the plot) are evident for the material to which SA was applied, as compared with the material that was ex-service or lab-aged without further heat treatment. This is also consistent with other data that showed improved creep properties for welded + aged material compared with welded material without further heat treatment.

Gap Analysis

Based on a summary of material properties needed for FFS and the material property data currently available from the literature, gaps in the mechanical property data have been identified. Each property should be measured on material that, as far as reasonably possible, matches the thermal history of the component being assessed, such as as-cast, as-welded, ex-service, and with or without SA treatment. For aged materials, care must be taken not to use too high temperature, because that may change the microstructural phases which can detrimentally affect the mechanical properties.

The following material property data gaps were identified:

Gaps in tensile properties

- Very limited data are available on tensile property values (YS, UTS, Elongation.) between 20°C (68°F) and 750°C (1382°F).
  - Only two manufacturers reported YS and UTS for as-cast material as function of temperature,
  - Limited tensile property data are available for as-welded and ex-service material, and
- Elastic modulus as function of temperature is not reported.
- No full stress-strain curves were found for as-cast or ex-service material for any test temperature.

Gaps in hardness

- None

Gaps in Charpy V-notch (CVN) impact

- Very limited CVN data are available for as-cast, welded, ex-service, or lab-aged material,
- No full CVN curves as function of temperature, for different aging conditions were identified, and
- CVN properties for material from different manufacturers are unknown

Gaps in Fracture Toughness

- No directly measured fracture toughness test data are currently available:
  - Only fracture toughness data available are values calculated from CVN impact tests,
  - Due to limited CVN data, correlation to fracture toughness not reliable,
  - Dynamic impact (CVN) is not a good indicator for quasi-static fracture toughness (J), which is a more realistic condition for fixed equipment,
  - Very limited CVN data are available for as-cast, welded, ex-service, or lab-aged material, and
  - No CVN data are available for different test temperatures.

Gaps in Stress-Rupture

- The literature identified relatively few (179 total) stress-rupture data-points
  - The number of stress-rupture tests is relatively small, because of all the variations in thermal history that these data represent: as-cast, as-welded, ex-service, lab-aged, solution annealed.
  - For FFS assessments, it is critical to use test results that reliably represent the thermal history of the components being evaluated.
- The manufacturers report as-cast minimum and average creep strengths that are *above* the curves constructed from the raw data in this literature review.

- The manufacturers data are non-conservative,
- The manufacturers do not report their actual data, but rather they tabulate creep strengths by 10,000 and 100,000 hours of life,
- Some manufacturers provide the data as LMP curves, which have to be converted for easy comparison. There is unknown uncertainty in the "minimum" and "average" curve fits in these LMP curves, and
- Manufacturers report mechanical properties only for the as-cast condition. However, research shows the properties can change significantly, even after short exposure at elevated temperature.

Gaps in Creep Data and Creep Rupture

- The literature review identified very limited data for creep-strain rates of Alloy 20Cr32Ni1Nb, for representative operating conditions and material thermal histories.

Gaps in Creep and Creep-Fatigue Crack Growth Rate

- The literature review identified no data-points for creep CGR of Alloy 20Cr32Ni1Nb, for any of the material conditions, either under constant load or cyclic loading.

Laboratory Testing Plan

Following the gap analysis, a draft Laboratory Testing Plan was developed, with reference to the five Example Scenarios and including a proposed minimum number of tests required for each property. Other scenarios could be proposed, but in this research only five main scenarios were selected. The plan is shown in Table 2.

Conclusion

Integrity assessments of SMR outlet manifolds require operational history data, the basic geometry of the component, its configuration within the system, size and shape of the flaw indication or defect, and knowledge of the material properties at ambient and elevated temperatures. The material properties are the most challenging to obtain, because they depend on many factors, including the original metal chemistry and thermal exposure history.

The information needed includes full stress-strain curves at different temperatures, CVN correlations, fracture toughness (J, K, or CTOD), creep/stress rupture data, creep fatigue curves, static creep growth rates (da/dt), and cyclic crack growth rate data (da/dN). It was found that relatively few mechanical property data are available for Alloy 20Cr32Ni1Nb, and ex-service properties, fracture toughness values, and crack growth rate data are particularly scarce.

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Example Scenario 1 – Assessment of fabrication issues (e.g., inspection indications at welds)
Example Scenario 2 – Possibility of increased start-up rate for SMRs
Example Scenario 3 – Making repair decisions during turn-around
Example Scenario 4 – Assessment of the need for solution annealing and post-weld heat treatment
Example Scenario 5 – Assessing effects of thermal history of SMR headers

#	Material Property	Test Method	Stress, Temperature	Base Metal As-Cast Example #	HAZ or Weld Metal As-Welded Example #	Base Metal, HAZ, or Weld Metal Ex-Service Example #	Base Metal, HAZ, or Weld Metal Lab-Aged Example #
1	Operating History	MTRs, Operational Data	Get from manufacturer, Get from Operator	Ask Manufacturer 1 - - - -	Ask Operators 1 - - 4 5	Ask Operator - 2 3 4 5	Ask Operator - 2 3 4 5
2	Micro-structural analysis	Light Microscopy, SEM	Before and/or after testing	min. 1 cross-section 1 - - - -	min. 1 cross-section 1 - - 4 5	min. 1 cross-section - 2 3 4 5	min. 1 cross-section - 2 3 4 5
3	Tensile Properties	ASTM E8	Ambient temperature; 100°C-900°C (212°F-1652°F) (@ 100°C [180°F] intervals)	min. 10 specimens/ manufacturer 1 - - - -	min. 10 specimens/ weld 1 - - 4 -	min. 10 specimens/ condition - 2 3 4 -	min. 10 specimens/ condition - 2 3 4 -
4	Hardness	ASTM E92	N/A	none	none	none	none
5	Charpy V-notch Impact	ASTM E23	Full curves ambient temperature to 900°C (1652°F)	min. 10 specimens/ manufacturer 1 - - - -	min. 10 specimens/ weld 1 - - 4 -	min. 10 specimens/ condition - 2 3 4 -	min. 10 specimens/ condition - 2 3 4 -
6	J-Fracture Toughness	ASTM E1820 CT-specimens	Ambient temperature, 700°C, 800°C, 900°C (1292°F, 1472°F, 1652°F)	min. 5 specimens/ manufacturer 1 - - - -	min. 5 specimens/ weld 1 - - 4 -	min. 5 specimens/ condition - 2 3 - -	min. 5 specimens/ condition - - - 4 -
7	J-Fracture Toughness	SENT Specimens	20°C, 800°C (68°F, 1472°F) at 2 a/W ratios	min. 4 specimens/ manufacturer 1 - - - -	min. 4 specimens/ weld 1 - - 4 -	min. 4 specimens/ condition - 2 3 - -	min. 4 specimens/ condition - - - 4 -
8	Stress-Rupture	ASTM E139	Moderately High Stresses and Temperatures to produce rupture in approximately 1,000, 1,800, 3,000 hours	min. 3 specimens/ manufacturer 1 - - - -	min. 3 specimens/ weld 1 - - 4 5	min. 3 specimens/ condition - - 3 - 5	min. 3 specimens/ condition - - 3 4 5
9	Creep	ASTM E139	Low Stress Levels at Typical In-Service Temperatures to produce low strain rates	min. 2 specimens/ manufacturer 1 - - - -	min. 2 specimens/ weld 1 - - 4 5	min. 2 specimens/ condition - - 3 - 5	min. 2 specimens/ condition - - 3 4 5
10	Creep-Rupture	ASTM E139	Low Stress Levels at Above-Typical In-Service Temperatures to produce short-term strain rates	min. 2 specimens/ manufacturer 1 - - - -	min. 2 specimens/ weld 1 - - 4 5	min. 2 specimens/ condition - - 3 - 5	min. 2 specimens/ condition - - 3 4 5
11	Creep Crack Growth	ASTM E1457	800°C (1472°F), 850°C (1562°F), Stress TBD	min. 2 specimens/ manufacturer 1 - - - -	min. 2 specimens/ weld 1 - - 4 5	min. 2 specimens/ condition - - 3 - 5	none - - - - -

Table 2. Master Test Matrix relating Example Scenarios 1 through 5 to proposed tests, with minimum number of specimens required per test condition.

Primary Reformer Air-Steam Coil Alloy 800HT Tube Failure

This paper will discuss the inspection and failure analysis findings and the effects of creep and high-temperature degradation on the Alloy 800HT Air-Steam Coil tubes in a Primary Reformer Convection Section. The recommendations, including planned replacement opportunities, will also be discussed. This paper will include the benefits of proactive process monitoring, which indicated a leak in the Air-Steam Coil before turnaround, and it will further highlight the importance of conducting destructive testing within turnaround scope in aging facilities to determine root causes of failures.

Samuel Okulaja
Nutrien
Calgary, Alberta, Canada

Justin Tomkins
Nutrien
Fort Saskatchewan, Alberta, Canada

Introduction

In 2018, a major turnaround was conducted at the Nutrien Fort Saskatchewan Nitrogen Operations facility, located in Alberta, Canada.

During this turnaround, a visual inspection of the Primary Reformer Air-Steam Convection Coil found a failed tube that was significantly bulged and contained a longitudinal through-wall crack approximately 4.5 inches (114 mm) long. Destructive testing was conducted on this tube which indicated creep damage and high-temperature degradation. The Convection Air-Steam Coil tubes are alloy 800HT material and have been in service since 1993.

Background

This facility was commissioned in 1983 and produces ammonia and urea fertilizer for the Western Canadian and export markets. The site includes a nameplate 1000 metric tons per day (MTPD) Kellogg ammonia plant and a nameplate 907 MTPD Stamicarbon urea plant. Current operating capacities are 1,350 MTPD of ammonia and 1,250 MTPD of urea.

The ammonia plant's primary reforming furnace is a top-fired Kellogg design, with a modified convection section arrangement consisting of three coils in the Hot Leg: the Air-Steam Shield Coil, the Hot Air-Steam Coil (main air coil), and the Mixed Feed Preheat Coil. In the Cold Leg, there are four coils: the Steam Superheat Coil, the Feed Gas Coil, the Boiler Feed Water Coil, and the Fuel Gas Coil. See Figure 1 for details.

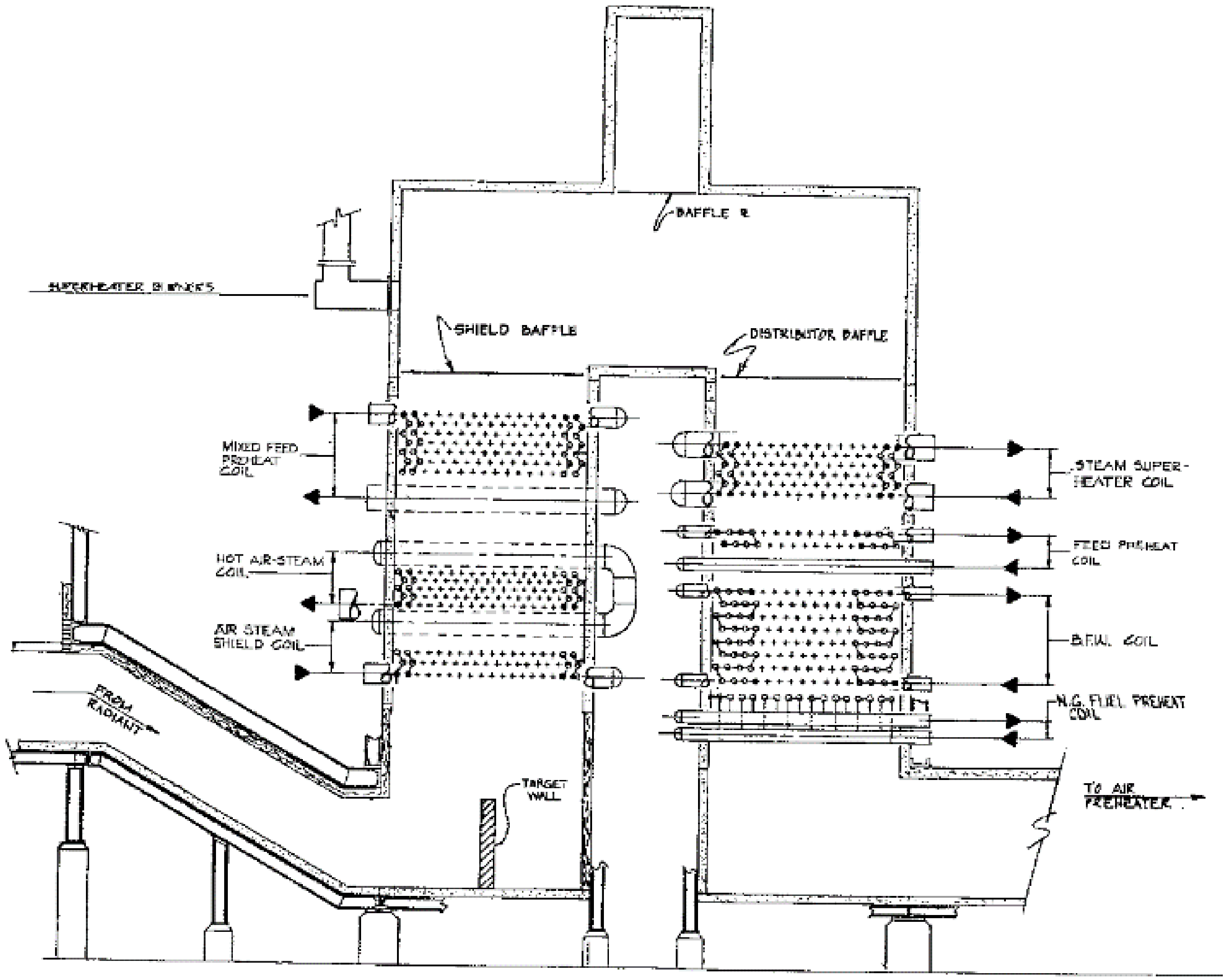


Figure 1: Primary Reformer Convection Section Layout

Similar longitudinal crack failures resulting from creep damage were previously discovered on the predecessor Hot Air-Steam Coil in 1990 and 1991. The Hot Air-Steam Coil was last replaced in 1993 when the design was modified from 5 rows to 3 rows to reduce the outlet temperature of the coil as there had been several failures at the coil outlet header.

The Hot Air-Steam Coil is designed for 575 psig (3964 kPa) at a fluid temperature of 1550°F (843°C). The coil contains 3 rows of 18 tubes per row. All of the tubes are 800HT material with a 0.66" (16.8mm) minimum wall thickness and are bare tubes (without fins). The flow pattern in this coil is counter-current, and the Hot Air-Steam Coil typically operates with a fluid inlet temperature of 950°F (510°C) and fluid outlet temperature of 1300°F (705°C). The process air-steam mixture in this coil is 95% air and 5% steam with a flow rate of 142,200 lb/hr (64,500 kg/hr).

Online Process Monitoring

During the normal operation of the Ammonia Plant, it was observed that the Process Air Compressor was running near its maximum capacity. At this facility, the air compressor often becomes a bottleneck when the plant is at high rates and the ambient conditions are warmer during the summer months. However, this situation occurred during the winter months in relatively cold ambient conditions. Process trending showed that the air demand for a fixed production rate had slowly increased over several months, as shown in **Error! Reference source not found.**.

Parameter	Normal Condition	Abnormal Condition
NH3 Production (MTPD)	1275	1275
Process Air Flow (sm^3/h)	48,000	51,500
Air/Gas Ratio	1.37	1.50
Synthesis Loop H/N Ratio	3.0	3.0

Table 1: Normal and abnormal Process Air Compressor operating conditions

Once it was discovered that the Air/Gas Ratio had been slowly trending up from 1.37 to 1.5, while the Synthesis Loop Hydrogen/Nitrogen (H/N) Ratio had remained constant at 3.0, the Operations Team began looking for potential sources of air leakage, such as at relief valves, vent valves, or drain valves. All these devices were found to be closed and not leaking. It was suspected that a leak had developed within either the Air-Steam Shield Coil or the Hot Air-Steam Coil in the Reformer Convection Section. As it was approximately 6 months until a scheduled major turnaround, the operational risk was evaluated, a decision was made to keep the plant running while some spare air coil materials were obtained, and a turnaround inspection plan was developed.

Turnaround Inspection and Repairs

Once the plant was shut down and the equipment isolated for the turnaround, a visual inspection of the process air coils was undertaken. On the top row of the Hot Air-Steam Coil, a tube had significantly bulged, and a longitudinal crack was evident, as shown in Figures 2 to 4. The failed tube was removed and sent for failure analysis as described in the next section. Measurements were taken on the remaining tubes in the top row, and it was found that all tubes displayed diametrical growth ranging between 1.1% and 3.4%, as shown in Table 2. Liquid Penetrant Inspection (LPI) was performed on the accessible welds, which revealed some minor weld defects, and these were repaired.

Figure 2: Failed tube section

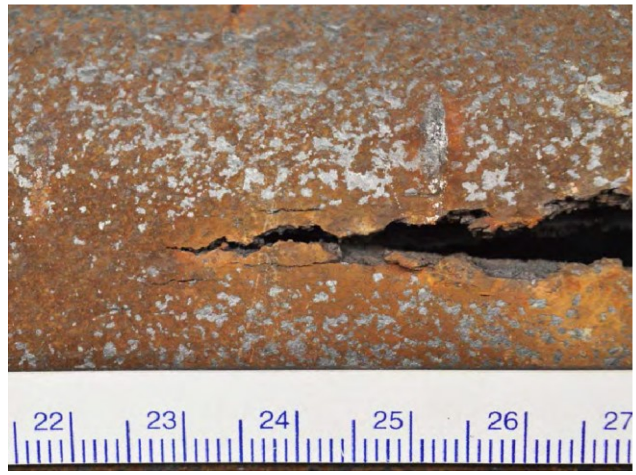


Figure 3: Close-up of the outside surface of the crack

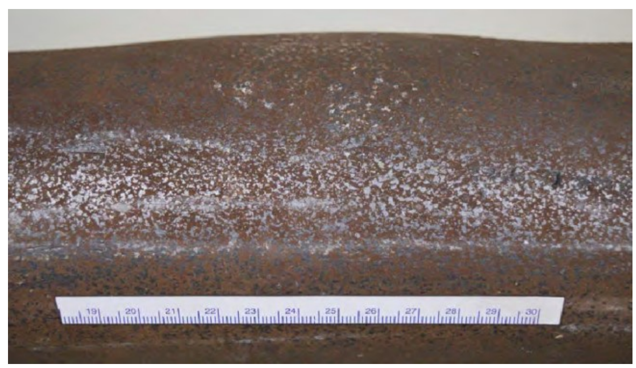


Figure 4: Bulging evident on the failed tube

In addition to the failed tube on the top row, 13 tubes had a diametrical growth greater than 2%. Since this exceeded the number of spare tubes available, it was decided that only the failed tube would be replaced at this time, and the balance of the tubes would remain in service, with a recommendation to replace the entire Hot Air-Steam Coil at the next turnaround.

Measurement Location (ft)	Tube Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
0	89	89	89	89	89	89	89	90	89		89	89	89	89	89	89	89	89
2	90	90	91	90	90	90	90.5	90	90		91	91	89	90	91	90	90	90
4	90	90	92	90	90	89	91	90	90		91	91	90	90	91	90	90	90
6	90	90	91	89	90	89	91	90	90	F	91	90	90	89	91	90	90	89
8	90	90	91	90	90	90	91.5	90	89	A	91.5	91	89	90	91	90	90.5	90
10	90	90.5	91	90	90	90	91.5	90	90	I	92	91	90	90	91	90	90.5	90
12	90	90	91	90	90	90	91	90	90	L	91	90	90	89	91	90	90	89
14	90	91	91	90	90	90	92	90	90	E	92	91	89	90	91.5	90	91	90
16	90	91	91	90	90	90	92	90	90	D	92	91	89	90	91	90	90.5	89
18	90	91	91	90	90	90	90	90	90		91	91	89	90	91	90	91.5	89
20	90.5	91	90.5	90	90	90	91.5	90.5	90	T	91.5	91.5	90	90	91	90.5	91.5	90
22	90.5	91	90.5	90	90	90	91	90	90	U	91	91	90	90	91	90	91	90
24	90.5	90.5	90	90	90	90	90	90	90	B	91	91	90	90	90	90	91	90
26	91	91	91	90	90	90	91	90	90.5	E	91.5	91	90	90	90.5	90	91	91.5
28	91	90.5	91	90	90	90.5	91	90.5	90.5		91.5	91	90.5	90	91	90	90.5	92
30	90.5	90	90.5	90	90	90	90.5	90.5	90.5		90.5	91	90.5	90	91	90	90	91.5
32	90.5	90	91	90	90	91	91	91	91		90.5	91.5	91	90	91	90	90.5	92
34	90	90	90.5	90	90	91	90	90.5	91		90	90	90	90	90	90	90	90
Max (mm)	91	91	92	90	90	91	92	91	91		92	91.5	91	90	91.5	90.5	91.5	92
Growth (%)	2.2	2.2	3.4	1.1	1.1	2.2	3.4	2.2	2.2		3.4	2.8	2.2	1.1	2.8	1.7	2.8	3.4

Table 2: Hot Air-Steam Coil top row diametrical measurement results

Failure Analysis

LPI was conducted on the failed tube. On the cracked side, the LPI identified the visible crack shown in Figure 5, while some crack-like indications were identified on the opposite side of the crack, as shown in Figure 6. The bulged cracked section was cut open for further fracture surface examination, which revealed a mid-section with multiple steps parallel to the inside diameter (ID). The fracture surfaces on the ID and the outer diameter (OD) were significantly rougher than the mid-section due to the precipitates, as shown in Figure 7.

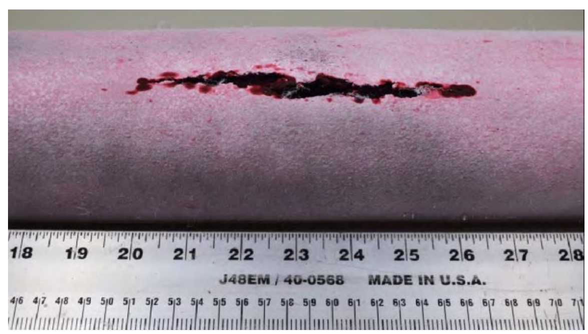


Figure 5: LPI of the cracked side

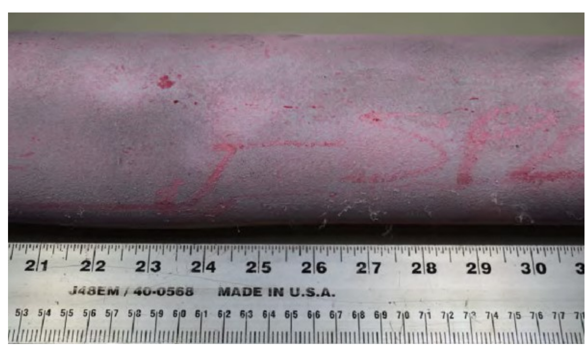


Figure 6: The side opposite the bulge had small crack-like indications

Figure 7: Close-up of the fracture. The mid-thickness area encased in the square is less rough than the other portions of the fracture

Two transverse metallographic cross-section samples, M1 and M2, as shown in Figure 8, were prepared from opposite sides of the bulged area. Multiple cracks were found on the OD. Some mid-wall cracks were observed that were not connected to the ID or OD. The tube ID had heavy precipitates with thicknesses of approximately 1.5mm (0.04 inch) for M1 and 0.9mm (0.03 inch) for M2.

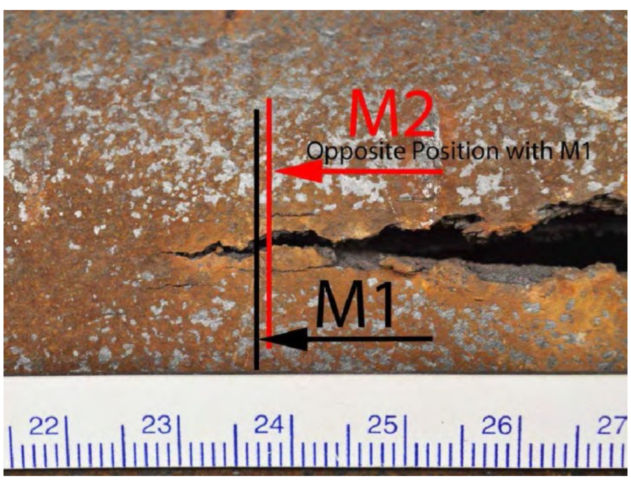


Figure 8: Transverse metallographic samples M1 and M2 were extracted from the areas identified. M2 was located diametrically opposite to M1

The main fracture was intragranular with a heavy scale and had multiple mid-wall cracks parallel to the main crack, characteristic of creep damage.

The microstructure consisted of austenite and carbides with precipitation of carbides at the grain boundaries, as shown in Figure 9. The fracture surface did not have isolated nickel filament, and therefore Stress Relaxation Cracking (SRC) was not a factor in this case since SRC is attributed to the presence of nickel filament around the deposited weld metal. Furthermore, fatigue was also not a root cause since fatigue failures are associated with transgranular cracks.

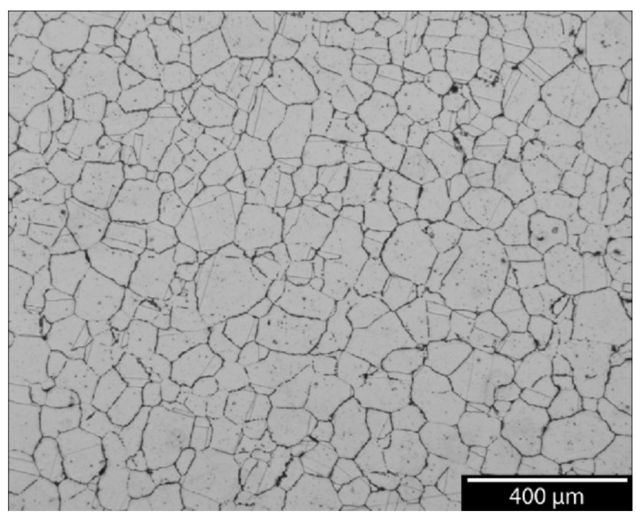


Figure 9: Sample M2 mid-wall microstructure, oxalic acid etched

The mounted and polished metallographic cross-sections were examined in a Scanning Electron

Microscope (SEM) by Backscatter Electron Detection (BSD) and Energy Dispersive X-ray (EDX) analysis. The IDs had heavily oxidized grain boundaries in both the M1 and M2 samples. The oxygen content next to the ID of M1 was significantly greater than that of the core microstructure. Larger voids were surrounded by metal with a different composition than the general structure. The darker grey zone surrounding the void indicates chromium depletion, which can be seen in Figure 10 and is characteristic of creep damage. The zones were richer in nickel and depleted of chromium towards the OD. The ID also had small precipitates with the shape of needles, which are associated with nitrides and are characteristic of exposure to high-temperature service. The sample had voids parallel to the main fracture. The OD of the samples had attacked grain boundaries and blocks of scale within the grains, which makes the material susceptible to cracking.

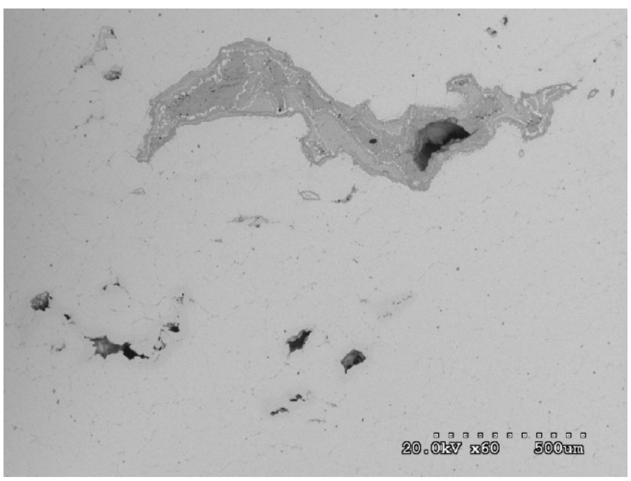


Figure 10: Sample M1 SEM image near the ID and fracture. The area surrounding the crack is chromium depleted

Hardness testing was performed on the metallographic cross-sections using Vickers macro hardness HV10/15. The results are shown in Table 3.

Sample	**Location**	**Hardness Values**
M1 (HV10/15)	~1mm (0.04") from the ID	150, 152, 161
M1 (HV10/15)	Core	112, 110, 105, 107, 102, 115, 115
M1 (HV10/15)	~1mm (0.04") from the OD	133, 137, 142
M2 (HV10/15)	~1mm (0.04") from the ID	125, 132, 129
M2 (HV10/15)	Core	117, 117, 114, 113, 107, 114, 117, 111, 114
M2 (HV10/15)	~1mm (0.04") from the OD	129, 135, 135
M1 (HV0.5/15)	<1mm (0.04") from the ID	165, 312, 343, 356, 394
M1 (HV0.5/15)	<1mm (0.04") from the OD	143, 143, 158, 161, 161
M2 (HV0.5/15)	<1mm (0.04") from the ID	149, 181, 195, 201, 262
M2 (HV0.5/15)	<1mm (0.04") from the OD	165, 169, 176, 181, 201

Table 3: Hardness results

Microhardness HV0.5/15 were performed on the ID and OD where indentations were close to the edges. The hardness values were greatest next to the ID of the failed section (as high as 394 HV0.5/15). These high values are associated with the embrittlement of the tubes and with work hardening as the tube deforms. The ID and OD hardness values of the non-failed section (as high as 262 HV0.5/15) were higher than those of the core (as an average 114 HV10/15). The core had lower values than typically expected for Alloy 800HT.

The EDX core analysis showed a chemical composition that is typical of Alloy 800HT.

The magnetic permeability of the OD of the tube was measured with a ferrite scope, and the results are shown in Table 4. These high readings in the cracked area are consistent with the nickel enrichment identified with X-ray Diffraction (XRD) toward the OD.

Location Distance	Ferrite Numbers	Comments
0”	21.4, 29.8, 24.1, 27.6, 26.4	West End
6”	23.1, 21.1, 19.6, 25.4, 26.9	
12”	24.3, 22.3, 24.7, 28.9, 30.1	
18”	32.6, 34.3, 27.8, 32.7, 35.8	
20”	24.4, 44.0, 29.0, 16.6, 42.8	
21”	19.4, 26.0, 23.3, 36.1, 36.2	
22”	45.2, 32.3, 30.3, 28.8, 37.3	
23”	22.2, 22.7, 23.6, 27.7, 22.3	Crack Center
24”	25.8, 32.2, 26.8, 21.0, 38.8	
25”	26.3, 20.1, 25.6, 27.1, 30.0	
26”	23.7, 20.6, 30.0, 21.8, 27.3	
28”	20.2, 23.5, 39.1, 26.0, 23.1	
34”	26.6, 22.7, 24.5, 39.8, 39.9	
40”	32.1, 19.3, 20.0, 18.1, 29.6	
46”	17.6, 21.2, 20.3, 18.0, 19.1	East End

Table 4: Ferritescope magnetic permeability measurements

The expansion of the tube was measured using π tape. The results indicated that the expansion was greater than 2.5% throughout the failed tube section, as shown in Table 5.

Location (inches)	Diameter (inches)	Expansion (%)	Comments
0	3.62	3.4	West End
6	3.62	3.4	
12	3.63	3.7	
18	3.63	3.7	
20	3.64	4.0	
21	3.68	5.1	
22	3.71	6.0	
23	3.72	6.3	Crack Center
24	3.70	5.7	
25	3.67	4.9	
26	3.63	3.7	
28	3.63	3.7	
34	3.61	3.1	
40	3.59	2.6	
46	3.59	2.6	East End

Table 5: Failed tube diameter measurements

Planned Replacement

Based on the failure analysis confirming the failure modes of the tube as creep and high-temperature degradation, which are time-dependent damage mechanisms, a capital project was initiated to replace the Air-Steam Shield Coil, Hot Air-Steam Coil, and Mixed Feed Coil. The Air-Steam Shield Coil requires replacement as it operates in similar conditions and is similar to the failing Hot Air-Steam Coil. The Mixed Feed Coil requires replacement as the end tubesheet refractory is damaged and difficult to repair, and it is more efficient to replace it in conjunction with the 2 coils below it. The inspection findings from the turnaround also necessitated the future replacement of the Radiant Section Catalyst Tube Harps. Therefore the scope of the project became a complete Reformer Revamp to meet the current and future reliability and process requirements of the plant. The revamp is scheduled to be executed in 2023, five years after this failure on the Hot Air-Steam Coil.

Conclusion

The integrity of Convection Coil tubes is vital to the continued operations of Primary Reformers. It is very important to schedule and conduct inspections of these tubes during turnarounds to ascertain their integrity. Alloy 800HT has proven to be an excellent material for this service, however, over a prolonged period, this material is susceptible to creep and high temperature degradation. Aging facilities should plan for replacements based on inspection and metallographic examination results.

Combatting Corrosion in the Fertilizer Industry

This article discusses case studies illustrating common forms of process equipment damage in the fertilizer industry and the inspection and non-destructive testing (NDT) techniques used to identify them: In all cases, competent, skilled personnel monitoring the equipment identified the damage before it became critical, and they used the inspection results to address the underlying problems.

Ana Benz, Matthew Bell
IRISNDT

Introduction

The fertilizer industry has varied and challenging processes: it requires corrosion-resistant materials at low and high operating temperatures.

Failures are prevented by using specialized mechanical design and materials. However, substantial corrosion and cracking damage can occur due to:

- Unforeseen contaminants,
- Severe service,
- Service condition changes,
- Material characteristics not covered in basic specifications, and
- Effects of long term service.

Vigilant inspections are essential since fertilizer processes can develop dangerous leaks and potential explosions.[1]

Chlorides Are Pervasive and Cause Damage

Austenitic stainless steel equipment is common in fertilizer plants. In the presence of chlorides and precipitated water, austenitic stainless steel can develop pits and stress corrosion cracks (SCC).[2] Pressure and residual stresses provide the tensile stress needed for the cracks to develop. The contaminants can have unexpected sources, as exemplified below.

The failed heat exchanger tube shown in Figure 1 had been in steam service for less than one year. Steam arriving directly from the power plant heated the tube outside diameter (OD) surfaces. The Liquid Penetrant Testing (PT) results in Figure 2 highlighted multiple branched cracks on the tube OD.

Figure 1. Failed austenitic stainless steel tube from a steam heat exchanger

Figure 2. Color contrast PT results

A metallographic cross-section through the 0.035 inch (9 mm) thick tube wall shows numerous cracks, see Figure 3. The cracks initiate from pits on the OD surface. The multiple, branched, transgranular cracks are characteristic of chloride stress corrosion cracking in stainless steel. Chlorides could not be readily identified on the fracture surfaces or in the cracks using Energy Dispersive X-ray (EDX) analysis. However, chlorides rinse out easily during the washing (e.g., to handle and ship the tubes as part of the PT procedure).[3]

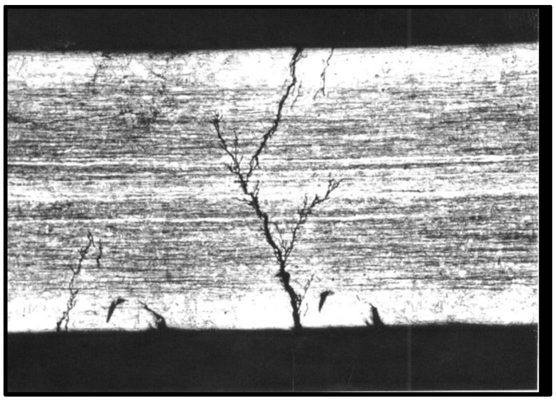


Figure 3. Metallographic cross-section of the austenitic stainless steel tube from the steam heat exchanger.

The investigation revealed that the make-up water for the steam had not been properly treated, and it contained chlorides. Since this heat exchanger was the first location downstream of the power plant, the chloride content was greater than for locations further downstream.

Austenitic stainless steel pressure components require vigilant chloride content control and inspections.

Pitting Attack of Austenitic and Duplex Stainless Steel Tubes

Corrosion often results in either generalized or pitting losses. Of these two, pitting corrosion can be more difficult to manage since it is more isolated and can be difficult to identify. As well, it can result more quickly in a leak. Should one manage pitting by changing the process conditions or the material? Changing the process is not easy. However, as illustrated below, battling pitting by changing materials is not simple.

Type 304L stainless steel condenser tubes in a fertilizer plant had developed pits and cracks on the OD shell side after several years of service (see Figure 4). The tube OD was exposed to cooling water below 260°F (130°C). The cooling water contained chlorides and chlorinated compounds. The OD had pits and multiple transgranular cracks typically associated with chloride SCC in austenitic stainless steel (see OD on the left side of Figure 5).

Figure 4. Type 304L stainless steel condenser tube with pits and cracks.

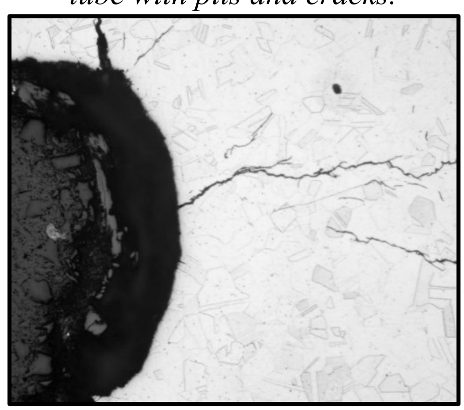


Figure 5. Type 304L stainless steel condenser tube pit and transgranular chloride SCC.

A new tube bundle with SAF 2304 duplex stainless steel was used to replace the Type 304L and prevent similar damage. SAF 2304 has a higher Pitting Resistance Equivalent Number (PREN) than Type 304L: 24 versus 18.[4] However, four years later, the SAF 2304 tubes had also developed pits (see Figure 6). Metallographic cross sections showed that the ferrite phase (orange in the KOH etch shown) was selectively attacked, while the austenite (white) was not (Figure 7). The pit was also examined with a Scanning Electron Microscope (SEM). The SEM showed a selective phase attack at the bottom of the pit (see Figure 8).

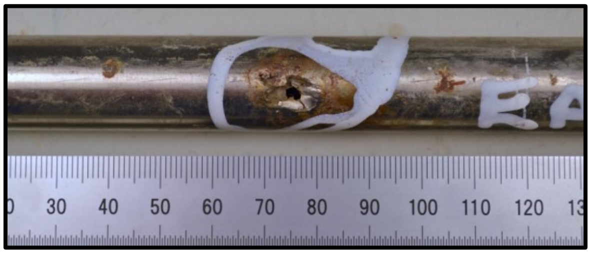


Figure 6. SAF 2304 duplex stainless steel condenser tube with externally initiated pits.

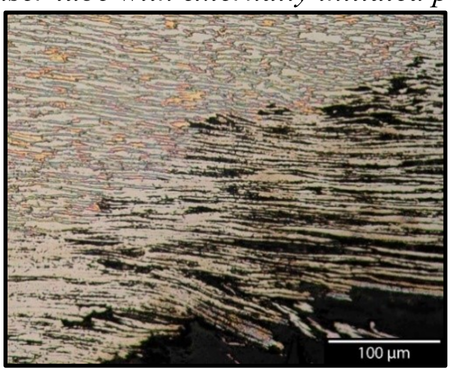


Figure 7. Selective phase attack of the ferrite phase in SAF 2304 duplex stainless steel condenser tube, KOH etch.

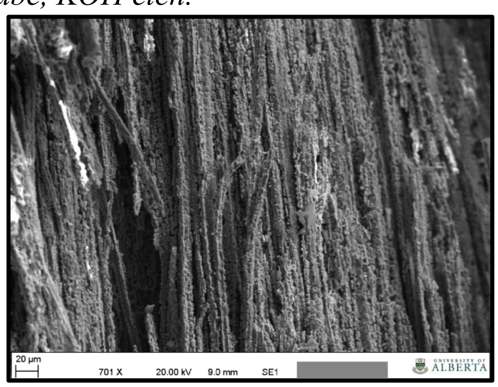


Figure 8. SEM image of selective phase attack of the ferrite phase in SAF 2304.

Finally, SAF 2507 tubes with a PREN of 42 were used, and the failures stopped. The pitting resistance equivalent number (PREN) is an excellent indicator of stainless alloys' pitting resistance in environments with chlorides. Duplex alloys have superior ESC resistance to austenitic alloys with similar PREN. However, the PREN determines the pitting resistance.

Corrosion under Insulation

Corrosion under insulation (CUI) is an insidious challenge to the integrity of fertilizer insulated equipment – even inland in the dry prairies.[5] CUI has been occurring ever since the industry started insulating equipment.[6] Why does CUI develop? Insulation provides[7]:

- An annular space or crevice for the retention and wicking of water and other corrosive media.
- A material that may contribute to contaminants that increase the corrosion rate.

Figure 9 illustrates a common condition for piping and equipment: wet insulation. The wet insulation was identified on the bottom side of the pipe with computed radiography. The installation details for insulation and cladding (jacketing) are often overlooked – frequently one of the last tasks before putting equipment into service. While the wet insulation may not immediately damage the steel beneath, with time, it is likely to lead to CUI.

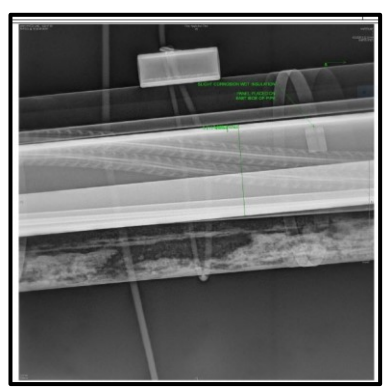


Figure 9. Computed Radiography image showing wet insulation on the bottom side of the pipe.

Figure 10 illustrates CUI in the form of widespread pitting damage in austenitic stainless steel pipe in a fertilizer plant. The pits were a consequence of wet insulation and chlorides, possibly from aged insulation. Figures 11 and 12 illustrate CUI in the form of chloride stress corrosion cracking in an 304L austenitic stainless steel thermowell. As the insulation aged, the inhibitors in the insulation surrounding the thermowell degraded, leading to the chloride-based damage shown.

Figure 10. External Pitting due to CUI on Type 304/304L stainless steel NPS 3 pipe

Figure 11. Penetrant Testing (PT) of thermowell with chloride stress corrosion cracking.

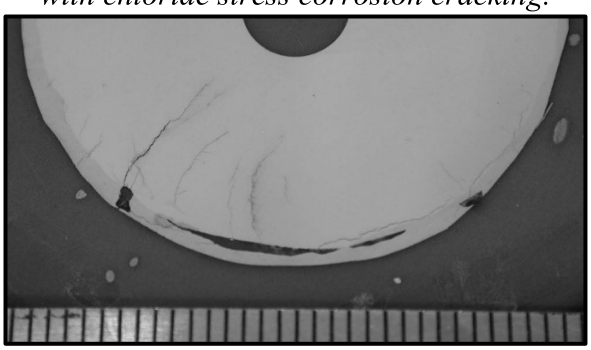


Figure 12 Metallographic cross-section of cracked 304L NPS 1 stainless steel thermowell.

While not shown, refrigerated lines should also be a focal inspection point in fertilizer plants. Key drivers to these CUI failures are cyclic icing and deicing due to intermittent operation or the presence of condensation in favorable ambient conditions. The consequences are well illustrated in a Dow Chemical Report.[8]

Crevice Corrosion Can Occur even in Commercially Pure Titanium (CP-Ti) Tubes

Commercially pure titanium is well known as a highly corrosion resistant material. However, like many other materials in the fertilizer industry, it can develop localized galvanic corrosion.[9] Crevice corrosion, a form of localized corrosion, can progress wherever two surfaces are close, and process fluids cannot be easily refreshed. A crevice is prone to corrosion between the outer surface of a tube and the inner surface of the tubesheet opening. Crevice corrosion losses in this type of equipment are exemplified below.

CP-Ti tubes in a heat exchanger developed leaks after almost ten years of service. The carbon steel tubesheet was clad with CP-Ti; the titanium cladding was on the channel side of the tubesheet. The CP-Ti tubes were rolled into the tubesheet, and seal welded to the CP-Ti cladding. The shell side process fluid was cooling water. The tube side temperature was below 400°F (200°C), and the shell side temperature was below 70°F (20°C).

The carbon steel tubesheet had deep losses found behind removed tubes (see Figure 13). The tubes leaked from through-wall pits; the tube pits progressed from the tube OD surface (see Figure 14). The pits developed between the tube-to-tubesheet seal weld and the first tube groove (i.e., a crevice). The tube OD surface had orange scales.

Figure 13. CP-Ti clad carbon steel tubesheet channel face and a location where a commercially pure titanium tube was removed.

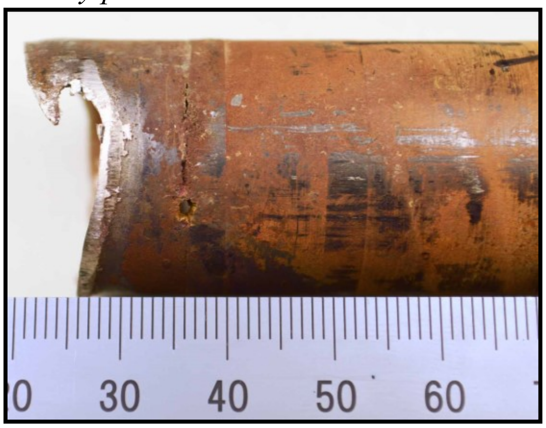


Figure 14. CP-Ti tube OD surface with through wall holes and bright orange scale.

The pits were steep, narrow, and tended to tunnel (see Figure 15). The orange scale on the tube OD was rich in iron and oxygen, consistent with the corrosion scale from the carbon steel tubesheet. The scale EDX spectrum identified a significant iron peak and smaller peaks consistent with other process contaminants (see Figure 16).

Figure 15. The CP-Ti tube pits are steep, narrow, and tend to tunnel. Kroll's Reagent Etch.

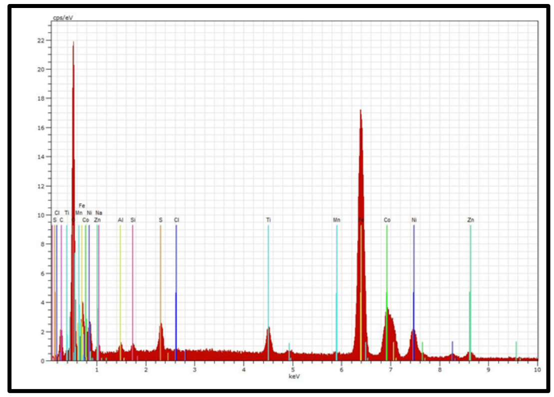


Figure 16. Energy Dispersive X-ray spectrum of the corrosion scale inside the through wall pits.

The orange scale is a corrosion product from the mild steel tube sheet. The pits are visible about 10 mm from the cut surface on the left. The CP-Ti tube failed due to the crevice conditions created between the carbon steel tubesheet and the titanium tube. Crevice conditions were particularly aggressive, and the iron corrosion products introduced galvanic effects that promoted further titanium crevice corrosion.[10,11] Flaws in the sealing tube-to-tubesheet welds likely allowed aggressive process fluids to enter the crevice between the tubes and the tubesheet. These welds require monitoring, refurbishments, and replacements during the exchanger's downtime.

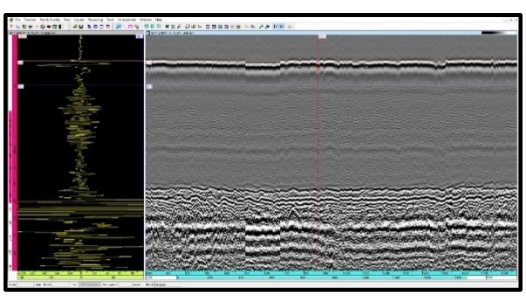
High Temperature Hydrogen Attack (HTHA)

Carbon steel and C-0.5Mo steel piping and vessels in ammonia and methanol plants are susceptible to HTHA. Though HTHA damage is minute, its consequences can be deadly such as the failure that caused the death of seven refinery workers during the 2010 Tesoro Anacortes Refinery Disaster.[12]

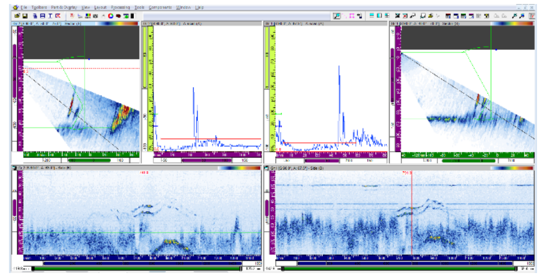
Identifying HTHA damage is challenging. Some NDT methods for identifying HTHA damage are best for examining base material, pipe to pipe, and plate to plate butt joints. However, different testing methods are better for inspecting nozzle and fitting joints.

Several techniques used to spot HTHA are:

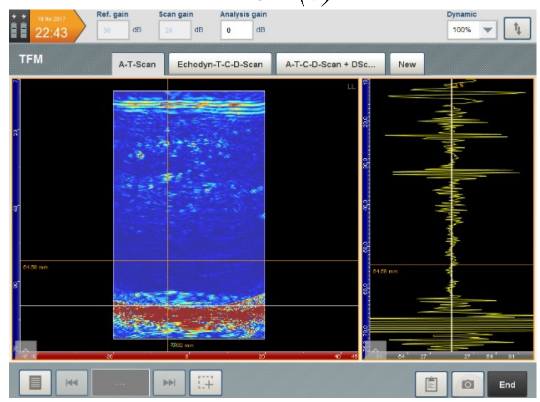
- Evolving advanced ultrasonic testing techniques. Time of Flight Diffraction (TOFD), Beam Forming Phased Array Ultrasonic Testing (PAUT), Total Focusing Method (TFM), and TOFD Ultra-low Angle (TULA) are now the industry accepted techniques for the early detection of HTHA. Third-party trained and certified technicians apply these techniques after training with real-world HTHA flawed samples. The samples are the fruit of extensive industry cooperation and research.[13,14] Industrial equipment HTHA damage identified by such personnel is illustrated in Figure 17. The new techniques have largely replaced Advanced Ultrasonic Backscatter Technique (AUBT). Nevertheless, ultrasonic backscatter is still a useful confirmation technique.
- Highly sensitive Wet Fluorescent Magnetic Particle Inspection (MT) of internal locations: a polished surface finish is required.
- In-situ metallography also called replication. This technique is used to monitor for HTHA during turnarounds. Metallographic replication is both an art and a science. The metal surface is carefully polished to a mirror finish and etched with chemicals. Soft plastic tape captures an impression of the metal structure. The tape is examined under a microscope. This inspection is exemplified below.



TOFD (a)



PAUT (b)



TFM (c)

Figure 17. Images of HTHA damaged steel pressure equipment from three advanced ultrasonic testing techniques

A carbon steel weld root in hydrogen reformer gas piping was inspected during a planned outage. The customer had chosen to inspect this weld root as a potential HTHA location based on their knowledge of the process. Replication verified that the root had a crack that appeared to be due to HTHA (See Figure 18). This replica was prepared before etching the material. Preparation artifacts are visible diagonally; replica artifacts are also visible (pale white streaks).

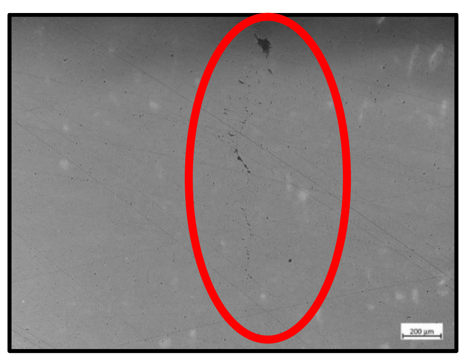
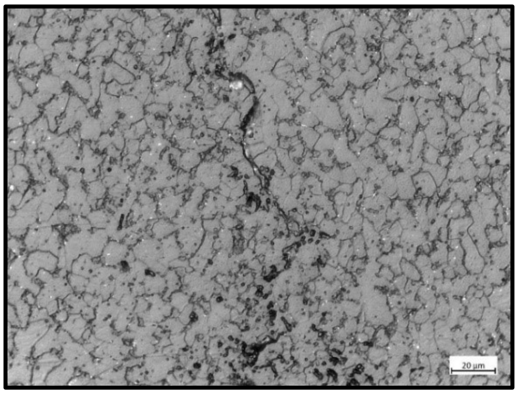
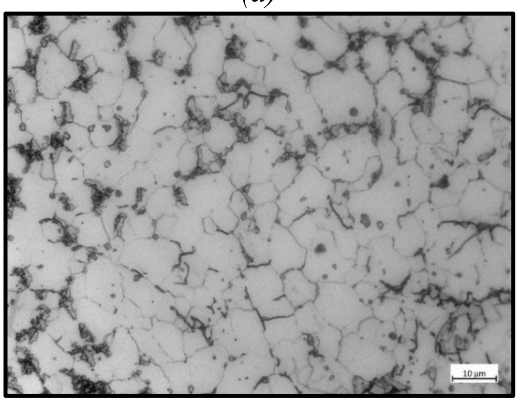


Figure 18. In-situ metallographic replication of HTHA suspect carbon steel weld root showing a small crack (within red ellipse).

The customer cut out the suspect piping and weld root for laboratory analysis. A metallographic cross-section through the indication showed the characteristic fissures and decarburization associated with incipient HTHA (see Figure 19). The carbon steel piping will be replaced with low alloy piping. Low alloy steel, with chromium additions, is more resistant to HTHA in this service.



(a)



(b)

Figure 19. Laboratory metallographic examination of suspect carbon weld root, 2% Nital etch.

Stress Relaxation Cracks

Stress Relaxation Cracks (SRC) develop in steam methane reforming (SMR) lines due to the pipe's chemical composition and the high temperature operations.[15] The cracks (microscopic as they initiate) grow at grain boundaries that tend to be weaker than the surrounding material at high temperatures. SRC occurs at high temperatures and is usually associated with high stresses (for example, residual stresses next to welds). SRC is exemplified below.

During a planned outage, PT on the Alloy 800H reformer outlet piping found extensive indications (see Figure 20). The cracks occurred next to the welds in large diameter piping. Cracks in this large diameter stainless steel piping can lead to explosions. Repairing these cracks became the critical path for the outage.

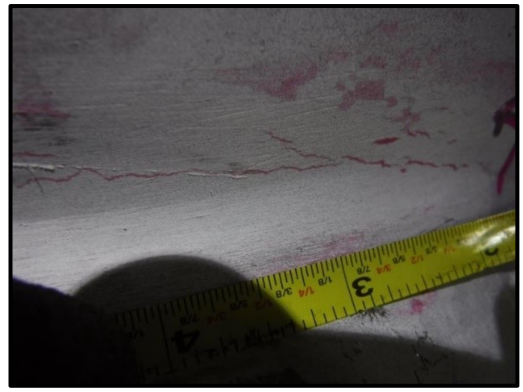


Figure 20. PT indications of SRC in Alloy 800H reformer piping next to weld cap

In-situ metallography was used to replicate the indications (see Figures 21 and 22). The indications had the halo and filament characteristic of SRC. In this instance, these cracks were removed by grinding, and then the material was replaced by weld repair. The removal of the cracks was verified with repeat applications of PT and metallographic replication. Nevertheless, with more time in service, these repairs will also be susceptible to more cracks. Previously repaired locations also had evidence of incipient damage. The customer has planned to replace the piping.

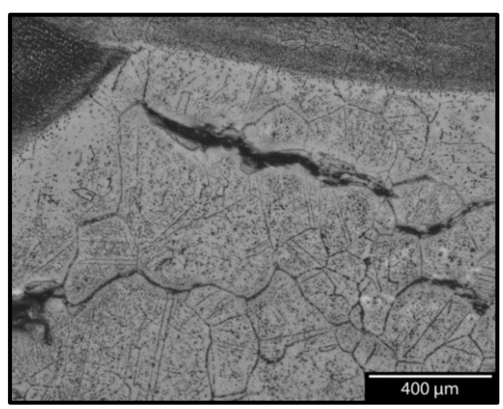


Figure 21. Replicated alloy 800H piping, 10% oxalic acid etch

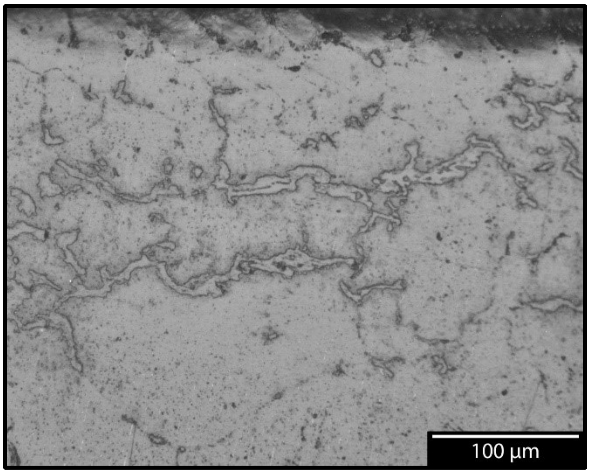


Figure 22. The replicated areas next to the weld have multiple intergranular features, 10% oxalic acid etch.

Industry understanding of SRC is improving as more research and identification of the mechanism occurs. API TR 942-B contains significant industry learnings about material susceptibility, design considerations, and heat treatments to mitigate SRC damage.[16]

Challenges when Welding New High Temperature Hydrogen Equipment

For the high temperature components used in the fertilizer industry, the basic specifications in standards may not be sufficient to purchase the right equipment. An example of this instance is given below.

Radiographic tests of a newly welded Type 347H fitting identified cracks. Equipment reliability was essential since it carried high pressure hydrogen. The full investigation identified that the cracks were due to hot cracking[17,18] (sometimes referred to as Constitutional Liquation) in the heat affected zone (HAZ) of the weld. The fitting grain sizes were coarse enough to be visible without using a microscope (see Figure 23). The prepared area in the figure is approximately 3 inches long by 1 inch wide (76 mm long by 25 mm wide). The fitting has austenite grains visible without a microscope (see red ellipse). The intergranular cracks were associated with these very coarse austenite grains (ASTM grain size ≤ 1) (see Figure 24). The deposited weld metal is on the top of the image. The cracks developed before the part went into service.

Figure 23. Type 347H cracked fitting with weld cap polished and etched, 10% oxalic acid etch.

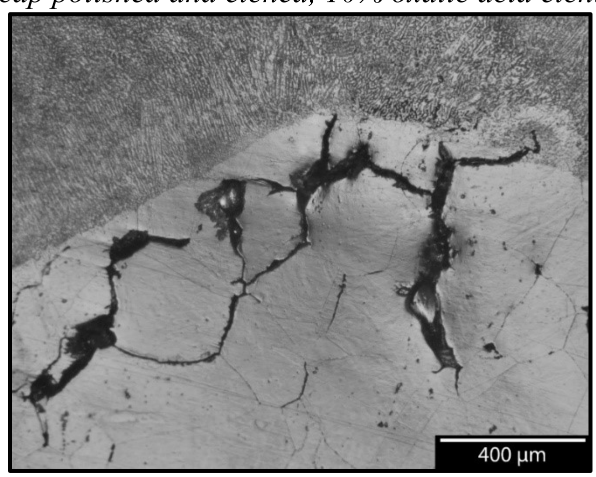


Figure 24. Type 347H cracked fitting with HAZ intergranular cracks. 10% oxalic acid etch.

The forged components and fittings were purchased as fabricated to meet ASTM A182 F347.[19] According to the standard, the forged components and fittings would have been subjected to a "solution treat and quench" as part of fabrication. Therefore, per the standard, the fittings need not have been solution annealed; properly applied solution annealing dissolves all secondary phases.[20] The fittings had anomalous grain size distributions and highly variable microstructures from one location to another. The Type 347H components with coarse grains were annealed at excessive temperatures for excessive hold times, leading to excessive grain growth and the formation of low melting point niobium carbide eutectics. The eutectics resulted in liquation cracking in the weld HAZs.

The coarse grains and networks of large precipitates make these weld HAZs prone to develop Stress Relaxation Cracking in the future.[21,22,23] Also, the high-temperature service could make the material significantly more difficult to repair as it ages (due to the continuing coarsening of precipitates and the formation of metallic filaments within the cracked grain boundaries). Note that cracking could be worse on the inside diameter (ID) process side of the welds since the ID was subjected to more heat cycles during welding than the accessible outer diameter (OD).

More than 1200 metallographic replicas were used to assess about 700 Type 347H components. Of the about 700 components replicated, approximately 30% had grains coarser than ASTM 3, and 20% had grains finer than ASTM 7. The components with grains coarser than ASTM 3 were segregated from the finer grained material. Figure 25 shows a typical metallographic replica.

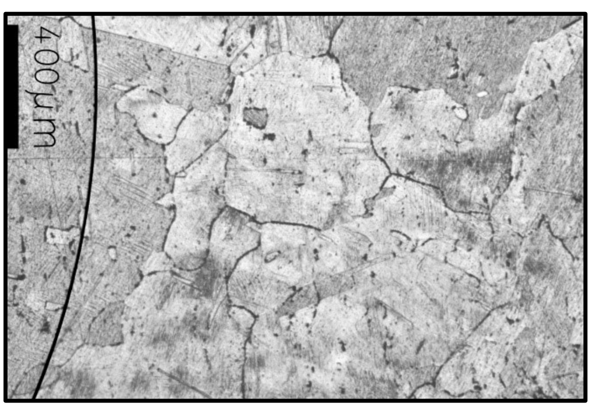


Figure 25. Type 347H Fitting replica microstructure, 10% oxalic acid etch.

Summary

In the fertilizer industry, new and aging process equipment need diligent inspections to combat corrosion and cracking. The consequences of failure can be disastrous. Experienced personnel is needed to assess the risks, and skilled inspection personnel using the appropriate NDT methods are needed to identify the damage.

Acknowledgements

The authors would like to thank Simon Butler (IRISNDT) for his great HTHA ultrasonic wisdom and images. Other colleagues also contributed to the images shown. We also thank understanding customers who have shared their findings with the industry through this article. Finally, we thank the IRISNDT management for their support.

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Reformer Operation Improvements Based on Inspection Data

Steam reformer catalyst tube inspection technologies are well established. Typically, the data arising from such inspections is assessed qualitatively to enable engineering judgement as to the fitness for continued service. However, behind these inspection data lies a wealth of information providing invaluable insight as to the health of the furnace over and above the initial replace or run decision. This paper provides describes a case study illustrating how analysis of inspection data can lead to recommendations to change operating practice and/or furnace design. In this case, inspection was undertaken using creep strain in the form of diameter growth as the primary indicator of damage.

Tim Hill
Quest Integrity USA, LLC

Alice Young, Charles Thomas
Quest Integrity NZL Ltd

Introduction

Managing steam reformer catalyst tube integrity is a critical part of ensuring safe and reliable reformer operation. Given that the output of the reformer is often a key determining factor for downstream production rates, reformer issues can also lead to problems for overall plant reliability. Progressive creep damage is the primary threat to catalyst tube integrity, with tube lifetime being determined by the rate of damage accumulation. This in turn is determined by the reformer operating conditions. Given the costs associated with replacing even a single catalyst tube, which can quickly run into the millions of dollars due to the necessary plant downtime, being able to predict tube lifetime and plan replacements in a way that will minimize these costs is extremely valuable for plant operators. Tube design lifetimes are rarely valid for the actual in-service conditions experienced, so inspection of catalyst tubes to monitor creep damage rates and predict actual remaining life plays a critical role in this.

Fundamentally, creep is a time- and temperature-dependent damage mechanism that causes permanent deformation. On a microscopic scale, damage is characterized by the formation of voids and cracks, typically at grain boundaries, which coalesce and/or grow over time. Macroscopic dimensional changes also occur and can be detectable even before significant void and crack formation. In reformer catalyst tubes, the primary dimensional change is an increase in tube diameter, due to the hoop stress from internal pressure being the dominant tensile stress acting. Established inspection methods for identifying creep damage include both flaw detection techniques such as eddy current, and diametric inspection for measurement of dimensional changes. Regardless of methodology, the goal of inspection is to enable a judgement to be made on the level of damage and the fitness-for-service of the catalyst tube.

However, high-quality tube inspection data can also contain a wealth of information about the reformer furnace. For example, it is possible to identify catalyst issues, problems with individual burners, even operational practices that have led to tube overheating. In this paper, we describe how analysis of catalyst tube inspection data can go beyond the typical fitness-for-service assessment and present a case study that illustrates how this can lead to recommendations for improved reformer operation. We focus on the use of diametric growth data as the primary indicator of damage and as a source of further information about the reformer as a whole.

Extracting Operational Information from Inspection Data

At the most basic level, tube inspection data can be used to make a qualitative judgement on whether the level of damage in a tube means it is fit for continued service, or it should be replaced. However, standards such as API 579-1/ASME FFS-1 (API 579-1) [1] provide methods for more quantitative assessment of damage and remaining life. These methods provide a starting point for extracting the operational information embedded within tube inspection data. For components subject to creep, creep strain and remaining life are calculated from operating temperature and pressure data using a material creep property model, but if measured strain data is available this can instead be used to back-calculate one of these variables. For reformer catalyst tubes, tube metal temperature is typically the greatest source of error, and it has been estimated that the uncertainties associated with on-line temperature measurement can lead to variations in remaining life predictions of -75% to +300% [2]. This is a significant level of uncertainty, meaning it is preferable to back-calculate tube metal temperature whenever possible.

However, it is important to recognize that the ability to accurately determine tube temperature from strain data is dependent on having a reliable material creep property model. For many alloys, a Larson-Miller or Omega model that assumes creep properties do not change over time in service is sufficient, and such models are provided in API 579-1 [1] and the API 530 tube design code [3]. Unfortunately, the creep behavior of the HP alloys typically used for catalyst tubes cannot be modelled using these approaches. HP alloys undergo aging during service, which results in significant microstructural changes and a decrease in creep strength over time [4]. There is no commonly accepted creep property model for these alloys, but that does not mean that a model does not exist. Over a decade ago, Quest Integrity (formerly Quest Reliability) developed a proprietary creep test database for aged and as-cast catalyst tube materials, from which a property model that captures the influence of aging on creep strength was created [4], [5]. This model has been validated through both laboratory experiments and application to hundreds of thousands of catalyst tubes in service, and is the cornerstone of Quest Integrity's LifeQuest Reformer™ methodology and software package for fitness-for-service and remaining life assessment of catalyst tubes.

The basic principle of the method used for determining tube metal temperature and predicting remaining life using this model is illustrated in Figure 1 and described as follows:

- Tube diameter data from the inspection is compared to the baseline (pre-service) diameter to identify growth and determine strain at a known point in the tube's lifetime. If no measured baseline is available, it can be estimated with a good level of accuracy by using the diameter at the inlet end of the tube as a reference. The inlet end of a catalyst tube typically experiences relatively low temperatures during service, meaning negligible creep growth occurs at this location.
- An effective tube metal temperature is back calculated by identifying the unique creep strain curve that best predicts the amount of strain in the tube at that point

in time. These curves are predicted by the material creep property model for a given stress, and temperature is varied to find the best match for the inspection data. Multiple inspection datasets can also be accommodated by effectively stitching together a sequence of partial curves.

- A threshold failure strain is specified, and the creep curve defined by the effective temperature is extrapolated out to this point. The predicted time from the inspection to the point where the failure strain is reached is then considered the remaining life of the tube. Note that this is dependent on the assumed future operating conditions.

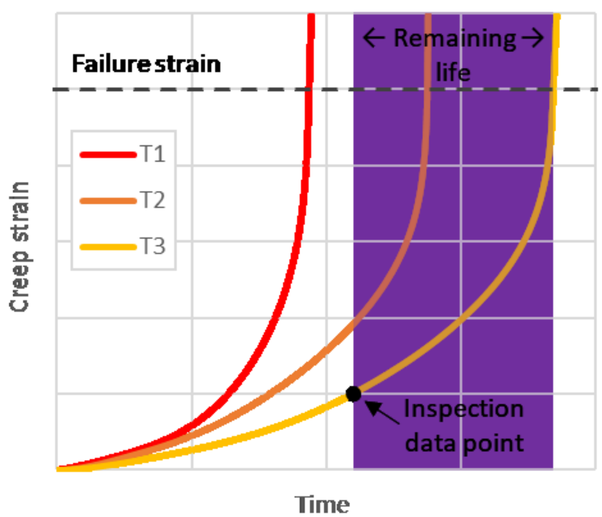

Figure 1: Illustration of back-calculation of effective tube metal temperature from measured creeps train and remaining life prediction.

It is important to be aware that the effective temperature is a single temperature that would produce an equivalent amount of strain over the time period considered – given that inspection intervals are typically on the order of years, it is not possible to capture every small transient. For a reformer operating relatively constantly under normal conditions, the effective temperature has been found to correspond well to the actual average on-line tube metal temperature. Deviations in the effective temperature indicate that there has been a discernible change in growth rate at some point during the time period considered and are therefore a key indicator of abnormal operating conditions. At a basic level, this can be used to identify patterns or anomalies in the overall temperature distribution across the reformer. At the highest level of assessment, provided the raw inspection data is of sufficient resolution, this methodology can be used to generate a full-length temperature profile for each tube, from which localized abnormalities such as hotspots on individual tubes can be detected.

Data Interpretation

Tube temperature profiles are extremely useful, but the ability to identify reformer operational issues from catalyst tube inspection data also relies on understanding the growth patterns that result from normal operation, and how these can be affected by external factors such as catalyst condition or burner control. Under normal conditions, tube metal temperature typically increases from inlet to outlet. This is primarily due to the endothermic nature of the reforming reaction, and the change in the driving force for reaction as the process gases move through the catalyst tubes. Near the inlet end of a tube, there is a strong driving force due to the high proportion of reactants in the process fluid. This causes a high rate of reaction and a large amount of heat absorption, which cools the catalyst tube. Moving towards the outlet, driving force decreases as the proportion of reactants decreases. At the outlet end of the tube, reaction rate and therefore the amount of heat absorbed is at a minimum, resulting in the highest tube metal temperatures. Given that higher temperatures will cause a greater rate of creep growth, a "normal" tube diameter profile is expected to show very little growth near the inlet end of the tube and a maximum in growth near the outlet. The temperature gradient is tempered by the fact that there is a pressure drop from the inlet to the outlet, decreasing the hoop stress in the tubes, but the temperature effect generally dominates creep growth rates. Example temperature and diameter profiles expected under normal operation are shown in Figure 2.

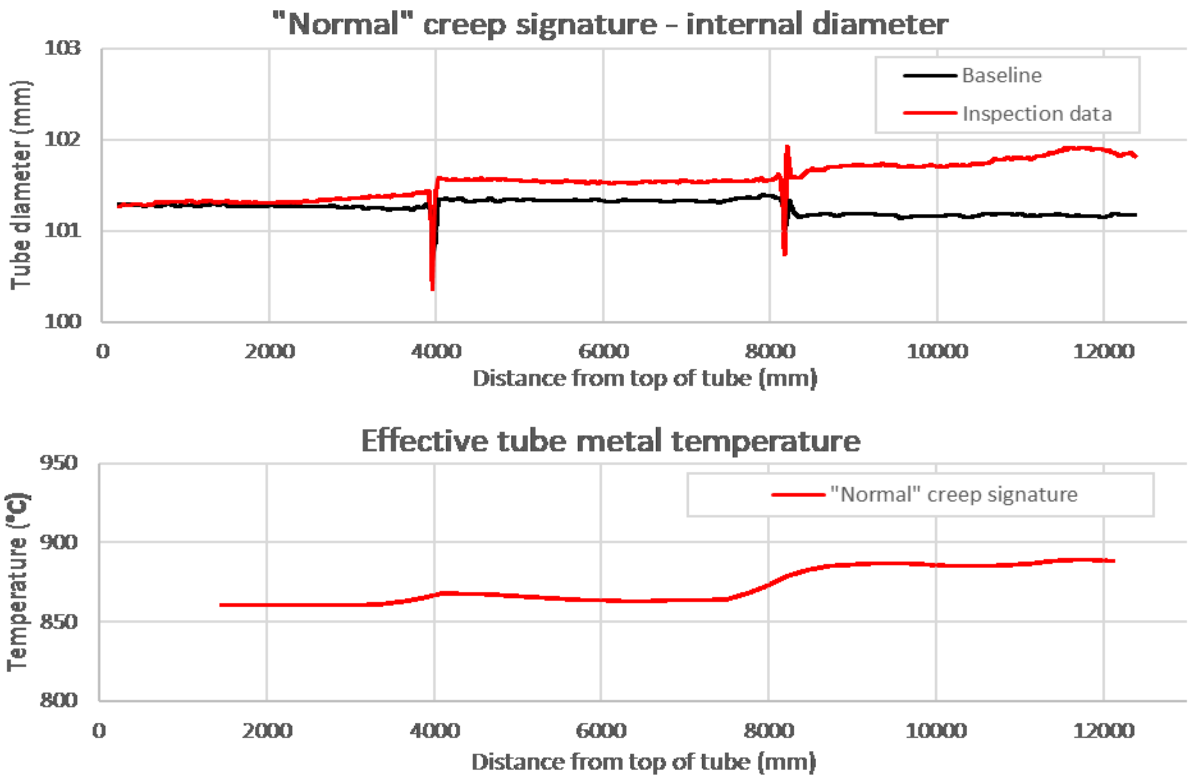

Figure 2: Example of a "normal" creep strain signature and corresponding effective temperature

In steam reformers, temperature typically plays the largest role in determining creep growth rates in the catalyst tubes, so abnormal growth patterns are most commonly caused by events or operating conditions that cause deviation from what is considered a normal temperature. There are a range of different ways this can happen in a reformer, but most leave a specific signature in terms of the growth patterns they produce. Some examples are described below, with accompanying illustrations provided in Figures 3**Error! Reference source not found.**-5.

Example 1: Furnace Balancing

In a reformer with a terrace-wall burner configuration and two rows of 78 catalyst tubes each, mapping of strain levels and calculated effective temperatures indicated that the tubes at the ends of the rows were experiencing higher temperatures and therefore higher rates of creep growth than those in the center of the rows, see Figure 3. This pattern indicated that the balancing of the furnace was not optimal, and some adjustment of the end burners was required to reduce the temperature of the end tubes. A re-inspection two years later showed that the adjustment had successfully improved the balancing of the furnace, and damage rates and tube metal temperatures were more uniform across the reformer.

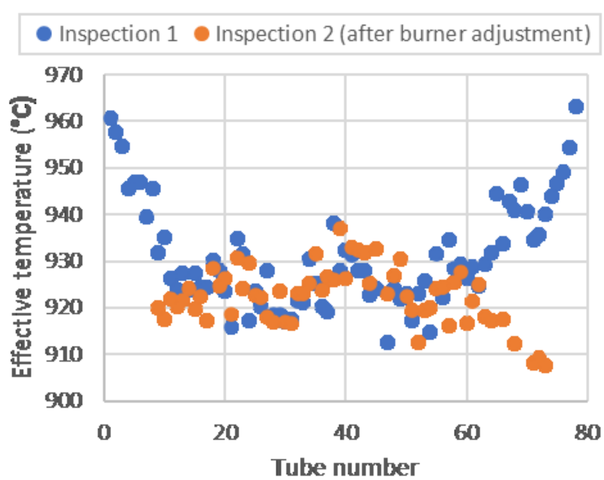

Figure 3: Effective tube metal temperature distribution along one row of the reformer before

and after balancing. Note that some of the end tubes were replaced between inspections.

Example 2: Burner Impingement

A top-fired reformer with three rows of 40 tubes each was inspected. Tube growth data and calculated effective temperatures indicated that a small cluster of tubes were experiencing abnormally high temperatures in the upper sections of the tubes, with one tube at the center of the cluster being particularly affected, Figure 4. The pattern of damage and the proximity of the cluster of tubes to a burner pointed to burner impingement. A subsequent inspection of the burner concerned found that the tip was eroded, which had allowed flame impingement on the nearby tubes.

Example 3: Internal Fouling

An internal inspection was undertaken on a small 32-tube reformer six years after the initial baseline inspection. The data showed areas on multiple tubes where the tube diameter had apparently decreased over this period, Figure 5. It is not possible for the internal diameter of catalyst tubes to decrease during service; instead, the inspection was detecting deposits or fouling on the internal surface of the tube. The reformer was known to operate at a low steam-to-carbon ratio, so it was believed that carbon deposition was the most likely cause. The effect of this was visible in a second inspection two years later: underneath the fouling, the tubes had evidently grown more rapidly than the surrounding unaffected areas due to a reduced heat transfer capacity and therefore higher tube metal temperature.

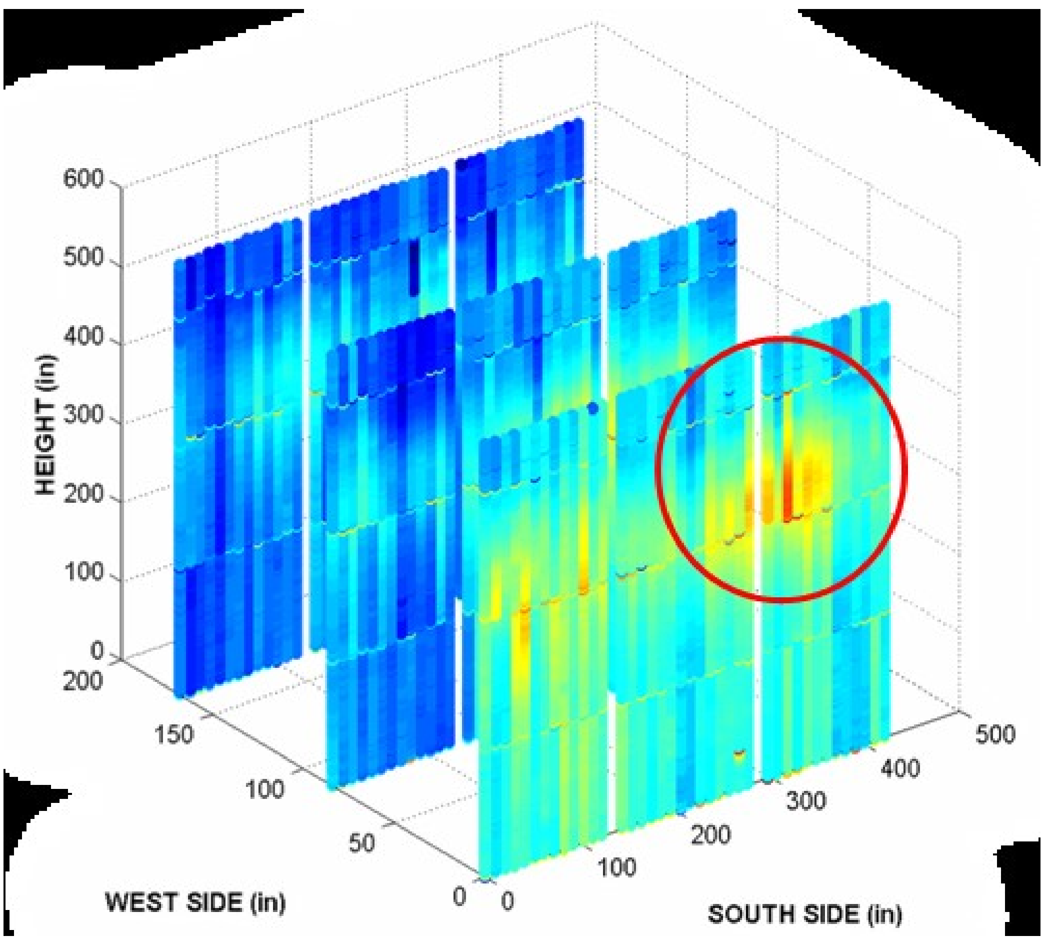

Figure 4: 3D map of catalyst tubes, color scale corresponds to measured diameter. Circled area highlights tubes with high growth and high calculated effective temperatures in an unusual location.

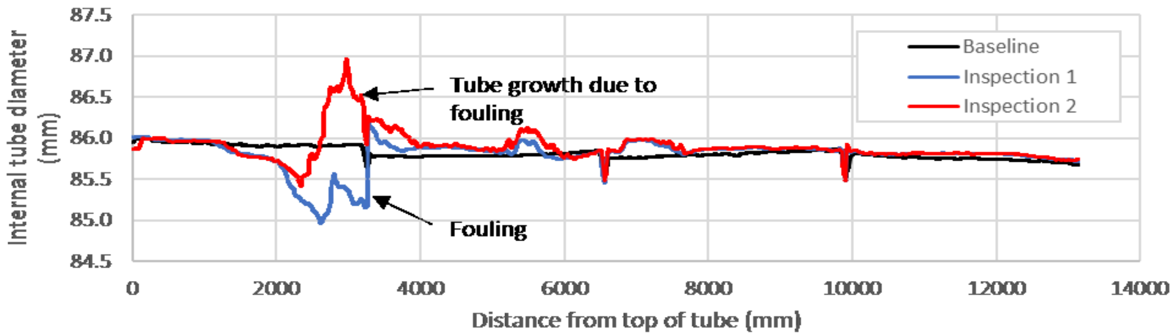

Figure 5: Internal diameter profile showing fouling and underlying tube growth due to reduced heat transfer capability in the affected area.

In all these examples, the worst-case scenario is that the issues identified could have led to premature tube failures if no remedial action was taken. Alternatively, if the inspection data had been used only to predict remaining life and there had been no additional interpretation of the damage patterns observed, it is likely that these issues would have resulted in either a greater number of replacement opportunities being scheduled to keep up with the uneven damage rates, or replacement of tubes with several years' remaining life to match the available replacement opportunities. Ultimately, either would have resulted in unnecessary costs to the plant operator. In many instances it is possible to detect these kinds of issues via other means, such as regular visual or infrared surveys of the reformer furnace and catalyst tubes, but accurately assessing their impact on tube life requires a measure of the damage incurred. In some cases the impact is negligible, particularly for minor short-term temperature excursions, and diameter profiles will show no sign of abnormal conditions despite temperature monitoring suggesting otherwise. However, there are some scenarios where the reverse is true i.e., significant damage is indicated by inspection data, but no over-temperature excursions have been detected from on-line temperature monitoring. This is rare, but the following case study illustrates how this may occur, and the crucial role of inspection data in diagnosing the cause.

Case Study

A series of inspections and life assessments were undertaken on the same reformer over a period of 8 years, with the first inspection taking place three years after installation of a full set of new tubes. The reformer in question was a top-fired design, with capacity for 64 catalyst tubes. The key events that occurred over the 11 years from installation to the most recent inspection are summarized as follows:

- In Year 3 of operation, three tubes ruptured during a start-up. Inspection revealed significant abnormal creep growth in the majority of tubes. Tube replacements were scheduled for the next available opportunity in Year 5, and one tube considered at risk of imminent failure was also removed from service.
- In Year 5, further inspection and assessment resulted in 23 tubes being replaced. It appeared that little additional damage had occurred between Years 3 and 5, but these tubes were predicted to reach the retirement threshold prior to the next replacement opportunity in Year 11.
- In Year 8, hotspots consistent in appearance with catalyst deactivation were observed on multiple tubes, and temperatures well above design were recorded over a period of several days. A catalyst replacement resolved the issue, but five tubes were assessed as being at risk of

failure prior to the Year 11 turnaround and replacement opportunity, so were removed from service.

- In Year 11, three more tube ruptures occurred during a start-up just a few months before the scheduled turnaround. The subsequent inspection yielded similar results to that from Year 3, where significant abnormal creep growth was observed in the majority of tubes. Due to limited availability of spare tubes, thirteen were replaced and eight removed from service.

A baseline internal diameter profile was recorded for all tubes before entering service. External diametric inspections were carried out in Years 3, 5, 8, and 11, and internal inspection was also undertaken in Year 11. Example diameter profiles from all inspections are shown in Figure 6, along with the calculated effective temperature profile for the Year 8 to Year 11 period.

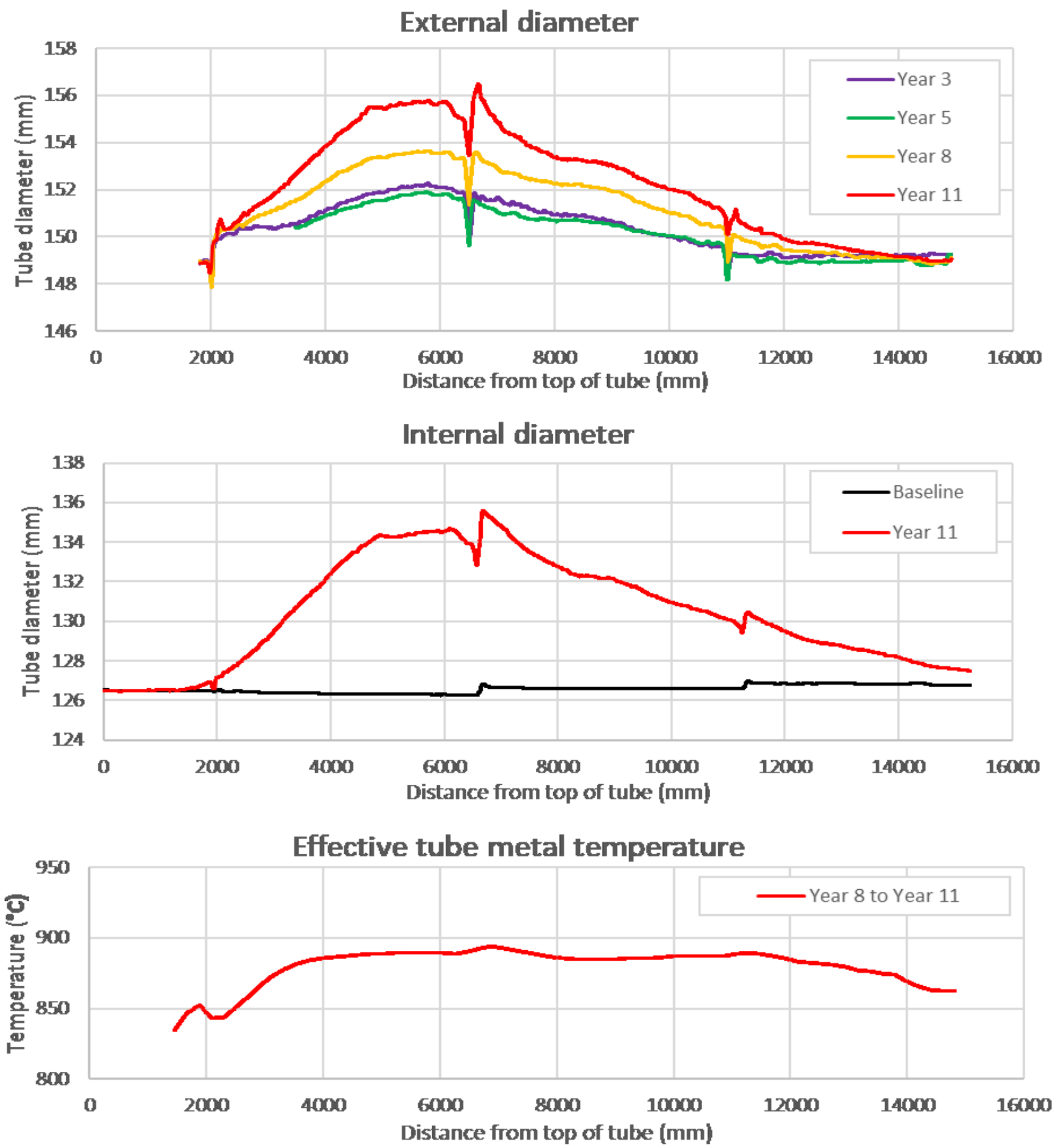

Figure 6: Example external and internal diameter inspection data from all historical inspections and calculated effective temperature profile for Year 8 to Year 11 period.

Comparison of the profiles shown in Figure 6 to the "normal" profiles in Figure 2 shows that the damage occurring in these tubes was clearly not the result of normal operation, as the maximum growth was located in the upper tube sections where temperatures should have been relatively low. All tube failures had also occurred in a similar location close to the inlet end of the tubes.

The damage accumulated in the tubes prior to the Year 3 inspection and the tube failures themselves were attributed to short-term overheat during start-up of the reformer. During start-up, operators must typically rely on process fluid temperature and pressure data to identify any problems; this data will not reflect actual tube metal temperatures, so tubes can be at risk of overheating if there is insufficient means of absorbing the heat from the burners before the endothermic reforming reaction begins. The consistent location of the damage in the upper sections of the tubes (close to the burners), the fact that almost every tube in the reformer had suffered similar damage, and the occurrence of the actual failures during a start-up all pointed to issues with overall process control during this transient period. In addition, on-line temperature monitoring gave no indication that the upper sections of the tubes were particularly hot during normal operation, despite the high calculated effective temperatures in this location. This mismatch between the measured and effective tube metal temperatures was a key indicator that the temperature excursions causing the damage were short-term and were happening outside of normal operation, and the start-up sequence was the only time this could feasibly have occurred. As further evidence, the appearance of the ruptured tubes was most consistent with failure due to short-term overheat rather than creep rupture, which would be the expected mode of failure if the tubes were subject to long-term temperature excursions. Examples of catalyst tube fracture appearance for these two different modes of failure are shown in Figure 7.

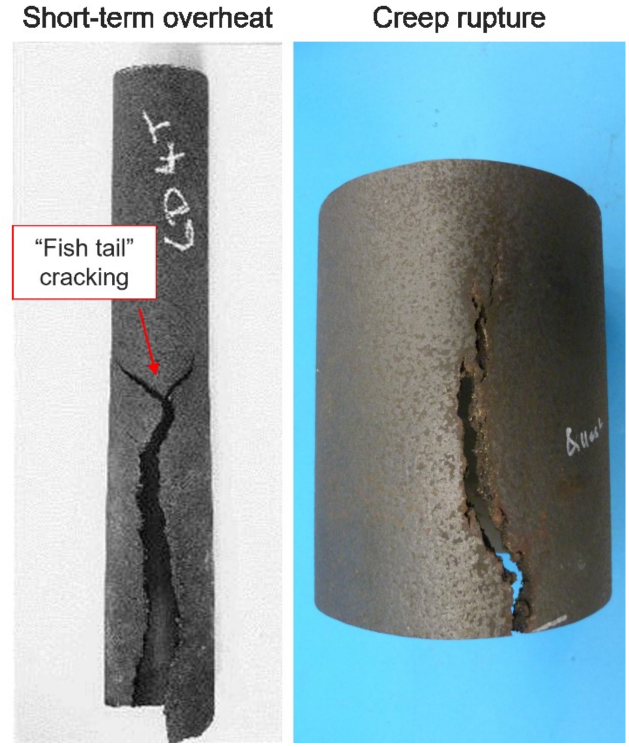

Figure 7: Examples of catalyst tube failures. Short-term overheat failure with characteristic "fish tail" cracking (left) and creep rupture (right).

Following the Year 3 inspection and assessment, a review of the reformer start-up and shutdown procedures was undertaken to address the overheating issue. A lack of further growth over the Year 3 to Year 5 period indicated that the issue had been resolved, although it is not known what actions were taken by the plant to accomplish this. The additional growth detected in the Year 8 inspection was feasibly explained by the hotspots observed earlier that year, which occurred in a similar location to the maximum growth observed in the Year 3 inspection. However, in retrospect, the similarity between the Year 3 and Year 8 growth patterns may indicate that the start-up issue had re-surfaced sometime prior to the Year 8 inspection. This suggests that whatever procedures had been implemented following the Year 3 tube failures had not been maintained. Together with the fact that potential start-up issues were seemingly not considered in the Year 8 assessment, this points to a general lack of communication around the history and operation of the reformer.

Regardless, the tube failures and tube growth observed in Year 11 were once again attributed to overheating during start-up. The pattern of damage and the appearance of the ruptured tubes was eerily reminiscent of that observed in Year 3. Regular on-line temperature monitoring carried out over the Year 8 to Year 11 period once again indicated that tube metal temperatures in the upper sections of the tubes were relatively low, well below the calculated effective temperatures for this period, and that the overall tube profiles were generally consistent with a “normal” profile such as that shown in Figure 2.

The Year 11 tube failures prompted a root cause analysis, which unearthed several red flags in operational data from past start-up sequences. Recommendations were made on actions that should be taken to reduce the likelihood of future overheating events, although the outcome of these is yet to be seen.

This reformer provides an excellent example of the value of inspection data beyond assessment of fitness-for-service and remaining life. In both Year 3 and Year 11, tube failures were the first indicator that there was any kind of issue, as tube metal temperatures were not monitored during start-up or shutdown. The tube inspection data revealed the nature and full extent of the damage. However, it also highlights the need for good communication around past issues, as the failures in Year 11 may have been avoided if the reappearance of the overheating issue had been identified earlier.

Concluding Remarks

The case study and other examples presented in this paper illustrate how deeper interpretation of inspection data can have benefits beyond assessment of tube fitness-for-service and remaining life. The case study in particular shows how issues can successfully be diagnosed from damage patterns and operational information embedded in the raw inspection data, even when there have been no indications of any problems during day-to-day operation. The overall health of the reformer furnace typically plays a large role in the reliability of the wider plant, so there is little justification for failing to make use of the wealth of information available from inspection. Although the cost of a high-quality program of regular inspection and assessment is not negligible, it can nonetheless provide a significant saving in comparison to the costs of unscheduled or potentially unnecessary shutdowns.

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Improvement in Process Safety Performance by Accelerated CUI Inspection Program

PT. Kaltim Parna Industri (KPI) suffered uncommon loss of primary containment (LOPC) event on piping system due to corrosion under insulation (CUI) during 2014-2017. The number of average LOPCs increased drastically from 2.57/year to 24.75/year as a consequence of non-technical long shutdown in 2013-2014.

Based on API 754 and CCPS classification, there was not a single LOPC that qualified as Tier 1 or Tier 2. Nevertheless, the financial loss was significant to repair and replace the piping or to cover the cost of inevitable plant shutdown. By implementing an aggressive CUI program with risk based inspection (RBI) methodology that condensed a 5 year inspection cycle into 1 year. The average LOPC decreased to 8.33/year, followed by process safety performance and on-stream days improvement.

Arif R. Hakim, Baskara A. Nugraha, Ilham A. Febryantho
PT. Kaltim Parna Industri, Bontang, East Kalimantan - Indonesia

Introduction

PT. Kaltim Parna Industri (KPI) is located in Bontang, East Kalimantan – Indonesia near the equatorial line with high rain intensity and extreme relative humidity. During its non-technical long shut-down period in 2013-2014, the corrosion under insulation (CUI) was predicted to occur due to the downtime duration and climate conditions. CUI will affect the process safety performance due to numerous loss of primary containment (LOPC) events. KPI has prepared the CUI program to counter this issue by condensing 5 years inspection cycle into 1 year. This program successfully reduced LOPC events specifically due to CUI, improved process safety performance, and larger number of on-stream days.

Background

Process safety performance in industrial sector is commonly measured by using leading and lagging indicators. The applicable standard broadly used worldwide are API 754 [1] and CCPS Guideline [2]. Lagging indicators represented by LOPC, an unplanned or uncontrolled release of any material from primary containment, including non-toxic and non-flammable materials (e.g. steam, hot water, nitrogen, compressed CO_2, or compressed air) that could have resulted in fire and/or explosion.

API 754 [1] and CCPS Guideline [2] classify process safety performance indicators into 4 tiers. Tier 1 is lagging and represents LOPC events of greatest consequence, while Tier 4 is a leading performance indicator as depicted in Figure 1.

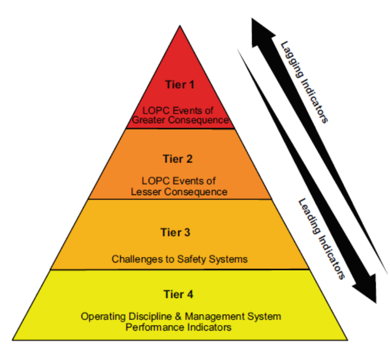

Figure 1. Process Safety Indicator Pyramid [1]

Basically, each LOPC event can be classified into Tier 1, 2, or 3 depending on the consequence. KPI chose to record Tier 3 LOPC event to maintain the trend of LOPC as a signal of precursor for a more significant incident potentially occurring.

Despite the absence of Tier 1 and 2 events, KPI experienced significant financial losses due to indirect cost to cover inevitable shut down, startup process, and production loss for several days. Also, when possible, the sources of the LOPC (i.e., pipe leak) need precaution to allow safe operation (i.e. installation of clamp).

For consistent LOPC event measurement, KPI implemented these methodologies:

1. Threshold quantity (TQ) units are in kilograms (kg)
2. Threshold release category using properties in Safety Data Sheet (SDS)
3. Rate of release is based on calculation
4. Any release from non-toxic material (e.g. steam, hot water, nitrogen, carbon dioxide, instrument air) is automatically classified as Tier 3 even though there is no TQ and other consequences

LOPC Record and History

KPI commercial operation began at the end of 2002, starting from this point, by utilizing Computerized Maintenance Management System (CMMS) software, all of the leakage events have been recorded in the database. After formal implementation of process safety management (PSM), these data would be analyzed as lagging indicators.

The first ever LOPC recorded due to CUI has occurred in 2006 affecting Medium Pressure Steam piping (P = 42 Kg/cm2.G (597.38 psig); T = 420 ^{0}C (788°F) around Steam Turbine Generator (STG). It was 1 (one) year earlier from common belief that CUI found to be significant in equipment more than 5 years old [3]. Afterwards, some LOPCs were found the next year ranging from 0 – 5 LOPC per year.

In 2013, due to non-technical issue, KPI suffered long shut-down period with only 65 on-stream days. In 2014 the condition was slightly better with 130 on-stream days. Details of on-stream time are shown in Figure 2.

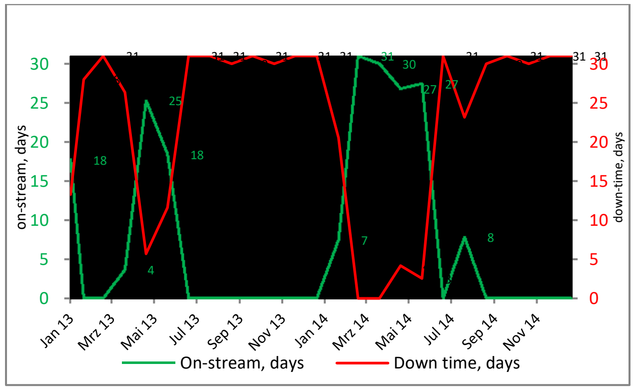

Figure 2.Downtime Days 2013 – 2014

Overall, the longest shutdown period was 247 days and 207 days in a row between May 2013 and January 2015.

A significant number of LOPC events were recorded in 2014 compared to 2013. 23 LOPC occurred, which gave an alert that CUI was an issue. The condition worsened in the next year with 25 LOPCs in 2015 (see Figure 3).

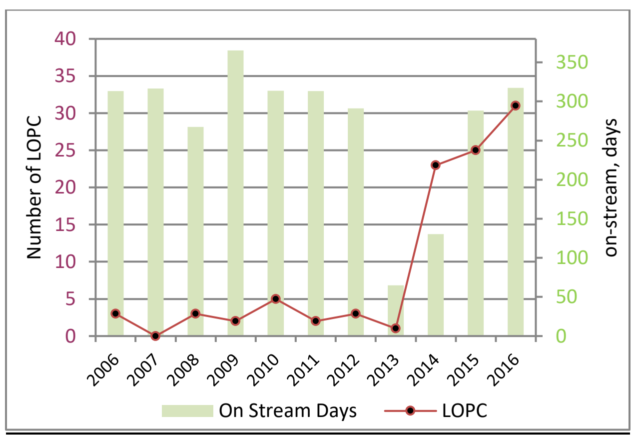

Figure 3. LOPC Count Due to CUI

The highest number of LOPC events were recorded in 2016, along with the greatest consequences. KPI suffered 2 unavoidable shutdowns– one in July and one in November – due to CUI. The losses, in Table 1, consist of downtime and indirect cost for startup (natural gas, chemical, and utility).

Parameter	Shutdown Period	
	July	November
Leakage source	E-0211	MSV-0204
Downtime (days)	3.82	13.09
Indirect cost (USD)	580,510	910,754
Production loss (MT) based on nameplate capacity 1,500 MTPD	5,730	19,635

Table 1. Shutdown due to CUI in 2016

Both July and November shut downs were triggered by LOPC due to CUI on ¾ inch piping containing natural gas shown in Figure 4.

Figure 4. CUI on bypass MSV-0204

Corrosion under Insulation (CUI)

CUI is defined as the external corrosion of piping and vessels that occurs when water gets trapped beneath insulation. CUI damage takes the form of localized external corrosion in carbon and low alloy steels [4]. In carbon steel material, which is widely used in industry, corrosion occurs not because it is insulated, but because it is contacted by aerated water.

CUI requires special attention since it is invisible from visual inspection. Because it can go undetected for long periods of time, it can cause severe damage to the piping and lead to leakage.

There are four types of insulation that are used in KPI, and all of these types are included in CUI program assessment:

1. Hot insulation
2. Cold insulation
3. Steam trace
4. Personnel protection

Some factors affecting CUI, identified in NACE SP0198-2010, Standard Practice, Control of Corrosion under Thermal Insulation and Fireproofing materials – A System Approach, are as follows:

1. Water
2. Contaminant
3. Temperature
4. Insulation
5. Weather and vapor barrier material
6. Design

The top three on the list are mainly affected by weather and environmental condition. The last three are operational and design related.

In a piping system, the potential areas for CUI can vary. The potential for CUI will be higher in certain areas such as flanges, dead legs, supports, valves & fittings [5].

Risk Profile of KPI

Located in a tropical country and near equatorial line, KPI has some disadvantages regarding the environmental conditions, which makes the corrosion phenomena more possible.

First factor is water, where the source to the piping is from rainfall infiltration or condensation. Due to its location, KPI is exposed to high rainfall intensity throughout the year averaging around 206.71 mm. Relative humidity (RH) is also high, averaging around 76% during the long-shutdown period. The higher relative humidity, the easier it is to form condensation. The environmental conditions are shown in Figure 5.

This situation worsens by the utilization of sea water cooling tower inside the plant. Not only does it create extreme humidity, but it also provides a potentially corrosive contaminant (chlorides) to stainless steel material. Since the insulation material is chlorides free, so the contaminant majority must be from the environment.

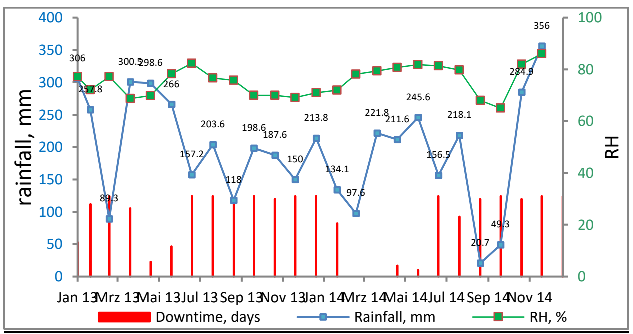

Figure 5. Monthly Rainfall and Average Relative Humidity 2013-2014

The ammonia plant utilizes many hot fluids (gas, steam, condensate, etc.) inside insulated piping. During normal operation, when temperature is mostly above 100^0C (212^0F), water can hardly condense within insulation. Conversely, during shutdown period, those piping are inactive and cooled down to ambient temperature, so the water content in its insulation is potentially condensed.

Risk Based Inspection (RBI) on CUI Program

Risk is a critical step to identify susceptible piping subject to CUI and develop a prioritized inspection plan and schedule. Risk, in general, is a function of probability (or probability) and severity of the consequence. This combination is typically represented in a risk matrix to be ranked and categorized.

In RBI, risk is a function of probability of failure (PoF) on demand of a component and consequences of failure (CoF) [6][7]. KPI defines PoF and CoF with maximum values of 50 and consider 5 (five) factors, including:

Probability factors:

1. Material (Pmt)
2. Temperature (Pte)
3. Fluid (Pfl)
4. Insulation (Pin)
5. Coating (Pco)

Consequence factors:

1. Operational Effect (Cop)
2. Pressure Exposure (Cpr)
3. Heat Exposure (Che)
4. Flammability (Cfi)
5. Toxic Exposure (Cto)

Probability of Failure (PoF) is formulated as follows:

$$PoF = Pmt + Pte + Pfl + Pin + Pco$$

While Consequences of Failure (CoF) is formulated as follows:

$$CoF = Cop + Cpr + Che + Cfi + Cto$$

Plotting the value of PoF and CoF simultaneously on the risk matrix will produce Risk (R).

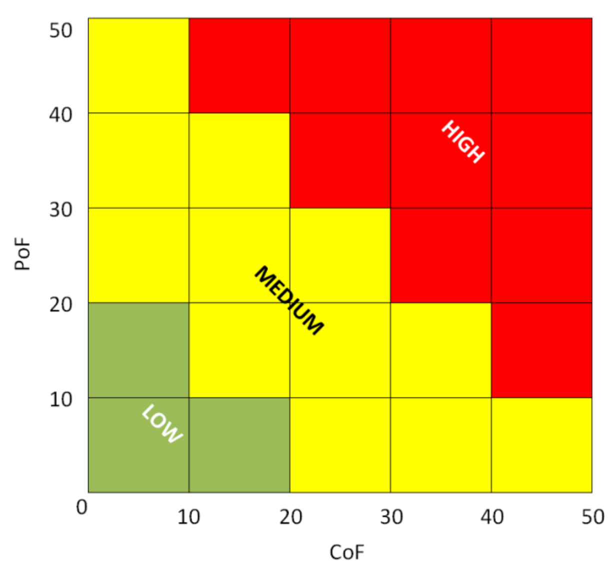

Figure 6. Risk Matrix

The risk is classified into 3 (three) category, low, medium, and high. This risk classification is used to predict where the CUI tends to occur as well as the consequence of its occurrence. The higher the risk, the more likely CUI is to occur and the higher the consequence, thus prioritizing in the inspection schedule.

Initiation of CUI Program

At the beginning of shutdown period on May 2013, and with the duration unknown, KPI realized that CUI will be a serious threat in the future. Literature study and preparation was started.

Since CUI Program was focus on insulated piping, it was essential to determining the number of insulated piping as a basis. KPI line index covers the total of 2,351 piping and it was found that 749 piping were insulated. Each of these piping underwent PoF and CoF evaluation, which was then plotted on the risk matrix.

LOPC history also collected to analyze the trend (material, dimension, fluid, corrosion rate, etc) and literature study was conducted to establish a more comprehensive understanding.

First Pilot Project

On March, 2015, KPI conducted a pilot project CUI program to measure the accuracy of risk classification. 15 piping samples which have highest risk were selected and inspected. If high risk piping were found in severe condition during inspection, it would prove CUI had already occurred, and the degree of accuracy could be accepted and could be used for further program.

However, contrary to the risk classification and prediction, inspection results found that all of the piping were in good condition. Meanwhile Failure piping (leakage) due to CUI was occurring on the other lower risk piping instead, shown in Figure 7.

The result of 1st pilot project concluded that risk method in defining inspection interval was not accurate. Nevertheless, the PoF region was quite accurate; it was the CoF that mainly caused inaccuracy. The actual failure occurred most on the piping with less consequence (e.g. steam, boiler feed water, etc.) which made the risk was in medium-high interface.

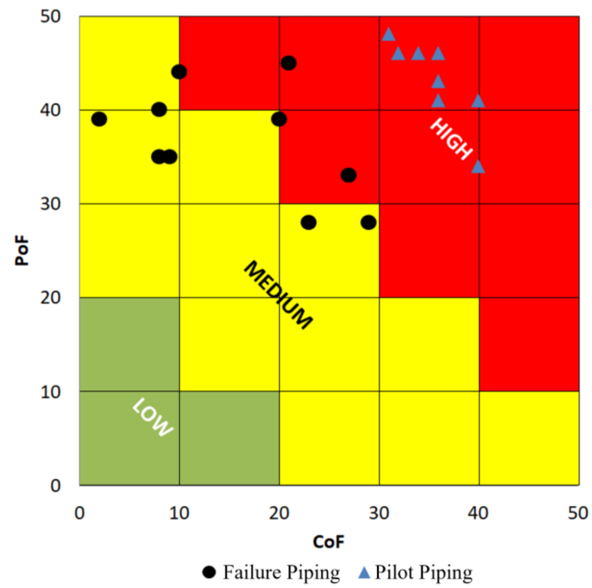

Figure 7. Risk Plot of Actual CUI Failure Piping vs Pilot Piping

Evaluation

There are two aspects that strongly affect failures, they are corrosion rate and original thickness. For material with certain level of corrosion rate, lower thickness piping will fail before thicker one.

From previous result of the First Pilot Project, Corrosion rate is associated with probability value. Therefore, it can be assumed that a piping having higher probability value will have higher corrosion rate, whereas a piping with zero probability value will not have CUI.

Corrosion rate value was determined by failures data that had happened in KPI plant. Corrosion rate can be calculated from piping thickness and piping service time. Due to the inadequacy of using the failure data, so only certain corrosion rate data gained that tabulated in Table 2.

Probability Value	Corrosion rate (mm/year)
40-50	N/A
30-40	0.33
20-30	0.35
10-20	N/A
0-10	N/A

Table 2. Corrosion Rate and Its Probability Value

Actual data for some ranges of probability value were not available; therefore it was calculated by linear regression with zero intercept. Zero intercept is based on assumption that chance for CUI occurrence with zero probability value is less likely to happen, shown in Figure 8.

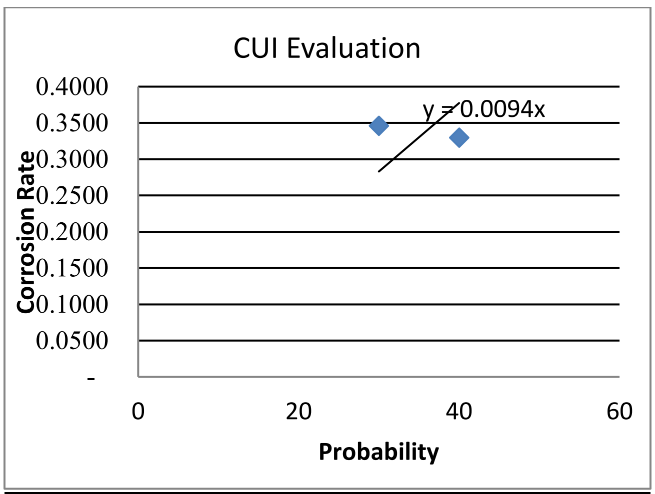

Figure 8. Corrosion Rate vs Probability with zero intercept

From evaluation results shown in Figure 8, we categorized the corrosion rate based on probability value as shown in Table 3. This corrosion rate value will be used to calculate Potential Failure.

Probability Value	Corrosion rate (mm/year)
40-50	0.47
30-40	0.38
20-30	0.28
10-20	0.19
0-10	0.09

Table 3. Corrosion rate based on Probability

Inspection Interval

PF (Potential Failure) interval is an estimated time required for piping initial corrosion until failure occurs. Piping will fail if its thickness is below minimum design thickness. Thus, it can be concluded that PF is the time required from initial corrosion until piping thickness is below minimum design thickness due to CUI. Minimum design thickness can be calculated based on ASME B31.3[8].

Minimum thickness calculation cannot be performed for every piping in KPI plant because there are so many piping variations, as well as miscalculation potential. Therefore, calculation of minimum design thickness was performed by a sample of 123 piping that represent all piping in KPI. Since minimum thickness value is different for every piping, it can be generalized by the percentage between difference of design thickness and minimum thickness with design thickness. This percentage is called SF (Safety Factor). SF was used for CUI analysis of all piping, the distribution of which is shown in Table 4. In design thickness, there is Ca (Corrosion Allowance) parameter that has same value for all of carbon piping.

SF	Piping Quantity	Percent
0 – 0.2	1	0.8%
0.2 – 0.3	3	2%
0.3 – 0.4	7	6%
>0.4	112	91%

Table 4. Safety Factor Samples Distribution

Based on table above, it was found that the lowest SF is 0.2. This value was used for PF interval calculation using the following formula:

$$PF = \frac{T * SF + Ca}{Cr}$$

where:

T: nominal thickness
SF: safety factor (0.2)
Ca: corrosion allowance (0.2 mm, KPI standard for all carbon steel)
Cr: corrosion rate

For preventing mechanical failure, inspection is done with maximum interval equal half of PF interval. The inspection interval for all piping is shown in Table 5.

A Half of PF Interval	Inspection Interval
2-3	2 years
3-4	3 years
4-5	4 years
>5	5 years

Table 5. Inspection Interval

Second Pilot Project

In October 2016, the second pilot project was conducted with a different approach. The inspection interval was no longer defined by the risk but was based on the PF interval instead.

After calculating all PF interval for each piping, 15 piping samples which have the shortest PF interval (5.2 – 5.3 years) were selected to be included in the second pilot project. From those samples, it was found that 6 piping samples had actual major corrosion failure.

Compared with the first pilot project results, it is concluded that CUI Inspection based on PF interval is more accurate and will be used as basis of future CUI program.

Establishment of CUI Program

Beginning with evaluation and improvement, the CUI program was established in January 2017. The program cycle was set to be done within 5 years and consist of several scheduled work-package.

The total insulated piping requiring CUI inspection is 749 items that are categorized into groups. The groups depend on the years of inspection interval and inspection period– either normal operation or scheduled shutdown – shown in Table 6.

Inspection Interval (years)	Group Qty.	Piping (Items) Qty.
2	24	126
3	36	286
4	48	177
5	60	160

Table 6. Inspection Interval Distribution

On the first five-year-cycle, the average piping to be inspected is 219 items/year. The item distribution is shown in Table 7.

Year	Piping (ea)
2017	205
2018	208
2019	232
2020	228
2021	221

Table 7. Initial CUI Inspection Schedule

CUI Acceleration Program

Due to huge losses caused by two emergency shutdowns in 2016, KPI management decided to accelerate the first implementation of CUI program in 2017 to prevent the recurrence. This acceleration program condensed the five year schedule down to one year for all piping items (749 piping). Those piping items were distributed over the 12 months as shown in Table 8.

Month	Piping (ea)
January	65
February	66
March	67
April	62
May	61
June	61
July	62
August	61
September	61
October	59
November	62
December	62

Table 8. Accelerated CUI Inspection Schedule

This acceleration program had huge impacts on man-hours and cost. For completing this one-year-program required 280,320 man-hours and spent approximately USD 248,000 for material and labor.

Outcome

The accelerated CUI inspection program is considered to be a success at KPI based on LOPC numbers. The LOPC numbers reduced significantly in the following year with an improvement on recorded on-stream days shown in Figure 9. Likewise, compared to the cost of the unexpected emergency shutdowns in 2016, the accelerated program is worth as much as USD 1,491,264.

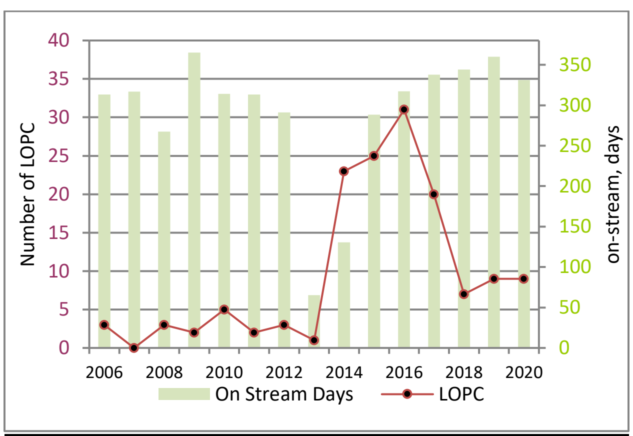

Figure 9. LOPC After CUI Program

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[6] API 580, 3rd Ed, February 2016, Risk-based Inspection

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How Stamicarbon successfully reduced the risk for loss of containment in urea plants

Operating a urea plant poses challenges in managing the corrosive environment, especially in the high-pressure synthesis section.

Several mitigation strategies have been developed successfully to minimize severe corrosion and, subsequently, loss of containment scenarios. Nevertheless, loss of containment still occurs occasionally, for instance, due to a tube rupture in a high-pressure urea heat exchanger. The severity of such a mishap will result in the release of a large cloud of toxic ammonia.

Stamicarbon introduced Safurex® stainless steels as the material of construction more than 20 years ago, and to date, the failure rate for a rupture of a single Safurex® heat exchanger tube is less than 10^{-7}. The application of Safurex® steels significantly improves the safety, reliability and availability of critical high-pressure urea equipment. This is also the case when exposed to severe process upset conditions and it offers excellent flexibility in plant operations. This paper presents some case histories to demonstrate this impressive achievement.

Alex Scheerder
Stamicarbon BV, The Netherlands

Introduction

One of the main challenges in operating a urea plant is managing the corrosive environment, especially in the high-pressure synthesis section. Ammonium carbamate is known for its extreme corrosiveness, and proper mitigation strategies are required to minimize the risk of a loss of containment scenario.
Several technologies have been developed successfully by different urea licensors, such as the introduction of passivation air and special urea grade stainless steels. Nevertheless, loss of containment scenarios still do occasionally occur, for instance, the rupture of a tube in a high-pressure urea heat exchanger due to (active) corrosion. Such an event typically results in the release of a huge amount of toxic ammonia.
Stamicarbon introduced Safurex® duplex stainless steels as a material of construction in 1996 [1], and to date, the failure rate for a rupture of a single Safurex® heat exchanger tube is less than 10^{-7}. These impressive statistics are obtained with more than 200 Safurex® heat exchangers in operation for more than 20 years worldwide with on average 2500 tubes per heat exchanger. This also includes heat exchangers exposed to severe upset conditions, as will be demonstrated in the following case studies.

Safurex® stainless steel

Safurex® INFINITY steel [2] is a super duplex stainless steel developed in cooperation with

Sandvik Sweden and introduced in the urea market in 1996. The first Safurex® high-pressure urea heat exchanger was commissioned in 1998, and the first complete greenfield plant containing Safurex® equipment was licensed in 2003. Safurex® INFINITY steel is a so-called super-duplex stainless steel having optimized corrosion resistant properties in ammonium-carbamate. It has proven its excellent performance in urea plants for many years, not only in Stamicarbon but also in non-Stamicarbon urea plants.

Figure 1: Safurex® stripper

Compared to austenitic stainless steels traditionally used in Stamicarbon urea plants like 316L UG and X2CrNiMo25-22-2, Safurex® steel is superior in performance with respect to passive (and active) carbamate corrosion, condensation corrosion, crevice corrosion, stress corrosion cracking, strain-induced intergranular cracking and under deposit corrosion. Passive corrosion rates are as low as 0.01 mm/y (0.0004 Inch/y), significantly lower rates compared to the traditional austenitic stainless steels, which have passive corrosion rates ranging between 0.05 mm/y (0.0019 Inch/y) up to 0.15 mm/y (0.0059 Inch/y).

Also, Safurex® steel does not require oxygen for passivation, allowing oxygen levels to be significantly reduced in Stamicarbon CO_2 stripping plants built with complete Safurex® high-pressure equipment. These urea plants operate at oxygen levels varying from 0.1 to 0.3 vol % providing significant advantages in operations, plant performance and safety.
In 2015 and 2017, Stamicarbon introduced two new Safurex® Steel grades, i.e., Safurex® STAR [3] and Safurex® DEGREE [4], with improved corrosion resistant properties compared to the original Safurex® INFINTY steel grade; i.e., approx. 20 % lower corrosion rate. Both steel grades are applied in high-pressure Strippers, the heat exchanger tubes are the Safurex STAR grade, and the liquid dividers (also known as Ferrules or swirls) are the Safurex® DEGREE grade. However, all case histories described in this paper refer to HP Strippers designed in the original Safurex® INFINITY steel grade.

Safurex® HP Strippers

The most severe conditions from a corrosion point of view are present in the heat exchanger tubes of the high-pressure stripper in both CO_2 stripping and in thermal stripping plants. The passive corrosion rate of the Safurex® INFINITY heat exchanger tubes in HP Strippers is comparable to that of austenitic heat exchanger tubes (X2CrNiMo25-22-2) and is typically in the range of 0.08 mm/y (0.0031 Inch/y) to 0.10 mm/y (0.0039 Inch/y). However, Safurex® INFINITY steel outperforms the austenitic heat exchanger tubes when exposed to upset conditions such as high stripper loading (flooding), low stripper loading (tubes partly dry), temperature excursions and loss of passivation air. These upset conditions will result in active corrosion of the x2CrNiMo25-22-2 heat exchanger tubes and can subsequently lead to tube rupture. An example is presented below.

Rupture of austenitic heat exchangers tube in HP Stripper

After commissioning a Stamicarbon CO_2 stripping plant, an unexpected tube rupture in the HP Stripper occurred only 14 weeks after start-up. The plant was designed in the conventional austenitic stainless steel; i.e., the heat exchanger

tubes were, X2CrNiMo25-22-2 with dimensions of: Ø 30 x 3.0 mm (Ø 1.18 x 0.118 Inch).
The safety valve of the HP Steam Saturator connected to the shell side of the HP Stripper which allowed the content of the synthesis loop to be released into the atmosphere, see figure 2. The rupture disk installed on the shell of the HP Stripper (set pressure 30 bar; 435 psi) did not rupture since the release of the full synthesis content was managed by the safety valve only (set pressure 25 bar; 363 psi).

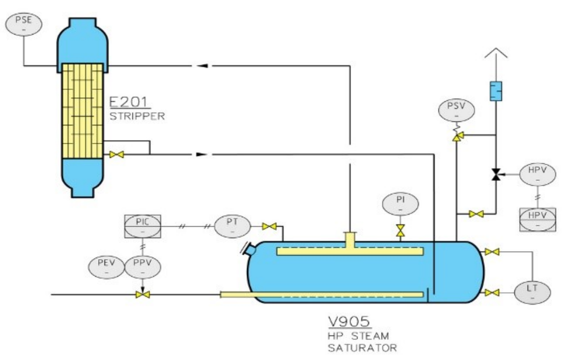

Figure 2: Configuration of HP Stripper and HP steam saturator, including PSV safety valve

60 tons of ammonia and CO_2 vapors were vented into the atmosphere and 140 tons of liquid urea and carbamate, which crystallized inside the plant premises, see figure 3. Fortunately, nobody was injured during this incident.

Figure 3: Ammonia-carbamate cloud released to the atmosphere.

The complete synthesis hold-up was released via one ruptured heat exchanger tube. The rupture occurred just below the top tube sheet. Active corrosion reduced the wall thickness relatively quickly until loss of containment occurred due to the internal synthesis pressure of 140 bar (2030 psi); see Figures 4 and 5.

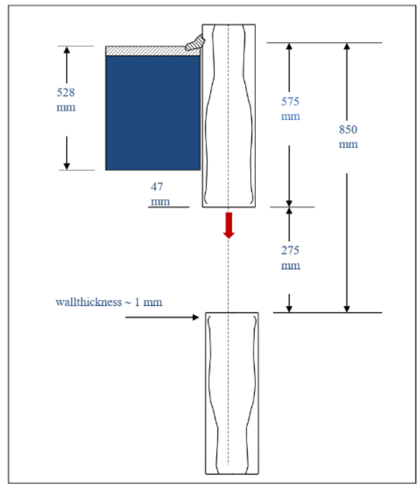

Figure 4: tube rupture just below top tube sheet

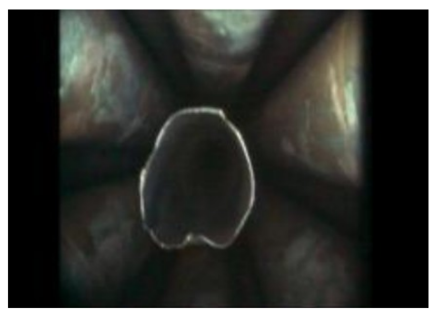

Figure 5: ruptured tube; surroundings tubes not affected

The root cause of the failure was the presence of a foreign object stuck inside the heat exchanger tube, most probably a steel brush left behind. This created a stagnant liquid level above the blockage. The stagnant ammonium-carbamate liquid level was slowly depleted of oxygen which resulted in the onset of active corrosion. The blockage prevented fresh CO_2 and oxygen from entering the tube from the bottom. The ruptured heat exchanger tube corroded actively only in the area of the stagnant liquid build-up. Below the blockage, the wall thickness of the tube was not affected by corrosion. Also, all other heat exchanger tubes showed no abnormal corrosion as expected after only 14 weeks of on-stream time. This incident shows the vulnerability of austenitic stainless steels to upset conditions in ammonium-carbamate service.

Excellent performance of Safurex® heat exchanger tubes in upset conditions

The previous example demonstrates the severe consequences of a tube rupture in a high-pressure Stripper. Austenitic stainless steel heat exchanger tubes are vulnerable to rupture if oxygen is depleted in the solution. In the next case, demonstrates the performance of Safurex® INFINITY heat exchanger tubes under similar upset conditions (i.e., oxygen depletion) but did not result in a loss of containment scenario.

Case history 1: Blocked tube in Safurex® HP Stripper

In a Stamicarbon CO_2 stripping plant, having a Safurex® HP Stripper (replacement), the stripper efficiency gradually declined, and the plant was shut down to solve this issue.
Following observations were made:

1. Severe fouling of oil residues on the top tube-sheet, including similar fouling of the liquid dividers. Approximately 30 % of the liquid dividers showed blocked holes, hampering the liquid entering the heat exchanger tubes, see figure 6. This fouling reduced the stripping efficiency. However, this fouling did not result in increased corrosion of the heat exchanger tubes, as confirmed by eddy current measurement.

Figure 6: severe oil fouling top tube-sheet, blocking liquid inlet holes

2. One Safurex® heat exchanger tube was blocked entirely, and the origin of the blockage is unknown but most probably clogged with oil residue. Figure 7 shows a video endoscope image of the blocked heat exchanger tube.

Figure 7: blocked Safurex® heat exchanger tube

However, the blocked Safurex® INFINITY heat exchanger tube did not rupture, and had no significant wall loss in the heat exchanger tube above the blockage, which was also confirmed by eddy current measurement.

Case history 2: Poor liquid distribution in Safurex® HP Stripper

Stamicarbon was contacted in 2010 to replace a bimetallic HP Stripper in a thermal stripping plant into a Safurex® HP Stripper. For this purpose, the standard Stamicarbon liquid inlet system (inlet from the side of the tube-sheet) needed to be modified into a central inlet design, see Figures 8 and 9.

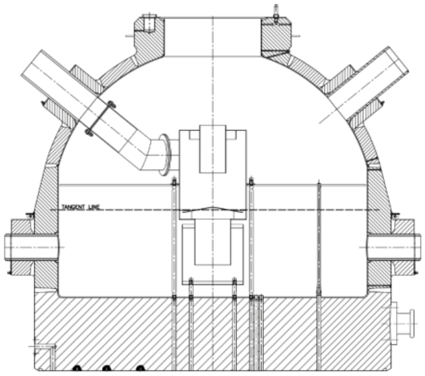

Figure 8: Modified central inlet system above the top tube-sheet

Figure 9: Top view central liquid inlet system

Unfortunately, the central liquid inlet box modification resulted in flooding of the heat exchanger tubes positioned in the first three rows around the central inlet box. The liquid entered these tubes via the liquid holes in the bottom and via the top of the gas risers due to too high fluid retention around the central liquid inlet. The extreme liquid level height around the central liquid inlet box is visible in figure 10 by the absence of an oxide layer on the gas risers closest to the central inlet box.

Figure 10: tubes centered around liquid inlet box flooded due to fluid retention.

The large volume of liquid entering the top of the heat exchanger tubes resulting in high vapor formation, hampering the ingress of CO_2 containing passivation air from the bottom. In this case, the flooding of the Safurex® heat exchanger tubes reduced the stripping efficiency but fortunately did not result in a tube rupture. The plant was shut down after a year to restore the stripping efficiency. The problem was solved by implementing additional modifications in the liquid inlet system. On this occasion, an eddy current measurement was performed to check the wall thickness of the heat exchanger tubes. Not only was the average corrosion rate as expected (0.08 mm/y; 0.0031 Inch/y), but also the flooded heat exchanger tubes did not show any increased corrosion. A similar central inlet design in a non- Safurex® HP Stripper (X2CrNiMo25-22-2) having similar flooding problems resulted in a tube rupture.

Case history 3: Extremely low liquid level in Safurex® HP Stripper

During normal operations of a Stamicarbon CO_2 stripping plant, the plant capacity gradually dropped well below the minimum design capacity. The liquid distribution system in the Safurex® HP Stripper was suspected. The plant was shut down for inspection, but no mechanical reasons for the poor performance of the urea plant were observed. In this case, the root cause was related to a foam-forming in the top of the stripper due to contaminants present at the process side.

However, during the inspection of the Safurex® HP Stripper, it became clear that the vessel was operated at extremely low liquid levels, as is seen in figure 11. The liquid level is clearly marked on the liquid dividers as a color change.

Figure 11: Extreme low liquid level on top tube-sheet, visible as color change.

Again, this adverse condition, which was maintained for several months, did not result in high (active) corrosion and tube rupture. The eddy current inspection of the Safurex® heat exchanger tubes also confirmed that no abnormal corrosion occurred; i.e., the corrosion rate did not increase, neither active corrosion occurred.

Safurex® steels allow higher flexibility in operations

The use of Safurex® steels reduces the risk for unwanted loss of containment scenarios, as demonstrated in the case histories above. In addition to this, the use of Safurex® steels also provides the plant operator with higher flexibility in plant operations without risking high (active) corrosion and, subsequent, loss of containment scenarios.

Examples of such advantages are:

1. Reducing the plant capacity beyond the designed turn-down ratio (typically 60 % of the nameplate capacity). As presented in case history #3, even an extremely low plant load will not result in abnormally high corrosion in the stripper heat exchanger tubes.
2. Longer blocking-in of the synthesis loop. For non-Safurex® plants, the synthesis loop cannot be blocked in for more than 72 hours (3 days) without the synthesis being drained and re-passivated. For Safurex® plants, blocking-in times of three weeks and longer are reported by the plant owner without any onset of increased or active corrosion.

Discussion

More than 200 Safurex® heat exchangers have been in operation worldwide, some of them for more than 25 years without a single reported tube failure. This statistic also includes heat exchangers exposed to severe upset conditions, as demonstrated in the three case histories. This equates to a failure rate of Safurex® heat exchangers in urea plants of less than 10^{-7}. This is a remarkable achievement and is because Safurex® steels do not require oxygen for passivation combined with the high mechanical yield strength of the material. Furthermore, its noticed that this achievement is obtained with the original Safurex® INFINITY steel grade introduced in 1996. In 2017 Stamicarbon introduced the next generation Safurex® STAR steel grade for heat exchanger tubes in HP Strippers with improved corrosion resistant properties compared to the original Safurex® INFINITY grade.

-The application of Safurex® steels as materials of construction in the high-pressure synthesis section of urea plants makes the plant less vulnerable to process upset conditions and significantly reduces the likelihood of a loss of containment scenario. The material is not only applicable in urea plants based on Stamicarbon technology but is also the best choice for non-Stamicarbon urea plants like thermal stripping plants. Furthermore, the use of Safurex® steels not only improves the safety and reliability of the plant but also creates higher flexibility in plant operations and reduces inspection and maintenance costs, i.e. reduces the total cost of ownership.

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[3] Safurex® patent WO 2017/0131180 A1;
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[4] Safurex® patent WO 2015/097253 A1; published 02.07.2015. (Safurex® DEGREE)

Successful Implementation of a CSA-B149.3 Certified BMS on a Primary Reformer

Nutrien's Redwater Fertilizer Operations successfully installed and commissioned a CSA-B149.3 compliant burner management system (BMS) on a 160 burner primary reformer. This paper will outline the primary challenges addressed throughout the extended design phase, not the least of which was the direct coupling of a gas turbine's exhaust stream as the oxidant supply. The paper will then discuss the installation and commissioning phases of the project and outline the strategies employed by the project team to ensure a successful startup. In the end, the plant was safely started up without any spurious trip events or delays due to the newly installed BMS.

Greg P. Dechaine
Nutrien

Introduction

It is no secret that one of the most dangerous unit operations within the ammonia process is the primary reformer. The potential for great harm always exists when such large amounts of combustible energy are present.

In Canada, the Canadian Standards Association (CSA) has a code, CSA B149.3, that regulates the implementation of controls regarding fired appliances. These control systems for fired appliances are generally referred to as Burner Management Systems or BMSs. In general, this standard relates to ALL appliances, big and small, although historically large industrial applications such as primary reformers were given a pass under this standard. However, in recent years (beyond 2010), the local regulatory body in Alberta which administers this national code has begun to require industrial users to adhere to this code.

This paper will describe the journey taken by Nutrien's Redwater Fertilizer Operations (RFO) to implement a CSA certified BMS on one of it's primary reformers.

Primary Reformer Description

The larger of two ammonia plants at Nutrien's RFO was originally built by EXXON/Imperial Oil Chemicals Canada in 1982 and started production in 1983. The original capacity of the plant was 1600 MTPD, which through various incremental projects over the years has increased to an annual average of 1830 MTPD.

The primary reformer is an EXXON/KTI designed 160 burner, bottom fired reformer divided into two parallel radiant cells each with 80 burners. There are a total of 400 catalyst tubes, with each cell containing 2 rows of 100 catalyst tubes. There are 4 rows of burners in each cell, one row on either side of the catalyst tube rows.

The original burners were a custom EXXON /KTI design. Their performance would be considered low-NO_x by today's standards (≈ 20 ppmv NO_x). The fuel supply to these burners is a mixture of natural gas, regen & depressurizing gas from two pairs of mol sieves, and a significant amount of tail gas from the purge gas hydrogen recovery unit (a cryogenic separation system, a.k.a. a cold box). This hydrogen recovery unit also processes the purge gas from a second, smaller ammonia plant, which adds an additional 40% purge gas/tail gas flow. The large proportion of tail gas in the fuel (≈ 40-50% on a volumetric basis) contributes to the low NO_x behavior of these burners by reducing the flame temperature (like flue gas recirculation).

One of the most unique aspects of this plant's design is the fact that the air/oxidant supply for the burners is the exhaust from a gas turbine (GT), as shown in Figure 1. This gas turbine is the driver for the ammonia plant's process air compressor, and the exhaust stream contains >15% residual O_2. In this configuration, the GT acts as a forced draft fan with air preheat since the exhaust gases are relatively hot (850-1050 °F, 454-566 °C). This reformer also has induced draft (ID) fans. Therefore, this reformer is considered a balanced draft unit (both inlet and outlet draft control).

Prior to implementation of the BMS, control of firing in the reformer was based on the process outlet temperature (referred to as coil outlet temperature, COT) cascaded to fuel flow for each cell. Air demand control for the burners was accomplished based on automatic control of firebox draft pressure cascaded to ID fan speed, coupled with manual control of the GT exhaust damper (i.e., venting excess exhaust).

In the case of safety protections for the furnace, the following Safety Instrumented System (SIS) protections were in place prior to the project:

- High process temperature (COT) trip (2oo2)
- High firebox pressure trip (2oo2)
- High and low fuel gas pressure trip (2oo2)
- This reformer did NOT have a no/low air flow or low O_2 trip. The reformer did have 6 O_2 analyzers (three per cell) on the crossover ducts between the radiant firebox and the convection section, and one O_2 analyzer at the inlet of the ID fans. There was also an O_2 analyzer on the exhaust from the gas turbine. Finally, there was a reformer trip on loss of 2 ID fans.
- There was no direct indication of flame status (i.e., no flame scanners) within the firebox.
- Ignition of the burner pilots was done manually using a propane torch, and the main burners were then lit from the pilots.

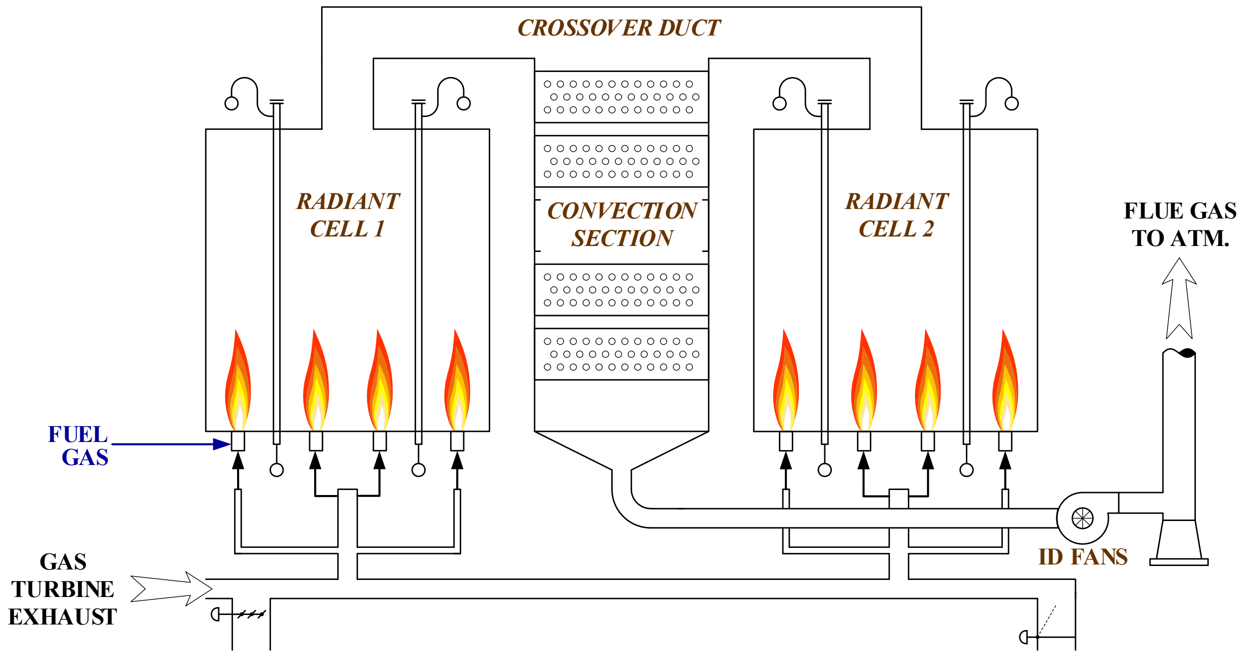

Figure 1: Schematic of the Primary Reformer

Project Description

The genesis of this project was the fact that the original Westinghouse GT was nearing its end of life and would require replacement. The initial project was initiated in 2009, 12 years prior to the actual installation! The GT at RFO was the last remaining turbine of its vintage in the world. It was a split-shaft design such that the power turbine and the axial compressor turbine were separate and controlled individually.

The new GT, a Baker-Hughes (formerly GE) Frame 5 MS5001PA, is a single shaft machine which is more efficient than the old machine. This results in a 200 °F (111 °C) reduction in exhaust temperatures. The reduced exhaust temperature equates to a reduction in energy contribution to the reformer from the gas turbine. This equates to less air preheat, which in turn requires that the furnace increase firing rate to offset the reduced heat load.

Testing was done at John Zink's Tulsa facility with a spare EXXON burner to determine if the existing burners could meet the increased firing demand. Unfortunately, the existing burners could not be fired hard enough to make up the lost heat load. At this point two options were considered: i) Adding a duct burner between the GT & reformer, ii) replacing the burners with new ones that could supply the additional heat load. The duct burner option was quickly ruled out since it negatively impacted the O_2 balance and firing characteristics of the existing burners (confirmed through testing). Therefore, as part of the GT replacement project new burners were procured for the reformer.

The new burners chosen were John Zink Coolstar®-11 low NO_x burners. These burners are roughly equivalent in NO_x production to the original burners, which is less an indictment of these burners and more a testament to the design of the original burners put forth by EXXON. Ultra-low NO_x burners were not considered for this application since the majority of the NO_x from this system (≈ 75%) is generated in the GT. The marginal gains in NO_x with Ultra-low burners were not deemed worthy of the added operating challenges posed by Ultra-low NO_x technologies.

In Canada, all fired appliances, and in particular the "*fuel-related components and accessories*", are governed by CSA B149.3[1],[2] (from here on referred to as "the code"), which is roughly equivalent to NFPA-85 in the US. Up to this point, the local regulatory body responsible for administering the code (Alberta Municipal Affairs or AMA) essentially grandfathered large industrial appliances such as primary reformers from adhering to this code. However, once the replacement of the GT required the installation of new burners, this approach is no longer applicable since AMA requires all new installations to be CSA B149.3 compliant. Therefore, since we were replacing the burners, we were now required to adhere to the code. Although not specifically mentioned in the code, the collective safeguards and controls laid out therein are colloquially referred to as a Burner Management System or BMS.

BMS Design

Code Requirements

As its name implies, the code covers a wide range of applications from small (e.g., appliances in your home) to large (package boilers, process furnaces, reformers). The code (in particular CSA B149.3-15[1] which was the revision in effect when the project was started) is a prescriptive standard, laying out detailed requirements for the fuel train control, as well as management of the burner including automated trip valves and flame detection on **each** burner.

In Canada, and Alberta in particular, all fired appliances must be inspected and approved for code compliance by so-called "inspection bodies" or IBs. These IBs are authorized by the regulatory body to approve installations as code compliant. As such, compliance with the code requires involvement of an IB all the way through the design phase up to the installation and startup. This can lead to challenges since approval of the final design is subject to the IBs interpretation of and willingness to deviate from the specific prescriptions laid out in the code. As such, selection of an IB is a critical choice very early on in the project to ensure a successful outcome. More specifically, selecting an IB with experience in large complex industrial combustion systems is particularly important.

Following revision of the code in 2020, and based on significant input from local industrial partners on the complexity of implementing this prescriptive code for large industrial appliances such as primary reformers, the local regulatory body (AMA) implemented a variance to the code[3] allowing for qualified engineers to approve designs which deviate from but still meet the intent of the code. This variance proved to be instrumental in Nutrien and its engineering partner, Spartan Controls, achieving the CSA approved design that was ultimately implemented.

Evolution of the BMS Conceptual Design

1. Initial Design Concept

The initial design based on CSA B149.3-15[1] targeted automation of every **second** burner (80 out of 160). This was done to meet the prescriptive nature of the original code. The total cost of this option was estimated at more than $24MM CDN! In addition, physically locating that much instrumentation and infrastructure beneath the furnace was not feasible. As such, a different approach to meet the **intent** of the code rather than the "letter of the law" was required.

2. Risk Based Approach

Given the magnitude of automating so many burners, the next approach investigated was a risk-based approach. Based on PHA analysis, risks associated with the combustion system and the overall reformer were assessed and used to determine the requirements of the BMS (e.g., layers of protection analysis, or LOPA). This included analysis of the potential gas flows into the firebox resulting from open burner valves. This approach is more in line with Nutrien's PSM programs and approach to safe process design. Unfortunately, this approach was rejected by the regulatory body and the design team was instructed to steward to the prescriptive nature of the code as much as possible.

3. Final Design Concept

The design team returned to the initial strategy and instead took the approach of determining the minimum number of burners that needed to be automated to meet the intent of the code. Per the code, once above auto-ignition temperature, flame detection and automation of the burners is no longer required. As such, it is only required to automate sufficient burners to bring the firebox above auto-ignition temperature (1400 °F/760 °C for methane). At that point, it is acceptable to release the remaining burners for ignition without flame detection or further automation.

Testing in the plant during a cold startup and with the facility's operator training simulator (OTS) determined that 24 burners per cell (30% of the total) would provide sufficient margin to bring the firebox above auto-ignition temperature.

Detailed Design of Key BMS Elements

The prescriptive nature of the code has many elements, some more challenging than others to implement within the context of a primary reformer. Some of the major elements are described below in more detail.

1. Logic Solver

Per the code, the BMS system MUST be managed by a dedicated logic solver (i.e., cannot leverage existing SIS PLCs). A Triconex SIL rated safety PLC was chosen for this application. All trips related to the fired appliance must reside within this logic solver, which in this case includes process trips such as steam-to-gas ratio, COTs, low process steam flow etc.

2. Fuel Train(s)

The original installation had a single automated double block and bleed to isolate the fuel flow to the furnace during a trip (an all or nothing approach). The new design implemented **four** new double block and bleed isolation trains, two for each cell:

1. One set of safety shutoff valves (SSVs) for each cell to cutoff supply of fuel to the cell (all burners) in the event of a reformer trip
2. One set of SSVs for the non-supervised burners (see next section for definition) such that they are disabled independently of the supervised burners. In this manner, the supervised burners are used to bring the furnace above auto-ignition while the non-supervised burners remain isolated

The control of the firing rate for normal operation remained largely unchanged. Firing demand is still controlled using the process outlet temperature (COT) in a cascade, however the base regulatory loop was modified from a flow control to a pressure control (i.e., a pressure regulator) per code requirements.

Per the code (§9.2.1[1]),

> *"Direct spark ignition shall not be used to ignite main burner gas, unless*
>
> *a) the main burner input is not in excess of 3.5 MMBtu/h (1025 kW) at the time of ignition".*

To meet this requirement, a second smaller pressure control valve was added in parallel with the existing control valve for startup. The pressure setting of this smaller "regulator" is fixed to limit the burner output to 3.5 MMBtu/h (compared to their rated output of 5 MMBtu/h). This is referred to as the "low-fire" state. Once the firebox has reached auto-ignition temperature, the larger control valve is released ("release to modulate" state) and operators can now fire the furnace as normal.

3. Individual Burner Controls

Burners equipped with flame detection and an automated isolation valve are referred to as "supervised" burners. Each supervised burner was equipped with:

- Individual flame detection (flame scanner)
- An automated, CSA approved safety shutoff valve (SSV) interlocked to the flame detection for that burner to isolate

the fuel if flame is not detected

- A CSA approved manual isolation valve

Non-supervised burners are equipped with a CSA approved, quarter-turn manual isolation valve.

4. Leak Detection System

An automated system for proving that the individual non-supervised burner valves are isolated and not leaking was implemented. The fuel supply headers are automatically pressured up with fuel gas by **briefly** (10 s) opening the main fuel SSVs and the low-fire pressure controllers (set at low-fire pressure), then closing the SSVs and controller to isolate the headers and monitoring the header pressure over time. If the pressure in the headers holds for a sufficient period, the header is deemed secure, and the system is released to the purge and ignition steps of the startup. If the pressure is seen to decay > 5% over 15 s, this is an indication of a leak or of burner valves open and the startup is aborted.

5. Burner Ignition

Automatic ignition systems for the supervised burners were considered. The initial intent of the design team was to keep operations personnel away from the firebox during ignition. However, having the ignitor permanently mounted in the flame zone poses long-term reliability concerns and as such a retractable design would be required. Upon consultation with operations personnel, it was determined that the added complexity and reliability concerns of automated, retractable ignition systems was not warranted for this installation since they would still require local operator intervention. As such, manual ignition using a handheld High Energy Spark Igniter (HESI) was chosen. In this manner, ignition of a supervised burner requires two operators: one operator to initiate the ignition sequence from the BMS control panel, and one operator at the burner to insert and operate the igniter until ignition has been confirmed.

The non-supervised burners are lit without a dedicated igniter. Since the firebox is already above auto-ignition when these burners are released, ignition occurs from the previously lit burners as well as from the heat within the firebox.

6. Auto-ignition Temperature Detection

A critical component of this BMS design is determining when the firebox has reached and/or exceeded the auto-ignition temperature for the fuel being combusted. During startup, the fuel is natural gas (methane) which has an auto-ignition temperature of 1400 °F (760 °C). The design team considered adding temperature measurements in the firebox for this purpose. However, given the difficulty in adding these sensing elements within the flame zone(s) as well as the severe service leading to reliability concerns, the design team decided to use the four existing crossover duct temperature measurements (crossover duct: duct connecting radiant and convection sections). In addition, four new elements were added to improve reliability for a total of 8 measurements (4 per cell). The auto-ignition detection uses a 2oo4 voting strategy.

Because the temperature at the crossover duct is always lower than the corresponding temperature in the combustion zone, the setpoint for the auto-ignition release was set at 1150 °F (250 °F lower than auto-ignition). The magnitude of this correction was based on CFD modeling of the firebox, and field measurements of the firebox temperature using a handheld pyrometer during startup. Per these sources, the crossover duct temperatures are > 300 °F (150 °C) lower than the combustion zone. Setting the auto-ignition release at 250 °F (121 °C) below auto-ignition represents a conservative setpoint ensuring that the combustion zone temperature will be above auto-ignition at the time of release.

7. Low Air Flow Trip

Unfortunately for the design team, this requirement of the code proved to be extremely difficult to implement for this system. The primary intent of this trip is to prevent firing the appliance in an oxygen deficient manner. For this unit, air is GT exhaust. This poses several major challenges in determining the stoichiometric air requirement:

- There is an insufficient straight run length on the duct between the GT and the reformer to install a flow element. The GT exhaust vent and the first burner supply takeoff are located very close to the GT exit flange. Therefore, it is not possible to measure the actual flow of oxidant to the reformer.
- The exhaust temperature and O_2 content of the GT exhaust is **variable** and depends on the process air demand, position of the GT's inlet guide vanes (IGVs), position of the inlet bleed heat controls, ambient conditions etc.
- The fuel composition is variable and depends on the tail gas flow (impacted by two plants), composition of the tail gas stream (affected by cold box performance), the mol sieve regen status, natural gas composition etc.

Therefore, it is not possible to measure nor determine neither the stoichiometric nor the actual fuel:air ratio without incorporating multiple compositional analyzers as well as a mass balance on the combustion section of the reformer. In past non-code applications, ID fan status coupled with damper position/status was considered sufficient to indicate air flow. However, this does not provide **proof** of flow and was not deemed acceptable by the IB.

In the end, the design team chose to add redundant oxygen (O_2) analyzers on the outlet of the convection section (upstream of the ID fans) and trip the reformer based on low residual O_2. Although it is generally advised by the IBs that analyzers NOT be used for this application, the inherent complexity of this combustion system left the design team no other viable option. Four tunable diode laser (TDL) analyzers were added for this application, with the trip configured as a 2oo4 voting strategy. Four analyzers were installed since analyzers require more frequent calibration and are more prone to reduced reliability. With a 2oo4 architecture, the site can take analyzers offline one at a time (sheds the trip logic to 2oo3) to perform preventative maintenance and/or repair a faulty analyzer. A full port ball valve was placed on the analyzer nozzle to allow isolation and maintenance of the analyzers while the plant is operating.

Unfortunately, there is still the need for some form of air flow measurement since per §9.2.1[1] of the code: *"the appliance control system shall provide a proven purge period prior to the ignition cycle. This purge period shall provide at least **four** air changes of the combustion zone and flue passages. The airflow rate during purge shall be not less than 60% of that required at maximum input"*.

To meet this code requirement, a flow measurement was implemented on the flue gas side of the reformer between the convection section exit and the ID fan suction. During the purge phase, there is no fuel in the reformer; therefore, the outlet flue gas flow is equivalent to the inlet air flow. Per the code, all flow measurements must be "*of the differential type*". Unfortunately, the convection section outlet duct is very large (147 in. x 82 in., 373 cm x 208 cm) and there are no off-the-shelf technologies available for ΔP based flow measurements at this scale. Simple pitot tubes were deemed inadequate due to the orientation of the duct, in particular because of several bends immediately before the chosen measurement point. As such, a custom venturi was designed and constructed for this application.

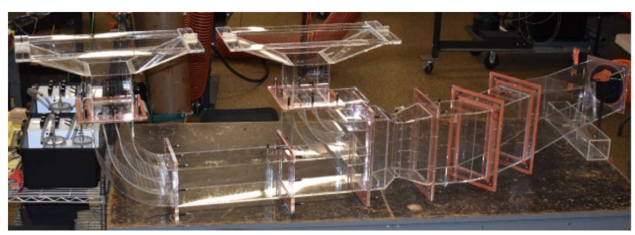

Figure 2: 1:12.5 scale model of the convection section outlet duct used for modeling of the custom venturi

To confirm the suitability of the venturi design prior to installation, a scale model of the outlet duct (see Figure 2) was constructed using Zeeco's Z-flo® method to validate the flow field in the duct and to validate the efficacy and validity of the venturi design.

Because this custom venturi does not have calibration curves available from literature, it was necessary to generate the ΔP vs flow curve empirically during the testing phase. The flow was determined from a combination of the fan curves and field flow measurements with a handheld anemometer and was correlated against the field installed ΔP transmitters. The flow measurement was also temperature and pressure compensated to account for the wide range of conditions at this point of the process.

This exhaust flow measurement is also used to provide minimum air flow protection for the reformer during startup. In the initial stages of warmup of the reformer, there is a significant excess of O_2 since there are significant volumes of air flowing through the unlit burners (dampers are not isolated). Therefore, the low O_2 trip is unreliable in this case. However, since the flow of fuel is low, and since the fuel at this stage is pure natural gas, a reasonable approximation of the required air:fuel ratio can be made, from which the minimum exhaust flow can be determined.

8. High and Low Fuel Pressure Trips

Per code requirements, the existing system was equipped with high and low fuel pressure trips. The existing trip interlocks were modified to make them 2oo3 (added redundant transmitters). The pressure trip setpoints were modified to suit the new burners which operate at much lower pressures than the original burners.

The high pressure trip setpoint was particularly challenging to define due to the varying nature of the fuel and firing rates used in this unit. The code[1] stipulates that "*In the absence of the burner manufacturer's requirements, the setpoint shall be set to not more than 125% of the normal operating pressure at the maximum firing rate*". For these burners, the maximum rated output is 5 MMBtu/h, while during low-fire state they must be limited to 3.5 MMBtu/h. Although the "normal" pressure depends on the amount of tail gas present in the fuel (RFO natural gas has a heating value of 927 Btu/scf, versus 688 Btu/scf with tail gas), it was not possible to determine the ratio of tail gas to natural gas in the fuel for scaling the burner pressure setpoint. In the end, the project team decided to use a dual setting approach, with a lower setpoint for the low-fire state and a step change to the higher pressure setpoint once release to modulate had been attained.

The low-pressure trip setpoint was set based on the minimum recommended firing pressure as specified by John Zink for the burners.

Project Testing

Extensive testing was completed at various stages of the project:

Burner Testing

1. Burner Ignition Testing

At the recommendation of our engineering partner, Spartan Controls, a test stand was built allowing for live-fire testing of the new burners. This test stand allowed Spartan Controls and Nutrien personnel to test the ignition and firing for the new burners, and to understand the firing dynamics of these burners under various non-standard conditions (e.g., high air flow at low firing).

This testing identified a significant issue with the location of the ignition port on the burner. The baseline location of this ignition port resulted in significant delays in ignition of the burner, which is problematic since the code requires proof of ignition within a pre-defined finite period. As a result of this testing, Spartan and Nutrien were able to identify the optimum location for the igniter and in turn redesign the ignition ports to provide much better ignition characteristics in line with code requirements.

2. Pre-installation of Test Burners

During the 2019 turnaround, two years in advance of the actual execution of the BMS and GT replacement projects, three of the new burners were installed into the reformer. This provided mechanical and field execution personnel with an opportunity to assess the scope and execution strategy for the remaining 157 burners. This effort identified interference issues between the oxidant supply ducting and the individual burner dampers and allowed the design team to implement a solution ahead of the main installation.

It also allowed for project execution planners to streamline the procedure/process for installation of these burners. This proved to be critical to the overall execution of the burner installation since the area below the furnace is congested and having a streamlined strategy significantly reduced the overall time required for execution. Small gains in installation time for each burner adds up to large gains over 157 burners. In addition to gains in project timelines and cost, having a streamlined installation strategy also resulted in a much safer execution, particularly considering the congested nature of the area underneath the reformer where these burners were installed.

3. Flame Detection Testing

Preinstallation of the three test burners also afforded the design team an opportunity to test several different flame detection options. The area under the furnace is very hot and the long-term reliability of flame detectors represented a significant unknown for the design team. Indeed, after installation and testing in-situ, most flame-scanners tested could not stand up to the operating conditions. In fact, this testing also identified a problem with most flame scanners on the market relative to the high amount of hydrogen contained in the fuel to this reformer. The hydrogen in the fuel created a water vapor "mask" over the flame envelope effectively absorbing the usual UV signal for reliable detection. After surveying the marketplace, the design team selected Zeeco ProFlame scanners as the best option for this application. This scanner was field tested for three months to ensure reliability, at which point they were incorporated into the design.

This testing also identified that very few (if any) flame scanners could physically withstand the high ambient temperatures at the bottom of this furnace for any reasonable length of time. As such, the design team developed an air-cooled shroud for the flame scanners to provide continuous cooling for the scanners and extend their life span. The cooling air for these scanners is supplied from the plant's process air compressor.

BMS Testing

1. PLC FAT Testing

Four days of factory acceptance testing (FAT) was done prior to shipping the PLC to the site. The purpose of this testing was to ensure that the logic programmed into the PLC met the design intent. This testing included the actual fuel train SSV skids, as well as a mockup of a set of supervised burners including the flame detection and the individual isolation valves. Every step of the BMS logic including purge, burner manifold pressure testing, ignition, auto-ignition release of non-supervised burners etc. was tested to ensure it worked as designed.

2. Fuel Train & Burner Valve Testing

As described in the Project Execution section below, the fuel train SSVs and supervised burner SSVs were installed prior to turnaround. This allowed for loop and function testing of the fuel train and burner SSVs prior to startup, and prior to the final system testing.

3. BMS SAT Testing

An extensive site acceptance test (SAT) was performed following project completion and prior to startup of the plant. Fortunately for the BMS project, the GT replacement project went longer than planned. This removed the live-fire burner testing procedure from the critical path and afforded the project team the opportunity to fully test the BMS without delaying the plant startup (which was the initial plan). The testing consisted of a combination of offline (non-fired) as well as live-fired testing. Every step of the startup and light-off sequence was tested, including all 48 supervised burners, over the course of 4 days.

Project Execution

Initial planning for the burner replacement, BMS, and GT replacement projects was indicating prohibitively long turnaround execution windows, on the order of 90 days. The design and execution teams for these projects were then challenged with finding ways to shift execution to prework to reduce the amount of downtime required for execution. The following changes resulted in significant reductions in the turnaround window and an increase in prework and testing:

1. The GT replacement project partnered with the BMS project to combine the control hardware (PLCs) into a single building (i.e., remote operating facility or ROF). This ROF was shop assembled and tested ahead of time. The ROF was installed prior to the turnaround and a significant amount of the instrumentation was also field wired to the ROF AND tested prior to the turnaround (see Fuel Train & burner SSVs below).

2. The Fuel Train(s) and associated SSVs for each cell were pre-assembled in the vendor's shop as skids and installed ahead of the turnaround. These trip valves were field wired, and loop checked ahead of the turnaround.

3. The supervised burner SSVs were pre-assembled in skids of 6 (4 skids per cell) and installed ahead of turnaround. These skids were located at the periphery of the furnace, which helped reduce the congestion below the furnace. This did result in slightly longer ignition times (lag time between valve opening and gas being present at the burner) which did require variance from the code stipulated trial for ignition times.

4. Significant portions of the project piping were pre-assembled in the field, including the cooling air piping and the supervised burner fuel supply headers. Only the final tie-ins were then required during the turnaround.

Following over 5 years of design and testing, the project was finally executed during RFO's 2021 turnaround. This turnaround was the largest turnaround in Nutrien's history, both based on duration (scheduled for 68 mechanical days, actual outage was 75 days) and on total expenditure.

System Startup and Operation

After 5+ years of engineering, testing, and planning, on Oct 6, 2021, RFO's plant 09 primary reformer and its new BMS were started up successfully on the first attempt. The reformer was brought up to full rate and steadied out with no spurious trips related to the BMS or the reformer.

The initial design of the control system (in addition to the BMS) was kept relatively simple despite having a great deal of additional information at the operator's disposal. The design team opted to keep the controls close to the original design initially to minimize the number of changes for the operator to assimilate. Now that the plant is running normally, and the site has had some time to digest the new system's capabilities, the plant process engineers, and operations personnel are working to streamline the controls to make the unit more efficient and more stable to process disturbances.

Conclusions

It is possible to implement a CSA (or NFPA) certified BMS on a primary reformer. Some of Nutrien's key learnings from this effort include:

1. Successful implementation requires a good understanding of the **intent** of the code more so than the prescriptive details.

2. A good working relationship between the owner/operator, the inspection body (IB) certifying the installation, and the engineering partner doing the detailed design is crucial to

arriving at a design that both meets the intent of the code AND meets the reliability and financial constraints of the owner/operator. It is particularly important for the IB to have prior experience and knowledge of the challenges of designing and operating large, industrial scale multi-burner fired appliances.

3. Testing, Testing, Testing! Given the complex and dynamic nature of these multi-burner fired appliances, extensive planning and testing is a necessity to ensure that all the details are properly accounted for. Successful implementation cannot be done quickly.

4. Consolidating automation into skids greatly simplified the final execution of the project, as well as addressed concerns around congestion and reliability of instrumentation in such a congested and difficult environment.

References

[1] "Code for the field approval of fuel-related components on appliances and equipment" CSA Group, B149.3-15 (2015)

[2] "Code for the field approval of fuel-related components on appliances and equipment" CSA Group, B149.3-15 (2020)

[3] STANDATA: Gas Code Variance, "Engineer Authentication at Oil and Gas Production Facilities", 20-GCV-02-Rev1 (2021)

Going Beyond Good Enough with IPL Design to Achieve Operational Excellence

A designed-for-purpose and robust-as-possible risk mitigation strategy performs well beyond the expectation of fully compliant systems with independent protection layer (IPLs) designed to minimally close the identified risk gap. Standard industry practice suggests having a good base process design, performing a thorough process hazard assessment (PHA) using an objective risk matrix, creating specific action items to close any safety and environmental risk gaps, and implementing corrective actions as soon as practical will result in a compliant, safe, and reliable operation. We have found that additional IPL design rigor and a focus on having as robust system as possible can achieve operational excellence even with significant numbers of action items still pending implementation.

Peter A. Henning, P.E., Christopher P. Horstman
Nutrien Lima Nitrogen

Matthew S. Davis, PMP, ISA/IEC 61511 SFS
The JDI Group, Inc.

Introduction

The Nutrien Lima Nitrogen Ammonia Unit, which was once referred to as "entering a death spiral" by a former executive in the early 2000s has completed its third straight year of continuous scheduled production without a serious safety or environmental incident as of the end of 2021. After starting up from a waste heat boiler repair in August 2018, the unit continued to produce each day for 735 consecutive days until the unit was shut down as scheduled for turnaround (TAR) outage starting in August 2020. Production resumed as planned 58 days later after routine maintenance and capital improvements. The unit remained actively producing the remainder of 2020 and the entirety of 2021 for an additional 432 consecutive days of production as of January 1, 2022.

Over the past decade, continually improving inspection, operator training and certification, preventative maintenance, and quality assurance combined with a detailed process safety management (PSM) approach that not only identified safety and environment risk gaps but also business risk gaps has strengthened plant operational reliability. Not only were operational loss and disruption risks identified, but stronger IPLs were implemented to fully mitigate all risk gaps even when business risk was orders of magnitude different than any identified safety or environmental risk. The holistic risk mitigation methodology led to assessing in detail how each component of the system could fail and identifying various common causes, which were removed from the system whenever possible.

Control and Safety System Infrastructure

The Basic Process Control System (BPCS), a uniform distributed control system (DCS) installed throughout the facility, and a network of unit emergency shutdown systems (ESDs) were previously very susceptible to several common cause failures that could result in large or even system-wide outages. The combination of not only losing all or large parts of one system but also incurring a large-scale outage in the other simultaneously made the resulting process disturbance very unpredictable and highly dependent on quick and effective operator action to avoid or mitigate unfavorable process events.

The most encountered infrastructure failures were caused by loss-of-power events. While an uninterrupted power supply (UPS) that was redundantly fed at the motor control center was nearly universally employed, the system had single components downstream of the redundant feeds that behaved more like a single source. The use of 120VAC I/O devices was extensive in not only the DCS and ESD but also in other critical devices like turbine governor and overspeed controllers. One UPS failure event not only caused the process to trip, by having safety critical inputs fail safe, but also placed demand on a seal oil turbine that could not start because the governor's power source was also removed by the same UPS failure.

The practice of staying with stable and proven versions of the DCS or ESD often left the system multiple major software and firmware revisions behind, making the emergency replacement of failed modules a potentially disruptive event. The ability to revert to older firmware isn't always possible and the system testing by the vendor doesn't always include excessively old versions. When the newer versions of firmware components are installed in the more vintage system, unanticipated and difficult to troubleshoot events can occur. One excursion occurred when a new parameter was introduced in a remote I/O module firmware upgrade could not be accessed from the legacy version of the configuration software. The default setting, which could not be changed, caused the downstream DCS modules which use FOUNDATION Fieldbus to communicate with field devices to begin to have intermittent loss-of-service events causing a significant amount of operational chaos.

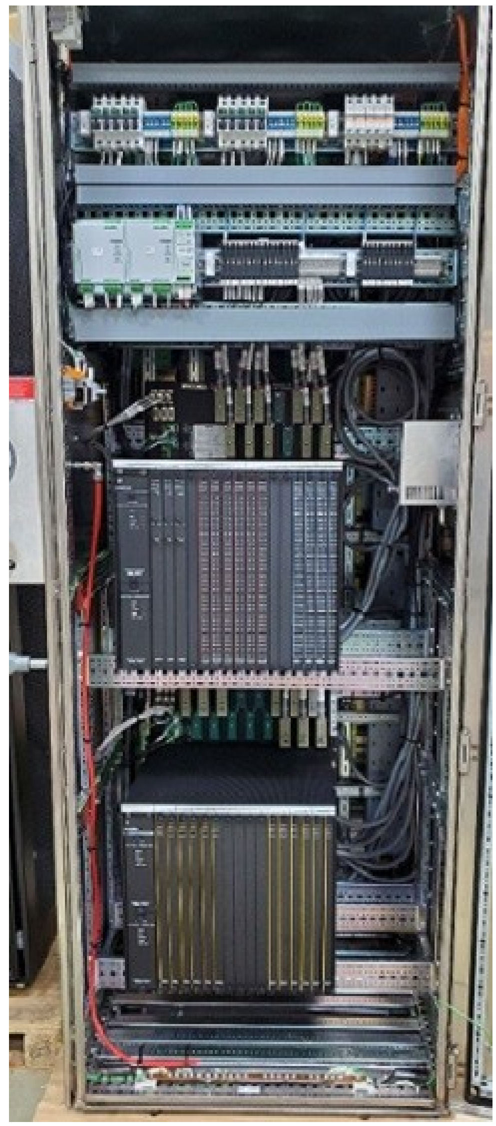

Figure 1: Front side of ESD control cabinet

While the quality of installation and safe work practices largely prevented loss-of-network connectivity, the opportunity for such an event existed as multiple optical fibers redundantly connecting both DCS and ESD components were typically run together in the shortest, easiest to install path. If the common cable tray was damaged by work or weather, the operators' view of the process and/or the remote I/O would be interrupted.

Figure 2: Back (I/O wiring) side of ESD control cabinet

Several control system upgrades and infrastructure improvements were implemented in the mid-2010s to address the vulnerabilities. Diverse sourced, redundant 24 VDC power was used throughout to ensure instrumentation continued to operate in the event of a power loss or UPS failure. 120 VAC components, typically solenoids and switches, were replaced with 24 VDC models to take advantage of the redundancy in the 24 VDC supply system. The implemented redundancy was much closer to the lowest levels of the system and greatly reduced common failures. Devices were protectively fused at proper levels on an individual basis to limit the impact of a single failed device. The latest supported version of both the DCS and ESD were achieved and subsequently maintained and updated in each turnaround (TAR) cycle. This resulted in better supported hardware and more predictability when replacing failed equipment. Redundant fiber optic communication rings and redundant high availability networking equipment were installed to provide multiple communication paths both among control and safety system components and at their interfaces with each other. The resulting DCS and ESD platforms are among the most redundant and robust forms available to provide highly reliable logic solver platforms.

Control and Safety System Function Independence

Although the Lima DCS and ESDs are distinct, independent platforms typically requiring collaboration from different developers to deploy composite functions, the desire to employ such schemes to limit the number of installed devices was quite commonplace in the early 2010s. The most glaring distortion of a safety function through intertwining the DCS and ESD was the low-level protection system for the CO_2 absorber.

The inputs used in the function were two DCS-connected remote seal diaphragm level transmitters and a low-level switch connected to the ESD that was often salted out due to challenges of being in potassium carbamate service and installed outside in a geographic location that experiences seasonal variation as colder weather increases the possibility of salting out. The logic controlling the decision to trip was in the ESD. The outputs were a DCS-controlled 20" motor operated gate valve (MOV) on the common line close to the exit of the absorber tower, two standard level control valves and two similar valves controlling the flow through the power recovery turbines, all of which had DCS-connected positioners and 120 VAC ESD solenoids to drive the control valves to fail state.

Since the DCS level transmitters were used as the basis for positioning the level control valves and the failure of that control loop could be an initiating event, an argument could be made that using various safety instrumented function standards provided no protection. It probably provided some protection, but it would have been an extremely complex calculation to determine how much. The logic implementation was also at least moderately complex to allow the diverse pieces to function together properly. Evolving the function for a modification like the addition of a third power recovery turbine would have been involved with a high probably of failing initial testing or not functioning properly when an unforeseen degradation occurred.

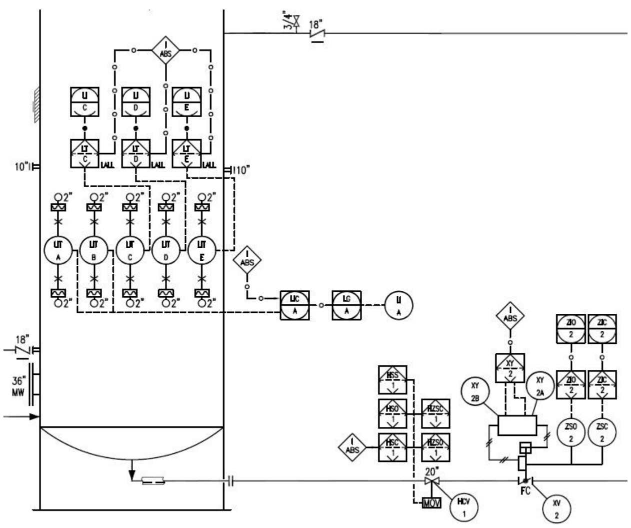

Figure 3: Absorber low-level protection system

The absorber low-level safety function was overhauled to achieve independence from the control functionality in two steps occurring in the 2014 TAR and 2015 expansion outages. The MOV was rewired to the ESD and its transition/operating speed increased to meet process safety time targets. Three additional level transmitters connected to the ESD were installed on the absorber tower and the problematic level switch was removed. The DCS level transmitters were removed from the trip function and used exclusively for alarming and control. Immediately downstream of the MOV, an ESD-controlled 20" pneumatic butterfly valve was installed, upstream of the flow splits. The 120 VAC ESD solenoids were removed from the level control valves to eliminate a chance for spurious trip in a UPS loss event. The resulting function not only could objectively meet safety integrity level (SIL-2) targets, but it also significantly reduced the probability of spurious trips that can easily escalate into unsafe and damaging events.

The enhanced low level protective function was activated in what was the most significant challenge to the 2018 – 2020 continuous production campaign. In preparation to remove one of the power recovery turbines for pump maintenance and replace it with the electric-driven spare, the field operator opened the bypass around the level control valve using a chain operator. He intended to barely unseat the valve to be ready for the coordinated effort of switching pumps with minimal disturbance to the absorber level. He pulled too hard and not only rapidly opened the valve to nearly fully open but also broke the chain operator. The DCS level control loop tried to preserve level, but it was not nearly fast enough for this disturbance and the ESD function engaged. The ESD function successfully brought the CO_2 removal system and the entire ammonia production unit to a safe state, limiting the equipment damage to the chain operator. The reformer stayed lit at minimum fire and after urgent maintenance on the chain operator was completed, the unit resumed production roughly 20 hours after the incident.

Secondary Functions to Prevent Trip Escalation

Another system design consideration that was showcased in the previous absorber low level incident was the use of automatic secondary functions to help prevent the trip from escalating.

When the absorber low level function engaged, the ESD immediately engaged the methanator shutdown, also contained in the ESD. Invoking the methanator trip caused the process gas vent in between the absorber and methanator to become the temporary destination for the front-end stream that was now very likely significantly above CO_2 limits with the removal system offline. The methanator trip invoked the synthesis gas compressor emergency shutdown prior to compressor surge being a concern. Since the synthesis gas compressor is driven by a steam turbine, which is the dominant high pressure steam user, another series of secondary actions engaged, including triggering the DCS to bring the reformer firing to a minimum setpoint.

Although the triggered secondary actions are not designed or credited as independent protection layers, the highly coordinated response is quick, reliable, and consistent, allowing the operators to focus on other concerns while the primary event is rapidly unfolding. If one of the secondary actions fails to perform, the appropriately designed and credited ESD function will engage and bring the unit to a safe state. Because the secondary actions act rapidly, demand on designed protective functions such as surge controls are avoided and only a minimal amount of the plant is removed from the normal production state, allowing significantly faster restarts after necessary repairs are made and root causes determined.

Although an argument can be made that the operator could make the same adjustments to achieve the same state without the extra logic complexity and additional interlock testing to ensure the actions function, we have found that operator effectiveness at avoiding escalations is highly inconsistent and typically fails in approximately 75% of attempts. The high rate of failure may be a function of the response time required due to Lima's expanded capacity, which now exceeds 150% of original design. The additional logic complexity is managed through strictly employing the Management of Change (MOC) process. The logic complexity and interlock testing load increase of 30% have proven to be a small price to pay for the significant benefits when steady state failures or process disturbances occur.

Approach to Input Group Selection and Functional Redundancy

Spurious trips and device failures that could not be remedied without sizable risk eroded confidence in the protective system even when control system infrastructure improvements and capable secondary system actions to avoid trip escalations were effective at reducing safety function demand. Striving for independence between control and protective functions also enabled higher capability functions with less common cause defeats to be utilized, but still a use gap remained.

Figure 4: Pressure and flow input devices

The first step in eliminating this gap was to determine the protective function's spurious trip cost, which can be considered a mid-campaign unplanned protective function activation. It was quickly discovered that all continuous processes with normal runtime exceeding a week could reduce anticipated spurious trips enough using the

ESD as the solver for all discrete trip functions so that use of DCS-based trips was eliminated in all but very specific situations.

The analysis also showed that universally implementing two-out-of-three (2oo3) input transmitter voting groups to provide trip triggers had an expected payback in one year or less. The input strategy now allowed the grouped instruments to continue operate with a minor voting degradation instead of shutting down to repair or continuing to operate with a sizable risk gap that comes with removing the entire protective function. The input voting arrays combine with other design factors that support uptime, including rotating equipment largely having installed spares, control valves having manual bypasses and isolation valves to allow for an onstream repair. Input voting arrays proved to be so beneficial in continuous processes that all new trip inputs implemented used a 2oo3 voting arrangement even when only a SIL-1 function was required.

Although 2oo3 voting groups alone solved approximately 90% of the likely input reliability challenges, the remainder required the implementation of diverse voting groups to ensure a protective function could still function even if the primary detection inputs degraded over the campaign. The most prevalent use of the multi-input group strategy is seen when a high outlet temperature trip is used to protect downstream equipment from a temperature excursion that challenges the maximum allowable working temperature (MAWT). An input voting group, using a calculated compensated flow ratio between two streams that combine in a reaction vessel, is used in conjunction with the high temperature trip to provide highly reliable detection of an unfavorable event, even if several of the temperature elements are degraded. Degradation of temperature elements in severe service commonly occurs from a thermocouple junction forming before the tip, causing the measurement device to report a temperature that is lower than it really is at the tip. Even though the elements are in wells, they typically cannot be successfully removed and replaced. The element often breaks and leaves residuals in the well, making the installation of new element nearly impossible without removal of the well.

The Lima KBR Reforming Exchanger (KRES™) is protected by both a direct high temperature trip and a process air to primary reformer gas flow ratio that is calculated from a vast array of pressure, temperature, and flow transmitters located in less severe service areas, which are serviceable in production. A similar function is also used in the nitric acid plant where the ammonia to process air ratio input voting group combines with a high gauze temperature trip. In both cases, the high temperature trip voting group can be degraded and even removed, and the protective function still meets the SIL-2 target.

Figure 5: Input and output devices on a skid

Approach to Output Group and Component Selection

As anyone who has ever done SIL calculations knows, the best logic solvers and input redundancy schemes can only influence the probability of failure on demand (PFD) of combined function so much, because typically the output reliability and redundancy together form the dominant term. Even with highly redundant inputs that could largely be maintained in production, some ESD functions still fell short of their desired targets when the ideal TAR testing interval was considered. The reliability of the output instrument equipment to perform a SIL-2 function when tested at a 60-month interval versus a 12-month interval is significantly different.

Figure 6: Reformer fuel isolation valves with online testing bypass

The various site protective functions were first investigated to determine an ideal testing interval. The ammonia and urea plants were striving to run for five years between TARs, so the 60-month target was ideal for them. The nitric acid unit has gauze replacement several times a year and typically several days of planned maintenance yearly. Two years was determined to be ideal for testing in the nitric acid plant to allow the years in which there were ammonia and urea TAR to be skipped to provide for better technician load balancing (fewer periods of unusually high demand for technicians). The other plant areas, including product shipping, were determined to be more batch-like and annual testing could be accommodated.

To achieve the desired long duration between testing intervals in the ammonia and urea units, one or more of the following strategies had to be employed regarding the output devices: provide a way to bypass and fully test output devices in production, devise a methodology to count system activations as testing, perform a partial stroke test, or use the most reliable components available according to various failure rate sources. Using system activations as output proof test results is still being explored, but the various difficulties, including most notably unpredictable timing, in getting such a program to be credible has prevented investing too much in this approach. Partial stroke testing provides some diagnostic coverage but comes with the chance of a possible disturbance event on a complex production system. Lima employs partial valve stroking sparingly with most of the applications isolated to steam turbine trip valves.

While manual bypassing to allow online full valve shutoff testing is utilized, most notably with the reformer fuel valves, it is used as a last resort and avoided whenever possible because of the necessary administrative controls. Ensuring that a proper test is completed without risk of a spurious trip event or compromising the function and not allowing it respond to a valid demand is challenging even with the best logic and physical setup. The fuel gas bypass installation Lima employs allows only one of the two shut-off valves to be removed at a time, reducing the probability of failure on demand when the shut-off valve is being tested.

Pursuing series installations of the best available process-suitable components in terms of their published failure rate data has been the strategy most often employed to extend SIL-2 functions to long duration test intervals. The methanator shutdown is an example where the ESD-based logic with a voting array consisting of nine unique temperature indications could not achieve the SIL target at the 60-month testing interval with the single 10" generalized butterfly valve and actuator equipped with 120 VAC safety solenoid. The output device was replaced with two 16" SIL certified butterfly valves in series with high reliability spring-return actuators activated by redundant diagnostic solenoids.

The change from a single 10" butterfly in a one-out-of-one (1oo1) function required to mitigate the hazardous event, to two 16" certified butterfly valves in a series, one-out-of-two (1oo2) function, not only increased output fault tolerance that significantly improved the function's PFD but also reduced pressure drop and allowed a modest production rate increase. The diagnostic solenoids are deployed in a two-out-of-two (2oo2) manner where both solenoids must de-energize to close the output device. The 2oo2 configuration reduces spurious trip risk but increases the chances of latent dangerous failure. To discover latent dangerous failures, the ESD executes a solenoid cycling sequence once every 24 hours to discover if either solenoid has degraded using diagnostic pressure switches. If the diagnostic test fails, an alarm is generated to alert the operator to enter a request to get the solenoid repaired. The redundant diagnostic device can therefore both reduce the chance of spurious trips from a single device failure and also improve the protective function's PFD.

Much like the nearly exclusive use of the ESD for trip logic and 2oo3 input voting arrays, the use of redundant diagnostic solenoids and the highest quality output devices became commonplace for all new installations regardless of desired SIL target. In the 2020 TAR outage, a replacement synthesis loop isolation function converted the DCS-based logic controlling general ball valves driven by MOVs, to ESD-based logic controlling pneumatic high-reliability rising stem ball valves driven by redundant diagnostic solenoids.

Loss and Disruption Risk Mitigation Strategy

The need to deploy safety instrumented functions where necessary to mitigate unacceptable process safety or environmental damage risks is largely consistent throughout the greater nitrogen industry. How and when to deploy ESD functions in response to production loss and disruption events, however, is viewed from several distinct vantage points. The two predecessor companies that formed Nutrien saw loss and disruption risks differently. We believe loss and disruption risks should be pursued with a similar vigilance as the more universally accepted safety and environmental risks, with the safest state for a nitrogen production facility (other than shutdown and secured) being steady-state production. Numerous empirically high-risk operating modes must be safely traversed to restore failed equipment if an online repair cannot be made.

Although the Lima facility's base design can tolerate a large amount of rotating, electrical, or control equipment failures, several large compressor trains are intended to run from one TAR to the next with only minimal preventative maintenance. Using the same process hazard analysis (PHA) methodology, it can be determined the likelihood of an event that may have loss and disruption consequences that are orders of magnitude higher than the safety or environmental consequence for the same event. One such event is a loss of lubrication oil on one of the compressor trains intended to operate from TAR to TAR.

On several of the vital compressor trains throughout the facility, three independent layers of protection are provided to mitigate the loss of lube oil to a critical compressor, which can be caused by loss of the primary lube oil pump or failure of a control valve or regulator. A BPCS logic-based function will be triggered to start the auxiliary lube oil pump by a single pressure transmitter for the first layer of protection. Although not credited as an IPL due to response time concerns, the BPCS pressure transmitter will alert the operator of the abnormal state. If starting the auxiliary oil pump cannot eliminate the hazard, a separate 2oo3 pressure transmitter voting group can initiate a machine shutdown through the ESD for an additional two layers of protection. Due to the desired test intervals discussed previously, additional fault tolerance is often required in the device or devices that halts the machine to achieve two layers of protection. Lima has installed additional output devices to eliminate loss and disruption risk and while difficult to quantify payback precisely, we believe the enhanced functions have provided benefits far exceeding their monetary and opportunity costs.

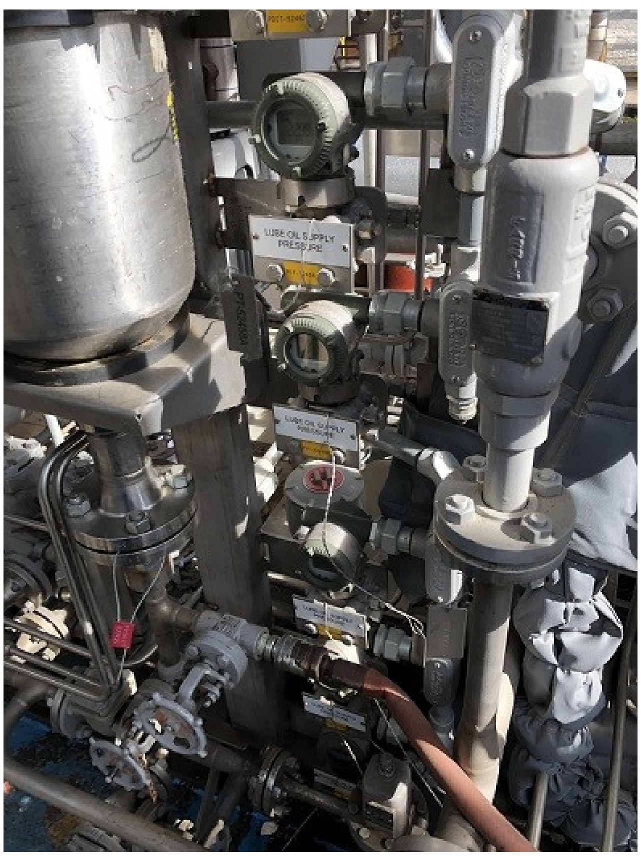

Figure 7: Turbine oil low pressure protection

Packaged Units Mitigation Strategy

Nitrogen facilities are increasingly dependent on packaged units to reduce project costs. While prefabricated integrated units can vary widely in their designs and robustness, the same risk identification and mitigation targets must be applied to the packaged units as the ones applied to the main process. A complex manufacturing system is only as strong as its weakest link. Packaged units that are typically highly cost-focused and commoditized can lack robustness that places demand on protective functions or causes unnecessary loss and disruption risk.

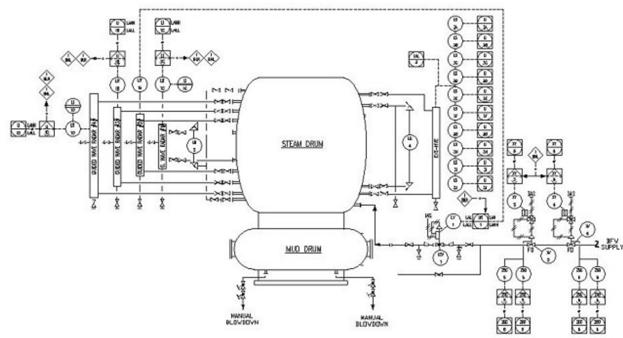

Figure 8: Boiler steam drum level protection system

Since the Lima ammonia unit employs a terrace-fired reformer without an auxiliary boiler and has a KRES that transforms some of the waste heat into additional reforming capacity, it is especially vulnerable to disturbances from the two packaged boiler units each supplying up to 150,000 pounds per hour of 900 psig steam. Both packaged boilers were redesigned and extensively modified to meet the same robustness expectations of the main process. While boiler firing controls remained in the DCS, the DCS-based burner management systems (BMS) were replaced with ESD logic systems to increase their reliability and robustness. 2oo3 input voting arrays, output valves with excellent failure rate data, and diagnostic solenoids were utilized throughout these systems.

The facility experienced two significant loss of boiler steam drum level events in its 50+ year operating history that resulted in a serious threat to onsite personnel and costly loss and disruption to the boiler equipment. The boiler drum is manually blown down by the utilities operator several times a week, resulting in a very high chance of human error. This potential error, combined with the consequence, requires four independent layers of protection to mitigate the risk. The boiler level control loop, using a compensated guided wave radar, provides the first layer of protection for the operator-initiated event. A diverse Eye-Hye discrete level detection device that independently generates an alarm alerts the board operator of the abnormal situation. An independent 2oo3 voting group of compensated guided wave radars provides the final two layers of protection by tripping the BMS. In the case of level loop failure, the alarm and BMS low level trip are credited again meeting the risk mitigation target.

Conclusion

In Spiderman, Uncle Ben tells Peter Parker that "With great power comes great responsibility." The same can be said about protective functions provided by an ESD system.

Often overlooked or regarded as the primary solution provider's responsibility, instrument and control infrastructure and designed fault tolerance is as critical as process, rotating, or electrical components in enabling successful continuous campaigns. Even as modern market share-leading DCS systems employ embedded ESD systems making the sharing of devices more accessible than ever, segregation of the DCS and ESD is valuable in making the system more robust from various common cause disturbance events caused by both equipment failures and human action. As facilities have increased throughput and complexity, required response time and the operator's ability to respond to abnormal events have decreased, leading to the need of using designed secondary functions to reduce demand on other protective functions and prevent trip escalation.

ESD inputs and output arrays of the highest quality can be utilized to minimize spurious trip risk and allow testing intervals spanning years instead of months. Loss and disruption risk is real and should be completely mitigated to risk tolerance level, when possible, to give the facility the best chance of staying in a steady state envelope effectively and efficiently producing. Packaged units can be the weakest link in otherwise stout systems and oftentimes the system will only perform to the abilities of the most fragile system component.

While the risk mitigation strategy described here was at various times under significant pressure to reduce costs and just be good enough to be compliant, going beyond proved to be worth the additional cost and effort in terms of overall performance, reliability, and uptime.

Methanator Temperature Runaway Results in a Fire

In the 1990s and early 2000s there were at least two known methanator runaways in North America that resulted in equipment overheating and loss of containment. The particular incident addressed in this paper is one of those two. It occurred during startup of a hydrogen plant while reducing a fresh charge of methanator catalyst. Piping in the methanator circuit overheated, resulting in a large fire. Although this incident occurred almost three decades ago, it underscores the importance of having and following well written procedures, safety instrumented systems, layers of protection, and risk awareness.

Ken Wohlgeschaffen
Chevron Products Company (a division of Chevron U.S.A., Inc.)

Introduction

Chevron operated a 1960s era hydrogen plant at one of its refineries. This relatively large plant (70 MMSCFD H_2) was designed to use natural gas or naphtha feed and produce a 96% pure hydrogen product at a relatively high pressure of 980 psig (68 barg). The process configuration was typical for conventional hydrogen plants of that era. It consisted of traditional desulfurization, steam reforming, high and low temperature shift conversion, and Purisol (n-methyl-2-pyrrolidone, "NMP") solvent CO_2 removal, followed by methanation. The 1994 incident occurred in the back-end purification section of the plant during a startup.

Figure 1 shows the layout of the back-end purification section of the plant. Process gas leaving the Purisol CO_2 removal absorber is heated up in the two E-312A/B feed-effluent exchangers, and then in the trim E-303 methanator preheater which uses high pressure (875 psig or 60 barg) steam from the waste heat boiler as the heating medium. The product hydrogen exiting the methanator is cooled in the E-312A/B feed-effluent exchangers. It is cooled further in the E-314 air cooler followed by the E-315 water cooler. Condensed water is separated from the gas in the V-308 product hydrogen knockout pot.

Sequence of Events

Fresh NMP solvent was charged to the system earlier in the week, and additional NMP was transferred from storage into the unit. The Purisol unit was brought online. The CO_2 analyzer on the absorber overhead was calibrated. Process gas was introduced into the methanator from the Purisol unit as the absorber overhead gas analyzer was showing 1.4% CO_2. During normal operation the absorber overhead gas contains 1% CO_2.

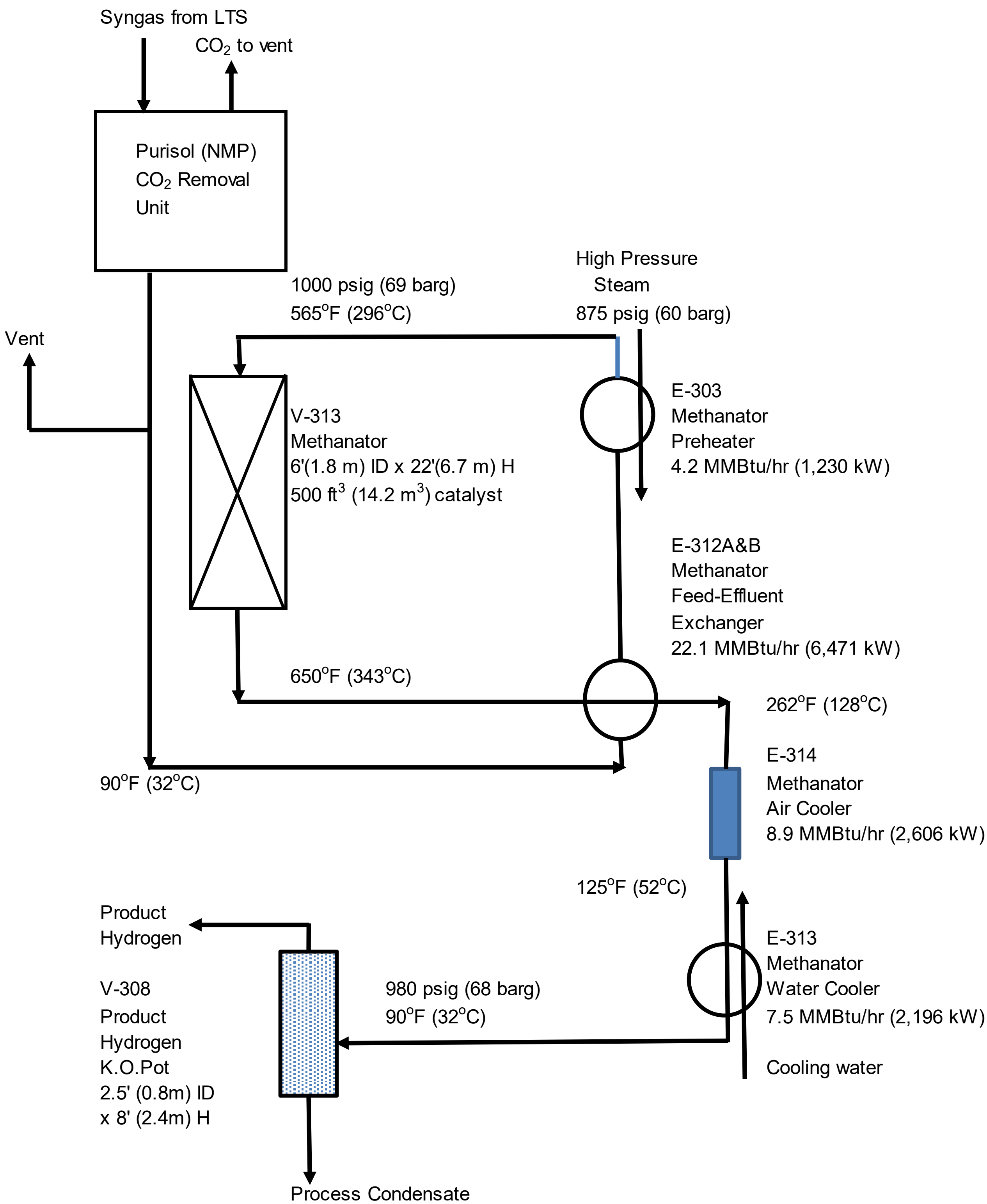

Figure 1: Back End Purification Section

The methanator was loaded with new, unreduced catalyst in its upper ("A") and lower ("B") beds during the major turnaround. The reduction procedure requires the process gas inlet temperature to be raised to 600ºF (316ºC) followed by a 24 hour "soak" at this temperature. Typical inlet temperature during normal operation is 565ºF (296ºC).

The methanator inlet temperature was slowly raised from 520ºF (271ºC) to 539ºF (282ºC) over a period of two hours. Five minutes later bottom bed temperatures in the methanator started to heat up at 2ºF/minute (1.1ºC/minute). Ten minutes later the heat-up rate increased to 5ºF/minute (2.8ºC/minute. At this time there was a very high level of condensate in the V-308 product hydrogen knockout pot which the automatic level control valve could not handle. It had to be manually drained. After seven minutes the heat-up rate jumped up to 12ºF/minute (7ºC/minute), and within two minutes it was 49ºF/minute (27ºC/min).

The high exit temperature alarm, which is set at 800ºF (427ºC), rang in two minutes later. Seconds later the methanator B bed bottom temperature indicator (the blue line in Figure 2) went beyond its maximum range. This was followed by the methanator outlet temperature indicator (the green line in Figure 2) a minute later. Two minutes later the A bed bottom temperature indicator (the orange line in Figure 2) went off scale high. These instruments are ranged 0-1000ºF (0-538ºC). See the temperature trends in Figure 2.

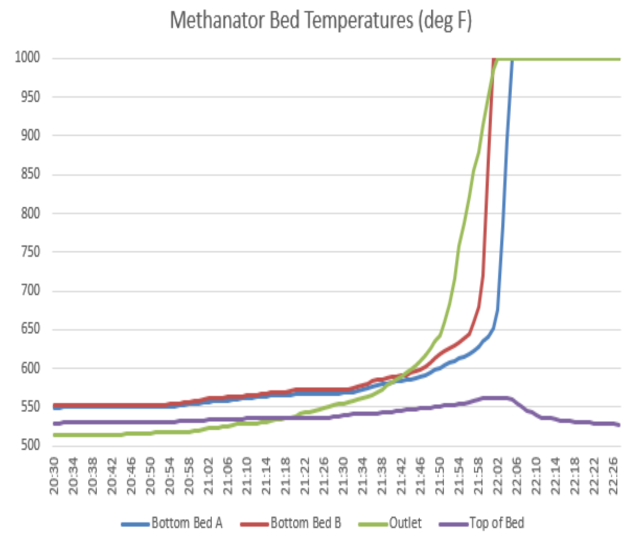

Figure 2: Methanator Temperatures

A visual field check was made of the methanator and the preheaters. It was noticed that the methanator outlet line and the E-303 preheater inlet line were glowing cherry red. A pyrometer measurement showed the E-303 preheater inlet piping was approximately 1200ºF (649ºC). It was decided to start to line up equipment to apply steam to cool the hot areas.

An attempt was made to rescale the bed A bottom bed temperature indicator to 0-1200ºF (0-649ºC) in order to determine the true bed temperature. However, the attempt was unsuccessful.

Attempts were made to reduce the methanator outlet temperature by lowering the inlet temperature. Over a nine minute period the inlet temperature was reduced from 539ºF (282ºC) to 522ºF (272ºC) by reducing the steam flow to the E-303 preheater. The top beds in the methanator started to cool (the purple line in Figure 2), leading to the belief that the bottom bed temperatures were also decreasing and the exotherm had been stopped. However, the temperatures in the bottom of both beds had continued to increase undetected. Sixteen minutes later the inlet piping to the E-303 methanator feed preheater ruptured at an elbow. See Figure 3 showing the equipment layout and failure location.

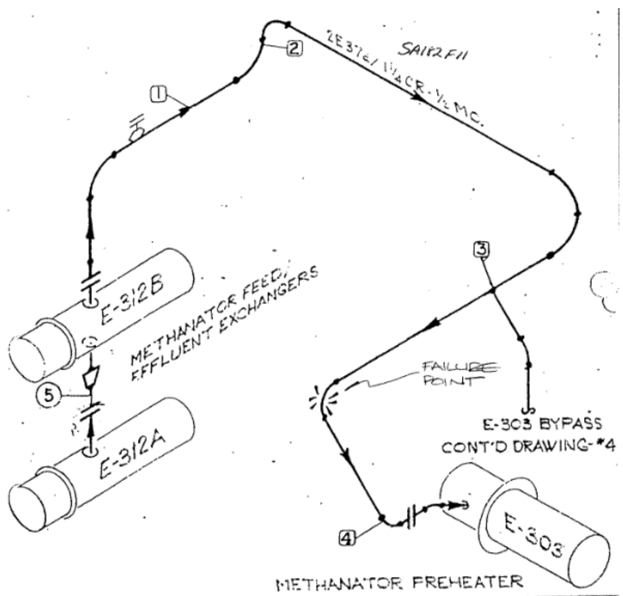

Figure 3: Methanator Feed Circuit

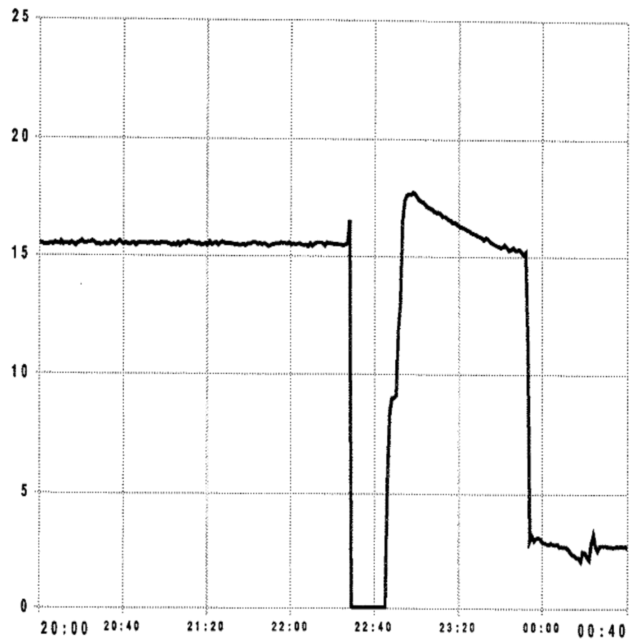

Figure 4: Plant Feed Rate (MMSCFD)

The released gas immediately caught fire. It burned up an area of concrete foundation approximately twenty square feet (1.9 square meters) by three inches (7.6 centimeters) deep and damaged equipment nearby. Fortunately no one was in the area at that time.

The Fire Department was notified and a plant emergency shutdown immediately initiated. Hydrocarbon feed was pulled, and nitrogen was introduced into the front end of the plant to extinguish the fire. Figure 4 shows the plant hydrocarbon feed being taken out and replaced with nitrogen.

Investigation Findings

It was suspected that incorrect material of construction may have led to the piping failure. The equipment materials and inspection reports for the methanation loop were checked. It was confirmed that the materials of construction were correct according to the original design specifications. See Figure 5.

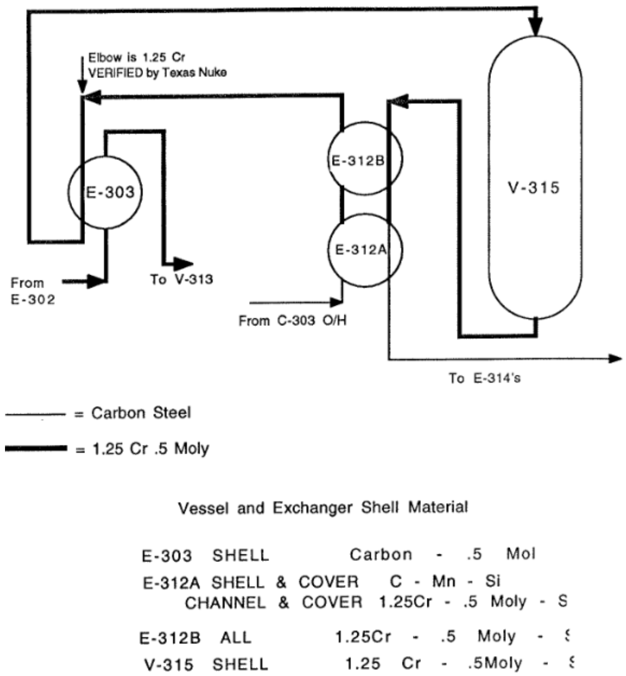

Figure 5: Materials of Construction

It was assumed that the NMP solvent was in good condition because fresh, pristine solvent had been charged to the system. So no check was made to verify its condition. However, the wet solvent from the storage tank that had been added to the fresh solvent charged to the system contained a high concentration of water. Water inhibits the NMP solvent's absorption capacity. A sample was taken from the V-328 low pressure CO_2 flash drum after the incident. Analysis showed the NMP contained as much as 15% water. The normal specification for proper absorption of CO_2 by the lean solvent is a maximum water content of 0.3%. This means that the solvent was not properly absorbing the CO_2 from the raw hydrogen gas.

When the methanator catalyst was partially reduced and the methanator inlet temperature reached 525°F (274°C), the methanation reaction started. Until that point there was no exotherm in the reactor. 1% CO_2 in the gas entering the methanator generates a temperature increase of approximately 108°F (60°C). The high concentration of CO_2 in the gas reacted very exothermically with the hydrogen, generating ten to twenty times the heat that would be generated during normal operation, and the runaway occurred. This caused the rapid rise in the temperatures of the catalyst beds, heat exchangers, and piping.

The procedure did not specify the steps to be taken for reducing a fresh charge of catalyst. This caused attention to be diverted. The focus was on simply heating up per the normal procedure and monitoring the inlet temperature to the V-315 methanator rather than the bed exotherm across the reactor. It was not understood that the methanation reaction occurs at 525°F (274°C) at which point the exotherm starts.

The CO_2 analyzer was found to be malfunctioning, despite the calibration check. This led to the instrument erroneously showing a false low CO_2 concentration of 1.4% (Figure 6). A value of less than 2% CO_2 concentration is required before introducing gas into the methanator. No sample of the gas was taken and analyzed to verify the CO_2 concentration.

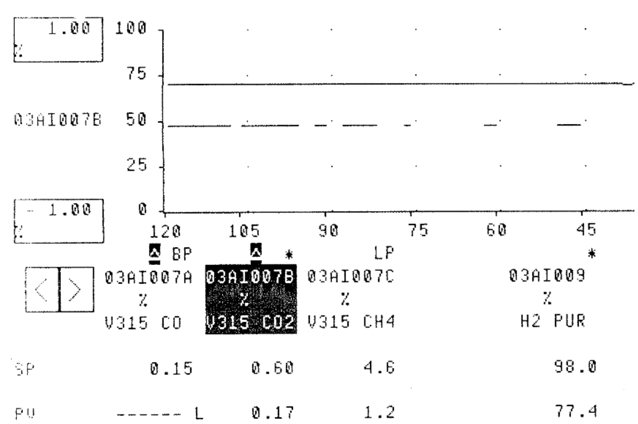

Figure 6: CO_2 Analyzer Trend

A high pressure drop was seen across the C-303 Purisol absorber during the incident. The pressure drop had increased from it normal value of 7.2 psi (0.5 bar) to 20.4 psi (1.4 bar). See Figure 7. It was not recognized that this indicated that the gas flow rate through the entire column was much higher than normal. This was because the NMP wasn't absorbing all of the CO_2 in the gas entering the column,

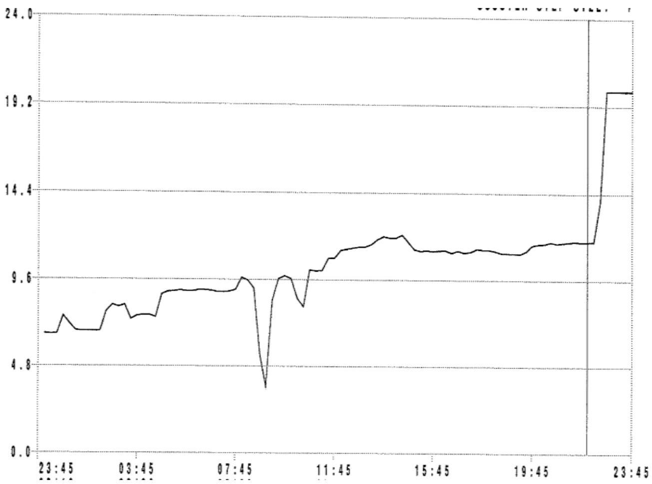

Figure 7: C-303 CO_2 Absorber Pressure Drop Trend (psig)

There was no automatic trip system on the methanator in this plant. The methanator was to be manually bypassed if the exit temperature exceeded 850ºF (454ºC), depressurized, and purged with nitrogen per the operating procedure. However, it was not bypassed when the exit temperature increased above 850ºF (454ºC). When the inlet temperature was lowered and evidence of some cooling was observed, it was mistakenly believed that the exotherm had been stopped, when in fact it hadn't.

It was not recognized that the high level in the V-308 product hydrogen knockout pot, which overwhelmed the automatic level controller and had to be manually drained, was due to the large quantity of water being generated by the methanation reaction:

$CO_2 + 4\ H_2 = CH_4 + 2\ H_2O$

In addition to the water being generated by the reduction reaction:

$NiO_{(s)} + H_{2(g)} = Ni_{(s)} + H_2O_{(g)}$

Key Lessons Learned

It is extremely important to maintain and follow written procedures covering potential safety scenarios, to ensure appropriate safety systems are in place, and to ensure safeguards are functioning properly.

It is important to have clear written procedures which cover unusual situations and recognize safety risks. The procedures at the time of this event did not include causes and effects of high liquid level in the V-308 product hydrogen knockout pot, or high pressure drop in the C-303 absorber. There was also no discussion of the catalyst reduction requirements in the start-up procedure which was written for standard plant start-ups. The operating procedures were revised to include clear guidance for these situations.

It is also important to follow written procedures. In this case, the NMP solvent was not checked for water content to verify that it was low. More importantly, the methanator was not bypassed when the outlet temperature rose above 850ºF (454ºC).

This incident also emphasizes that safety instrumented systems are needed to safeguard against high-risk scenarios. To protect against methanator runaways, hydrogen plants are now equipped with highly instrumented trip systems which quickly bypass the methanator on high bed temperatures using a voting system. Previous technical papers presented at this symposium have discussed methanator trip systems in detail.[1],[2],[3]

Finally, safeguards which are in place need to be checked to ensure they are functioning properly. In this case the CO_2 analyzer was incorrectly displaying false low CO_2 concentrations. Layers of protection are important. In this case a second layer of protection would have been to manually sample and analyzed the gas to verify it contained less than 2% CO_2 before feeding it to the methanator.

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Improved Process Performance and Safety via Autonomous AI: Dyno Waggaman experience

Achieving zero incidents while maximizing process uptime and efficiency has always been the key vision for Dyno Nobel Waggaman. This paper talks about Dyno Waggaman's digital transformation journey and the early outcome of their implemented initiatives.

An important building block towards improving the operational performance and safety is establishment of a proactive risk mitigation culture, supported by effective technologies and sound management workflows. Studies show that most incidents and unexpected process failures can be avoided if the risks are identified at their initiation stage in a way that operating teams get timely information about them and take preventive actions early on. This can be accomplished by having: (1) a proactive management, (2) an effective workflow, and (3) an enabling technology.

At Dyno Waggaman, the management decided to make a change and bring forward the proactive culture. Also, "Dynamic Risk Analyzer™" based on recent breakthroughs in autonomous AI/machine learning, was identified as one of the enabling technologies. Finally, in time, a workflow was established to achieve the best results.

This presentation will focus on the following areas: (1) sharing of management workflows, (2) challenges that were undertaken to help drive a proactive risk mitigation culture, and (3) experience and applications of an autonomous AI/machine learning technology, along with real-life lessons and case studies.

Ashutosh Shukla, Marc Hermus
Dyno Nobel Inc

Ankur Pariyani, PhD, Ulku Oktem, PhD
Near-Miss Management

Introduction

Minimizing incidents, while maximizing process uptime and efficiency is an important goal for most production companies. This goal can be achieved using the latest digital technologies; however, companies also need to consider change management aspects and carefully plan how to adapt their "organizational culture" shift. Along this process, it is equally important for them to ensure that employees fully embrace changes and recognize their benefits. This paper offers a modern approach for the companies to transform their organizational culture and workflow from "reactive" to "proactive" and improve their operations' performance significantly – by utilizing new developments in digital technology, particularly autonomous AI/Machine Learning.

Dyno Waggaman Ammonia plant is a new facility and hence, most of the basic frameworks/tools for operational excellence such as Historian, Plant Resource Monitoring (PRM), Plant Monitoring (Insight), Incident Reporting and Management, were setup from the beginning. With time, the plant was further supplemented with alarm rationalization and machine diagnostic tools (System1). However, some of the investigations on process upsets brought out shortcomings in picking *weak signals* before the upsets – which led Dyno Waggaman to look for new enabling technological options.

An important step towards achieving operational excellence and improved safety is the establishment of a proactive risk mitigation culture, which in turn, is supported by effective technologies and sound management workflows. Studies show that most incidents and unexpected process failures can be avoided when risks are identified early on and operations teams take proactive-corrective actions to resolve them in a timely manner, as opposed to being delayed due to either a lack of information on the developing risk or a lack of an effective workflow [1-5]. Therefore, improving operational excellence can be accomplished by having: (1) a proactive management, (2) an enabling technology, and (3) an effective workflow.

A successful organizational change can be accomplished first by setting up and agreeing on priorities between the stakeholders (operations, maintenance, engineering, etc.) and management. Ideally, building a culture on these priorities is the best practice that should occur before any project is undertaken. This process of developing a proactive organizational culture can best be organized through the following steps: first, the goal to achieve a proactive culture should commence from the plant management – starting with implementation of clear priorities that would allow the transformation plan to be successful. The goal and plan must be reviewed with the operation staff to ensure that there is ownership at the appropriate level. The next important step is to select the right digital tool(s) that would enable this transition. Efficient implementation of those tools is equally critical so that the resources can be utilized, without over-stretching of any areas. Once the tools are selected and they are functionally in place, it is critical to develop a workflow that allows engineers and other operations members to integrate the tools into their schedule and use them efficiently. Undefined or unclear workflows often lead to failures of such initiatives early on. Furthermore, when employees are stretched to cover multiple projects, this often leads to a lack of ownership, so having the right balance is important.

In summary, attention to change management is a key attribute for a successful digital transformation. While the right digital tool is an important enabler, true change occurs at the organizational culture level. Furthermore, an efficient workflow is critical that allows for integration of newly generated insight into daily practices and enables operations teams to successfully achieve significant improvements.

Digital technologies for early risk identification

With the recent advances in data science and computing power, currently there are several approaches and directions available for the processing industry to identify problems at their early stages, compared with traditional monitoring and alarm systems that often notify the operating team much later – once the risk is further developed. While many of the available technologies are in more mature stages and are already being utilized commercially, some others still require more development and validation. Furthermore, different analytics categories offer diverse insights that often do not overlap with each other.

In practice, there is no silver bullet that can address all concerns and solve all problems. Successful companies must choose the right combination of digital technologies to address their needs.

This section briefly explains the five most promising digital technologies (shown in Figure 1) that allow for identification of process problems at an early stage.

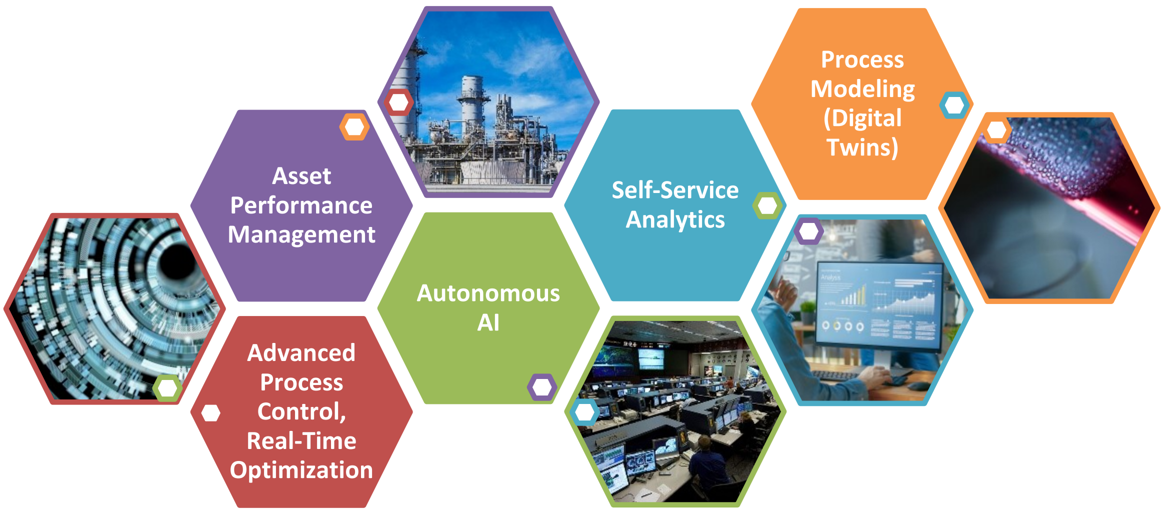

Figure 1. Promising Digital Technologies for Early Identification of Process Problems

Process Modeling (Digital Twins)

Process Modeling approach, also referred to as creating a "Digital Twin" for a process or equipment, is based on building custom first principal models by domain experts. These models are developed based on a fundamental understanding of underlying physical and chemical phenomena, such as mass balance, energy balance, heat transfer, reaction kinetics, and the key operational steps, such as heating, cooling, pumping, etc. Once a model is developed, tested for different operational conditions and a reliable model is achieved, it can be used to detect a mismatch between model-estimations and real-life sensor measurements, which may be indicative of a problem. For example, if there is a significant deviation between model-based pressure prediction versus sensor-based pressure reading, that could be an indication of a processing issue or an instrument problem. This approach can also allow for estimation of parameters that cannot be measured easily (called "virtual metering"), such as, the temperature inside a furnace, and can be used to predict some of the potential outcomes if conditions do not change.

Conversely, the models are prone to drift over time and require periodic tuning by experts. The creation and maintenance of models is a resource intensive process, often spanning several months, and requiring CAPEX investment. Furthermore, when a new piece of equipment is added or an existing process is modified or when an equipment condition slowly deteriorates or after a major turnaround, the models most likely need to be rebuilt or re-calibrated.

Asset Performance Management

Asset Performance Monitoring tools are based on building custom baseline models (for an asset/equipment) by domain experts that use a combination of "normal signatures" and "failure signatures". The normal baseline is built using data from good plant operating conditions in the past. When a mismatch is detected between the real-life sensor measurements and normal baseline, the system prompts the user of a potential problem. Often additional "failure signatures" are provided as an input (by domain experts) to better characterize a developing problem. Using this failure signature library, these systems can recognize the failures in their initial stages and can help detect *recurring* problems early on.

Like digital twins, the creation and maintenance of baseline models (library of signatures) is a resource intensive process, which needs to be carefully handled by domain experts together with the operations staff to avoid false negatives and false positives. These models also require tuning and re-calibration periodically as changes (aging, turnaround, etc.) occur in the process. If a new type of failure or abnormal condition occurs (e.g., combination of multiple failures), there may not be an existing failure signature to compare against. Furthermore, if a piece of equipment is re-built or the standard operating procedure for a process is changed, the resulting data may not completely align with the previous asset signature in the library, which means the baseline needs to be re-established again.

Self-Service Analytics

Self-Service Analytics tools are toolboxes with advanced statistical options (such as regression, classification, clustering, model fitting, etc.), allowing the operations staff to do in-house data analysis, without the need to write their own software code. For example, the user can view the plant process data from the historian, analyze it using different statistical options provided by these tools, compare it with different time periods and set up alerts. With easy installation and maintenance, these systems can help improve the knowledge and skills of the team members in understanding their process data, whenever needed. When an in-depth look at a specific problem is required, these tools can be useful.

In contrast, when individuals or teams are bombarded with large amounts of information or are required to make decisions within a short period of time, they often resort to mental shortcuts or heuristics (referred as Cognitive Bias) that can lead to inaccurate interpretations. Even the most experienced operators and engineers are not impervious to these biases [6-7]. Because the results are dependent upon the user, their use may lead to different interpretations and hence, may not reliably identify problems every time.

Autonomous AI/Machine Learning

Autonomous AI/Machine Learning systems analyze large volumes of historical process data and autonomously learn the characteristics of normal and abnormal performances, using self-optimizing, unsupervised algorithms. Unlike traditional machine learning, there are no models to build or maintain and hence, the operations staff do not need to tune/calibrate them, making it easy to install and maintain, saving engineering resources and avoiding cognitive bias. This approach enables continuous self-learning, allowing the system to adapt autonomously to dynamically changing conditions in the plant. Therefore, they can be an excellent overarching way to provide early identification of developing issues anywhere, across the whole process. These systems can also be helpful for timely maintenance scheduling by pointing out the emerging problems before an emergency, allowing issues to be addressed when it is easier, quicker, and less costly. The specific application and case studies developed by Dyno Waggaman, utilizing this technology, are discussed in the Section on 'Dyno Waggaman Experience in using Autonomous AI'.

While enabling early identification of needed process corrections and maintenance, this technology is not applicable for process optimization. Since it does not include any custom-built first principle or baseline models, its predictive power is limited to pointing out the problem but not a solution or an option.

Advanced Process Control (APC) and Real-Time Optimization (RTO)

Advanced Process Control (APC) refers to control techniques such as Model Predictive Control, Feedforward Control, etc., that address specific performance or economic improvement opportunities in the process and are deployed in addition to basic process controls. Real-time Optimization (RTO) refers to optimization strategies that maximize (or minimize) an economic function for the plant such as Overall Yield, Product Concentration, Raw Material Costs, etc. while respecting the existing constraints (related to quality, safety, environmental compliance, etc.). The common objective is to maintain the process at desired operating conditions while taking process constraints in account, even though the plant is subjected to nonlinear behavior and frequent disturbances [8].

Although they are primarily used for control and optimization of a process and are not directly designed as an early risk identification technology, they can be used as such by engineers to identify deviations with respect to some meaningful set-points, established by SMEs. As the process moves away from those desired set points, the operations staff get notified about the deviations, allowing for an early intervention.

In practice, both APC and RTO are limited to controlled variables only, which form less than 10-20% of the total variables in the process. They do not monitor manipulated variables, variables that are taken out of control for one reason or another, or disturbance variables, which is where, the problems originate in many cases.

In summary, although the above solutions identify problems from different perspectives, they often complement each other. For example, in a steady state, a basic control system attempts to maintain a process variable (controlled variable) by modulating the control element through its entire range (0-100%). However, an enabling AI technology, with its statistical analysis capability, would flag an anomaly if historically the basic control had steadier output – thus prompting the operator to deep dive and investigate. Successful companies must understand these differences, their advantages and drawbacks and use a combination of these solutions to leverage their available benefits. If possible, companies looking to implement new digital technologies should consider more than one solution to ensure a successful early problem identification and resolution program.

Lastly, besides the advantages and disadvantages, it is also important to consider the resource requirements (financial and engineering resources) for the full implementation of the technology as well as its continued maintenance over the years.

How to Successfully Adopt Digital Technologies

Management support

One of the important factors for the successful and sustainable adoption of a digital technology is the support and guidance provided by the management. This chain of support can start from the top management, such as the plant manager or the CEO, and extend all the way to the shift supervisors, each one recognizing their role in this "change management" as described below.

Management support that leads to successful implementations comprises of several factors, such as, clearly defined goals and objectives of the new application, well developed workflow, recognition of achievements and benefits, continuous improvement, making any course corrections – if and as needed, and providing consistency and encouragement, until the new practice becomes a standard. For example, a plant manager can hold a town hall meeting to introduce the new application and the roles and responsibilities of different support functions. He/she can also periodically meet with the operations group to: (a) learn about benefits observed by the operations team, (b) discuss any challenges that the team might be facing (such as not having enough resources, or not having easy access to computers at the facility, etc.), and (c) recognize their efforts in adapting to the new technology. This would also be a good opportunity to hear suggestions for any workflow improvement or potential new applications of the technology.

Why are we adding a new technology?

When selecting a new digital technology to add to an existing system, that operating team members are already accustomed to and feel they have been using "successfully", they may ask, "Why is this change necessary?" Especially if they think the operations have been running well. This question must be addressed by management at the beginning of any implementation. One or more of the following goals can be key drivers: improving productivity (both in terms of process and people), reliability, safety, quality, profitability, etc. It is important to address this topic head-on and present a sound case that justifies looking at one more report or screen, maintaining another software, updating servers, etc., which can be viewed as an additional unnecessary task by the operating team members. Therefore, the management, in its leadership and forward-looking role, needs to address such concerns at the beginning to be able to get the necessary buy-in from everyone, for a successful implementation.

Well-defined workflow

When evaluating digital technologies, they should not be considered as "one size fits all". Different digital methods require somewhat different approaches, efforts, and workflow. Management, together with key users, should identify a workflow, preferably something that meets the needs of different levels. Top management may set how often they would like to be informed of the progress (can be weekly or monthly). While the middle management may have a more frequent update, the critical level – operating team members – may need to interact with the technology daily.

With time, an efficient workflow will allow integration of new technologies/insight into daily practices and enable operations teams to successfully achieve significant improvements.

Change Management

Whenever a new technology is introduced, it brings with it an element of disruption. Therefore, each application should be considered from a "Change Management" perspective and its effect on an existing process must be evaluated. This includes several factors, such as, human behavior, roles and responsibilities, accountability of individuals, impact on existing processes, and existing priorities in decision making, etc. Also, new applications may impact critical success factors – changing or modifying them. Standards of what may have been acceptable may be no longer be acceptable. A new hierarchy, including more stakeholders, may need to be established. Whatever is needed must be defined and encouraged by management teams.

Dyno Waggaman Experience in using Autonomous AI

At Dyno Nobel Waggaman, after understanding the critical benefits of early risk detection, the management took the decision to further embrace its proactive risk mitigation culture. Based on recent breakthroughs in autonomous AI/machine learning, Dynamic Risk Analyzer™ ("DRA") was identified as one of the enabling technologies. Upon implementation of the software, over time, supporting workflows were established to achieve optimal results.

While the plant was already equipped with a historian, alarm management software, automated process KPI reports, System1 for machine diagnostic etc., a new enabling technology was envisaged for early risk detection and as a diagnostic tool to bridge the gap between a human's ability to pick anomalies through alarm and monitoring *versus* an enabling technology which could consistently and comprehensively scan for anomalies across an entire process, providing operators and engineers with an autonomous review and unbiased information.

DRA obtains process data from the historian, performs its analysis autonomously, and the results are available via a web-based dashboard and reports. Currently, middle management and process engineers have access to the system to review DRA results once a day, at their morning meeting or at the beginning of each shift. As a next step, Dyno Waggaman plans to cascade DRA access to shift leads, support engineers and operators. Furthermore, with an upgrade of the historian server, DRA is now equipped to pull data continuously, thus providing real time deviations, if any.

In terms of how software results are communicated, the dashboard feature provides an overview of the overall risk index based on anomalies detected, which can also be further drilled down to individual plant sections and tags.

The system indicates the number of variables with varying anomalies and provides a quick view to zero in on the affected section of the plant and drill down as needed.

Case Studies

Since embarking on utilizing DRA in daily risk assessment, Dyno Waggaman has benefited from the early identification of plant problems leading to the avoidance of potential process safety and plant reliability issues. Below are three case studies identified by DRA provided as examples:

a) Early identification of rising bearing temperature at 1st stage of the process air compressor

At the Dyno Waggaman plant, the 1st stage bearing of the process air compressor has always been hotter than other stages but remained constant since the start of the plant in 2016. In the plant's first turnaround (TA) in January 2021, the compressor was inspected, and the bearing replaced. Post TA, the bearing temperature again stabilized to pre-TA values.

During September 2021 (Table 1), the plant ran after the Hurricane IDA shutdown, DRA triggered an anomaly on the 1st stage bearing temperature (Figure 2), even though this tag did not trigger an alarm on DCS value set by the Original Equipment Manufacturer (OEM).

This DRA finding initiated detailed discussions between the OEM and lubrication experts by Dyno Waggaman reliability engineer. A DECON™ lubrication product was added to the oil in the process, to remove some of the varnish, which again stabilized the 1st stage bearing temperature. In this case, early detection provided sufficient time for Dyno Waggaman personnel to engage with SMEs and the OEM to temporarily address the issue, until an opportunity presented itself to rectify the problem. This way an impending shutdown situation could be avoided.

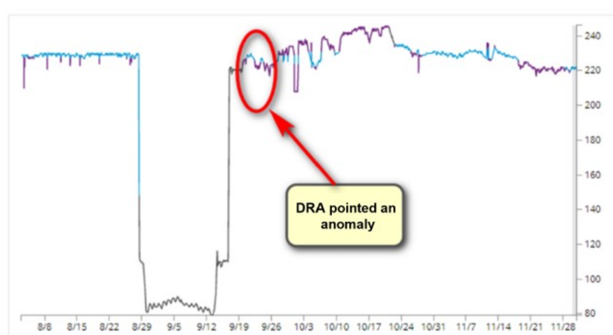

Figure 2. Bearing temperature detection by DRA

Time Line		
	TI3100B Deg F	Comments
August-16	223	Plant commissioned
April-18	226	
October-19	229	
February-20	231	
January-21	231	
	TA	Inspection and replacement stage 1 and stage 2 bearings. Varnish. No installation defects found.
June-21	228	
August-21	229	
September-21	228	
October-21	246	Discussion Siemens, IOWA fertiler. Design issue. HiPer bearing recommended. MOC created
	Decon I	Decon added
December-21	223	
January-22	250	
	Decon II	

Table 1. Turnaround timeline

b) Early detection of an erroneous anti-surge flow transmitter on the refrigeration compressor

Dyno Waggaman's ammonia refrigeration compressors have 4 stages. Each stage is equipped with its own kick back line fed by common discharge, a typical setup for this equipment. In one case, while the plant was running at steady state, a 3rd stage anti-surge flow deviated low, and DRA triggered an anomaly (Figure 3).

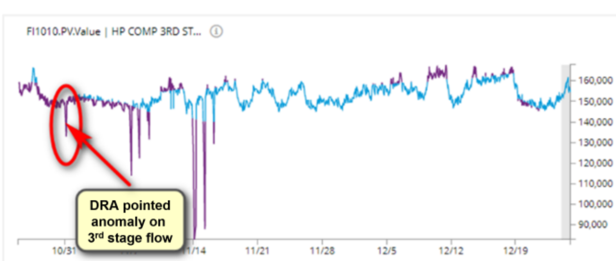

Figure 3. Flow detection by DRA

Upon further investigation, it was found that the anti-surge flow controller, which was fed with two independent flow transmitters (for enhanced reliability), had one flow transmitter deviated low. As part of a machine surge protection system, the 2oo2 transmitter was configured in a way that took the lower of the two-transmitter reading as its input (Figure 4).

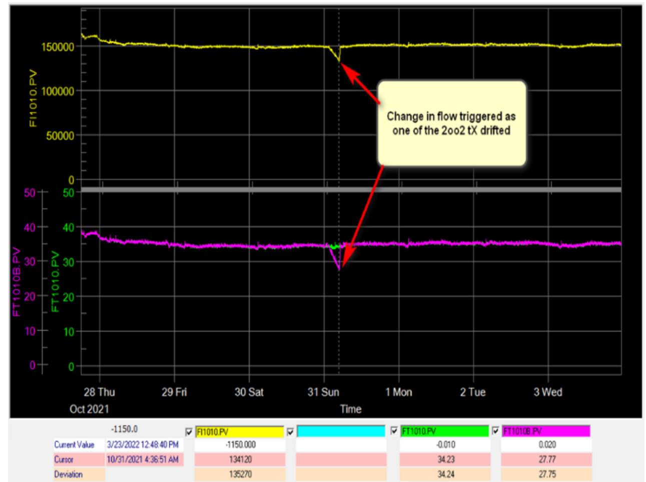

Figure 4. Further analysis through historian

Due to this finding, the erroneous transmitter was bypassed for trouble shooting. Ultimately, it was discovered that the transmitter had faulty installation resulting in NH_3 condensation in one of its legs (during lower ambient temperature conditions) – causing the lower reading. The tapping of the transmitter was modified for self-draining, and the transmitter was placed back in service without causing any process upset.

c) Early detection of erratic pressure control valve on chiller

The Ammonia plant at Dyno Waggaman has a chiller to cool down the methanator effluent. The temperature is controlled by cascade control of the pressure on the chiller. Lately, this caused fluctuations in temperature, pressure and level in the chiller level. DRA detected an anomaly on the output of the control valve, which led to further investigation by plant personnel (Figure 5). The problem was found with the hand jack assembly of the valve, which was later corrected.

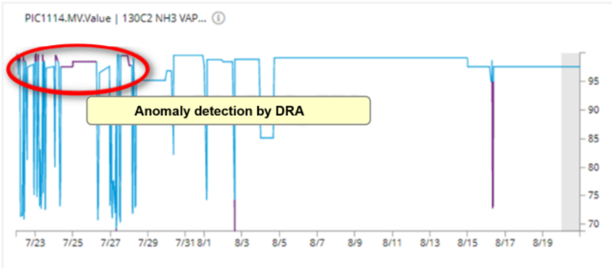

Figure 5. Pressure controller output

Conclusion

This paper aimed to outline key aspects of adapting to a proactive approach in dealing with early risk identification and rectification of issues flagged via DRA technology at the Dyno Waggaman plant.

DRA has been running for more than a year at Dyno Waggaman. It has helped plant personnel to: (a) become more cohesive in dealing with plant issues through early identification, effective prioritization in the planning/scheduling and execution process and (b) involve the right resources in a timely manner, which would not been possible if the issues were not detected early.

It has resulted in better awareness amongst the plant personnel as they believe that the problems are more focused now and can be identified by them much earlier. It has also given the organization a belief that knowledge and skills alone cannot guarantee a proactive mind set –it needs to be complimented with enabling tools to sustain the continual improvement journey.

Dyno Waggaman anticipates that the reliance on DRA within the organization will continue to mature over time, as its access is expanded to include more operations and maintenance team-lead and supervision. The key to success would depend on slowly sensitizing the work force to this new technology and how it works in tandem with the basic controls.

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First industrial experience with iron-chromium-free HTS catalyst in ammonia plant

Until recently, all commercially viable, high-temperature shift catalysts have been based on iron and chromium and have not undergone any major changes in over 100 years. The main challenges with the conventional formulation are not only the minimum required plant steam-to-carbon ratio, but also the risks associated with handling and operating a product that contains a certain amount of hexavalent chromium. With the introduction of the zinc spinel-based SK-501 Flex™ catalyst these risks are now eliminated.

Free of chromium, SK-501 Flex™ eliminates the risk of handling carcinogenic hexavalent chromium during catalyst loading and commissioning, catalyst unloading, and final disposal of the product. At the same time, this new product allows more operational flexibility, making it possible to increase production capacity by 3–5% in a modern, large-scale ammonia plant. The first installation of SK-501 Flex™ in an ammonia plant will be presented, focusing on the experiences gained during catalyst handling and operation.

As the first of its kind, the catalyst is a key element in the future of traditional ammonia production, meeting growing pressure from legislative bodies and safety standards while continuing to push the boundaries of operational excellence.

Chad Taylor
Haldor Topsoe Inc.

Mads Feddersen, Kaj Mikael Jensen, Sigridur Ingimarsdottir
Haldor Topsoe A/S

Introduction

The Haber-Bosch process marked the beginning of the industrial-scale ammonia production and also the start of high-temperature shift (HTS) catalysis. Many areas of the ammonia production process have been improved during the last 100 years; however, within the area of HTS, new developments have been limited. Today's catalyst formulation is only marginally different than the catalyst employed back in 1913. This also implies that the industry is still relying on a catalyst formulation which possesses risks of exposure to the carcinogenic hexavalent chromium (Cr6) during catalyst production, loading, operation, unloading, and final disposal. With the recent introduction of the SK-501 Flex™ there is now an alternative which eliminates these risks.

The toxic character of Cr6

Hexavalent chromium is a carcinogen and a reproductive toxicant for both males and females. Exposure to hexavalent chromium occurs through breathing, ingestion, and contact with the skin. Although most of the known health impacts are related to inhalation, there is recent data, linking ingestion of hexavalent chromium, such as through drinking water, to severe health effects.

In 2008, the National Toxicology Program (NTP) under the U.S. Department of Health and Human Services published the results of the two-year toxicity and carcinogenicity studies [1] on a hexavalent chromium compound. NTP reported that sodium dichromate dihydrate in drinking water caused oral cancer in rats and small intestine cancer in mice.

In addition to cancer and reproductive harm, short- and long-term exposures can lead to eye and respiratory irritation, asthma attacks, nasal ulcers, dermal burns, anemia, acute gastroenteritis, vertigo, gastrointestinal hemorrhage, convulsions, ulcers, and damage or failure of the liver and kidneys.

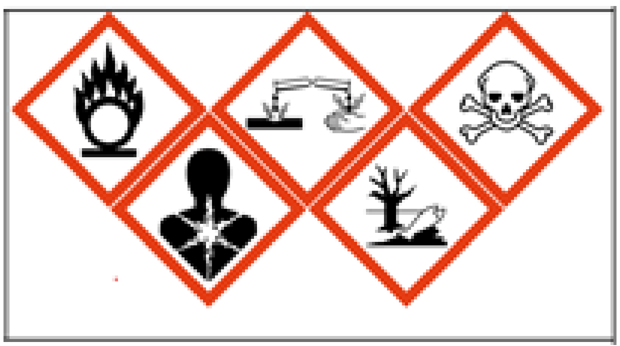

Figure 1. GHS pictograms for a CrO_3 (Typical Cr6 compound).

Cr6 regulations

Growing pressure from legislative bodies is increasing the demand for minimal levels of Cr (VI), and future regulations may require the complete elimination of chromium from HTS catalysts. Below (Table 1) lists the regulations in a few key regions.

Region	Substance	Value type	Value
U.S. Federal, Workplace	Hexavalent chromium compounds OSHA OELs for specifically regulated substances Hexavalent chromium inorganic compounds, including Chromite ore processing, as Cr (VI), inhalable Fraction	OSHA Action level OSHA Time weighted average (TWA) 8-Hour Exposure Limit (TLV-TWA)	0.0025 mg/m3 0.005 mg/m3 0.0002 mg/m3
China	CHROMIUM TRIOXIDE, CHROMATE, DICHROMATE, AS CR	8-hour Time Weighted Average (TWA)	0.05 mg/m3
European Union	CHROMIUM (VI) COMPOUNDS, Substance Expressed as: as chromium. Carcinogen Category: 1	8-hour Limit Value expiration date of this limit: 17 January 2025 8-hour Limit Value Valid from 17 January 2025	0.010 mg/m3. 0.005 mg/m3

Table 1. Cr6 limits in different key regions [2].

It should be noted that in some of the countries in the European Union (EU), a more strict national limit is in place, and countries like Italy and France are significantly below the EU limits.

The risks associated with Cr6 throughout the HTS catalyst lifecycle

Traditional HTS catalyst is based on an iron-chromium formulation which in most cases is promoted by a few percent of copper to boost the activity. During the production of the catalyst, up to 3.5 weight% of Cr6 is being formed as a result of the production conditions due to the following reaction.

$$2Cr_2O_3 + 3O_2 \rightarrow 4CrO_3$$

Some catalyst manufacturers would then carry out a subsequent reduction of the Cr6, so that most of it is converted back to Cr_2O_3, whereas others would just leave it as is.

Typical Cr6 contents of commercially available HTS catalyst are shown in Figure 2.

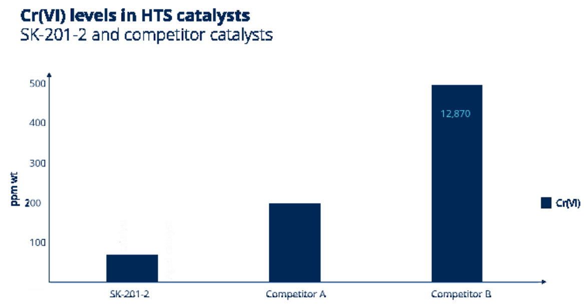

Figure 2. Cr6 content in different fresh HTS catalysts.

Catalyst manufacturing

The different catalyst manufacturers will have to comply with local legislation when producing the HTS catalyst, including minimizing the exposure of their employees to the Cr6 present in the production line. When producing the traditional SK-201-2 product this has meant continuous focus on improvements of the production process by applying the three-level barrier model, meaning:

- Implementation of technical means, including containment of all processes and equipment, segregation in order to minimize contamination
- Specific written procedures for production, cleaning and maintenance as well as regular training of all operators
- Use of special personal protection equipment (PPE)

Furthermore, half-yearly monitoring programs are in place ensuring validation of exposure levels.

Catalyst transportation

Once the produced HTS catalyst has been packed into approved steel drums or big bags, the Cr6 is in principle isolated from the outside. However, these packages may be punctured or opened by mistake, which could expose people, such as truck drivers in warehouses or other persons in the logistic chain, to Cr6. In most cases, these people will have no knowledge of the harmful character of Cr6 and how it can impact their health.

At the ammonia facility, the HTS catalyst will normally be stored in a warehouse prior to the catalyst loading. In some cases, the material may be stored outside under tarpaulins, and here it is of course very important to ensure that the packages are intact and that there is no risk of water getting in contact with the HTS catalyst, as this could result in the soluble Cr6 being washed out and end up in the surroundings.

Catalyst loading

In most developed countries, the catalyst loading is carried out by specialized loading companies, and they would have their own standards for handling hazardous materials. In less developed countries, the loading may be carried out by less specialized companies, and, in some cases, it may actually be the maintenance crew of the plant itself carrying out this task. With less specialized companies doing the loading, the risk of human exposure to Cr6 increases significantly both due to lack of protective gear (Figure 3) and also lack of knowledge on how to handle hazardous materials or maybe even realize the character of the Cr6 material.

Figure 3. Loading crew with protective gear during final stage of HTS catalysts loading.

Catalyst commissioning

Once loaded in the reactor, the HTS catalyst needs to be commissioned by exposing it to process gas. Catalyst with a high level of Cr6 needs to undergo a special time-consuming reduction step in order to control the highly exothermic reaction when the Cr6 is being reduced by the process gas. On top of this, some HTS catalysts also require an even longer desulfurization step in order to remove sulfur impurities in the product and avoid poisoning of downstream LTS catalysts. On both occasions, the process gas is vented downstream the reactor, and the commissioning is delayed by typically 6–36 hours. If condensation occurs during start-up from cold conditions, then Cr6 will be present in this condensate and will end up in the process condensate system or in the sewage system of the plant. However, more serious upsets can also occur during the initial start-up, and such an incident occurred back in August 2011 at the Kooragang island production facility in Australia. After an overhaul of the plant, the new charge of HTS catalysts having around 2 wt% of Cr6 were subject to excessive condensation during the initial commissioning phase, and the condensate containing the soluble Cr6 was then sprayed to the surroundings through one of the vent stacks, resulting in the plant and neighboring community being exposed to Cr6. This incident is described in detail in [3] and resulted in the plant being shut down by the authorities for a period of six months.

Catalyst operation

During normal operation, the Cr6 content in the HTS catalyst is very low and remain stable, as it is in a very reductive environment; however, mishaps occur, and there is a number of cases where air is still being routed to the secondary reformer, even though the hydrocarbon feed has been stopped. Such an incident was reported in a previous AIChE paper in 2014 [3]. The continued air addition results in a rapid oxidation of the catalysts in the secondary reformer and also in the HTS reactor (Figure 4), leading to a significant Cr6 formation, and as the HTS in most cases will be unloaded after such an event due to poor mechanical strength then this Cr6 will be exposed to the surroundings, which brings us to another pitfall when unloading HTS catalyst.

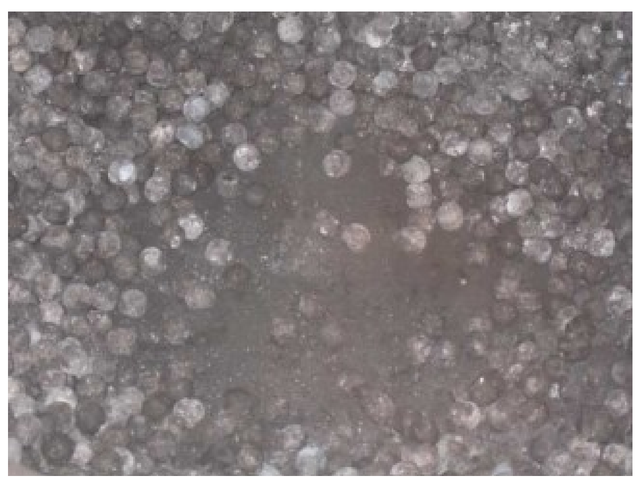

Figure 4. HTS catalysts with high degree of oxidation.

Catalyst unloading

The unloaded HTS catalyst is normally strongly self-heating due to its reductive character being mainly reduced iron. When the catalyst comes into contact with air, it will start to heat up as it oxidizes, and this will result in Cr6 being formed. In order to control the oxidation, it is common to spray water on in order to limit the heat generation. This may solve the heat up of the catalyst, but, at the same time, it transfers the soluble Cr6 into the water, which then would have to be treated in an appropriate manner in order not to get into contact with the environment. In order to minimize the effect from the oxidation during unloading, one may decide to unload under nitrogen blanket and collect the catalyst in containers / drums which can be closed after being filled.

Catalyst disposal

Finally, the unloaded catalyst will have to be discarded. In developed countries, this is normally done through catalyst handling companies which have the right setup to manage hazardous materials. As HTS catalyst does not contain significant amounts of any valuable metals, disposal of such catalysts carries a certain cost which for the time being is around 700 USD per metric ton [5]. As chromium and Cr6 are becoming more and more expensive to treat, this cost will surely go up in the future and is something that plant operators should think of when procuring next charge of HTS catalyst.

The Cr6-free alternative

With the introduction of the SK-501 Flex™ (Figure 5), there is now an alternative to the risks associated with operating a Cr6-containing product.

Figure 5. SK-501 Flex™.

This new catalyst contains no iron or chromium and is based instead on zinc aluminum spinel. This fundamental composition has long been known to have some degree of activity for the water-gas shift reaction, and the addition of certain promoters and an effective preparation method gives the new catalyst an activity superior to the activity of conventional iron chromium based HTS catalysts. Being free of iron also means that there are practically no limitations to the steam / carbon ratio at which it can operate. In summary, the benefits of this new product include:

No risk to personnel and safety

As the catalyst is free from hazardous materials, it is easy to handle during catalyst installation and catalyst unloading. No special requirements are needed for the loading, which is just as straightforward as loading of an LTS reactor.

Not pyrophoric during unloading

Due to its very low content of reduced material, the catalyst is stable in air and can be unloaded without the use of nitrogen. Once unloaded, the catalyst can be left in containers before it is being transferred to the disposal packaging.

Low environmental impact

The SK-501 Flex™ can be disposed of in an environmental sound manner. The metals (Figure 6) used to produce the catalyst can all be reclaimed and would not require special permits as for chromium-containing materials.

Figure 6. Main components of SK-501 Flex™.

Exceptional activity and stability

The formulation of the SK-501 Flex™ results in a catalyst with an activity which is significantly higher than for the traditional HTS catalysts. Coupled with a different and less pronounced deactivation mechanism, this results in a catalyst which can operate not only at lower steam carbon ratios, but also a catalyst which can operate at reduced inlet temperatures. This again results in higher conversions due to exothermic character of the water gas shift reaction. Below temperature profiles confirm that the catalyst is able to convert the process gas to equilibrium at low inlet temperatures, confirming the high activity (see Figure 7).

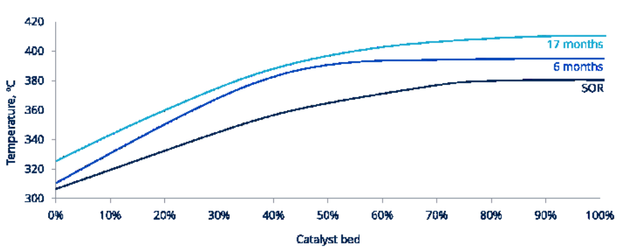

Figure 7. Temperature profiles of SK-501 Flex™.

Extended operational flexibility

The composition of SK-501 Flex™ (Figure 6) described in patent US8119099B2 offers groundbreaking benefits to ammonia producers. With the possibility to operate the plant at steam/carbon (S/C) ratios previously unattainable with commercial catalysts, producers can achieve improvements in capacity increase. As an example, a decrease in S/C from 2.8 to 2.5 can result in 5% more ammonia production for a stand-alone ammonia plant being limited on throughput (Table 2).

Steam/carbon	**2.8**	**2.5**	**Difference**
Feed	100%	108%	+8%
Fuel	100%	92%	-8%
Feed+Fuel	100%	103%	+3%
Production	100%	105%	+5%

Table 2. Reducing S/C and the impact on production.

Improved energy efficiency

Additionally, low S/C ratios make it possible to significantly reduce energy costs. At a modern ammonia plant, operation with SK-501 Flex™ could reduce energy consumption by 1% (Table 3). Such energy savings would be achieved from reduced steam input and from an overall reduction in natural gas consumption. The exceptional activity of SK-501 Flex™ also contributes to better energy efficiency. The activity allows for lower inlet temperatures, keeping conversion high even at lower plant S/C ratios (Figure 7). This translates into lower pressure drop over the reactor and less energy consumption by the compressors.

Steam/carbon	**2.8**	**2.5**	**Difference**
Feed	100%	102%	+2%
Fuel	100%	93%	-7%
Feed+Fuel	100%	99%	-1%
Production	100%	100%	+0%

Table 3. Reducing S/C and the impact on feed and fuel amounts.

Minimum by-product formation

With SK-501 Flex™, there is no longer a risk of over-reduction at low S/DG ratios. There would be no formation of the higher hydrocarbons, acids, or esters catalyzed by over-reduced iron oxide, even at extremely low S/C ratios (Figure 8). This would eliminate the consumption of valuable hydrogen and the contamination of process condensate due to these by-products. The only by-product formed is a small amount of methanol which is formed over any type of HTS catalyst due to the equilibrium reaction for methanol from the reaction of CO_2 and H_2.

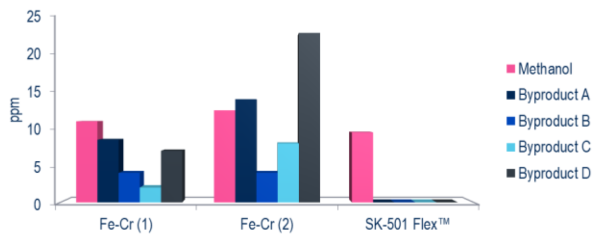

Figure 8. By-product formation across different HTS catalysts.

Hassle-free start-up

Like Topsoe's ultra-low hexavalent chromium SK-201-2 catalyst, start-up is easy and hassle-free with the chromium-free SK-501 Flex™. There is no need for extra start-up procedures that are normally needed when hexavalent chromium is present in the catalyst. With SK-501 Flex™, activation is fast and takes place in connection with the start-up of the reforming section, saving producers costly downtime (Figure 10).

Industrial experience

The first charge of SK-501 Flex™ was installed in a French hydrogen plant back in 2014. Since then, a number of hydrogen producers have opted for this product due to its environmental benefits and also its ability to work at steam carbon ratios where traditional iron-chromium-based catalyst would not be able to operate. Figure 9 shows the activity development for the first SK-501 Flex™ charge.

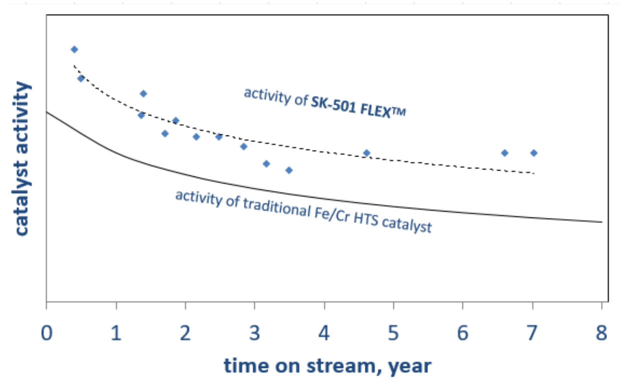

Figure 9. Activity of SK-501 Flex™.

The performance of the catalyst shows an increased activity level compared with traditional iron-chromium-based products, and at the same time the deactivation is very modest.

The first installation in an ammonia plant was at a Southeast Asian producer and below graph shows the temperatures in the HTS reactor during the commissioning of the catalyst.

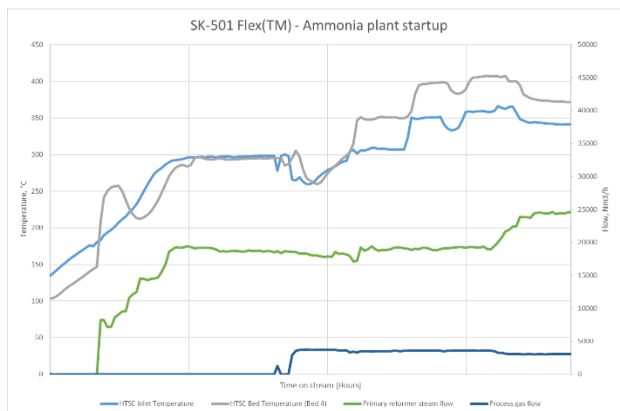

Figure 10. temperature development during commissioning of SK-501 Flex™ HTS.

Since the commissioning, the catalyst activity and the catalyst pressure drop have been very stable. These are shown in Figure 11 and 12.

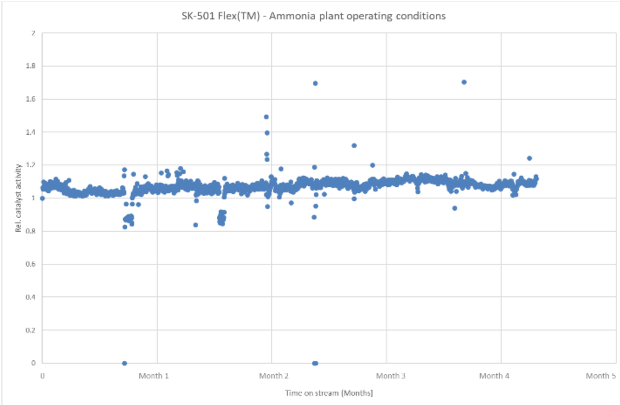

Figure 11. Graph showing relative catalyst activity of the SK-501 Flex™ charge.

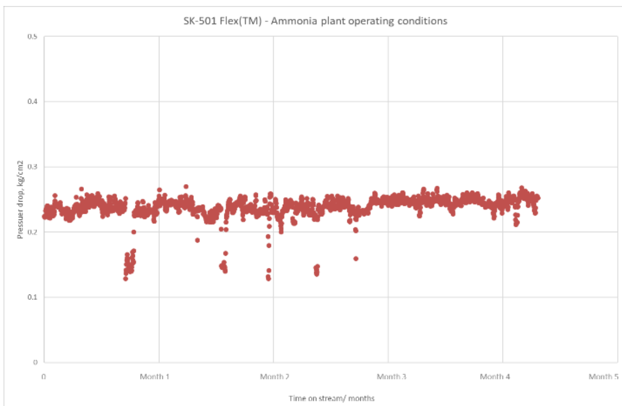

Figure 12. Graph showing pressure drop of the SK-501 Flex™ charge

Recently, two more ammonia producers have ordered SK-501 Flex™ for their plants. Combined with the references gained within the hydrogen segment, this means that globally there are 24 SK-501 Flex™ references, as illustrated in Figure 13. In spite of some of these references reaching +8 years of operating time, the first reference is yet to reach end of run and be replaced.

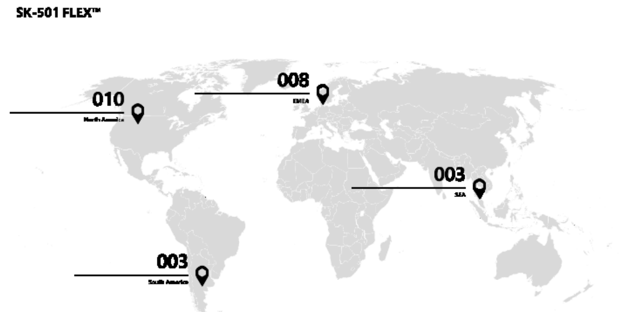

Figure 13. SK-501 Flex™ references worldwide.

Conclusion

Prevention of exposing people and environment to dangerous and toxic chemicals is high on the agenda everywhere. In many cases, a viable solution to mitigate these risks comes at a cost either on CAPEX or OPEX side. With SK-501 Flex™, a toxic component in the traditional iron-chromium-based HTS catalyst can be totally eliminated and substituted with a patented catalyst with improved performance due to higher activity and flexibility. The increasing number of references confirm the industries' interest in having more sustainable products in their facilities and also the need for more energy-efficient solutions. SK-501 Flex™ gives them that.

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Unconventional Strategy for Revival and Sustained Operation of 50 Years Old Ammonia Plant

The Pakistan natural gas crisis from 2010 till 2019, forced intermittent plant operation and several start-up and shutdown cycles of the 50-year-old Ammonia plant. Plant preservation remained a unique challenge which later became more profound due to a prolonged outage of 786 days. Special preservation techniques were developed while maintaining operational readiness for plant start-up due to uncertain gas supply. Implementation of a robust preservation regime followed by second party audits by experienced cross-functional teams enabled safe plant start-up and its subsequent sustained operations to achieve Ammonia plant service factor of ~98% for two years following the resumption of gas supply.

Abdul Ghaffar, Adnan Mahmood
Pakarab Fertilizers Limited, Pakistan

Faisal Jamal, Kamran Arif Chaudhry
Fatima Group Head Office, Pakistan

Introduction

Fatima Group (FG) is one of the largest and most progressive business conglomerates in Pakistan, operating in diversified sectors including Fertilizer, Textile, Sugar, Energy, Packaging, Mining and Trading of commodities. FG owns three fertilizer manufacturing facilities located strategically in the fertile belts of Pakistan, with the product range of Ammonia, Urea, Nitric Acid, CAN (Calcium Ammonium Nitrate) and NP (Nitro Phosphate). From a safety standpoint, combined safe man-hours of fertilizer facilities are over 80 million, while Fatima Fertilizer, located in Sadiqabad, has recently set a Guinness World Record for clocking more than 60 million safe man-hours in the fertilizer sector globally.

Pakarab Fertilizers Ltd. (PFL), one of Fatima Group companies, is a compound fertilizer manufacturing complex situated in Multan, Pakistan. PFL operates a natural gas-based steam reforming Ammonia plant designed for 910 MTPD capacity by M.W. Kellogg Ltd commissioned in 1978. A Petrocarbon designed cryogenic Purge Gas Recovery Unit was installed later and commissioned in 1986 to increase the production to 960 MTPD, whereas the plant has achieved the highest production capacity of 1,067 MTPD.

Pakistan's industry was impacted due to gas shortfall driven by a decline in indigenous gas production. Consequently, the PFL plant remained intermittently operational due to forced gas curtailment. This paper describes the challenges faced during intermittent operation and prolonged outage, mitigation strategies, and outcomes. Focused discussion on the following areas is covered in the paper:

1. Key learnings from PFL’s unique experience of successfully managing innovative preservation techniques for a 50 year old Ammonia plant during intermittent and prolonged shutdown.

2. Revival through setting-up unprecedented gas processing facility (details covered under “Indigenous Gas Arrangement” section)
3. Achieving operational sustainability of the highest standards during subsequent operations.

Background

Over the last decade, Pakistan industry has been adversely impacted due to gas shortfalls driven by a continuous decline in indigenous gas reserves. Consequently, fertilizer plants connected with the national gas supply network, including PFL, faced severe gas curtailment resulting in intermittent operations, frequent plant start-up and shutdown cycles. Curtailment of PFL gas supply initiated in 2011 and continued till 2017, after which the plant faced a long shutdown of 786 days till start-up in 2020 through indigenous gas sourcing arrangement:

Year	Ammonia plant Operating Days	No. of Startups
2011	171	9
2012	74	8
2013	43	2
2014	43	2
2015	267*	2
2016	193*	3
2017	213*	4
2018	0	0
2019	0	0
*Operation on Regasified Liquefied Natural Gas (RLNG)		

Ammonia plant average service factor during 2011-19 remained ~30%. Plant preservation during offline periods and management of frequent start-ups (fatigue cycles) upon natural gas availability remained as key challenges.

Plant Preservation Techniques

During the offline periods, plant stationary equipment, machines, catalysts, and piping health were safeguarded through implementation of specialized and conventional preservation techniques developed in consultation with OEMs and Water Treatment Experts. Preservation techniques developed were intended to cover short- and long-term shutdown scenarios while ensuring operational readiness for plant start-up due to uncertain gas supply.

Following sections of the Ammonia plant were identified for the application of Preservation techniques as per the following guidelines:

Boiler System

The **water-side** surfaces of boilers are vulnerable to corrosion when air contacts moist metal surfaces during out-of-service periods. Therefore, to prevent corrosion, the boiler water-side surfaces were protected through the adoption of wet storage and dry storage methods. Wet storage is typically used for short-term outages or where the boiler may have to be returned to service quickly. Dry storage is recommended when a boiler is intended to be put out of service for an extended period, i.e., more than 3 months. The dry storage method was applied to old redundant boilers. For dry storage, moister-absorbing material, such as quicklime ~~at a rate of~~ (0.9 kg for every m^3 boiler volume), was placed on trays inside the drum to absorb moisture from the air. The manholes were closed, and all other connections on the boiler were tightly blanked. The effectiveness of the desiccant and replacement was determined through regular internal boiler inspections.

Steam, Condensate and BFW Piping

Steam and condensate piping uses carbon steel as the material of construction, with some exceptions for special processes. These circuits are prone to corrosion due to the presence of oxygen and water during shutdown periods which becomes evident from the condensate color when the steam system is put into service after shutdown. During the outage period, it was necessary to purge the steam circuits with inert gas and hold positive pressure to avoid an internal corrosion attack. The following steps were ensured in this regard:

1. Close all the drains, vents and any other points to contain nitrogen in the selected loop.
2. Ensure a pressure gauge is installed on the selected loop to monitor the nitrogen pressure.
3. Pressurize the loop with nitrogen from inlet points up to 3 kg/cm^2g (42.7 psig).
4. After holding for 1-2 hrs, start venting from purge points up to a pressure of 0.5 kg/cm^2g.
5. Repeat this pressurization and depressurization system till O_2 content is reduced to 2-3%.
6. After purging, preserve the system under nitrogen pressure by maintaining nitrogen pressure from 0.5–1.0 kg/cm^2g.
7. Continue monitoring O_2 content daily.

Cooling Water Circuit

A specialized cooling water preservation regime was developed to ensure system health during the idle period while maintaining operational readiness for plant start-up on gas supply resumption. Salient steps of the wet lay-up technique applied are summarized below:

1. Maintain Corrosion and Scale Inhibitor concentration four to five times the normal operating level for adequate corrosion and scale protection.
2. Shock dose Non-Oxidizing Biocide based on the normal operating regime (while keeping blow-down in closed position).
3. Discontinue cooling water system circulation once the required concentration level of chemicals is achieved (customized in view of gas constraint).
4. Analyze cooling water for zinc and phosphate reserves daily.
5. Monitor total bacterial count in the cooling water system and initiate cooling water circulation once it reaches 1000 CFU/ml.
6. Once a week, maintain Cooling water circulation for at-least 12 hrs while maintaining free chlorine concentration level of at least 0.5 ppm. During extreme gas curtailment period, PFL installed lower capacity rental power generators for management of critical plant load and intermittently operated one low-pressure cooling water pump (normally 3 pumps of low pressure and 1 of high-pressure circuit were kept operational, both circuits shared a common cooling water basin and return header). Cooling water supply circulation during outage periods, therefore, remained limited to low-pressure circuits.
7. Replenish depleted concentration of zinc / ortho-phosphate, add scale/bio-dispersant chemicals as per normal operating regime and maintain all other parameters within Safe Operating Limits (SOL) during the weekly circulation period.
8. Check total bacterial count at the end of the circulation period.

Catalysts

All catalysts in the Ammonia plant were put under a positive pressure of nitrogen to eliminate any chances of oxygen ingress into catalysts, especially:

- Hydrotreater
- Low-Temperature Shift
- High-Temperature Shift
- Methanator
- Synthesis

Zinc Oxide catalysts were also kept under nitrogen as it contains natural gas either in an absorbed or unabsorbed state.

Catalysts were preserved by keeping them under nitrogen, maintaining pressure from 0.5–1.0 kg/cm^2g.

A regular regime of Catalyst bed temperatures monitoring was in place by the Operations team on an hourly basis, and Process Engineers verified daily to ensure safe system preservation.

Natural Gas Circuit

The natural gas circuit was kept pressurized and periodically checked for any condensate which was drained from the lowest point in the circuit.

Process Gas Circuit

The Following process circuits were kept under a positive pressure of nitrogen 0.5–1.0 kg/cm^{2}g to eliminate any chances of Oxygen ingress:

1. Ammonia plant Process Piping.
2. Catacarb Circuits: First, transfer the solution to storage, wash them with Demineralized water and keep them under a slight positive nitrogen pressure.

Machinery

Rotating equipment, including steam turbines, gas turbine generators, compressors, pumps, blowers etc., are prone to rust and corrosion while in storage or during plant shutdown due to moisture ingress into the enclosures. To avoid corrosion during storage, the relative humidity in storage areas was maintained below 40% at ambient temperature. Moisture accelerates the rate of corrosion of turbines, compressors and their components leading to:

1. Deterioration of parts and components
2. Malfunctioning / increased downtime
3. Decrease in life and efficiency

Sophisticated and expensive components include rotors, compressor parts, bearings, buckets and blades, seals, gearbox parts, couplings etc. Studies show that corrosion products are produced exponentially when RH exceeds about 60%.

An extended standstill period can also lead to bowing of the rotor shaft, which needs to be prevented by taking appropriate measures, including ratcheting/barring and slow roll operations.

a. Steam Turbines

The turbines must be stored to prevent corrosion while not in use to save various parts of the turbine, which are expensive to replace and maintain. Turbines and engines that are taken out of operation for up to one month must be preserved to avoid corrosion.

Condensing turbines are more sensitive as a large quantity of water is collected as condensate; when the turbine is in idle or shutdown condition, this water evaporates with time resulting in corrosion of various metallic parts of the turbine.

Key preservation guidelines include.

1. Prevent steam leaks to the turbine by means of existing steam locks on all lines to the turbine.
2. Keep the inner space of the turbine dry by induction of dry air (dew point <-20 C, RH <10 %) or nitrogen 98%.
3. At least once per month, put oil pumps for 1 hour into operation. All control valves (CCCV) devices shall be moved once from completely closed to completely open during this period. Control system alarms are to be also verified. Turn the turbine rotor manually or, if applicable by an existent barring gear during oil circulation for approximately 2 turns. Afterwards, turn at 45 degrees from the last position, record this in the turbine logbook/history card. Most commercial turbine oil brands contain corrosion inhibitors that provide reasonable protection against rust.
4. Take oil samples fortnightly for moisture analysis. Operate centrifuge weekly for moisture removal.
5. For auxiliary oil pumps, no special preventive measures need to be taken. Protection

against rusting is achieved by turning on the oil pump every month.

6. Check all lubricating lines to see if any tubing, piping, tank or sump covers have been removed. Cover all coupling breathers, and seal drains/leakage points.
7. External visual inspection for any degradation, corrosion, leaks, external moisture/dust, faulty gauges, RTDs and report in daily logbook.
8. Even if the machines are idle for long periods, it is important to replace oil charges as per OEM recommendations (even if the machines remain idle for long periods).

b. Centrifugal Compressors

Key preservation guidelines include:

1. Install plastic curtain at the suction of air compressors to prevent moist/dirt ingress.
2. Keep the inner space of the compressor dry by induction of dry air (dew point <-20 C, RH <10 %) or nitrogen 98%.
3. At least once per month, put oil pumps for 1 hour into operation. Turn rotor manually or if applicable by an existent barring gear during oil circulation for approximately 2 turns afterwards turns at 45 degrees from the last position, record this in the logbook/ equipment history card.
4. Check for any moisture content by draining the casings weekly.
5. All control valves, including -anti-surge, are to be tested and logged weekly.
6. Check all lubricating lines to see if any tubing, piping, tank or sump covers have been removed. Cover all coupling breathers, and seal drains/leakage points.
7. External visual inspection for any degradation, corrosion, leaks, external moisture/dust, faulty gauges, RTDs and report in daily logbook.
8. Special analysis of Lube oil after a prolonged outage to ensure oil is fit-for-use and is not degraded.

c. Gas Turbines Generators

Gas Turbines were weekly tested on no/low load to ensure reliability.

d. Other Equipment

Apart from Steam Turbines, Centrifugal Compressors and Gas Turbines, all other plant rotating equipment, e.g., Pumps, Blowers etc., were operated or rotated at least once per month for a period of at least 1 hour to ensure operational reliability. Furthermore, seal flushing lines of pumps were dismantled and cleaned before the plant restart to avoid blockage.

Validation Techniques

The effectiveness of applied preservation techniques was ensured by implementing regular audit and inspection regimes (including thickness monitoring, visual inspections, application of corrosion coupons, monitoring of corrosion under insulation, etc.).

Indigenous Gas Arrangement

Because of prolonged gas curtailment driven by continuous decline in indigenous gas reserves, focused and coherent efforts were made to secure long-term sustainable gas supply solutions. After extensive research and conducting feasibility studies of potential solutions, gas supply was restored by securing gas from Exploration and Production (EP).

Unique Project features and challenges included:

1. Development of unprecedented greenfield gas processing facility ~350 km away from PFL plant site for raw gas compression and de-hydration to achieve pipeline specifications.

2. Construction of 24 km pipeline for transportation of processed gas to national grid; involving extensive Right of Way (ROW) challenges and numerous government approvals.
3. Implementation of Pakistan's first third party access arrangement for transmission of processed gas to PFL plant.

Start-up Readiness after Prolonged Shutdown

After a prolonged outage of more than 2 years, Plant start-up readiness was ensured through the development of specialized start-up procedures and implementation of pre-start-up remedial measures:

1. Despite extensive preservation, Steam blowing/purging of critical loops was carried out, including steam network, Instrument Air headers etc.
2. In view of the possible carry-over of heavier hydrocarbons and soot, the natural gas inlet line to the complex was thoroughly blown out, up to the Ammonia plant inlet battery limits.
3. The Air Compressor Suction chamber downstream of the filters was thoroughly cleaned of debris and dust deposits.
4. Pre-start-up safety reviews of all modifications were carried out, and field verification of all modifications was ensured.
5. A special regime was put in place for extended monitoring upon start-up of each machine for the initial few hours of restart w.r.t vibration and bearing temperatures. This regime helps identify the post-restart problems early and avoids many failures.
6. Detailed inspection of Piping supports and gaskets.
7. Manning and skill gaps identification and mitigation.

Start-up readiness was further strengthened via 2nd party audits utilizing in-house resources from Fatima Group. Total of seven operational reliability and start-up readiness audits were conducted, covering the following areas:

1. Safety and Environment risk management.
2. Preservation of machines and equipment based on best practices.
3. Review and availability of SOPs and start-up checklists. Training validation of new staff on developed SOPs.
4. Heath assessment of critical machines, instrumentation, control and electrical systems.
5. Interlocks verification/logic testing and stroke checking of all control valves.
6. Catalyst and Chemicals requirement and availability.
7. Mechanical Integrity of equipment and piping.

All audit observations were categorized based on their risk rating and closures ensured before initiation of plant start-up.

Successful Start-up and Sustainable Operation

After an extended shutdown of 786 days, plant start-up was initiated on Jan 17th, 2020. After a safe and smooth start-up, Ammonia production resumed on Jan 20th, 2020. Subsequently, the Ammonia plant achieved sustained and reliable operations and a service factor of 97.7% and 98.5% during years 2020 and 2021, respectively.

Key features facilitating successful start-up and its subsequent sustained operation include:

1. Preservation procedure compliance.
2. Machines and equipment reliability audits.
3. Operational readiness audits.
4. Process start-up procedural compliance.

5. Stringent and extensive monitoring of Process Parameters, Lab Analysis and machines post start-up. Monitoring frequency was kept high during the initial period and was gradually normalized over a period of time.
6. The replacement frequency of different filters was high during the initial few weeks of plant restart after a prolonged outage. Accordingly, extra vigilance and monitoring on these filters were ensured, and adequate stock was maintained for timely replacement.

Key Learnings

A rigorous preservation regime, extensive audits, inspections and methodical restart approach helped PFL in a smooth restart, sustainable operation and accomplishing excellent service factors in a subsequent operation. However, there were a few learnings from subsequent operation which are being shared for the benefit of readers for future improvement:

Critical Piping Leaks

After two years of operation, and minor pin-hole leakage was observed from process gas piping at the CO_2 absorber inlet. Upon detailed thickness mapping, thickness loss around the pinhole vicinity was also observed, indicating the possible formation of carbonic acid, especially during intermittent plant operation. It signifies the importance of thoroughly purging the critical process piping and keeping it under positive Nitrogen pressure during the offline period.

Catacarb Circuit Passivation

The passivation layer of Vanadium in the Catacarb circuit, is prone to dislodging after a prolonged outage, and it essentially requires additional chemical dosing to ensure that a new layer is available on the piping/equipment. It is also equally important to remove the dislodged layer through extensive filtration and with additional focus on Lean/Semi-lean solution pumps' strainers to avoid cavitation. PFL experienced frequent choking of these strainers during initial few weeks and additional focus was applied to promptly change-over these pumps upon strainer choking to avoid damage to these pumps due to cavitation. Furthermore, increased filtration through activated carbon was also witnessed, requiring frequent replacement of activated Carbon filters, especially during the initial few months post-start-up. Extensive filtration and regular cleaning of strainers helped maintain good solution chemistry and thus avoiding any process upset in the Catacarb system.

Cooling Water Circuit Deposit

Despite a very rigorous CW preservation regime and no apparent signs of corrosion based on monitoring of corrosion coupons, PFL observed deposits of iron chips on a few exchangers on high pressure cooling water circuit (dedicated to the Nitric Acid plant) in which CW circulation was not established during outage period due to gas and power availability constraints after the changeover to smaller capacity rental generators for managing critical plant load. Mud deposits were also observed on dead-end exchangers, which signifies the importance of maintaining regular weekly Cooling Water circulation at full velocity covering all circuits.

Conclusion

PFL plant, over the last decade, underwent a prolonged sequence of intermittent operations followed by an extended outage period which has no known precedence in the fertilizer industry. A unique challenge of maintaining plant health during the referred period was successfully managed by utilizing conventional and specialized preservation techniques, later validated through seamless plant restart followed by its sustained and reliable operation afterwards. However, key learnings gained through this unique experience have been captured to facilitate the industry in the implementation of an even improved preservation regime during short and long-term outages.

Decarbonize with blue ammonia

With increasing global concern about atmospheric CO_2 levels, the chemical industry is seeking to reduce CO_2 emission. Ammonia produced from hydrocarbon has inherently an adjacent unavoidable CO_2 production. This CO_2 needs to be sequestered or used for producing new chemicals, if emission to the atmosphere shall be avoided/reduced. Typical ammonia plants release CO_2 in connection with syngas preparation and as part of the flue gas from steam reformers and fired heaters. To sequester or use the CO_2 for new chemicals, it needs to be relatively pure. The CO_2 from syngas preparation is sufficiently pure, whereas the CO_2 in the flue gas must be separated at a relatively high cost. The CO_2 in the flue gas should therefore be minimized or transferred to the syngas preparation for removal. This opens for multiple new process solutions.

Over a very short period it has become an obligatory task to reduce CO_2 emission in grass root projects, and soon existing plants are likely to be met by similar requirements. This paper addresses this required ammonia technology transition, that must be made without compromising the reliability and safety of the resulting process.

Ameet Kakoti, Per Juul Dahl
Topsoe

Introduction

Global concern continues to increase over atmospheric CO_2, and all eyes are on the world's chemical producers and their efforts to reduce emissions. When derived from hydrocarbons, ammonia carries an inherent and unavoidable carbon cost. Since much of the world's ammonia is still produced from fossil sources, minimizing the environmental presence and impact of carbon emissions, whether through sequestration or downstream use, is necessary.

A typical ammonia plant releases CO_2 in two ways:

- As a result of syngas preparation, which produces a sufficiently pure CO_2 stream for sequestration or use.
- As a portion of the flue gas emitted from steam reformers and fired heaters, which is of insufficient purity and requires additional cost for separation.

To minimize the financial impact, producers should reduce flue-gas CO_2 to the extent possible and direct it to the syngas-preparation stage for removal. This challenge, rather than representing a roadblock to ammonia success, provides an opportunity for the implementation of innovative, highly efficient, and beneficial process solutions.

As such, it has become an obligation – and crucial business objective – to reduce the CO_2 emissions of grassroot projects, and existing plants will likely be subject to similar requirements soon. This paper addresses the ammonia-technology transition necessitated by these requirements, which must be made without compromising neither the reliability nor the safety of the resulting process.

Green or Blue considerations - Lack of standards

Conventional ammonia based on steam methane reformer (SMR) technology without any CO_2 reduction mechanisms leads to about 0.48 kg CO_2/kg ammonia (1.05 lb CO_2/lb ammonia) and Topsoe SynCOR^{TM} process emits about 0.31 kg CO_2/kg ammonia (0.68 lb CO_2/lb ammonia).

An international standard for blue chemicals is not yet established. Decarbonizing flue gas has in most cases had a practical/feasible limit at 90 % CO_2 capture, and this has in some cases therefore been used as the limit for blue chemicals. The possibility to rearrange process layouts and efficiently remove pure CO_2 from synthesis gas, as well as more efficient flue gas capture units has changed the practical/feasible limit to 90% - 99% capture. Moreover, the capture % is driven by the expectation of CO_2 tax on emission and possible income from selling the captured CO_2. On this basis, the market trend for new blue chemicals project is at least to meet carbon recovery of 90% or higher. That translates to a CO_2 emission which is less than 0.20 kg CO_2/kg ammonia (0.44 lb CO_2/lb ammonia).

Decarbonization is presently defined as kg CO_2 emission/kg product or as the percentage of the carbon into the process which is captured and utilized for other chemicals or stored.

Ammonia process configurations vary in their energy imports and exports. Some processes produce its own power and others import power, some processes produce its own oxygen, and others import oxygen etc. For comparison of different processes, it is important that CO_2 emission from imports is added to the emission, similarly that CO_2 emission from exports is subtracted, if these exports has a value. This will give a correct comparison and thereby an optimal selection of process design.

Ways to produce blue ammonia and prepare for the future

Producing ammonia from hydrocarbon feeds inherently results in CO_2, which must be removed as part of the process. The hydrocarbon feed is via different reforming technologies converted to a synthesis gas comprising H_2, CO, and CO_2. The CO is then shifted with H_2O to form H_2 and CO_2, resulting in a synthesis gas comprising H_2 and CO_2. This is then followed by a CO_2 removal step wherein practically pure CO_2 is separated from the synthesis. This CO_2 product can be used for other chemicals, such as urea or methanol, or it can be stored. For reforming technologies involving air reforming, the synthesis gas will also contain N_2. This CO_2 product is unfortunately not the only CO_2 source from an ammonia process. Especially the reforming step requires heat to take place and this heat is traditionally supplied by burning hydrocarbon fuel, resulting in CO_2 emission via the flue gas. Two ways of reducing the flue gas CO_2 emission are pursued. Technologies for capturing typically 90% of the CO_2 from the flue gas have been available for many years. This technology has been used as a revamp feature in several Topsoe designed ammonia plants, in relation to Urea plants where the hydrocarbon feed used for the ammonia production is lean in carbon, so the recovered CO_2 from the synthesis gas is not enough to convert all ammonia into Urea. It was therefore selected for new build ammonia plants, based on lean gas, to increase the capacity of the synthesis gas generation section and thus produce more CO_2 product and excess Hydrogen. The excess hydrogen was used as fuel in the reforming section. This alternative to CO_2 flue gas capture has shown to be an advantage also when the goal is decarbonation. In most cases, it is considerably cheaper to produce hydrogen for replacement of hydrocarbon fuel, compared to having to remove CO_2 from the flue gas. Table 1 shows a comparison between pre-carbon capture (process capture) and post carbon capture (flue gas capture) for hydrogen produced using tubular steam reforming. It is evident that even for a 32% excess hydrogen generation in the pre-capture case, the resulting levelized cost of hydrogen is 16.3% lower. The drawback of this result is, however, the increased size of the tubular steam reformer, which will limit the maximum single line capacity for technology.

Carbon Capture	OPEX	CAPEX	LCOH	Excess Hydrogen %
Flue gas capture	100	100	100	0
Process capture	92,1	74,5	83,7	32

Table 1. Comparison between flue gas capture and process capture

Reforming technologies

Based on the above findings the optimization of the decarbonation is then directed towards the required heat input to the reforming section.

Almost all ammonia plants in operation, use steam reforming as part of the synthesis gas generation. More than 20 years ago, i.e. before the decarbonization took off, Topsoe introduced the SynCOR^{TM} concept for large scale synthesis gas generation. The SynCOR^{TM} concept is a synthesis gas generation technology using autothermal reforming, operating with a steam carbon ratio below 1.0, typically at 0.6. The technology has today achieved more than 100 years large to very large scale industrial reliable operation. This SynCOR^{TM} concept can be used for many different products including ammonia as shown in Figure 1.

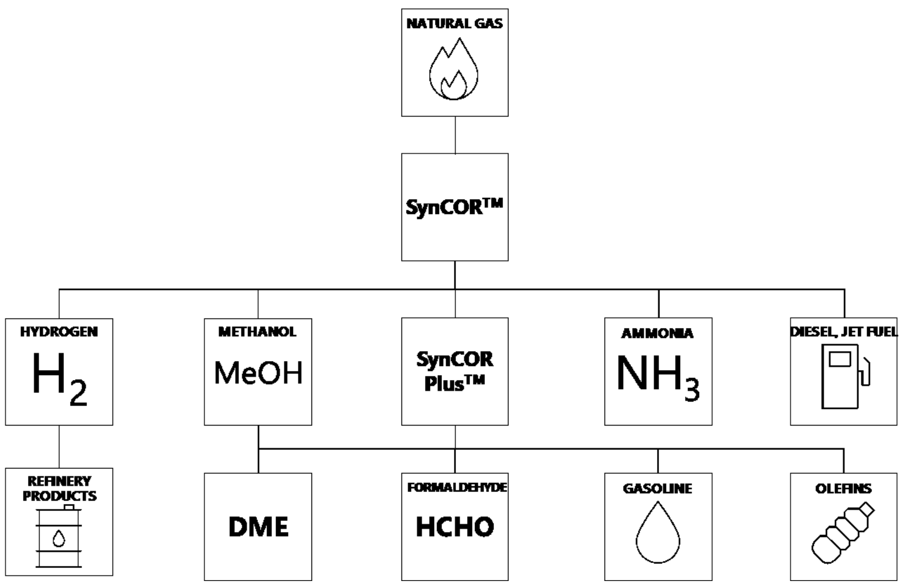


Figure 1. SynCOR^{TM} technology applications.

The latest success for SynCOR^{TM} is for hydrogen production. Within the hydrogen industry, the tubular reformers have become too large, and too costly due to the size of the units increasing proportionally to the plant capacity, and therefore the SynCOR^{TM} solutions have generated interest. Same applies to blue ammonia production where large scale single trains bring economy of scale. A SynCOR^{TM} ammonia plant as shown in Figure 2 is basically a SynCOR^{TM} hydrogen plant followed by nitrogen addition and an ammonia synthesis. Synthesis gas generation corresponding to 10,000 MTPD ammonia or 8,000 MTPD blue SynCOR^{TM} ammonia can be produced in one SynCOR^{TM} reactor which makes it fundamentally different from all other available reforming solutions. The defined major difference is the operation with a low steam to carbon ratio of 0.6, which is about 4-5 times less than required for tubular steam reforming. This reduces the amount of heat input for the reforming section drastically, and thereby the fuel requirement directly leading to a lower CO_2 emission.

On the same basis, a steam reformer-based ammonia plant captures approximate 75% CO_2 directly from the synthesis gas where the number for a SynCOR™ based plant is approximate 85%.

Therefore, in case of a desire to decarbonize, the use of SynCOR™ is beneficial since it either requires a smaller flue gas capture unit or less need for excess hydrogen for fuel, which is a major advantage against steam reformer-based solutions.

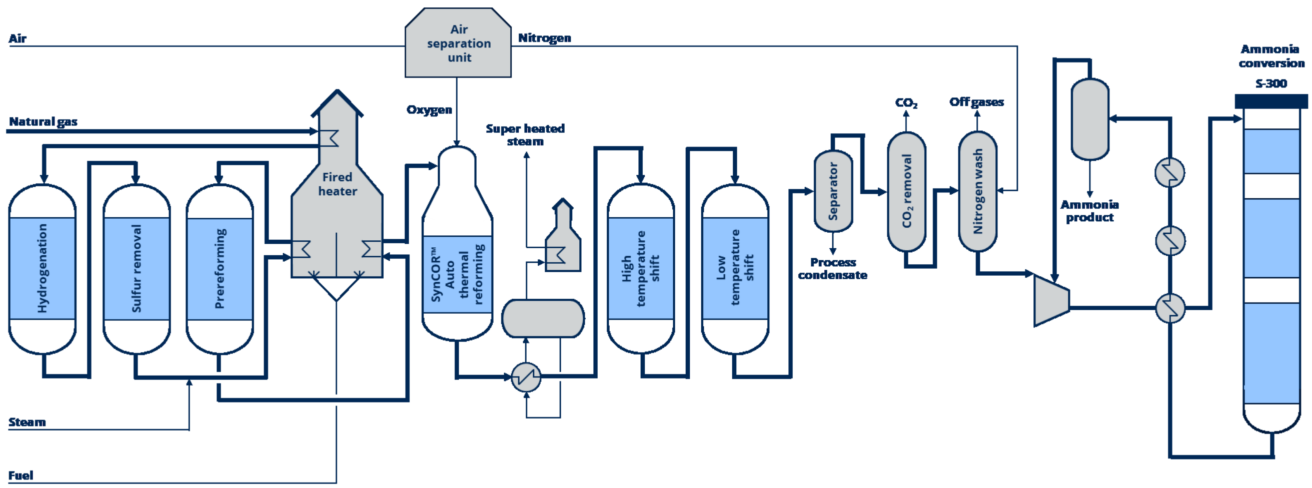


Figure 2. SynCOR™ ammonia process layout

CO_2 removal technologies

The technology for removing CO_2 from the synthesis gas also needs to be optimized for blue. For many years, MDEA based units has been a preferred choice because of its low energy consumption. The less efficient CO_2 removal technologies can, however, be an efficient alternative, when integrated in a SynCOR™ synthesis gas generation unit. Topsoe finds that all well referenced CO_2 removal technologies can be used efficiently in decarbonized ammonia plants, all the way up to more than 99% CO_2 capture.

New, less proven technologies have, however, entered the market based on PSA and cryogenics. New carbon capture solutions will especially be considered for required carbon capture percentages better than 97- 98 % and where the product CO_2 shall be delivered at high pressure. The new solutions include the recycle compressor and supply the CO_2 product as liquid, as opposed to the normal low-pressure gas phase CO_2.

Drivers for rotating equipment

The ammonia process comprises several rotating equipment, requiring either electrical power or steam drives. Intensive use of the sensible heat from the ammonia process is therefore used for steam production to cover the main part, if not all the energy for the rotating equipment. This approach is optimal in terms of energy consumption but not necessarily in terms of CO_2 emission. To the extent that less CO_2 emitting power is available, then the optimal criteria for the ammonia process changes towards less steam production. This change is difficult for the steam reformer solution, where the available sensible flue gas heat is not easily reduced. For SynCOR™ based solutions, steam production can be reduced to the bare minimum only making the required process steam.

Impact of oxygen and steam/electricity import/export

SynCOR^{TM} and other ATR (autothermal reforming)/POx (partial oxidation) solutions require oxygen. How does oxygen requirement count in the energy/CO_2 emission balance? The energy used to produce oxygen can either come from steam or from electricity. In both cases, this energy consumption shall be added to the total energy cost for producing ammonia using oxygen as part of the feed. Similarly, the CO_2 emission related to the electrical power production or steam generation, if external, shall be added to the total CO_2 emission. This ensures that different process layouts can be compared on equal terms. It also results one solution to fit all cases cannot be made.

Gas and electricity prices and CO_2 emission connected to the power production now and in future have an impact on the optimal solution. The availability of more renewable power in the future can be considered while balancing the energy for the overall complex.

Carbon taxes

Last but not the least, the tax on CO_2 emission and/or CO_2 product price/cost will have an impact on the optimal layout of an ammonia plant. Another factor is the requirement to CO_2 emission or capture. It started out being 80 % capture, related to what can be done with carbon dioxide removal (CDR) process from flue gas. In the present market, 90% capture has become a standard, but it is going towards more than 99% capture. Does it make a difference? The answer is yes. The CAPEX increase going from 90% to 99% is in the order of 6-7% and OPEX is increased by 5-6%.

Comparing cases

The technology steps for blue ammonia are well proven and reliable. Selecting the technology best suited for a specific project will depend on multiple parameters, including carbon intensity(CI)/carbon recovery(CR), as well as the levelized cost of ammonia (LCOA). The parameters (LCOA and CI/CR) should be looked into, with due consideration to energy balance in the full blue ammonia facility, including auxiliary boiler emissions as shown in Figure 3.

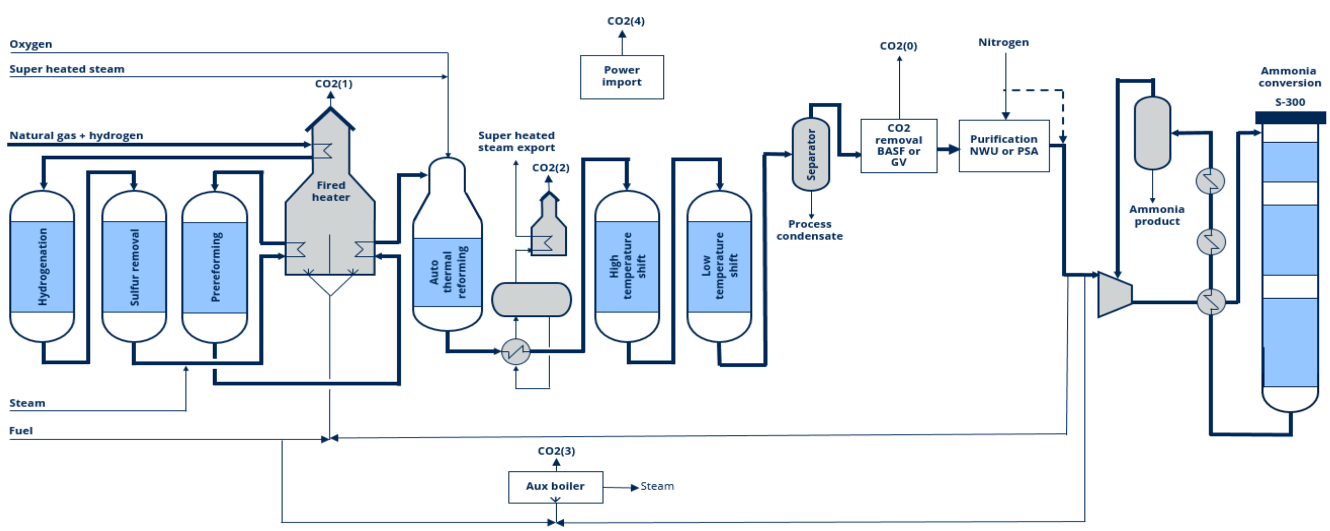


Figure 3. Schematic diagram of SynCOR^{TM} Blue NH_3 process for 90% carbon recovery

SynCOR^{TM} is the preferable choice at higher capacities, because of low capital expenditure (CAPEX) and operating expenses (OPEX). Its single reactor layout and very low steam-to-carbon ratio operation enables the SynCOR^{TM} design to benefit more from economy of scale.

Carbon intensity (CI) or carbon capture/recovery rate (CC%) is now widely considered the most effective way to measure the success of a blue ammonia technology, in terms of reductions in CO_2 emissions. The desired capture rate will have an impact on overall CAPEX and OPEX. However, if planned, the blue ammonia plant can start with lower capture rate, which could be potentially revamped to a higher carbon recovery rate, when needed.

Reducing CI from the process gas is more straightforward than capturing CO_2 from flue gas and is therefore normally the first step in CO_2 capture. SynCOR^{TM} achieving very low CI, is fully feasible by removing the CO_2 formed in the process gas only. This feature makes these processes ideal for blue ammonia production. The advantage of less firing duty required in SynCOR^{TM} blue ammonia, is reflected in low steam to carbon operating mode.

For a fair comparison, four cases are presented below with the basis that all plants are based on SynCOR technology with a capacity of 4000 MTPD.

Case C1(Base case), is a newly built standard SynCOR^{TM} ammonia unit with no additional means to reduce carbon recovery, with shift section, and pre-combustion carbon capture, as in traditional ammonia plants. The captured CO_2 is compressed to 162 barg (2350 psig) and liquefied for transportation or sequestration. The syngas is purified in a cryogenic nitrogen wash unit to prepare inert free make up gas. Fired heating duty is provided by natural gas and off-gases from nitrogen wash unit

Case C2 (Minimal hydrogen firing), is similar to base case with the exception that part of syngas/hydrogen rich gas is used as a fuel to enhance carbon recovery to 90%. Due to hydrogen firing, additional syngas is produced in the syngas generation section of the unit.

Case C3 with hydrogen rich gas is the main fuel for the fired heater to assure a higher carbon recovery, set at 99%. The major difference from C2 is, that the natural gas firing in the heater is reduced to bare minimum as for pilot burners, and balance is hydrogen rich fuel. Normally all of the methane containing off gases from purification unit is recycled to the reforming section and the balance used as fuel. Due to hydrogen firing, additional syngas is produced in the syngas generation section of the unit. Haldor Topsoe A/S has a patent pending on this technology.

Case C4 with post combustion capture is similar to base case C1, with the addendum of a post combustion capture unit to the fired heater to obtain a carbon capture of 90%.

The following utility prices were considered for the purpose of the evaluation:

Utility	Unit	Price
Natural gas	€ / MMBTU	4
Power	€ / MWh	100
DMW	€ / m^3	1
Steam	€ / ton	13.5
CO_2 credit for emission avoided	€ / ton	25

Table 2. Assumed utility prices capture

Additionally, the following parameters were considered for the current study:

Parameter	Unit	Value
CO2 emission due to power import	g / kWh	255
O&M cost	€ / year	4% of TIC
Discount factor	%	12
Yearly hours of operation	Hours	8500
Plant lifetime for LCOA evaluation	Years	20

Table 3. Basis for LCOA evaluation

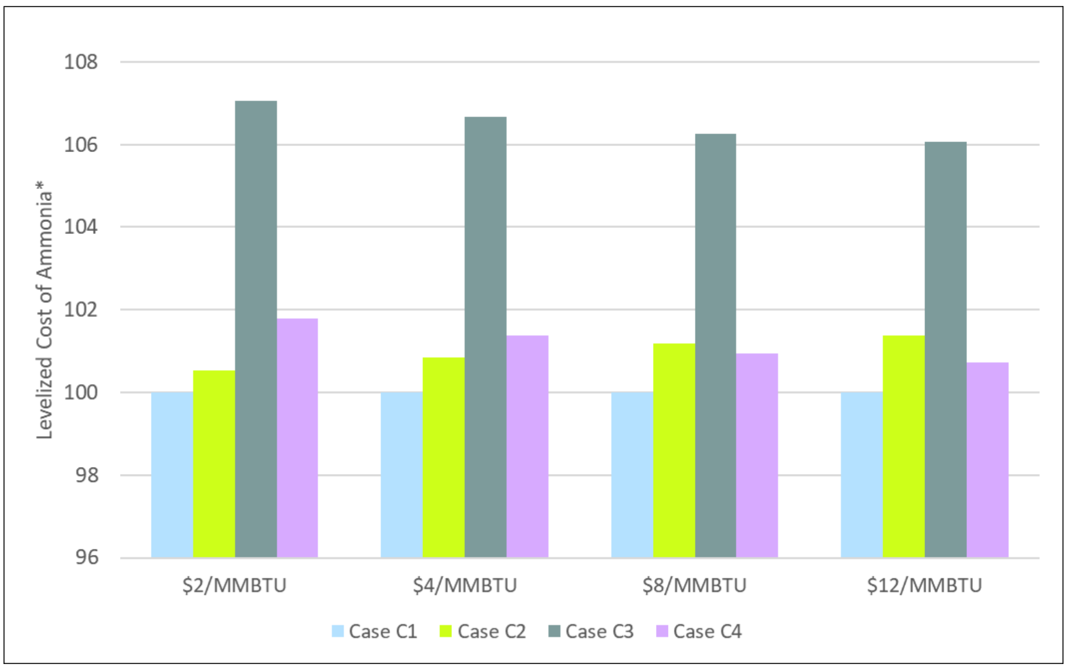
Table 4 shows operating and capital expenses, based on the defined cases and assumptions listed in Table 2 and Table 3.

	Case C1	Case C2	Case C3	Case C4
Carbon recovery %	87	90	99	90
Excess H_2 Production for fuel, %	0	4.3	15.3	0
LCOA	100	100.9	106.6	101.3
OPEX, $/h	100	101.9	107.4	101.7
CAPEX, MM$	100	102.4	109.2	104.6

Table 4. Comparison between cases

Table 4 gives the overall CAPEX and OPEX comparison for the different cases considered:

- Base case C1 gives lowest OPEX and CAPEX.
- Case C2 shows that producing excess H_2 for hydrocarbon fuel replacement has attractive CAPEX at 90% capture rate resulting in lower LCOA. However, post combustion case (C4) improves OPEX and in some scenarios (e.g. lower capacities), C4 case can be better than C2.
- Case C3 shows that there is a certain increase in both OPEX and CAPEX with increasing carbon capture requirement 90% to 99%.



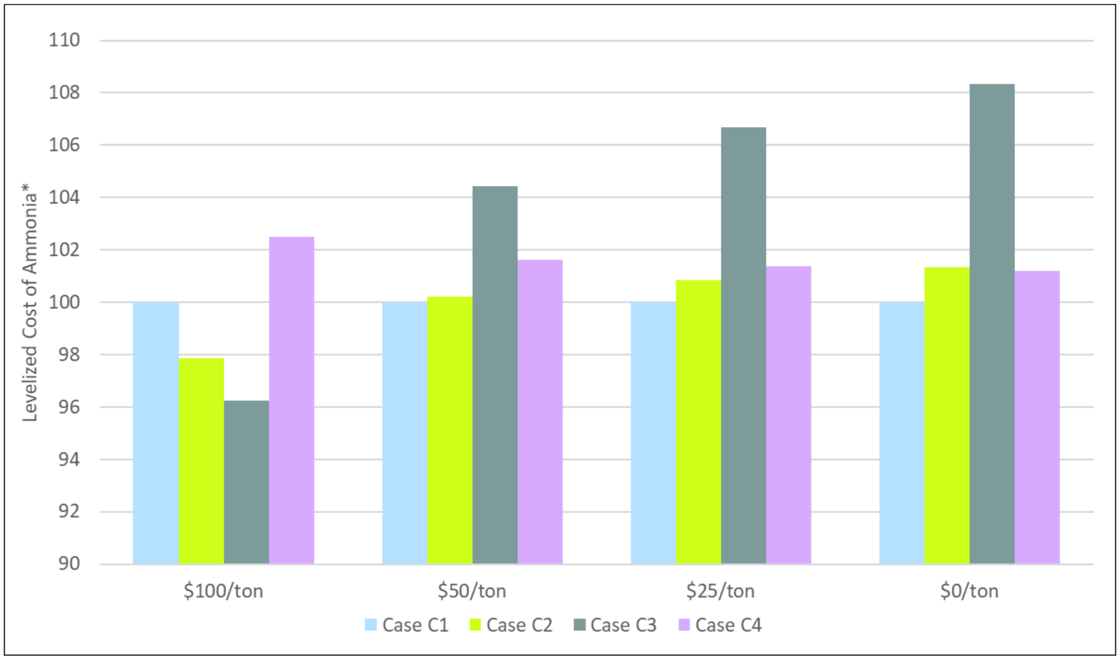
*Normalized to base case C1

Figure 4. Levelized cost of ammonia (LCOA) with varying natural gas (NG) price

The choice of technology ultimately depends on achieving certain targets as cost-effectively as possible. Levelized cost of ammonia is an important factor to consider, which will indicate the selection of layout on the basis of utility cost, CO2 tax, and credit and other associated costs of operating plant together with CAPEX. This case study shows that, as expected, low emission gives higher cost. But just as important, selecting the correct technology match to the boundary conditions can have similar impact on the result. The main learning is, that within the 'blue' we should not aim at a one fits all solution but aim at an adjustable concept which can be optimized to the local boundary conditions. Figure 4 shows the impact of natural gas prices variation on LCOA for all cases. Case C3 shows highest LCOA because of excess hydrogen production and higher CAPEX and C1 the lowest. That remains valid at different bands of natural gas price.

However, when carbon credit is taken into account, the layout selection becomes more critical. Figure 5 shows the impact of CO_2 credit variation on LCOA. It is clear that with no credit, case C3 shows highest LCOA and C1 is most favorable, however C3 case becomes attractive at higher CO_2 tax.

It shall be stated, that all four cases evaluated are comparable in most cases and attractiveness of layout can change relatively from case to case.



*Normalized to base case C1.

Figure 5. Levelized cost of ammonia (LCOA) with varying CO_2 credit

Conclusion

Blue ammonia will be one of the major solutions in the fight for climate change and achieve decarbonization. Blue ammonia will create a need for larger than ever built capacities. The traditional tubular reformer-based solutions are well proven but will be challenged at higher capacities both on operational and capital expenses. Needless to say, higher flue gas emissions in steam methane reformer plants, which will bring in additional cost to capture the high volume.

There are different, well-proven, mature methodologies available to achieve blue ammonia production. Depending on desired criteria and with foreseen availability of more renewable power, the SynCOR^{TM} blue ammonia process delivers with the lowest levelized cost of ammonia to go with lowest carbon intensity. The solution will provide economy of scale with the lowest carbon intensity.

As with energy transition, availability of more renewable power in the foreseeable future, also presents a viable option to design and operate in a way to integrate zero carbon power to further bring down emissions.

Optimization of the Ammonia Decomposition Process

Ammonia will play an important role in a future hydrogen economy as an energy carrier. The biggest hurdle is the geographical distance between renewable-rich locations and consumer countries. Thereby hydrogen transport is a challenge. The safe and proven alternative to transporting large quantities of hydrogen is shipping it in the form of hydrogen embedded in the ammonia molecule. In this case, the shipped ammonia has to be converted back to hydrogen at the destination point for further use.

This article describes the technical options for the ammonia decomposition process and their energy efficiency and CO_2 intensity, which – among others – also depend on the selection of the process heat source. This also impacts the decision between centralized and localized hydrogen production.

Johannes Elischewski, Alexander Kleyensteiber
thyssenkrupp Uhde

Introduction

The cracking of ammonia is a technology almost as old as its synthesis. The study of this reaction commenced as early as the 1920s, and for the last about five decades, small scale cracker units have been commercially available. But with the wide availability of industrial hydrogen, ammonia decomposition was used for niche applications only.

With the increasing importance of green technologies and the vision of energy supply avoiding CO_2 emissions, the cracking of ammonia regained widespread interest, and technological advancements took up momentum.

The central element is the CO_2 emission-free production of hydrogen by electrolysis of water ("green hydrogen"), taking place in locations with abundant availability of renewable power (e.g. solar, wind). In contrast, the high demandfor hydrogen or energy is in a region without such renewable power. Thus, hydrogen must be transported there, often from one continent to another. Several options for this exist. The transport of pure hydrogen, however, is a complicated task because of its low energy density as a gas and the need for extremely low temperature (-252 °C, -422 °F) for transport as a liquid, leading to high energy consumption for refrigeration and reheating, as well for new technology and infrastructure.

These difficulties are resolved when ammonia is used as the medium for hydrogen transport. Conversion of hydrogen to ammonia and transport of liquid ammonia by ship over long distances are proven well-established and low-risk technologies. In contrast to other suggested shipping media such as methanol, ammonia can be produced from hydrogen only with the addition of nitrogen from air, without the need for a carbon source.

At the point of energy use, ammonia can be converted back to hydrogen. Also, this decomposition or cracking process is known but not used on a large scale today. In addition to the established utilization of hydrogen, new ones emerge today, from hydrogen-fed gas turbines to its use as a reducting agent in steel production.

As with all new technologies, a great deal of optimization work is required for all these applications. This is an ongoing process at thyssenkrupp Uhde to offer an efficient and sustainable solution.

Fundamentals

Ammonia cracking or decomposition takes place according to reaction (1), which is the exact reversal of the ammonia synthesis:

$$2\ NH_3 \rightarrow N_2 + 3\ H_2 \qquad (1)$$

The five basic process steps shown in Figure 1 are required to produce a hydrogen stream of defined purity from refrigerated liquid ammonia as feedstock. They are referred to as the ammonia cracking process.

The liquid refrigerated ammonia feed stream is first evaporated and the resulting ammonia gas is preheated to the desired reaction temperature. Then it is fed into the heated catalytic NH_3 cracker, where the decomposition reaction takes place, producing hydrogen and nitrogen. The hot process gas leaving the cracker is cooled before entering a purification section, where the hydrogen product is purified to the desired level by removing nitrogen and unreacted ammonia. Separated components either leave the system as an off-gas stream or are used otherwise.

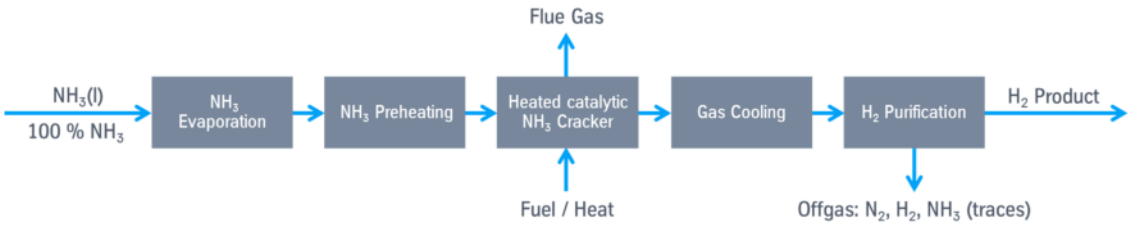


Figure 1: Ammonia cracking process.

Ammonia cracking units for small quantities of hydrogen products are commercially available as electrically powered package units. They usually serve a market where only small quantities of H_2 are needed in situations where its cost does not play an important role. They cannot be economically used for large-scale production both from investment and operation costs.

Therefore, different process options and optimization approaches for large-scale decomposition applications considering an investment, operation cost, product yield and greenhouse gas (GHG) emissions are discussed.

Process Options

Factors shaping the final ammonia cracking process are, amongst others:

- Source of reaction heat and selection of temperature profile
- Selection of catalyst
- Reaction parameters
- Design of downstream processing, especially the recovery of ammonia and hydrogen
- Availability of renewable energy

Source of Reaction Heat and Selection of Temperature Profile

The cracking of ammonia, forming one molecule of nitrogen and three of hydrogen from two molecules of ammonia, is strongly endothermic at 46 kJ/mol NH_3. Any technical application requires heat input to drive the reaction. This heat may be given all at once and stored at a higher temperature from which the reaction is then powered in an adiabatic way, or it may be sent into the reaction incrementally for a quasi-isothermal reaction profile. This heat can be generated within the reaction medium or outside and then transferred into it.

Both choices between temperature profile and location of heat generation have their advantages and disadvantages. In theory, all four combinations of the above options are shown in Table 1 and can be built using existing technology.

		Heat generation	
		Inside of process	Outside of process
Temperature profile	iso thermal	radiation-induced nano-catalysts	the tubular reactor, fired or electrically heated *comparable: reformer tubes in fired box*
	adiabatic	autothermal reaction (partly combustion) *comparable: autothermal reformer*	the fixed-bed reactor, fired or electrically heated upstream *comparable: pre-reformer with an upstream heating coil*

Table 1: Options for ammonia cracking reaction design and comparison with methane reforming technologies in italics. Cells with thick borders are discussed in more detail in Table 3.

Considering the reaction mechanism and process conditions, a comparison of the ammonia cracking reaction with steam methane reforming suggests itself. Therefore, corresponding versions of the steam reforming reaction are shown in Table 1 in italics and are discussed below.

External heating brings the disadvantage of a requirement for effective heat transfer. An isothermal reaction condition may be realized in a reactor similar to a steam reformer, consisting of catalyst installed in parallel vertical tubes heated from outside by firing or by electricity.

Adiabatic reaction conditions may be realized by one or more fixed beds with intermediate heating either by utilizing heat from flue gas or, again, electricity.

For the internally heated adiabatic ammonia cracking, a design similar to that of an autothermal reformer can be used. It is simpler in design than a steam reformer analogue but requires its combustion air at pressure, increasing the process's energy demand. The main drawback is that the combustion products remain within the process gas. The combustion of ammonia and hydrogen creates a large amount of nitrous oxides, which must be removed from the reaction mixture to a very high degree, primarily if hydrogen is produced for fuel cell applications. Also, the combustion produces water, which must be removed by condensation, and will take some ammonia along by dissolution. This ammonia must be recovered, which is energy-intensive.

The supply of energy by irradiation of nano-catalysts with light or UV radiation is a very new field of study (e.g. [1]). Small scale units have been built with efforts to improve their energy efficiency. As this process provides the total energy from electricity, its demand for electrical power is very high.

Selection of Catalyst

The catalyst to drive the ammonia cracking reaction is a field of intense study. Historically, nickel and ruthenium are known to be efficient catalysts and are commercially available. Nickel is the less active one and requires higher reaction temperatures of 650 to 900 °C (1,200 to 1,650 °F). Current developments aim at application at a lower temperature.

Ruthenium is more active and, therefore, applicable at lower temperatures around 500 °C (930 °F). Its scarcity and cost do not make its large scale application seem feasible. Other catalysts are being investigated, but as none of them is close to being commercially available, they are not discussed here.

Therefore, nickel seems the catalyst of choice, although it is not without challenges. Due to the high process temperatures, it requires an effective integration of process heat to minimize losses. At high temperatures and pressure, ammonia causes nitriding of steel pipes on one end of the reactor, and hydrogen may cause high-temperature hydrogen attack (HTHA) on the other, requiring smart choices of construction materials and process parameters to minimize these effects.

Reaction Parameters

The endothermic ammonia cracking reaction (1) increases the number of molecules from two to four. Therefore, high conversion is favoured by high temperature and low pressure.

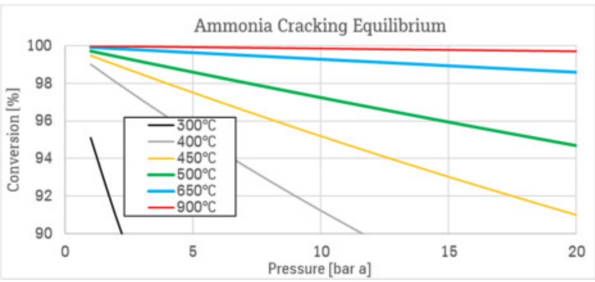


Figure 2: Ammonia conversion as function of temperature and pressure.

Figure 2 shows ammonia conversion rates dependent on equilibrium temperature and pressure. At 900 °C (1,650 °F), the effect of a pressure increase is nearly negligible; even at 20 bar (290 psi) pressure, the conversion reaches well above 99 %. At 500 °C (930 °F), however, typically for a ruthenium catalyst, conversion rates of only 95 % are reached at a pressure of 20 bar (290 psi). Lower temperatures are not suitable for technical application at higher than atmospheric pressure. However, running a large-scale process at low pressure is not efficient in terms of material cost for the considerably larger equipment and piping required.

The optimal process conditions seem to be an elevated, but not very high pressure to cap the capital cost of the plant, and high, but not extreme temperature to avoid the worst of the adverse material effects of both educt and product. For example, at 650 °C and 20 bar pressure (1,200 °F, 290 psi), the nickel catalyst provides equilibrium conversions of higher than 98 %, meaning a residual NH_3 content lower than 1 %.

Design of Downstream Processing

According to the block flow diagram (Figure 1), two more process units are required downstream of the reactor. The cracked gas leaving the reactor must be utilized in efficient heat integration measures to improve the efficiency of the plant. Those may include steam production, feed gas preheating, heating of combustion air, and boiler feedwater. Combustion of the off-gas typically available (see below) is the other heat source in the process; between those, the preheating duties can be shifted for a good fit.

Lastly, nitrogen and ammonia's undesired components must be separated from the cracked gas. Ammonia, if present in a significant concentration, may be removed by absorption into the water and then released by rectification. This supports the advantage of the ammonia being of high purity and fits for recycling into the feed, but it incurs the cost of energy in the form of steam or electricity to separate wash water and ammonia.

The separation of hydrogen and nitrogen can be facilitated in several ways. Cryogenic separation is possible but requires very high inlet pressure and very high energy demand, rendering it virtually unsuitable for this application. The same goes for membrane separation.

For industrial hydrogen production, pressure-swing adsorption (PSA) has been state of the art for decades. A PSA can operate at a moderate pressure of 15 to 25 bar (220 to 360 psi), ambient temperature and can produce hydrogen at a fuel cell quality of 99.97 %. A drawback is the less than full hydrogen yield, as some hydrogen is lost during bed regeneration. The PSA off-gas, consisting of almost all NH_3 and N_2 from the inlet stream and some H_2 loss, can however be utilized as fuel and replace a part of the fuel in the combustion. Besides, it improves the combustion behaviour of ammonia.

There is one more way to treat residual ammonia: by minimizing it in the reaction. At very high conversion rates, the little remaining ammonia can be removed in the PSA as well, folding ammonia recovery and hydrogen purification into one step, thus optimizing the way of downstream processing.

Availability of Electricity from Renewable Sources

The two largest consumers in the overall heat balance of an ammonia cracking plant are the reaction itself and the evaporation of the liquid ammonia feed. Losses are incurred by heat release to a cooling medium, ambient, and flue gas. Further, if ammonia absorption is employed, the reboiler of the regenerator column is another consumer of heat.

This demand can be met by process heat downstream of the reactor and from the combustion of the PSA off-gases. But these two sources alone cannot close the balance. Either additional fuel (e.g. ammonia or hydrogen) must be burned, or electrical preheating may be used if sufficient power is available. To keep the theme of CO_2-neutral technology, electricity from renewable sources is preferred.

Replacing combustion heat with electrical heat frees up more ammonia for cracking and increases hydrogen yield. This is more difficult in processes with a reformer-like reactor, as the flue gas contains most of the process heat requirement. But in a sequence of adiabatic fixed bed reactors, less ammonia is required for combustion but can be used as a hydrogen source if the heat is provided electrically upstream of each reactor.

Metrics for Process Comparison

Process optimization needs a metric for the efficiency of the process. Two metrics make sense:
Molar efficiency: The actual hydrogen production is divided by the maximum possible hydrogen production. The latter is defined by ammonia's hydrogen content, which is 0.1776 kg/kg.

$$\eta_M = \frac{m_{H2}}{m_{H2,max}} \qquad (2)$$

Energy efficiency: This is the energy contained in the hydrogen product divided by the energy input to the process

$$\eta_E = \frac{m_{H2} LHV_{H2}}{m_{NH3,in} LHV_{NH3} + E_{fuel} + E_{el}} \qquad (3)$$

with:

- LHV_i lower heating value of i
- E_{fuel} energy input by additional fuel input
- E_{el} energy input by electricity input

It can also be expressed as energy input per ton or m^3 hydrogen product:

$$e_E = \frac{m_{NH3,in} LHV_{NH3} + E_{fuel} + E_{el}}{m_{H2}} \qquad (4)$$

The energy of feedstock, product and externally supplied fuel (if applicable) can be expressed by their heating values (LHV). For consideration of electric power, see the following section.

Factors preventing attaining a molar efficiency of 100 % are:

- A small amount of unconverted ammonia at the reactor outlet, in the range of a few per cent (depending on the process conditions): Separated downstream but loss if it is not recovered.
- Hydrogen loss with the PSA off-gas.
- Using feed and/or product as fuel: This can be the largest contribution. The molar efficiency of the process depends much on the rate of this fuel usage. As a benchmark, if the energy for the cracking reaction is entirely supplied by combustion of feed and/or product, the yield is 0.1550 kg H_2 / kg NH_3, or molar efficiency $\eta_{M,ref}$ = 87.32 % as per (2). This means that about 13 % of the feed is consumed by the process and is not available as hydrogen product.

The definition of the relative yield (in %) is an indication of the produced quantity divided by the production of this benchmarking process:

$$p_{rel} = \frac{m_{H2}}{m_{H2,ref}} = \frac{\eta_M}{\eta_{M,ref}} \qquad (5)$$

Factors preventing to attain an energy efficiency η_E of 100 % are, besides the above reasons, the energy loss to the atmosphere by heat loss and efficiencies of utilized machinery.

The third metric for process valuation is its greenhouse gas emission. The cracking process should be energy-efficient and low in CO_2 or GHG emissions.

The basic process does not emit any greenhouse gases. However, if natural gas or another source is used for energy supply, it does. Further, the combustion of ammonia produces N_2O, which is a greenhouse gas about 300 times as potent as CO_2. However, technologies for its removal exist and are assumed to be installed here. Thus, only CO_2 is considered as GHG in the following.

Since ammonia cracking is one element in a process chain of delivering hydrogen to the consumer, all elements of this chain have to be considered. This includes emissions from the production of ammonia and electricity which consumes.

$$f_{GHG} = \frac{\sum_i m_{CO2,i_i}}{m_{H2}} \qquad (6)$$

Comparison of Processes

Process Configurations

From the parameters discussed above a range of possible plant configurations arise. The following three have been investigated in more detail by thyssenkrupp Uhde and are discussed here, distinguished by the ammount of energy supply:

- Case 1: Self-sustaining process: The required energy is provided by the combustion of a part of the feed and/or product stream. Two versions are discussed as Cases 1a and 1b.
- Case 2: Process with external fuel source. The required energy is provided by combustion of a fuel supplied from outside.
- Case 3: Process with electrical heating. The required energy is provided by electric heaters.

Figure 3 shows the flowsheet in a simplified form for Case 1b. The other cases are derived from this:

- Case 1a: No pre-reactor;
- Case 2: No use of NH_3 for firing, replaced by natural gas firing instead;
- Case 3: No use of NH_3 for firing, pre-reactor replaced by adiabatic reactors with intermediate electrical heating.

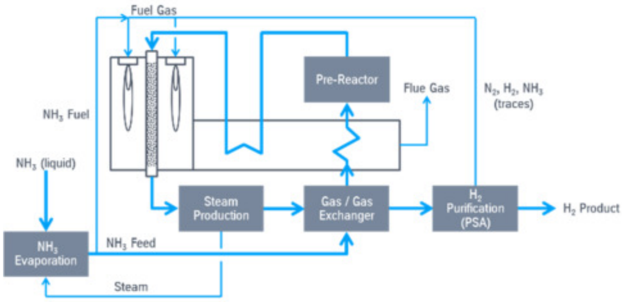


Figure 3: Simplified flowsheet for the cracking process, Case 1b.

All processes are designed in such a way that they do not export any off-gas or steam. Waste heat is utilized by the process as far as reasonably possible. The battery limit conditions are set as per Table 2.

Ammonia feed	-33 °C, 3.0 MPa a (-27 °F, 435 psi a)
H_2 product	42 °C, 1.6 MPa a (108 °F, 232 psi a), purity 99.97 % H_2
NG fuel	25 °C, 0.11 MPa a (77 °F, 16 psi a), assumed as 100 % CH_4
Scope of evaluation	Process with feed, fuel, electricity; plus electricity for cooling water supply

Table 2: Battery limit conditions for all process configurations.

Efficiency Comparison

Table 3 shows a qualitative comparison of the processes.

A quantitative analysis is provided in Table 4. In all cases, the theoretical total H_2 content of the input is 2,198 kmol/h.

The simple process from Case 1a has been improved about its efficiency by adding an adiabatic pre-reactor, see Case 1b. This efficiency increase mainly originates from lower overall firing duty and less heat loss with the flue gas. The pre-reactor design is therefore adopted also to Cases 2 and 3. It also helps to solve some design challenges associated with Case 1a.

Obviously, the molar efficiency (eq. 2) from Cases 1a and 1b can be increased if less feed / product is used for heating by replacing it with another fuel or electricity. This is done in Cases 2 and 3. The theoretical maximum plant yield is therefore determined by the hydrogen yield of the pressure swing adsorption unit. However, this does not necessarily increase the energy efficiency (eq. 3). The additional fuel has to be accounted for by its heating value, same as the other contributions.

But how to handle electric power input? For a process consuming fuel and electric power, a common unit of measurement must be created to allow for a fair addition of these two energy sources. This can be done by considering a specific conversion efficiency when the combustion of a fuel produces electric power.

All of the above processes consume a small amount of electricity for pump and compressor power. In Cases 1a, 1b and 2, the electric power supply is only 0.7 % of the total energy of the process. Therefore, the way if its valuation does not have a big impact. In Case 3 however, a significant amount (8 %) of the energy comes as electric power, and its proper valuation had a significant impact on the efficiency figure. For Table 4, 40 % conversion efficiency has been used.

For comparison: H_2 production by steam methane reforming has an energy consumption of approx. 140 MJ/kg, expressed by the natural gas LHV.

All processes generate an off-gas stream containing unconverted ammonia. In Cases 1 and 2 this is sent to the cracker firing. Since this is an attractive solution, this is also done in Case 3 with the electric heating. Therefore, also this process contains a firing, and only part of the energy is supplied by electric power. The high electricity consumption of Case 3 per ton of H_2 produced (Table 4) is about 9 % of that of H_2 production by water electrolysis.

	Case 1	Case 2	Case 3
Description	Process with internal fuel source (self-sustaining process)	Process with external fuel source	Process with electrical heating
Advantage	No direct CO_2 emission	High yield by full conversion of feedstock to H_2	High yield by full conversion of feedstock to H_2 Less energy loss by flue gas
Disadvantage	Lower yield by consumption of feedstock as energy Energy loss by flue gas	CO_2 emission depending on selected fuel Energy loss by flue gas	CO_2 emission depending on selected power source Expensive energy source

Table 3: Pros and cons of different process configurations. Options can also be combined with each other.

		Case 1a	Case 1b	Case 2	Case 3
Feed NH_3	kg/h	25,000	25,000	25,000	25,000
Product H_2	kg/h	3,437	3,470	3,771	3,777
Molar efficiency etaM	%	77.25	78.00	84.76	84.91
p_{rel} (eq. 5)	%	88.66	89.52	97.28	97.45
Feed + fuel	MW	128.9	128.9	140.1 (3)	128.9
El. power	MW	0.9	0.9	1.0	11.2
Energy efficiency (1) / (2)	%	87.84 / 86.95	88.70 / 87.79	88.70 / 87.79	89.44 / 79.85
Energy demand (2)	MJ/kg H_2	137.39	136.07	136.07	149.61

Table 4: Comparison of efficiencies of the process configurations. Notes: (1) no efficiency factor for electricity / (2) 40 % efficiency factor for electricity / (3) incl. 11.2 MW nat. gas fuel.

CO_2 Emission

Another comparison is made to the CO_2 emissions of the whole process chain of ammonia production and cracking. This is done by assuming different production pathways (green and blue) for the ammonia fed to the cracking processes (Cases 1b, 2, 3), whereby each cracking process can be differentiated again by the CO_2 load of the electric power used (e.g. renewables only vs. average grid).

To achieve a low CO_2 footprint, the ammonia has to be either green or blue. Specific CO_2 emissions for ammonia production are:

- Green ammonia: Ammonia from hydrogen from water electrolysis and nitrogen from air separation, both driven by renewable power. No GHG emission by the ammonia process and electricity generation, but GHG emission associated with the installation of the facility, e.g. in a wind farm [2]: 0.112 kg CO_2 / kg NH_3
- Blue ammonia: Ammonia from steam reforming of natural gas, CO_2 emissions reduced by CO_2 capture and sequestration: 0.2 kg CO_2 / kg NH_3. (Expressed as hydrogen, this would mean 1.1 kg CO_2 / kg H_2, which would satisfy the conditions of being below 2.0 defined by the US Infrastructure Bill 2021 [3] for "clean hydrogen". There is no unique definition and CO_2 emission standard because several degrees of CO_2 capture are possible.)

For comparison: A convectional ammonia plant based on steam reforming of natural gas has a CO_2 emission of 1.7 kg CO_2 / kg NH_3.

Example figures for CO_2 equivalents of electric power sources for the cracker are listed in Table 5. One has to bear in mind that the purpose of using ammonia as a hydrogen carrier is based on the idea that ammonia is produced in a place where renewable power is abundantly available at a low cost, and it is transported to a place where such renewable power is expensive (like Europe). Therefore, it is realistic that renewable power is available in a limited amount at a high cost only at the cracker location.

Description	CO_2 equivalent kg CO_2 / kWh	Reference	Remark
Wind power	0.0112	[2]	"wind" in Table 6
Grid mix Germany 2018	0.5	[4]	"DE2018" in Table 6

Table 5: Examples for CO_2 equivalents of electric power.

The resulting specific emission factors for the full process chains are shown in Table 6.

		Case 1b	Case 2	Case 3
CO_2 emission, using green ammonia				
• NH_3 decomp. "wind"	kg CO_2 / kg H_2	0.812	1.332	0.776
• NH_3 decomp. "DE2018"	kg CO_2 / kg H_2	0.937	1.458	2.228
CO_2 emission, using blue ammonia				
• NH_3 decomp. "wind"	kg CO_2 / kg H_2	1.464	1.933	1.376
• NH_3 decomp. "DE2018"	kg CO_2 / kg H_2	1.590	2.058	2.828

Table 6: Comparison of CO_2 emission factors f_{GHG} (eq. 6) of different cracking processes for green and blue ammonia, using different electricity sources for the cracking process.

For Case 2, a comparison with 1b shows that heating by natural gas increases the CO_2 emission by about 0.5 kg CO_2 / kg H_2.

For Case 3, a comparison with 1b shows that electric heating has a small net CO_2 saving if cracking power is from renewable sources. It is a significant increase if it is taken as a grid mix.

All cases can be compared to other ways of H_2 production:

- steam reforming: approx.
  7.5 kg CO_2 / kg H_2
- "clean hydrogen" [3]:
  2.0 kg CO_2 / kg H_2, e.g. as blue hydrogen, steam reforming with 73 % CO_2 emission reduction
- green hydrogen:
  0.63 kg CO_2 / kg H_2 [4], own calculations

The best option from Table 6 has a CO_2 emission of the chain H_2 production – conversion to NH_3 – re-conversion to H_2 23 % higher than that of green hydrogen. The worst is 350 % higher.

Centralized vs. Local H_2 Production

An element discussed in the context of using ammonia as a transport vector for hydrogen is the question of where the re-conversion to hydrogen shall take place. Assuming NH_3 transport by ship from a distant location to, e.g. Europe, the two extreme scenarios are:

a) Conversion to H_2 at the place of import in a large, centralized unit, further distribution to consumers inland only as hydrogen (compressed gas tanker or pipeline);
b) Transport of liquid NH_3 by tanker or pipeline to many small, localized crackers for conversion to H_2 close to the consumers.

The two scenarios have different characteristics for required transport infrastructure and transport risk. In addition to that, their environmental impact and the cost of the units would be different. Like in most chemical processes, if a production capacity is realized in a few large units, the investment is less than for many small units by the economy of scale. The same also holds for the operating cost, e.g., lower manpower requirements.

For the cracking process, another aspect becomes important: the selection of the process from Cases 1, 2, and 3. For a large unit with a feed of several hundred or thousands of tons of ammonia per day, the design with the fired reactor, looks similar to a reformer, is available.

For small plants for a few tons per day, it becomes complicated with the firing inside the box and heat utilization from the flue gas to keep it efficient. Here, electric heating can simplify energy management because it avoids a hot flue gas stream. But the unit as per Case 3 with electric heating produces an off-gas which is burnt to recover its energy. If Case 3 is modified by recycling this off-gas back to the process, this increases the electric heating for its replacement and requires an additional compressor. The recycling needs another treatment of the PSA off-gas to keep the NH_3 residues within the process and only emit uncontaminated N_2. Thus, simplifying the process in one place makes it more complicated in another. And as seen in Table 6, the electrically heated unit has a high CO_2 footprint if the electric power is not generated fully from renewables.

Thus with large, centralized units, both the highest energy efficiency and the lowest CO_2 emission can be ensured.

Summary

Ammonia decomposition or cracking to hydrogen is an important process step in the context of CO_2 avoidance in a future hydrogen economy and the use of ammonia as a transport medium for hydrogen. All steps of this process chain (green or blue hydrogen – ammonia synthesis – ammonia decomposition to hydrogen) are offered by thyssenkrupp Uhde.

The ammonia cracking process has a minimum energy consumption of approx. 13 % of the energy is contained in ammonia. This energy can be made up by combustion of a part of the feed or product or it can be supplied from outside by fuel or electricity. While the latter two measures increase the hydrogen yield per ton of ammonia input, they also increase the specific CO_2 emission. The only exception is when the cracker is heated with electricity from renewable (CO_2-free) sources.

Centralized and localized hydrogen production both have their pros and cons in the aspects of safety, economic feasibility and CO_2 avoidance. The safety of both options strongly depends on the selections made for inland transport and storage of ammonia and hydrogen, while process economics and avoidance of CO_2 emissions favour the ammonia cracking in large, centralized units.

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The Dakar Ammonia Accident: Analysis of the Worst Incident at an Anhydrous Ammonia User

The Dakar ammonia accident, in Senegal on March 24, 1992, is the worst ammonia industrial accident ever. This anhydrous ammonia industrial catastrophe claimed 129 lives and injured another 1,150 workers and citizens.

The accident happened at a peanut oil processing facility where ammonia was used to detoxify the product. Anhydrous ammonia was stored in a portable tank commissioned in 1983 and repaired in 1991 before the incident. The weld repairs made were on cracks detected on the tank's surface. Frequent overfilling of the tank ("authorized" to hold 17.7 tonnes) was one of the primary causes noted in the reports. An overpressure inside the tank led to its catastrophic failure releasing 22 tonnes of pressurized ammonia. A heavy white cloud of ammonia aerosol plus vapor spread a significant distance causing fatalities and injuries.

This paper presents an analysis of the incident and the resulting consequences.

Dharmavaram, S.
Air Products, Allentown, PA, U.S.A.

Pattabathula, V.
S.V.P. Chemical Plant Services, Brisbane, Australia

Introduction

Understanding and managing the hazards of pressurized anhydrous ammonia is extremely important to prevent significant accidents. Many incidents have occurred in the industry in producing, transporting, and using anhydrous ammonia.

The Dakar accident is the worst ammonia accident in terms of fatalities [1]. This paper describes the incident and an analysis of the consequences observed. It is important to review the details of the accident to derive lessons that all stakeholders can utilize.

Of course, the worst industrial accident was the Bhopal accident [2] on December 4, 1984, which resulted in significant consequences and desirable changes in industrial focus on process safety and regulations implemented worldwide [3]. Like Bhopal, the Dakar accident (see Figure 1) deserves equal attention as the worst accident among ammonia handling facilities that we can all learn from. The news report in Le Soleil (The Sun) newspaper from the day after the incident (Fig. 1) headlined the "cloud of death" following the explosion of an ammonia tank. There were similar news reports published in U.S. newspapers describing the immediate consequence of the accident [4-5].


le soleil
UNE CITERNE D'AMMONIAC EXPLOSE : 41 TUÉS, 403 BLESSÉS
LE NUAGE DE LA MORT

Figure 1. Dakar accident news report (Ref. 1)

An understanding of the hazards of pressurized gases (like ammonia, chlorine, etc.) and the consequences of hazardous events can lead to good decisions for minimizing process risk. This has been continuously emphasized for numerous industries publicized by the Center for Chemical Process Safety (CCPS) [6-7], the U.S. Chemical Safety Board (C.S.B.) [8], and other organizations for a variety of different hazardous chemicals.

Figure 2. Dakar, Senegal, Africa

Dakar Accident

Around 30 years ago, on March 24, 1992, the country of Senegal (see Figure 2) experienced its worst industrial accident in Dakar, Senegal, at a peanut oil mill (operated by Sonacos SA) near the Dakar port. The debris from the explosion of the tank truck also pierced process equipment (e.g. hose) containing liquid ammonia under pressure. The release of 22 tonnes of liquid ammonia was reported [1]. A two-phase flow of ammonia fluid (vapor plus liquid as fine aerosol) formed a dense vapor cloud and spread over a significant distance resulting in injuries and fatalities. The dense plume settled over the oil mill, nearby offices, and adjacent restaurants where people were present at lunchtime. Forty-one (41) people died immediately, and many others were transported to the nearest trauma center. Ultimately (after a month), the total numbers were determined to be one hundred twenty-nine (129) fatalities and one thousand one hundred and fifty (1150) injuries.

Figure 3. Peanut Oil Mill [1]

Most of the injuries and fatalities resulted from inhalation of ammonia at high enough concentrations that caused respiratory lesions, edema in the lungs, and skin/eyes irritation. Near the release location, many of the fatalities resulted from direct skin exposure and cold burns and inhalation of high concentrations. Fortunately, because of the Ramadan holidays, the schools nearby were closed, and restaurants were less crowded. Otherwise, the number of fatalities and injuries could have been much higher.

Process Operation & Incident Details

Peanuts and peanut oil were among the top commodities exported from Senegal in the 1990s. To extract peanut oil from peanuts, anhydrous ammonia was used to detoxify the product at a peanut oil mill in Dakar which Sonacos SA owned.

Anhydrous ammonia was brought to the Mill by a road truck from a fertilizer company nearby that stored large quantities of cold liquid ammonia in spheres. The tank was then placed at the Mill for use as a storage vessel since no other storage tanks were present at the Mill.

The details of the ammonia tank that exploded are as follows [9]:
Diameter: 2.2 m
Thickness: 11 mm
Volume: 33.5 m^3
Construction material: Annealed hardened steel
Construction year: 1983
Last maintenance year: 1991

The tank was built by a French company in 1983 and certified as compliant with regulations. From 1983 to 1991, the tank truck was frequently overfilled beyond the "authorized" 17.7-tonne filling limit. The overfilling led to overpressure and crack formation that was detected in 1991. The crack was welded but not annealed. After the repairs were done, the truck continued to be overfilled on the day before the accident. The tank was filled with 22,180 kg of liquid ammonia under pressure and was placed at the Mill.

Around 1:30 to 2:00 PM (during shift change), on March 24, 1992, the tank suddenly burst open along the middle with the two portions propelled in different directions. The collision from the tank contacting the buildings caused significant damage and debris (Fig. 4 – 6). The chassis and axle from the truck were found up to 200 meters away beyond the facility boundary. Anhydrous ammonia from the tank was released almost instantaneously, and heavy, dense clouds spread well beyond the facility into the industrial and residential neighborhoods. The debris caused the failure of a hose connected to the process vessel, with the discharge continuing for at least half an hour.

Figure 4. Front of the Tank View 1 [1]

Figure 5. Front of the Tank View 2 [1]

Figure 6. The rear of the tank [1]

Weather Conditions

During the time of the accident, the weather conditions were as follows [9]:
Temperature: 26 C
Wind speed: 4 m/s

Wind direction: North

These weather conditions were used for the consequence analysis discussed below.

Medical Treatment

On April 2, 1992, U.S. Ambassador Katherine Shirley declared a disaster and requested the purchase of emergency respiratory and cardiac monitoring equipment. Pulse oximeters and E.C.G. cardioscopes with accessories were procured and immediately dispatched to Senegal. The equipment was donated to the intensive care unit at Dakar's Trauma Center, where victims seriously injured by accident were being treated. Nine days after the equipment was received, USAID/Senegal representatives met with the Trauma Center staff and were told by the physician in charge that the equipment had made a difference between life and death. Of the more than 400 patients admitted to the Center, only 31 remained under treatment. In mid-April. the total death count from the accident was 129 people.

The patients treated for minor skin lesions developed pulmonary edema (fluid build-up in the lungs) in the trauma center. Most of the people killed near the tank explosion and release were in semi-confined locations (Mill, restaurants, damaged buildings, and in the streets nearby). Among the injured were emergency responders that were ill-prepared to deal with an event of this magnitude.

A detailed chronological study [10] based on an autopsy of people that died revealed that the victims were between 3 months and 74 years old. The cause of death was identified as the after-effects of pneumopathy (pulmonary infection, bronchiectasis, and pulmonary fibrosis). The intensity of lesions and mortality was proportional to the quantity of inhaled ammonia per m^3 of air.

Primary Cause: Overfilling

A systematic root cause analysis of the Dakar accident can yield multiple causal factors (related to design, operation, hazards management, etc.) resulting in the incident. However, there is one primary cause (overfilling) that is obvious and has resulted in and continues to cause numerous incidents throughout the world.

Understanding the hazards of overfilling and determining the "Filling Ratio "for a variety of containers (cylinders, tanks, etc.) to avoid incidents like this Dakar accident has been widely recognized [11-13]. Overfilling of high pressure compressed gases can result in overpressure and loss of containment.

Filling Ratio

The filling ratio is defined as "the ratio of the mass of gas to the mass of water at 15°C that would fill completely fitted ready for use" [13]. For high-pressure liquified gases (like anhydrous ammonia), the filling ratio is determined such that the settled pressure at 65 °C does not exceed the test pressure of the pressure receptacles. The minimum test pressure typically required is 1 MPa (10 bar). If relevant data are not available for high-pressure liquified gases, the Maximum Filling Ratio (F.R.) is determined as follows:

$$FR = 8.5 \times 10^{-4} \times d_g \times P_h$$

where d_g = gas density (at 15°C, 1 bar)(in kg/m^3)
P_h = minimum test pressure (in bar)

Receptacles	Max. Allowable Working Pressure (bar)	Min. Test Pressure (bar)	Maximum Filling Ratio
Cylinders, Drums		29	0.54
Portable Tanks	20 - 29		0.53
Tanks		26 – 29	0.53

Table 1. Filling Ratio for Ammonia Receptacles [13]

Table 1 [13] provides the published Maximum Filling Ratios for anhydrous ammonia. The pressure testing is typically done every 5 years for ammonia receptacles.

For a tank (or any other receptacle) containing anhydrous ammonia under pressure, it is best to ensure that the filling ratio does not exceed 0.53.

The tank in the Dakar accident was overfilled to almost the full volumetric capacity of the vessel (33.5 m^3) before the day of the accident.

Consequence Analysis

An analysis of the consequences of the ammonia releases during the incident on March 24, 1992, can be done using the release and weather data that is available. The Emergency Response Planning Guideline (ERPG) concentrations published by the American Industrial Hygienists Association [14] can be used to determine the acute toxicity effects. The ERPG-2 and ERPG-3 concentrations for ammonia are 150 ppm and 1500 ppm, respectively. ERPG-2 is a concentration above which irreversible injuries can occur. Very serious injuries and potential fatalities can occur based on exposure time at concentrations above ERPG-3.

The probability of fatality can be determined using Specified Level of Toxicity (SLOT) and Significant Likelihood of Death (SLOD), and Dangerous Toxic Load (DTL) data published by the U.K. Health and Safety Executive [15].

Substance name	CAS number	'n' value	SLOT DTL (ppm^n.min)	SLOD DTL (ppm^n.min)
Anhydrous Ammonia	7664-41-7	2	3.78×10^8	1.03×10^9

Table 2. SLOT and SLOT DTLs for Ammonia [15]

On March 24, 1992, around 22 tonnes were instantaneously released when the tank exploded. In addition, loss of containment from a hose connected to the process tank continued for a significant period of time.

The DNV PHAST model [16] was used to model the release and dispersion of the heavy gas cloud from the two scenarios (Instantaneous Release: 22 tonnes; and Continuous Release: Hose Failure).

The maximum footprint generated by the instantaneous release of 22 tonnes is shown in Figure 7. The injury concentrations (ERPG-2) extend to more than 4 km and with a width of about 4 km. The distance to ERPG-3 is about 1.5 km, the zone within which there might have been serious injuries and fatalities. The cloud would have been visible only up to a 900 m. Figure 8 shows an estimate of distances for the higher probability of fatalities. Up to a distance to almost 200 m, the probability of fatality is 100%, and then it drops to 0.1% by 500 m, primarily because the exposure time is shorter for an instantaneous release.

The maximum footprint generated by the continuous release from a 3-inch hole (e.g., hose failure) is shown in Figure 9. The plume is narrower (less than 1 km), but the injury concentrations (ERPG-2) extend to almost 5 km. The distance to ERPG-3 is less than 1.5 km, again the zone where there might have been serious injuries and fatalities. The visible range would have also been around 900 m. Figure 10 shows an estimate of distances to a high probability of fatalities. Up to a distance of almost 400 m, the probability of fatality is 100%.

Based on the proximity of the population near the paper mill that has been reported, it is therefore not surprising that 1150 people were injured, and there were 129 fatalities. Because of a religious holiday (Ramadan), the population off-site, especially in nearby schools and restaurants, was a lot lower. If this incident had occurred on any other day, the injuries and fatalities would have been higher.

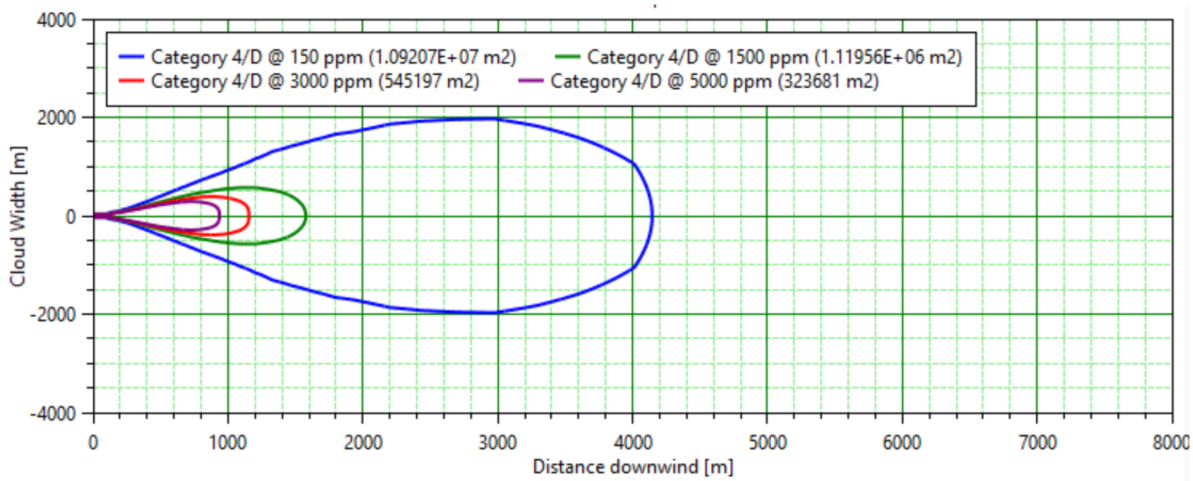

Figure 7. Maximum Footprint for the Instantaneous Release of 22 tonnes

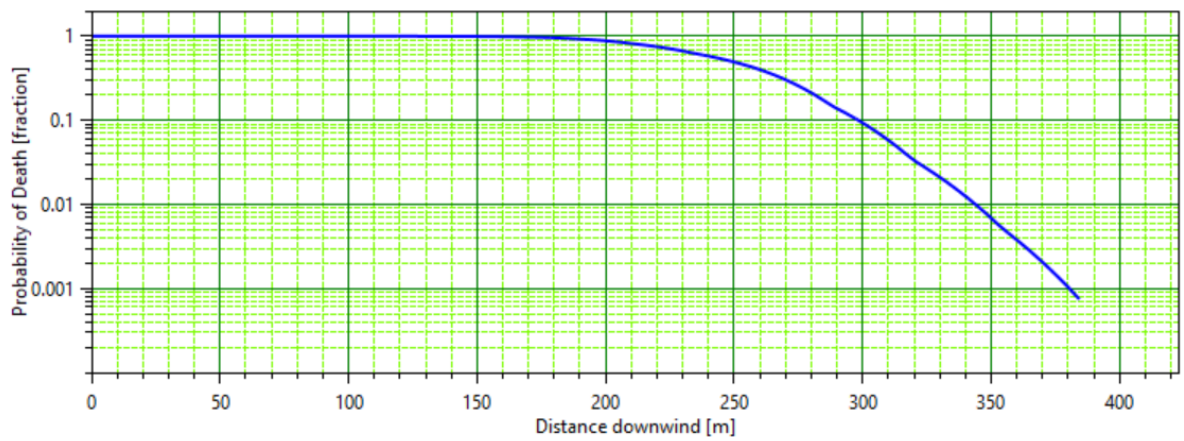

Figure 8. Probability of fatality vs Distance for the Instantaneous Release of 22 tonnes

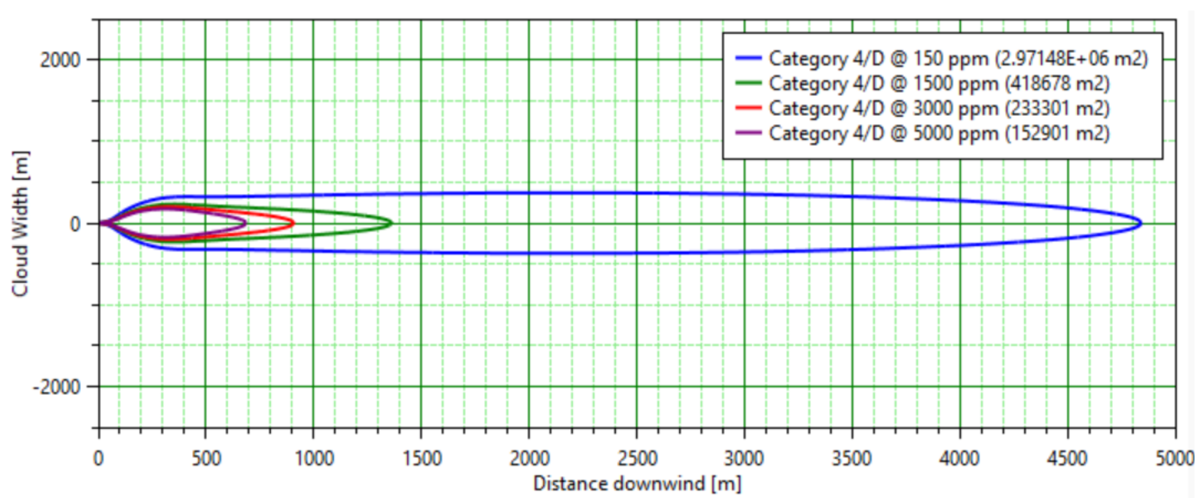

Figure 9. Maximum Footprint for the Continuous Release from a 3-inch hose

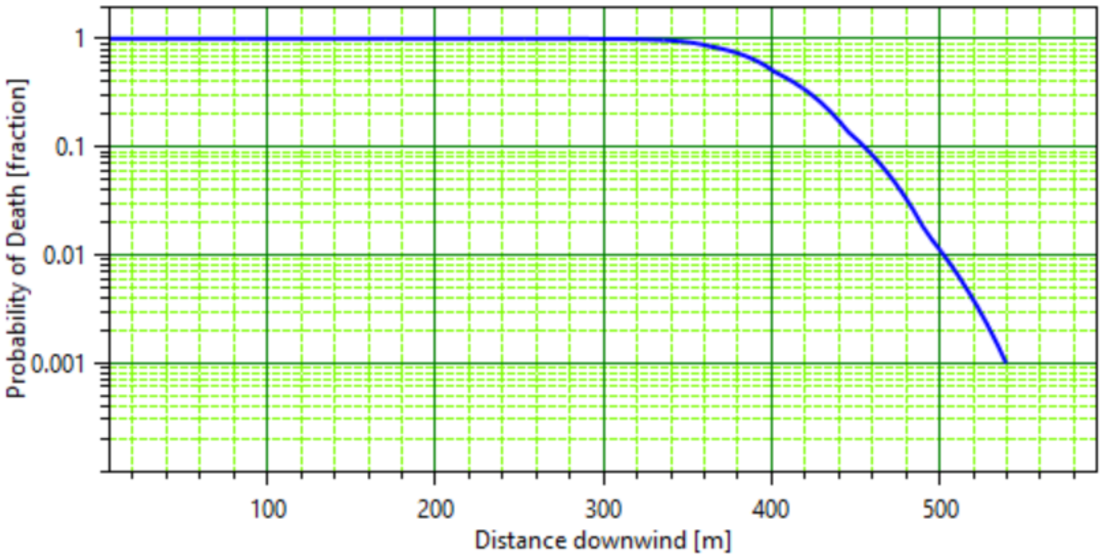

Figure 10. Probability of fatality vs Distance for the Continuous Release from a 3-inch hose

Lessons Learned

A detailed analysis of the causal factors can only be done using evidence (preserved/protected) and related data from the day of the accident. After a period of 30 years, it is almost impossible to reconstruct all the details based on limited data that is currently available in public literature. However, some general lesson categories (related to technology, operations, management, etc.) and generic causes can still be extracted. Table 3 below provides a summary of lesson categories and high-level causes, that can be broadly leveraged to prevent such incidents from happening.

In addition to the primary cause (i.e. overfilling) noted above, there were many failures in the following categories: technical; operations; facility/corporate leadership; government oversight; and industrial standards/governance. These are all important for safe operation of ammonia facilities in all global locations.

An industrial standards organization for ammonia (like they exist for other chemicals like chlorine – Chlorine Institute, Eurochlor) might improve process safety performance in all jurisdictions, particularly in developing countries. The production and use of anhydrous ammonia is expected to increase dramatically across the world in the next few years.

In Senegal, anhydrous ammonia will continue to be used in large quantities since it is needed to detoxify agricultural commodities (i.e. nut oils) to eliminate aflatoxins. The demand is high and likely to increase over time. Ammonia is currently seen as a "formidable and indispensable killer" resulting from the Dakar accident in Senegal [17]. Lessons from Dakar and other incidents can be effectively used & leveraged to improve the perception of ammonia and promote its safe handling everywhere.

Lesson Category	Potential Causal Factors
Technical	Poor understanding of hazards of anhydrous ammonia under pressure
	Improper design and utilization of equipment and protection systems; inadequate design basis documentation
	Inadequate or no hazard reviews, consequences, and risk analysis
Operations	Lack of training & competency development
	Poor emergency response planning & procedures
	Improper testing and inspection of equipment & control systems
	Failure to understand the gravity of an abnormal situation and potential consequences
Leadership	Lack of safety concerns at senior leadership levels
	No policies, procedures, or guidance documents related to process safety
	Lack of risk assessment & management practices
	Failure to be open/receptive, bad safety culture
	No sense of vulnerability and failure to equip plants with required resources
Government Regulations/Industry Standards	Lack of process safety regulations, standards
	Absence of toxics substance management policies & procedures
	Poor emergency management and lack of coordination of community response
	Adhoc siting of hazardous industrial operations
	Lack of controlling land use and poor zoning of land use
	Poor implementation of safety audits & recommendations

Table 3. Potential Lessons that can be Learned & Leveraged from Dakar Accident

Summary

The Bhopal accident was the worst industrial accident, but the Dakar accident on March 24, 1992, is the worst ammonia industrial accident ever. It was also the worst industrial accident in Senegal.

High pressure in a portable tank resulted in the crack spreading and splitting the tank into two parts and a loss of containment of 22 tonnes of ammonia. The debris also damaged process equipment and resulted in an extended release from a hose failure.

An analysis of the consequences of the ammonia release scenarios demonstrates that the estimated distances for potential fatalities (1 km) and injuries (4 to 5 km) is very significant, with several fatalities (129) and injuries (1150) that occurred on March 24, 1992.

It has been well argued and proven [3], that accidents like those that occurred at Bhopal and Dakar in the developing countries (India and Senegal), can occur in developed countries, too, even with more robust regulations and industry standards. But it is essential to continue developing and implementing standards for safe designs, operations, and governance and thus improve process safety performance at anhydrous ammonia storage & handling facilities.

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Ammonia Pipeline Integrity and Risk Management

The potential green use of ammonia as a hydrogen source will necessitate signification expansion of ammonia distribution infrastructure. Ammonia pipelines have provided the safest and most economical mode of transportation. This paper provides a framework for understanding pipeline risk along with logical and defensible risk assessments that allow for tailoring management strategies for risks along the pipeline. The framework also includes a review of updated pipeline risk damage mechanisms and mitigation techniques with lessons learned from existing ammonia networks including those in North America with 50+ years of history. The product of this process provides a basis for prioritization and practicality of risk mitigation strategies for new or existing pipelines.

Dorothy F. Shaffer
Joshua Bruce-Black
Sean Berg, Ph.D., P.E.
Baker Engineering and Risk Consultants, Inc.

Introduction

Above and below ground pipelines that distribute materials over long distances are a cost effective means of transportation with comparatively low risk. Pipelines commonly convey cold product several kilometers to a shipping port above ground, or at warmer than frost temperatures in underground networks to other regions. With green energy potential, the previous ammonia destinations of croplands and chemical manufacturing sites will be supplemented by new energy production destinations that require robust and safe transportation. Lessons learned from past pipeline incidents combined with the improved design, risk assessment, and mitigation tools of today has resulted in better methods for managing the potential hazards of pipelines for both existing and new facilities.

A few major ammonia pipeline networks have crisscrossed large areas for decades. Their construction and reports of damage and failures yield information on damage mechanisms and failure modes. Inspections have evolved to reduce the likelihood of releases. The challenges of transporting cold products, including ammonia, over long distances is generating evolving methods for cold ammonia transport design. The risk assessment techniques and mitigation options for evaluating and reducing impacts on people and the environment are also evolving. Regulations including the US CFR 49 Part 195[1] provide a detailed structure for managing pipeline operations and maintenance to reduce failures and their effects. These regulations cover physical aspects of the pipeline from design, operating stress level, leak history and cause, inspection requirements and intervals, evaluations, and history. The risk assessment considers information about physical conditions plus consideration of failure impacts along the pipeline route.

Pipeline Failure Modes:

Causes of pipeline failures vary widely depending on their location, breakdown of information, and the scope of the review. In Europe, excavation causes were cited in ~50% general pipelines incidents. In the US over the past 5 years for highly volatile hazardous liquids (which includes ammonia), excavations were cited in just 4% of incidents as compiled by the US Pipeline and Hazardous Materials Safety Administration[2]. Major concerns of ammonia pipeline incidents include:

- Material/Weld/Equipment Failure
- Corrosion
- Incorrect Operation
- Excavation/Collision Mechanical Damage

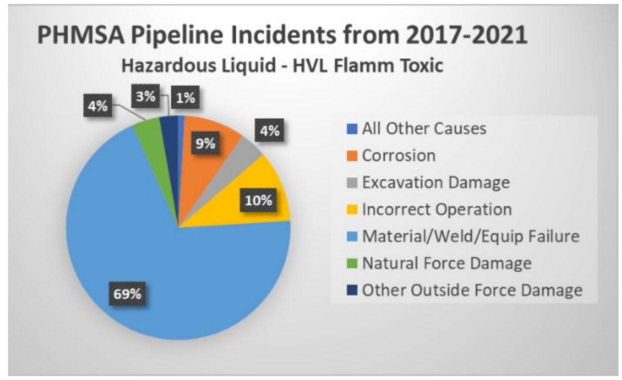

Figure 1. Highly Volatile Liquid Pipeline Incidents in the United States[2]

Applicable damage mechanisms for typical pipelines are listed in Table 1.

Damage Mechanisms	Risk for Ambient or Cold Service	Mitigations
Ammonia Stress Corrosion Cracking (SCC)	Both	Add 0.2% water Material selection Control oxygen contamination
Atmospheric/ External Corrosion	Both	Coatings particular to above or underground installation Insulation seals on cold pipelines Cathodic protection
Brittle Fracture	Both	Material selection Operating temperature control
External SCC	Both	Coatings particular to above or underground installation Insulation seals on cold pipelines Insulation specification on contaminants Cathodic protection
Corrosion Fatigue Cracking	Both	Coatings to avoid corrosion initiators Cathodic protection Monitor by pigging
Corrosion Under Insulation	Both, Cold: Higher Risk	Coatings particular to above or underground installation Insulation seals on cold pipelines Insulation specification on contaminants Cathodic protection
Crevice Corrosion	Both	Metal and Fabrication Quality Control Coatings (External)
Fabrication or Metal Defects	Both	Metal and Fabrication Quality Control
Freeze Damage/Frost Heave	Cold, underground	Design and seal for cold operation (double pipe system). Ambient, limit operating temperature.
Mechanical Damage (external)	Both	Warning signs or installations Monitor to prevent catastrophic break
Mechanical Fatigue Cracking	Primarily Welds	Design and Weld Quality Control

Table 1. Typical Pipeline Damage Mechanisms

With the exception of Ammonia SCC, which is easily managed, ammonia is generally minimally corrosive with reports of 0.00034 mm/yr (0.0134 mil/yr).[3] Remaining damage mechanisms are limited to external corrosion, material/fabrication, and/or installation issues. Four recent BakerRisk pipeline incident investigations involved fabrication flaws. Most of these combined with typical corrosion mechanisms to create a weak area that prematurely failed the piping.

Much of the cross-country pipeline network in the US is long-seam welded pipe. Before the 1960's and early 70's, Low Frequency Electrical Resistance Weld (LF-ERW) techniques were used with operating temperature specifications at 10°C (50°F) or above. Weld practices then transitioned to High Frequency (HF-ERW) which improved the Charpy impact test values markedly, providing better resistance to brittle fracture in auto-refrigeration conditions. Overall better weld quality was achieved with HF-ERW along with improved resistance to lack of fusion and the formation of hook cracks. Other types of welds are used in addition to HF-ERW for long seam pipe still in use today.

Above Ground and Underground Pipelines

In 2008, Fertilizer Europe [4] compiled guidance for inspection and leak detection of pipelines, which included a tabulation of 25 European pipelines. The data included:

- 19 above-ground pipelines with an average length of 5 km (3.2 miles).
- 6 underground pipelines with an average length of 17.2 km (11 miles).

Above ground piping is practical where the transited areas are controlled, which allows management of hazards over a short distance, such as damage from mobile equipment. Cold ammonia systems can transfer directly to or from ships and barges and vapor generation can be more easily returned.

The data also indicates that above ground pipelines operate in a mix of cold (<-20 C) and above freezing temperatures, but only two of six underground pipelines operate at cold temperatures, and they are relatively short. For cold pipelines, water infiltrates the smallest breach in insulation seals to condense, leading to Corrosion Under Insulation (CUI) and inviting External SCC, which are well-known damage mechanisms in ammonia facilities. Corrosion is more common at piping supports and on welds. CUI conditions can be more easily monitored and corrected in above ground pipelines.

For underground pipelines, operation at cold temperatures requires rigorous protection to prevent issues or failure caused by icing.

Amoco Incident

A 1967 incident involved a 6.4 km (4 mile) 203 mm (8") low ammonia temperature pipeline loading failure where it passed underground at a road crossing. At these sections, the line was wrapped in vinyl for corrosion protection, was cathodically protected, and then installed in a 305 mm (12") pipe sleeve with rubber casing seals at each end as the installation was below the water table. However, the operation cycling between cold and ambient temperatures drew moisture in, resulting in icing. Freeze-thaw cycles between pipe and the pipe sleeve caused a failure of the ammonia line.[5] Piping strain due to frost heave stress was also postulated.

Poly-coated lines can be used to avoid external CUI and SCC. Stainless pipe avoids CUI, but must be coated to resist external SCC. Advancements in double pipe or multilayered insulation systems can help avoid freeze damage.

The Fertilizer Europe data confirms that, on average, above ground pipes run for much shorter distances than underground pipe. Above ground piping is practical where the routing path is controlled, allowing better management of mobile equipment or potential security threats. For longer distances, however, full control of the route is impractical. Burying the pipe at a meter or more underground limits the risk of security and traffic issues. Longer pipelines typically operate at ground temperature.

Case Study, Tekemah Incident

The 2016 MAPCO Tekemah release of 500 tonnes of ammonia resulted in a fatality and provides a case study of fabrication/installation issues, damage mechanisms, and inspection techniques.

This section of ammonia pipeline was installed in 1968 by third party contractors with MAPCO supervision. In 2016, while operating normally at a pressure of 5.5MPa (800 psi), a crack ruptured on the 203 mm (8”) diameter line at a location where a gap in the tar paper spiral wrap allowed External Corrosion to occur, followed by a Corrosion Fatigue step progression that led to the failure (see Figure 2). While most tar paper spiral wrap adhered to the surface, several areas exhibited flaws in the wrap, including gaps, “tents,” and locations where the wrap folded back on itself, which compromised the exterior wall protection. External corrosion was identified at several of these locations.

Figure 2. Corrosion Fatigue Cracking Rupture

Mitigation: The difficulties of maintaining quality control in field installation practices must be considered in evaluating risks, though it was decades before the full extent of these particular issues arose.

Mitigation: By regulation and good practice, risk mitigation would require that exposed piping be inspected to determine its condition. If issues are found, further inspections would determine the extent of the condition to be examined and addressed.

An extensive integrity investigation was undertaken by the US National Safety Transportation Board (NTSB) and MAPCO. *Mitigation: While the investigation was ongoing, the NTSB set limitations on the operating pressure that were substantially less than the pressure at the time of rupture.*

The pipeline section’s history revealed twelve loss of containment events that required repairs, including a “seam failure” with 8.2 tonnes of ammonia released with no cause identified. The remaining releases were 285 kg (630 lbs.) or less of ammonia, with four identified simply as “pinhole leaks” and two as “defective pipe.”
Mitigation: Investigate failures thoroughly. The company was cited for incomplete investigations into these failures.
Mitigation: The pipeline’s hydrotest history also resulted in a number of repairs. Hydro-testing had been performed in 2008, including a spike hydrotest[6] to identify potential weak points (results shown in Table 2). For “Stress Corrosion Cracking”, the type and location (internal or external) were not identified.

The CFR 49 Part 195 regulations require that assessment (inspection) techniques are evaluated for their ability to detect flaws and predict growth rates. In-Line-Inspection devices (ILI) are useful for underground piping network and pipelines for ammonia import or export shipping lines, and are available for 150 mm (6 inch) diameter or greater piping. Mapco had used ILI on the section of line, but the tests did not pick up a number of defects.
Mitigation: Following the hydrotest results, Mapco undertook a recalibration of the ILI to increase its sensitivity.

Milepost Location of Failure	Failure Description
MP 225.25	A seam failure rupture 857mm (33.75 inch) long × 32 mm (1.25 inch) wide due to either a lack of fusion or a hook crack
MP 230.14	A pipe body rupture 178 mm (7 inch) long × 25mm (1 inch) wide (failure mechanism not determined)
MP 232.45	A pipe body rupture 318 mm (12.5 inch) long 51mm (2 inch) wide due to Stress Corrosion Cracking
MP 239.45	A pipe body crack 38 mm (1.5 inch) wide that leaked but did not rupture during the hydrostatic test
MP 245.46	A pipe body rupture 330 mm (13 inch) long × 76 mm (3 inch) wide due to Stress Corrosion Cracking

Table 2. Hydrotest Results

Figure 3. StarTrak In-Line Inspection Device

As indicated, ILI devices can be intentionally calibrated to improve the accuracy of the results. BakerRisk has assisted in the calibration of ILI equipment through metallurgical characterization of ILI indications found during ultrasonic inspection. Multiple transverse specimens were metallographically examined at regions where ILI indications were recorded, and dimensional measurements were taken in the as-polished condition in the metallographic specimens, including length and depth of the indication in the pipeline wall. This was compared with the ILI device data to help calibrate the equipment.

Risk Assessment

Risk assessments can vary but typically follow the methodology as shown in Figure 4.

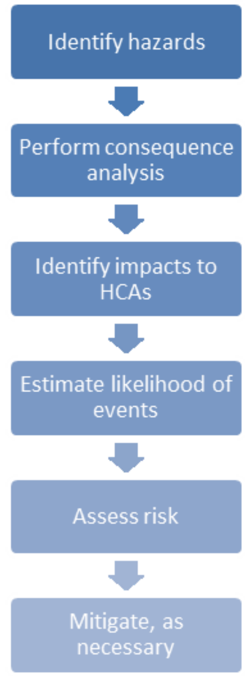

Figure 4. Steps in Risk Assessment

Pipeline Hazard Identification & Consequence Analysis

Risk assessments begin with identification of hazards presented by the physical conditions of the pipeline. Factors involved would include the design specifications (pipe diameter), the operating pressure, temperature, and whether it is above or below grade piping. These factors along with release assumptions from small leaks to full bore rupture determine the range and quantity of the potential releases.

The consequence analysis focuses primarily on the toxic impact of the ammonia release, and the local atmospheric and geographical conditions that would impact an area the size of the resultant cloud.

For ammonia at ambient temperature well above the -34°C (-29°F) atmospheric boiling point, a significant percentage of the liquid ammonia will flash upon discharge. After flashing, the remaining ammonia will be at the atmospheric boiling point and will pool on the ground. The dispersion of the ammonia vapor is generated from the initial flashing vapor and pool evaporation. Typically, the amount of vapor generated from the initial flash is much higher than from pool evaporation. On the other hand, pipelines with cold ammonia near -34ºC (-29ºF) will have limited flashing, and therefore the vapor dispersion will depend primarily on pool evaporation.

Consequently, a release from pipelines with "warm" ammonia predominantly results in longer downwind dispersion distances. However, scenarios involving significant topographical variations can cause even "cold" ammonia to have greater spill extents that results in larger dispersion clouds.

These topographical variations can lead to significant changes in spill and subsequent dispersion extents compared to a flat terrain assumption. Models that account for the effect of an uneven terrain can reveal variations in the extent of the liquid spill along the pipeline route as shown in red in Figure 5.

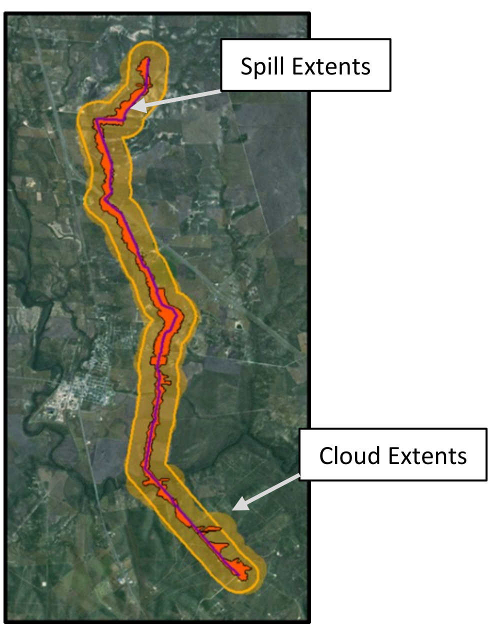

Figure 5. Comparison of Flat and Uneven Terrain Model, Spill and Cloud Dispersion Extents

The subsequent dispersion extents in Figure 5 show differences between assuming a flat terrain (bright orange outline) which follows the pipeline at a constant distance compared to the cloud generated by uneven terrain. Note the difference at the bottom right where the ammonia flows away from the pipeline that impacts the cloud location. Models that examine overland and water spill extents should consider the effects of liquid run-off, liquid deposition, pooling, evaporation, and potential transport into and by way of rivers and streams.

Having established these concerns, the natural next step is to examine the pipeline routing for its potential impacts. US regulations require the identification of the endpoints for each High Consequence Area (HCA)—sensitive areas that can include for example, dense population areas, sensitive receptors such as schools, drinking water sources, or ecological areas.

Risk and Mitigation

Consequence analysis identifies potential hazards in HCAs. Identifying and quantifying the factors that add to risk provides better management for reducing the likelihood of an occurrence. Baseline pipeline risk assessments typically utilize industry average pipeline failure rate data based on the pipeline diameter and the intervals between release cases to estimate a release frequency. A more detailed analysis of pipeline failure rate can be performed as needed to account for pipeline design specifics and location. Pipeline design specifics include aspects such as age, material of construction, thickness, cathodic protection, external coatings, design pressure, and maximum allowable operating pressure. The pipeline location includes routing above ground or underground; if underground, consideration should also be given to the water table level or the depth of cover, pipeline routes that traverse vehicular crossings, and whether earthquake zones or weather events could affect release likelihood.

The frequency of each event is calculated by multiplying the frequency of a release by its corresponding impact. This results in a table of impacts that identify the highest risk pipeline segments for comparison with risk tolerance values to identify areas that may require mitigation.

Risk results should be compared to tolerance criteria and risk mitigation should be identified where necessary. Pipeline mitigation strategies should consider elimination to prevention first where possible, then reduction of release size and impacts through detection and isolation, and emergency response.

By understanding the drivers of risk in a pipeline segment, decisions can target more effective reductions in risk. Elimination/reduction of the hazard would include rerouting the pipeline around high consequence areas to an area with lower consequence. The choice of prevention mitigations can be targeted to the frequency of the initiating event.

Revisiting major concerns provides insight to mitigation:

- Material/Weld/Equipment Failure
- Corrosion
- Incorrect Operation
- Excavation/Collision Mechanical Damage

Material/Weld/Equipment Failure & Corrosion: Pipeline integrity includes design and quality control on installations and repairs. Increased inspections assist in maintaining integrity for an area with corrosive soils or a past history of repairs. Trending data on repairs and inspection findings can provide insight that may prevent a failure from occurring.

Incorrect Operations: Operations training and procedures should be robust and learn from past incidents and close calls. Past events have clearly shown that operator response is critical in reducing the size of releases, as these rare events can generate disbelief and a delay in taking action. National Transportation Safety Board reports provide resources for pipeline failure investigations that include operations considerations.

Automation changes and/or improved control systems can reduce operating errors that lead to incidents. Mitigations can also include reduction of a release size by monitoring through mass flow measurement, pressure loss detection, control system monitoring, and installation of manual or remotely-operated shutdown valves (RSV). US regulations now require RSVs in HCAs for new pipeline installations.

Excavation/Collision Mechanical Damage: The causes of failures resulting in full bore or major releases are a key concern, and can result from mechanical damage by external forces such as excavation or collisions, or natural hazards such as flooding or earthquake.

Preventive measures are preferred! A recent analysis of Dutch pipeline data [7] showed that increasing the depth of cover from 1 meter to 2 meters (3.3 feet to 6.6 feet) reduced the hit frequency by a factor of 10 in rural areas and a factor of 3.5 in suburban areas. Also in that analysis, information from British Gas observed that adding concrete barriers above a pipeline was found to reduce the damage frequency by a factor of 5. When used in combination with warning tape, an improvement of up to a factor of 30 was observed.[8]

A number of new technologies for ammonia detection are emerging, from temperature detection along the pipeline [9] to thermal imaging or gas detection cameras at potential flange leak points at loading stations. For remote areas, monitoring for excavation by air is possible.

Lastly, emergency response includes evacuations and training of the public.

Fertilizers Europe's publication [10] provides good background and more detailed information on certain damage mechanisms, and examples of risk mitigation measures for above and below grade pipelines. A listing of other resources is provided at the end.

Other Risk Considerations

Uncommon risks can impact pipeline viability.

The former MapCo/Magellan ammonia pipeline ceased operations in late 2019, citing operating and maintenance costs of its 50+ year old network. In addition to the expense of incidents such as Tekemah, a fine of $3.65 million USD and additional mitigation measures were levied by the US Environmental Protection Agency in 2009 after two ammonia spills resulted in fish kills.[11]

Risk from political events is also evident in the case of the shutdown of the Russian/Ukrainian pipeline: four of seven Russian Togliattiazot ammonia plants feeding the pipeline were shuttered due to the conflict as of April 2022 [12].

A paper by Haifa Chemicals provides their analysis of considerations for a wide varierty of pipeline risks [13].

Conclusion

Management of pipeline risk begins with a thorough integrity program with preventive measures for multiple pipeline failure and risk hazards. While certain regulations can be difficult to navigate, this valuable guidance can help achieve more robust programs, most often built upon decades of experience and lessons learned.

Understanding the damage mechanisms, failure modes, and the lessons learned from previous experience and incidents provides a basis for addressing piping risks. Trending data from inspection findings and examining results from event investigations can help mitigate a more serious event. Performing logical and defensible risk assessments can support a company's management strategies to tailor risk mitigation properly along the path of the pipeline. The results of this process provide a basis for prioritization and practicality of risk mitigation strategies for new or existing pipelines that will be essential as ammonia pipeline infrastructure is expanded to accommodate the potential green use of ammonia as a hydrogen source.

References

[1] US Department of Transportation CFR 49 Part 195. https://www.phmsa.dot.gov/pipeline/annotated-regulations/49-cfr-195

[2] US Pipeline and Hazardous Materials Safety Administration.

[3] Luddeke, D.E., "Ammonia Pipeline Maintenance and Repair," AICHE Ammonia and Related Facilities Safety Symposium, 1974.

[4] Fertilizers Europe, Guidance for Inspection of and Leak Detection in Liquid Ammonia Pipelines, 2008 ed, Issue 2013.

[5] Miller, R.W., Caserta, L.V. "Failure of a Low Temperature Ammonia Line," AICHE Ammonia and Related Facilities Safety Symposium, 1970.

[6] *"A Spike Hydrostatic Test is a test in which the test-pressure-to-operating-pressure ratio significantly exceeds the minimum value of 1.25 as required by federal regulations (49CFR §195, Subpart E) and the duration of which is considerably shorter (1/2 hour to 1 hour) than the minimum time of 8 hours also required by federal regulations."* NTSB, 12/6/2019. https://data.ntsb.gov/Docket/?NTSBNumber=DCA17FP001

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[8] Ibid

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Seeing Inside the Box: Innovative developments in reformer monitoring and optimization

Optimizing the primary reformer is key to making ammonia as efficiently as possible, with ca. 30% of the total natural gas demand consumed by driving the reforming reaction.

Johnson Matthey has proprietary models, such as REFORM™, which have been developed and tested over decades in the industry, that take account of many parameters that contribute towards this optimization. However, accessing accurate data has been a barrier to continued optimization in the field.

The use of OnPoint's ZoloSCAN™ TDLAS (Tunable diode laser absorption spectroscopy) technology makes continuous in-situ flue gas analyses achievable. This paper details how, when coupled with process data and Reformer Imager data providing insight into the tube wall temperature profiles across the reformer, it has enabled benefits such as lowering fuel demand, excess air, and so with it NO_x emissions and CO_2 footprint.

Matt J. Cousins and Kate McFarlane
Johnson Matthey

David A. Brinkmann
OnPoint Digital Solutions LLC

Pierre Coddeville
Yara France, Le Havre

Introduction

The steam-methane reformer is at the heart of most world-scale synthesis gas plants for ammonia, methanol or hydrogen production, and its optimum performance will maximize plant production and efficiency. This paper studies the wide variety of parameters that need to be considered if a steam methane reformer is optimized.

The work has been to utilize Johnson Matthey's **REFORM** modelling package as part of a future continuous monitoring system (CMS).

The work has interpreted process data, tube wall temperature data and thermometric and gas compositional radiant section data. These data streams are used together to develop new insights into what is happening inside a reformer cell. This creates an opportunity for improved reformer optimization.

The work referred to as **REFORM CMS** was led by Johnson Matthey (JM) in partnership with On-Point Digital Solutions LLC and delivered to Yara Le Havre, who pioneered the system's use.

The benefits of the **REFORM CMS** work include:

- Enhancement of asset integrity programs to improve plant reliability
- Optimization of hydrogen production to maximize ammonia production efficiency
- Optimization of excess air to maximize combustion efficiency
- Enablement of continuous improvement culture by translating information into knowledge and supporting the implementation of improvement actions.

Background

Steam-methane reforming has been used as an industrial means to realize hydrogen since the 1920s. Over the last hundred years, our understanding of this process has grown enormously enabling developments that make it possible to reform a wide range of hydrocarbons in various licensed reformer designs. However, many reformers operate without the ability to measure and optimize all the parameters that affect their operation.

The steam reforming process reacts purified hydrocarbon feedstocks with steam to produce hydrogen and carbon oxides. In the reformer, a series of interconnecting reactions take place over the catalyst. The two hydrogen forming reactions, steam-methane reforming and water-gas shift are detailed below:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \quad \Delta H = +206 \text{ kJ.mol}^{-1} \tag{1}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -41 \text{ kJ.mol}^{-1} \tag{2}$$

Following reaction (1), process conditions can be optimized to maximize the conversion of methane, at equilibrium, by higher temperature, lower system pressure and increased steam partial pressure.

As shown in reaction (1), steam-methane reforming is strongly endothermic, and large quantities of heat are required to drive the reaction to the hydrogen product. To provide the process heat to overcome the heat of reaction, a reformer is designed to hold the catalyst within tubes in a furnace.

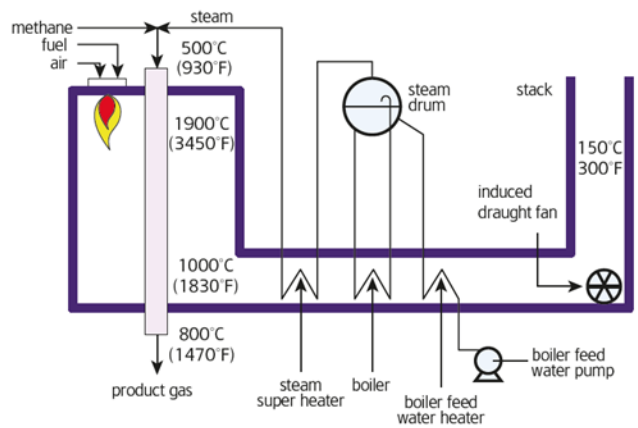

Figure 1. Outline diagram of a steam-methane reformer, showing typical process conditions.

This combination of catalytically driven reaction and furnace operation results in one of the most complex process units on the ammonia plant. Much technical know-how and insight is required to ensure safe and efficient operation across the reformer. Reference [1] describes in detail some of the issues that can arise from the sub-optimal operation of a reformer, including:

- Inefficient operation - poor conversion of hydrocarbon feedstock, poor use of fuel
- Tube rupture - during normal operation, the tubes are within the creep region and have a limited lifetime. Operation at higher temperatures significantly reduces tubes' lifetime, and if this is exceeded, the tubes can rupture within

the reformer, with the potential for a serious incident. (Reference [2]).

- Carbon formation - high temperatures or catalyst poisoning can result in formation of solid carbon on the catalyst and within the tubes. This will reduce catalyst activity and increase pressure drop up to blocking tubes (Reference [3]).

The carbon forming reactions, and much more, are included in **REFORM**, Johnson Matthey's proprietary software to model the operation of steam reformers. It was initially developed by ICI in the 1960s to support their steam reformer operation, and since then has been continually improved and updated with more detailed models and to reflect changing reformer design (Reference [4]). **REFORM** is a powerful tool to design the catalyst loading, evaluate current operating performance, and assess optimized operating conditions.

Previously, when optimizing a steam reformer, the process was limited by the amount of data available and the one-time nature of the data-collection process. Tube Wall Temperature (TWT) data would be collected manually, and operation optimization would be carried out based on this data. However, over time, perhaps a few days or weeks, plant operating parameters would change, and plant operation would become sub-optimal.

The **REFORM CMS** work addresses this issue by considering a wide range of continuous data, covering many aspects of steam reformer operation. If the plant operation is required to change, updated TWT data can be gathered and analyzed quickly. This allows timely re-optimization and maximizes the time spent at peak operation. (Reference [5])

REFORM CMS work considers three differentiated data feeds, each targeted to supply a data input that drives the **REFORM** model: TWT, process and radiant box data, as depicted in Figure 2.

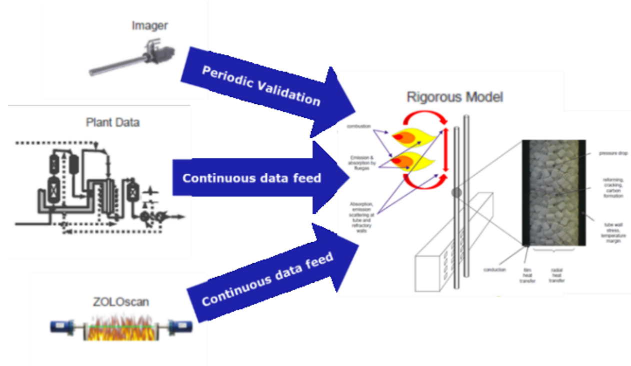

*Figure 2. Outline of **REFORM CMS** process.*

This allows the operator to understand:

Where there is an opportunity cost,

and

Which process parameters to target to optimize the operation

This paper now describes how **REFORM CMS** was deployed, looking at the components, installation, and interoperation of the first data.

Components of REFORM CMS

The data fed to the **REFORM CMS** work comprises three separate streams. Plant data (pressures, temperatures, gas compositions, etc.), Reformer Imager data of TWT for the tubes and ***ZoloSCAN™ TDLAS*** data for the radiant box.

In Figure 3, the data collection activities at the client site are shown in dark blue, which provide data input for analysis and reporting, shown in pink.

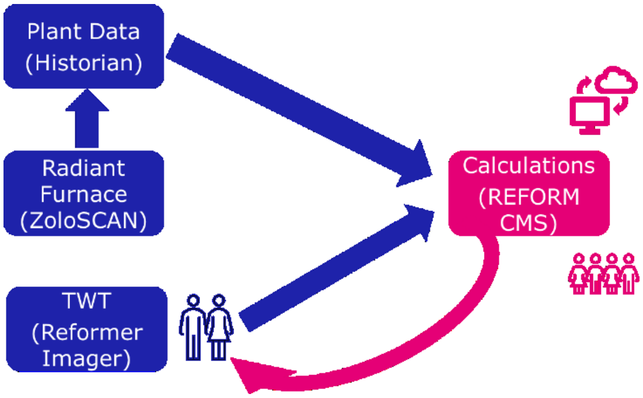

*Figure 3. Data flow within **REFORM CMS**.*

In comparison to a typical plant data set, **REFORM CMS** work considers:

a. More of the parameters affecting the reforming operation.
b. More granularity within the data, as it is not a global average. Data can be used to define different conditions across the reformer cell.

In the case of the Yara Le Havre reformer, the tubes are arranged in diagonal rows laid out in an unusual sawtooth pattern in each of two reformer cells (North/South) as shown in Figure 4.

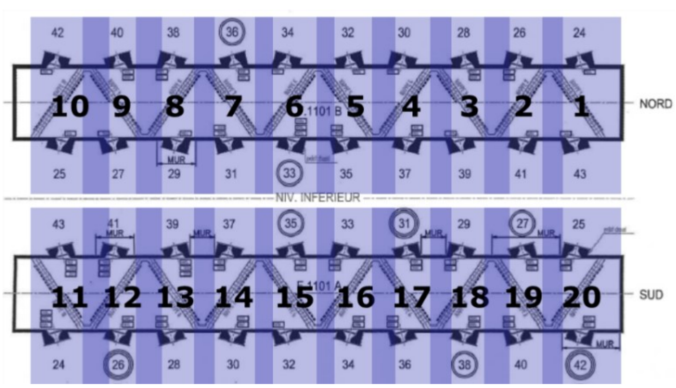

*Figure 4. Sketch of the reformer at Yara Le Havre, showing sub-cells as considered within **REFORM CMS**.*

For the purpose of modelling, as shown in Figure 4 each cell was split into 10 'mini reformers' or sub-cells. This required:

- Plant data provided process temperatures for the outlet header of each tube row
- Reformer Imager TWT data for each tube
- ***ZoloSCAN^{TM} TDLAS*** temperature data for the radiant cell in the vicinity of each tube row

Plant data

Plant data is already utilized regularly by the operations team in the safe running of the unit. It is also commonly used every few months to provide a snapshot that is used in data evaluations to assess the effectiveness of the process in the context of the reformer operation.

SFTP (Secure File Transfer Protocol) captures and transmits a comprehensive set of process data from the Yara historian to JM.

This provided the required detailed process data:

- Inlet gas composition
- Inlet process gas pressure
- Inlet process gas temperature
- Inlet gas flow
- Temperatures of each collector header
- Exit process gas pressure
- Exit gas composition

This provides a platform for regular data transfer and the daily data processing using the optimization tools developed for the **REFORM CMS** work. Using high-quality, consistent data allows the analysis to look beyond a global average.

Tube Wall Temperature Data

A standard visual inspection of the furnace is invaluable but gathering quantitative data on the TWT spread across the furnace is essential. There are three commonly employed pieces of equipment to measure TWTs; each option has its merits. Table 1 gives a summary of how these different reformer measurement devices function.

Tool	Optical Pyrometer	Gold Cup Contact Thermocouple	Reformer Imager
TWT Measurement	Yes – point	Yes – point	Yes – Universal
Background correction required	Yes	No	Yes
Time for Survey	Medium	Slow	Fast
Video Images	No	No	Yes
No. of data points	Single	Single	Multiple

Table 1. Comparison of different TWT measurement techniques

Based on these properties, the Reformer Imager has been selected to gather TWT data**.** The Reformer Imager supplied by LAND Instruments International Ltd. and developed as a portable reformer survey tool by JM provides more insight into the TWTs than any other available method.

The Reformer Imager can measure temperatures in the range of 600-1100°C [1110-2010°F], and the measurement wavelength of 1 μm maximizes visibility through the hot combustion gases. The Reformer Imager provides a wide viewing angle, so often, almost all of a tube row can be seen in one video image, more than can be seen visually. The videos are recorded directly to a laptop and can be taken away for further analysis. For more information on the technical specifications and capabilities of the Reformer Imager, please see Reference [6].

During a standard Johnson Matthey reformer survey using the Reformer Imager, data is gathered by manually moving it through different planes to capture as much of the reformer as possible. However, the natural variation resulting from this type of movement means that each video must be interpreted manually. This can be very resource intensive, and the interpretation of videos can often take several days of effort. As Reformer Imager surveys are not often carried out, this time is appropriate.

However, for the **REFORM CMS** work to be truly continuous, there was a need to enable more regular TWT data collections and interpretation with a quick turnaround. This need led JM to further develop the use of the Reformer Imager as a portable reformer survey tool and to include automation to speed up data extraction. To improve repeatability, a clamp was developed to hold and manipulate the Reformer Imager, rotating it in the same manner in every peephole while the thermometric video data was captured. The benefits of this are:

- Consistent positioning is achieved in each peephole
- Consistent movement takes place at every peephole
- Improved automation of data extraction

The picture in Figure 5 shows the Reformer Imager positioned in the JM Clamp. The clamp provides a collar located within a rotating set of bearings, enabling the Reformer Imager to be rotated through 360°. The clamp is lifted using the handle. The feet rest on the bottom of the peephole, and magnets aid the stability in use by providing easily reversible adhesion to the outer wall of the furnace. (Reference [7])

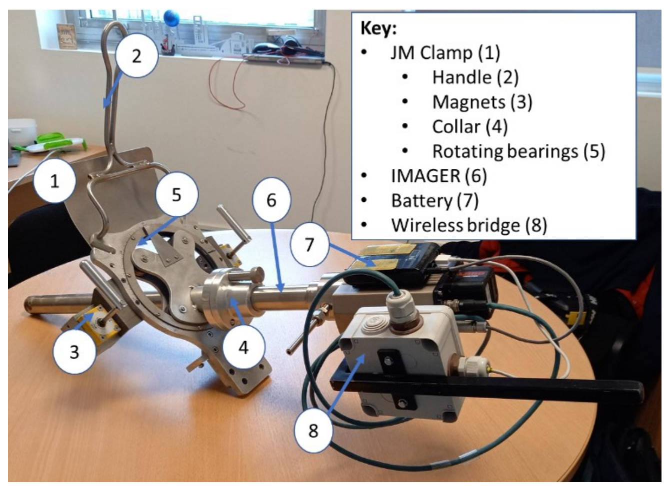

Figure 5. Complete set-up for the use of Reformer Imager as part of **REFORM CMS.**

A wireless bridge has been used to avoid the need for a wired data transfer connection between the Reformer imager and the laptop. A single battery powers both the Reformer Imager and the bridge. This wireless enablement of the Reformer Imager brought multiple benefits:

- Removed tripping hazard of the data transfer cable
- Improved connection reliability
- Decreased the time to complete a TWT survey

TWT Data Extraction

The streamlining of the data extraction process was enabled by the consistency gained from the use of the JM Clamp. The video captured as the Reformer Imager is rotated in the clamp is first stitched to form a single, complete image, and then TWT data was extracted from this image.

Figure 6 shows a still image from a video recorded by the reformer imager, displaying a partial view of the tubes within the furnace.

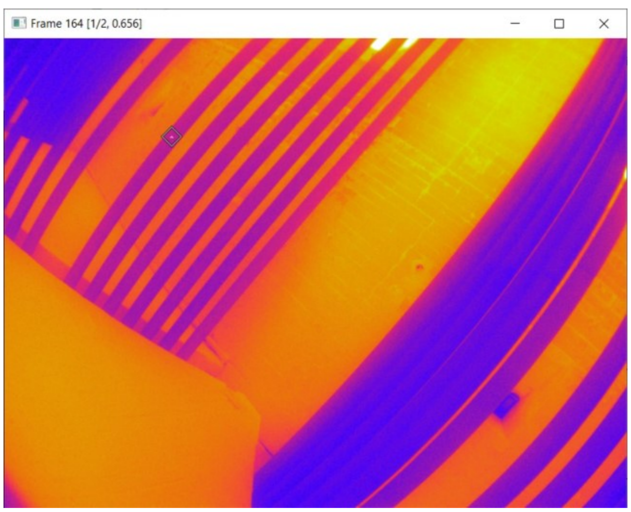

Figure 6. Still image from video recorded by Reformer Imager, showing sections of reformer tubes.

Stitching the individual images that make up the video into a single composite image provides the greatest possible field of view from the peephole without having to view and select multiple frames from video manually. This can be seen in the composite image in Figure 7, which shows many more of the tubes than the image in Figure 6.

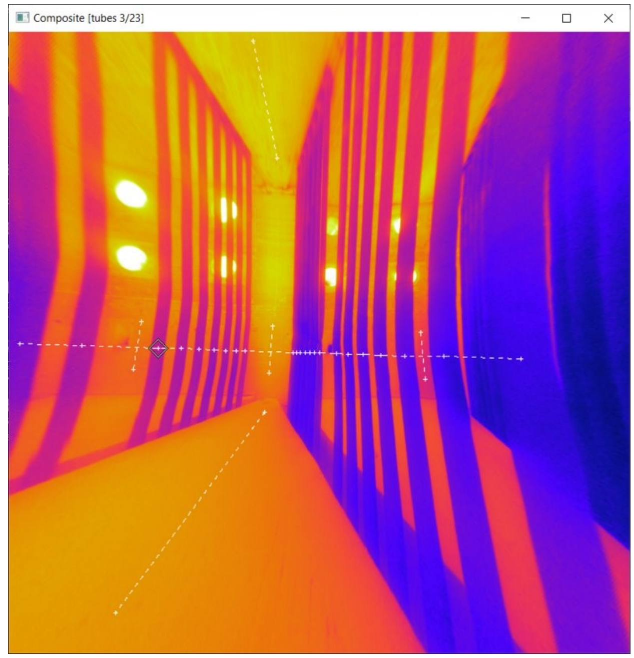

Figure 7. Composite image generated from complete Reformer Imager video, showing all visible tubes.

The single composite still image can now be processed to extract the thermometric data. This extraction has been semi-automated, with the potential to fully automate this process.

The requirement for background radiation correction was tailored for the reformer at Yara Le Havre and managed as part of the data interpretation.

Multiplexed *ZoloSCAN^{TM} TDLAS* system

The third data stream was provided by OnPoint's multiplexed ***ZoloSCAN^{TM} TDLAS*** system. This system monitors and describes the gas composition and temperature within the radiant box.

TDLAS measurements are based on molecules, each having a unique signature absorbance profile. An industry standard diode laser is tuned in wavelength across a tiny portion of the optical spectrum. A given combustion component absorbs light at the chosen wavelength, and the relative amount of absorption is proportional to the concentration of that component.

OnPoint's multiplexed ***ZoloSCAN***^{TM} ***TDLAS*** technology transmits multiple laser wavelengths simultaneously along a single path and measures an average across each path for each component simultaneously. This provides real-time, in-situ, measurement of temperature, O_2 and CO directly in the reformer combustion zone. The path layout also provides spatial representation profiles of temperature, O_2, and CO. The path layout was defined as it provided a path average data source into **REFORM** for each sub-cell.

The ***ZoloSCAN***^{TM} system for Yara Le Havre was designed to provide 22 laser paths across the reformer cells, with transmitting heads termed "Pitch" and receiver heads termed "Catch"; mounted on the outer walls of the furnace as shown in Figure 8..

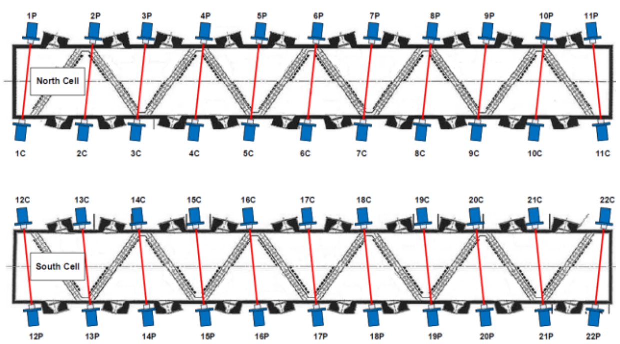

*Figure 8. Overhead view of Yara Le Havre reformer, showing **ZoloSCAN**^{TM} **TDLAS** laser paths, "pitch" and "catch" heads.*

Each pitch head periodically emits the combined laser light sources to the catch head maintaining alignment automatically and continuously. The light source transits across the reformer cell, following a path not impeded by the reformer tubes. Further focusing is enabled during operation using a steerable optic assembly within heads to maximize the signal strength. The path design places laser paths between the herring-bone arrangement of tube rows, so data is gathered associated to each row of tubes.

Installation of tools needed for the REFORM CMS work

Project implementation was hindered by the COVID-19 pandemic, which delayed the installation of the ***ZoloSCAN***^{TM} system, a key component, for many months. It took nearly 18 months to achieve project implementation, although the active working time was approximately 3 months.

Plant data

This was the easiest part of the installation. Clearly, the plant data already existed and was recorded by the historian. Yara and JM agreed on which instrument data were needed to model the reforming operation and prepared a list of associated instrument tag numbers. JM provided a SFTP connection, and data transmittal started.

Reformer Imager

The work required the development of the Reformer Imager clamp and wireless enablement of the Reformer Imager to avoid the communications cable becoming tangled.

Achieving Consistency – The clamp

The clamp was developed over several iterations, offering a bespoke design to integrate with the reformer peephole design employed at Yara Le Havre.

Figure 9. Photo of Reformer Imager Clamp in use on reformer peephole at Yara Le Havre.

Multiplexed *ZoloSCAN™ TDLAS* (Tunable Diode Laser Absorption Spectroscopy)

*Figure 10. Photo of installed **ZoloSCAN** sensor heads on the reformer at Yara Le Havre.*

The heads were mounted on sight tubes that had previously been fitted to the reformer during planned maintenance. These provided alignment between the pitch and catch heads. The sensor heads were then able to be fitted while the reformer was in operation, minimizing the required downtime.

The output from the ***ZoloSCAN™ TDLAS*** can be read directly from the control panel, as shown in Figure 11, or through the REFORM CMS dashboard.

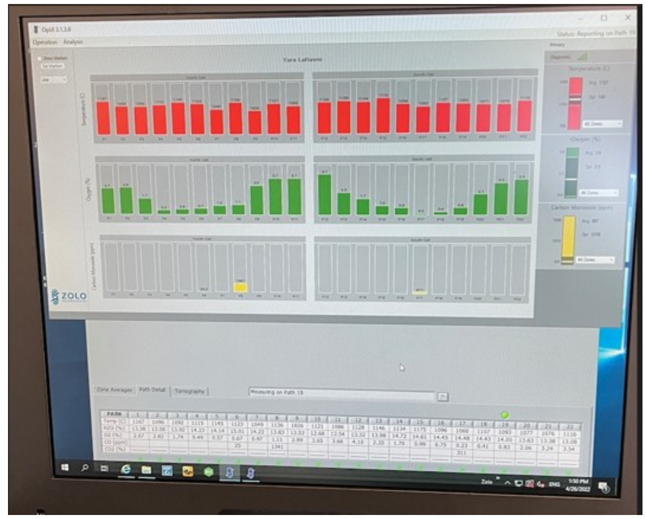

*Figure 11. **ZoloSCAN™ TDLAS** raw data output, showing temperature (top, red), oxygen content (middle, green) and carbon monoxide content (bottom, yellow) for each sub-cell.*

Training

JM provided training to Yara Le Havre covering the functions of the **REFORM CMS work**, practical use of the Reformer Imager and use of the thermometric analysis method for the captured videos. OnPoint provided full training in the use of the ***ZoloSCAN™ TDLAS*** system.

Figure 12. Training of Yara Le Havre staff in the use of Reformer Imager for TWT monitoring.

Use of REFORM CMS

Primary actions:

Integration with the existing Yara asset integrity program is of paramount importance. The TWT data is mapped, showing tubes that were too hot or too cold. To protect the tubes, the first action is to reduce the temperature of the hottest tubes based upon this data.

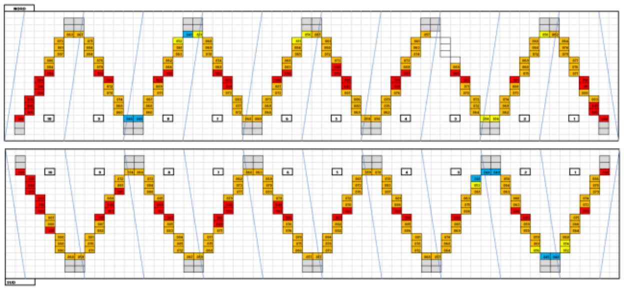

*Figure 13. Tube wall temperature map generated from Reformer Imager data by **REFORM CMS**.*

Secondary actions:

REFORM CMS runs based on each day's process and TDLAS data for each sub-section of the reformer cell. It produces KPIs (Key Performance Indicators) for each sub-cell, such as measured and optimized values for the

- Tube exit temperatures
- ATE (Approach to Equilibrium for the reforming reaction)
- Hydrogen make
- Excess oxygen in the flue gas

The dashboard visualizes the opportunity value for hydrogen make and excess oxygen. The opportunities are presented as a global value and broken out to show which zones present the best opportunity for improvement and which section of the furnace should be the focus. The basis of the optimization is to:

a. Reduce TWT variation and move the average towards the optimal value, thereby producing most hydrogen.
b. Excess oxygen towards a decreasing and agreed value. The effect of this is to move the unit away from the fan limit in the duct and directionally lower the NO_x in the flue gas.

Benefits of REFORM CMS

The measure of benefits can be assessed in numerous ways:

a. TWT reduction of hottest tubes, providing an extension of tube life
b. Increased product make from the same feed natural gas flow

These benefits are easily monitored by following the trends provided in the **REFORM CMS** dashboard, along with the excess oxygen. Other, less quantitative, but still crucial benefits include:

c. Increased number of focused discussions on reformer optimization, with data to back these up
d. Increased number of adjustments and interventions to optimize performance

Conclusions

The REFORM CMS work shows the potential opportunity from daily analysis of reformer performance and associated optimization.

The system that has been constructed can respond quickly to changes in rate, feed composition etc., and to re-optimize performance.

Reformer Imager data affords assurance from an asset integrity perspective before and after a change is made.

This project has shown the interconnectivity between the process data, the TWT and the combustion cell conditions, and that only when all three of these are considered can the operator truly "see inside the box".

Acknowledgements

The authors wish to thank all the staff at Yara Le Havre for their support and contribution.

Mike Davies at Johnson Matthey has provided essential expertise and insight for this project.

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[6] "The Value of Primary Reformer Temperature Balancing and Monitoring", Michael Dean, Kendra Briggs and Jamie Chisamore, AIChE Ammonia Plant Safety Symposium, 2015.

[7] M.J. Cousins et al (2021) *Method of Recording Images within a Furnace Using a Thermal Imaging Camera Comprising a Borescope* (GB Patent Application No. 2585483).

REFORM is a trademark of the Johnson Matthey group of companies.

ZoloSCAN is a trademark of OnPoint Digital Solutions LLC.

Ammonia Release During Ammonia Import Activity

On July 21, 2018, an incident occurred at CSBP Limited's import facility in Kwinana, Western Australia, that resulted in the accidental release of ammonia vapor.

A thorough investigation identified the causes of the incident, which resulted in the quick connect/disconnect coupler disconnecting from the ship manifold flange, releasing approximately 1,000 kg of ammonia. Thankfully no one was injured, but the incident provided key learnings for CSBP and industry on how to safeguard against similar incidents occurring in the future.

Naresh Patel
CSBP Limited

Introduction

CSBP Limited (CSBP) manufactures ammonia, nitric acid, ammonium nitrate, sodium cyanide, fertilizers and industrial chemicals. Operating in Western Australia for more than 100 years, CSBP has a long and proud history as a major manufacturer and supplier of chemicals and fertilizers to the mining, industrial and agricultural sectors.

Providing ammonia to both external customers and using it within its ammonium nitrate, sodium cyanide and fertilizer businesses, CSBP has a dedicated ammonia plant on-site at its Kwinana site. The plant can produce 750 t/day (826 STPD) of ammonia, with an annual production capacity of 255,000 t (281,000 ST), and 40,000 t (44,100 ST) of on-site storage capacity.

Each year ten to twelve ammonia vessels , approximately 250,000 t (276,000 ST) are imported by CSBP to supplement local production to meet its internal and external needs. The imports are carried out via the ammonia import facility, located at the Kwinana Bulk Jetty (Figure 1). Over the prior decade, 90 ammonia imports had been completed without incident.

Figure 1. CSBP's ammonia loading facility at the Kwinana Bulk Jetty

An ammonia import involves the following six-step process:

1. cooling down of the ammonia import line;
2. connecting the spool piece and loading arm to the import line;

3. cooling down of loading arm;
4. commencing the ammonia import;
5. hot gas purging of the loading arm on completion of the ammonia import; and
6. purging of the loading arm using nitrogen on completion of the hot gas purge.

Incident Summary

On Saturday, July 21 2018, at 10:30 am, an ammonia import was being conducted at the Kwinana Bulk Jetty. An incident occurred during the hot gas purging step resulting in approximately 1,000 kg (2,200 lb) of ammonia being accidentally released. Figure 2 illustrates an ammonia vessel's connection to the ammonia import line.

Figure 2. Ammonia import line connection

After the completion of the ammonia liquid import, hot ammonia vapor was introduced to vaporize the liquid ammonia from the pipeline, as per the normal operating procedure. As a result of the high flow of hot ammonia vapor combining with the inadvertent closing of the import valve, hammering started in the loading arm and the downstream pipeline. In addition, improper clamping of the quick connect/disconnect coupler (QCDC) resulted in the QCDC disconnecting from the ship's manifold flange.

The ship's captain identified the ammonia cloud from his control room and activated the emergency shutdown, stopping the ammonia vapor release (Figure 3).

Figure 3. The ammonia release captured by a port camera

What Happened?

A failure of different safeguards during the six-step ammonia import process led to the accidental release of ammonia.

Cooling down of ammonia import line

Liquid ammonia was pumped from the storage tank into the ammonia import loading pipeline and circulated to cool down the pipeline (Figure 4). The ammonia import line was cooled down without issue.

Connecting the spool piece and loading arm to the import line

The loading arm was connected to the import pipeline, with the connection completed without issue (Figure 5).

At the other end, the QCDC was connected to the ship's manifold (Figure 6). The investigation found the QCDC was not properly clamped, resulting in disconnection from the ship's manifold flange during the incident.

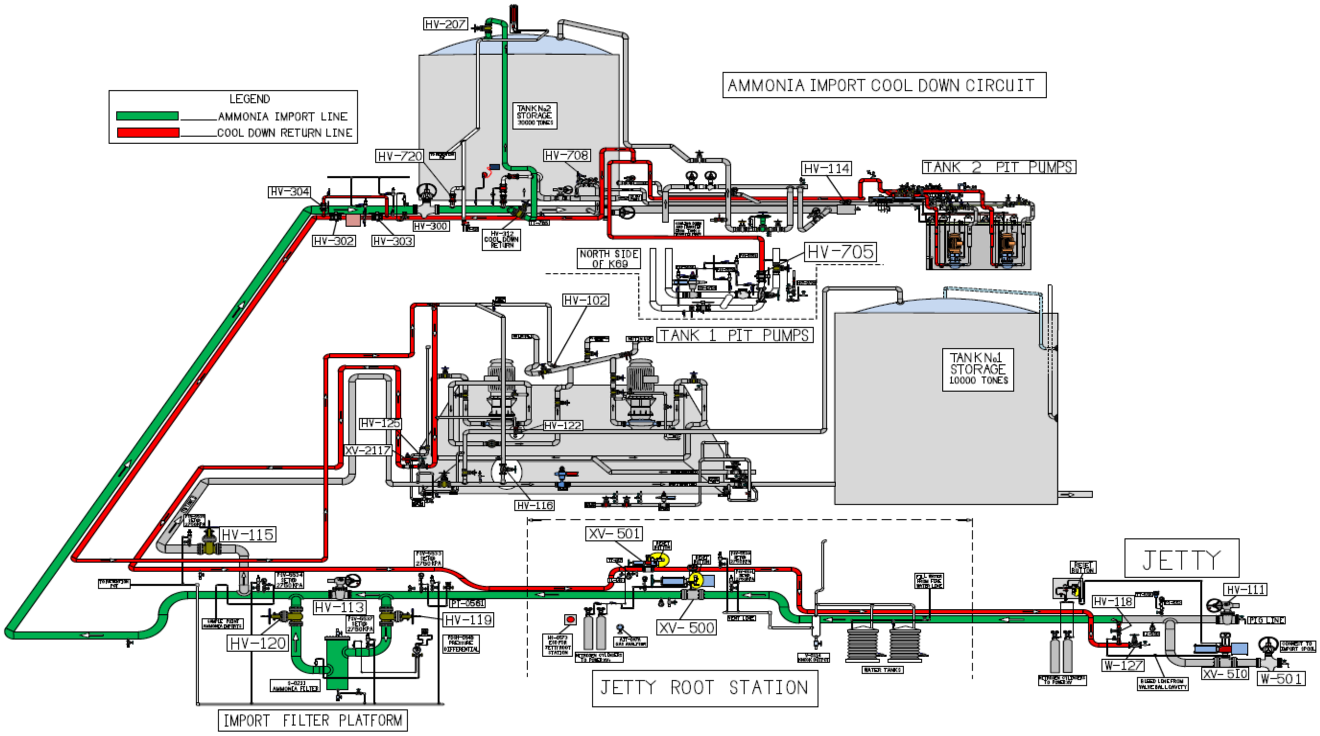

Figure 4. Import line cooling down set-up

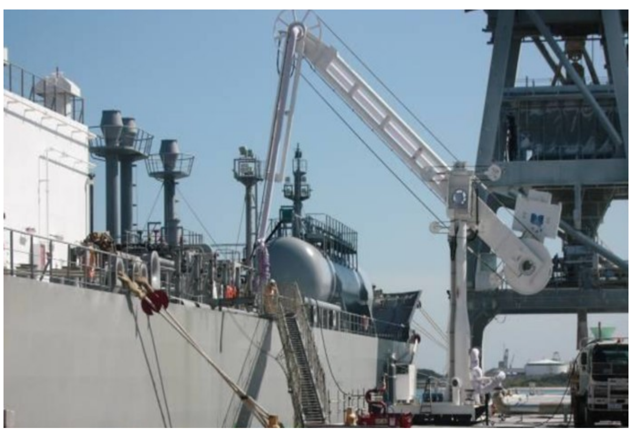

Figure 5. Loading arm connection to the ship

Figure 6. QCDC connection to ship manifold

Cooling down of loading arm

Cooling down of the loading arm was completed without issue.

Commencing the ammonia import

As there was no dedicated instrument air header to operate the import control valves, the operation of the ammonia line valves was managed using a nitrogen cylinder.

During import, the jetty's root station valves are operated using a manual hand jack and nitrogen supply mode. Ammonia import from the ship to CSBP's on-site ammonia storage tank was completed without issue.

The system arrangement for the ammonia import process is shown in Figure 7.

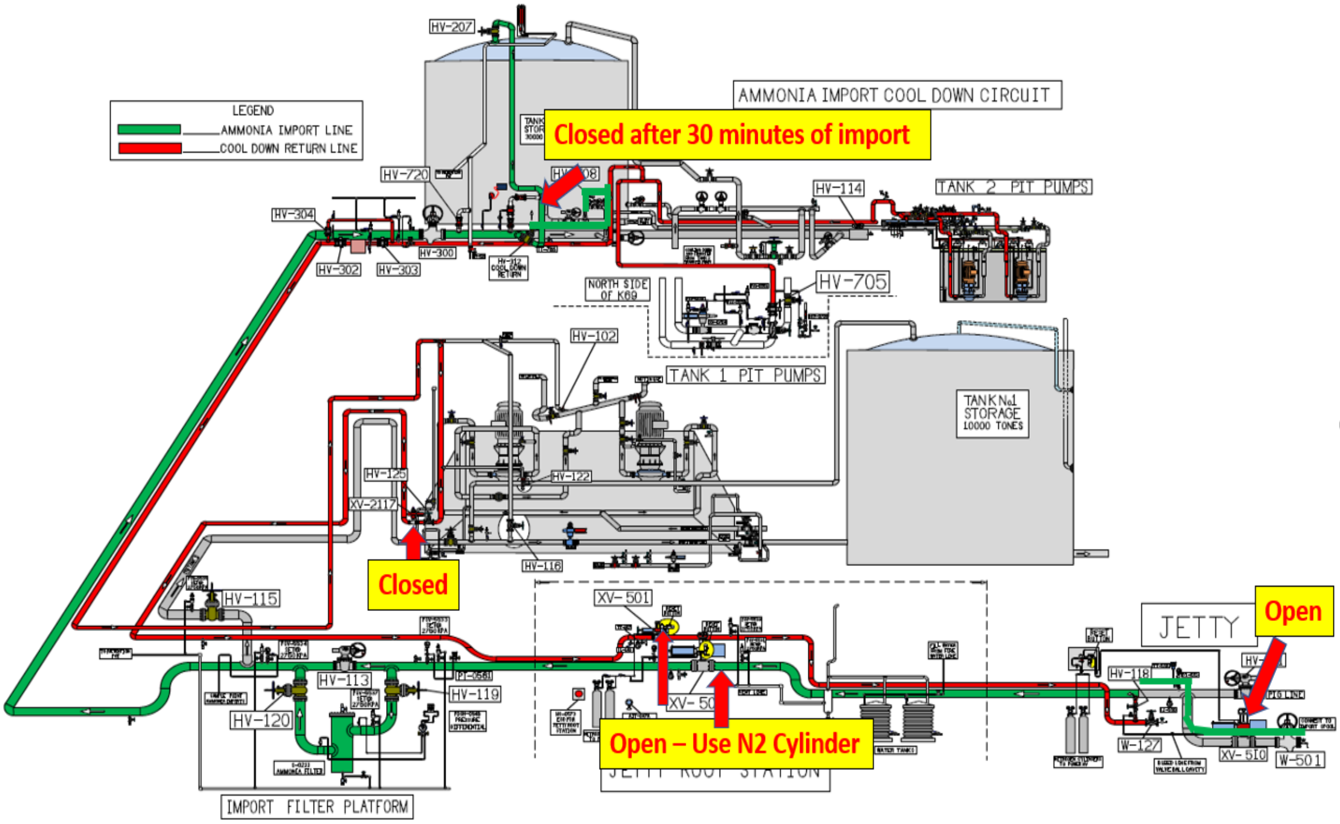

Figure 7. Ammonia import set-up

Hot gas purging of the loading arm on completion of the ammonia import

The operating procedure requires the liquid ammonia valves to be arranged as shown in Figure 8. Importantly, it required the root station valve to be hand jacked open and the nitrogen supply from the cylinder to be isolated. The line runner was instructed by the loading master to operate the liquid ammonia line root station valves using a hand jack.

Hot ammonia vapor was introduced from the ship's refrigeration compressor and discharged into the loading arm and import line through a small bypass line, in order to remove the liquid ammonia from the loading arm before it was disconnected.

During the hot gas purge process, the line runner (operator) was operating the hand jack, and as he was releasing it, the valve began closing, initiating the loading arm process trip.

As a result of the incorrect operation of the root station valve, the Emergency Release Coupling (ERC) ball valve closed and hammering started in the loading arm and import pipeline. When the ERC ball valve closed, pressure in the QCDC elevated to the purging ammonia vapor supply pressure of 300-500 kPa (44-73 psig), and the connection to the loading arm decoupled, resulting in the ammonia release from the ship's manifold.

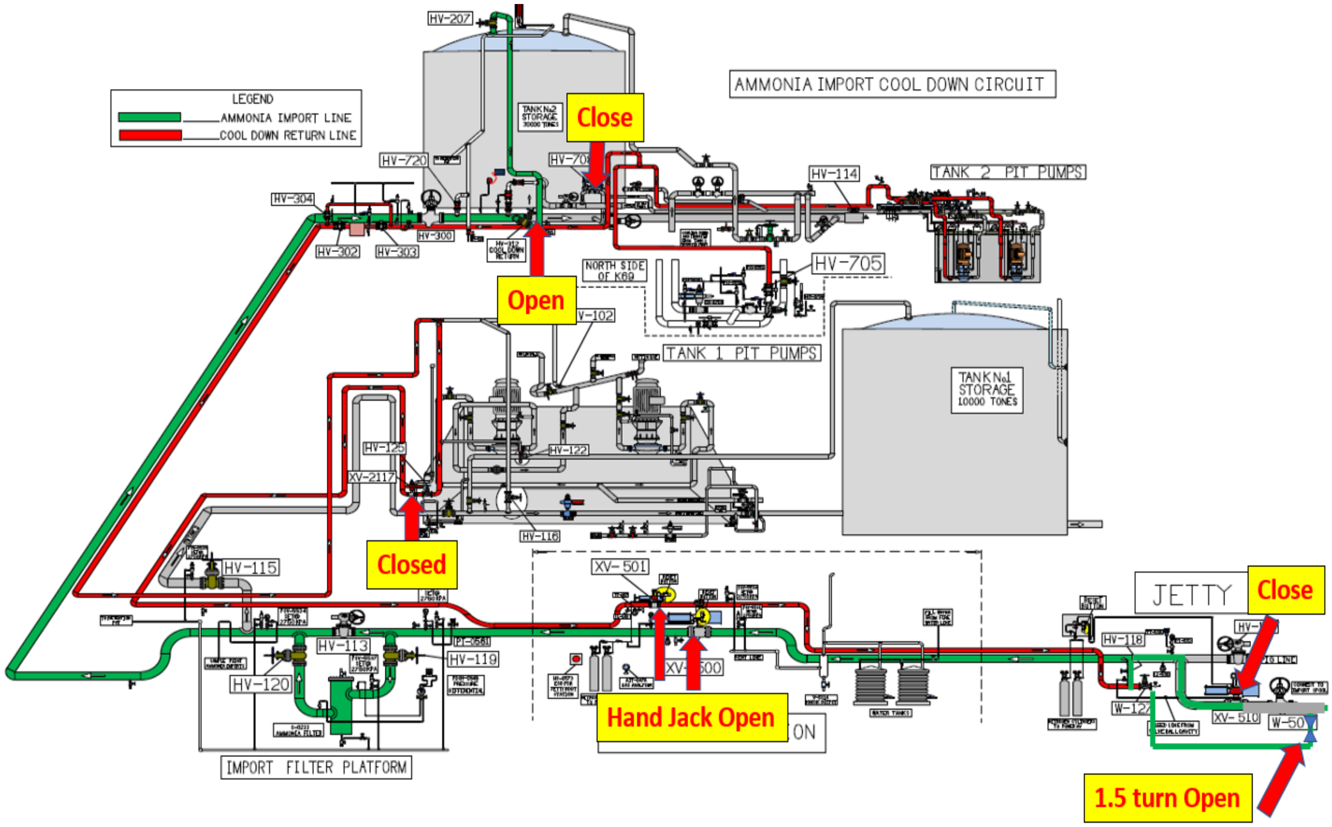

Figure 8. Hot gas purging set-up

Incident Management

Upon seeing the ammonia release, the ship's captain pressed the emergency stop button to close the manifold valve, shutting down the hot gas purge and immediately stopping the vapor release.

A contractor rang the guardhouse to inform them, and the jetty operator rang the central CSBP control room to report the incident. The alarm sounded on the wharf, and the emergency response team attended the site.

Five personnel (one CSBP employee and four ship crew members) were taken to the hospital for precautionary assessment and discharged the same day, suffering no ill-effects.

Investigation Outcome

Following the incident, CSBP initiated a comprehensive investigation to ascertain the cause and identify actions to mitigate the risk of future incidents. The investigation found the hand jack had not been operated in the correct sequence and the QCDC had not been correctly clamped.

Hammering in the loading arm and ammonia import line, and the subsequent build-up of pressure in the loading arm, was attributed to:

- Incorrect operation: The ammonia line root station valve hand jack was operated in the incorrect sequence, and the valve position was not visible.
- Poor communication: Hot gas purging was started while the operator was changing the position of the valve.
- Higher than normal hot gas purging rate: Although the ship's compressor discharge pressure was within the acceptable range, the flow rate was high, and the ammonia liquid contained within the pipeline created two-phase flow and initiated hammering. As the flow rate was managed manually, the flow

control was determined by the individual personnel operating the valve.

- Early closure of valves: When the operator released the hand jack, the root station valve started closing, triggering the “close” signal on the control system. The closure of the ammonia import line root station valve initiated the ammonia import trip to close the ERC valve, causing back pressure in the loading arm.

QCDC disconnection during the hammering

The investigation revealed that the QCDC was not properly connected due to:

- Design faults of the control panel: The operator relied on the “QCDC clamped” lamp on the control panel which was not derived from the actual close condition. It only indicated that the clamp had been activated and had no feedback that a close position had been reached.
- Visual impairment: The local visual indicator on the clamp had been painted with the same colored paint as the pipeline, so a visual check of the position of the QCDC was not possible, and procedures did not require the “QCDC locked” position indictor to be checked. (Figure 9)
- Incomplete preventative maintenance: the QCDC springs had potentially lost tension, due to being in service too long, which may have led to the QCDC not being able to clamp the flange properly.

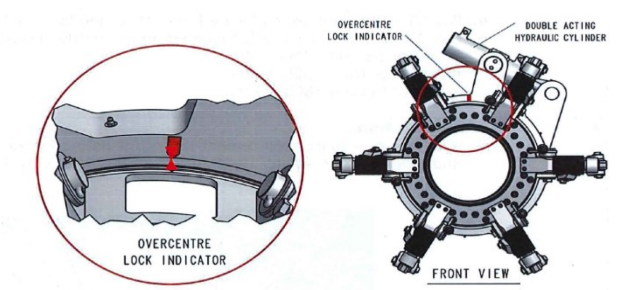

Figure 9. Hot gas purging set-up

In addition, the investigation found the absence of two trip mechanisms may have also contributed to the ammonia release:

- A “Ship to Shore” process interlock trip would have established a communication trip interlock between the ammonia loading facility and the ship, enabling the trip to close the manifold valve and instantly stop ammonia release.
- A high-pressure trip on the loading arm would have stopped vapor escaping from the ship when the QCDC disconnected.

Summary of Investigation

The investigation determined there were four factors contributing to the release of ammonia – design; maintenance; procedure; and human error (see Figure 10).

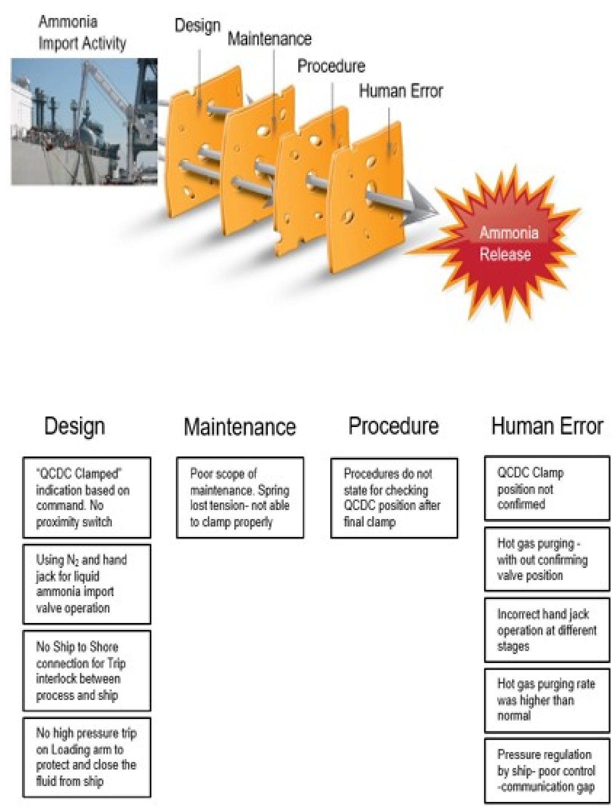

Figure 10. Factors contributing to the ammonia release incident

A range of actions were implemented after the incident investigation, including:

- QCDC removed, and flange-to-flange bolt connection used instead.
- "Ship to CSBP" trip logic was implemented to initiate ship manifold valve closing in case of loading arm shutdown.
- All process operators completed refresher training.
- Operating procedures were reviewed, refined and an additional checklist added for the loading master.
- Process engineers carried out complete trip checks for the loading facility.
- The loading arm vendor, SVT, was engaged to expand the scope of the routine maintenance program.
- SVT carried out a complete maintenance overhaul on the loading arm.
- Hand jack operation on ammonia line valves was removed and a back-up nitrogen supply established. Process operators are now required to perform routine checks.
- The nitrogen supply system was reviewed, and additional routine checks for nitrogen supply pressures are added.
- The scope of work for maintenance has been modified as per the vendor's recommendation.

In addition, the following projects have been initiated:

- A high-pressure trip on the loading arm.
- A QCDC clamp position proximity switch with interlock.
- An ERC open/close proximity limit switch installation, with connection to the loading arm trolley emergency shut down programmable logic controller.

Conclusion

A combination of factors led to the failure of different safeguards in the ammonia import process, resulting in the accidental release of ammonia vapor.

This incident has highlighted the importance of the following items:

- Refresher training,
- Procedural checks throughout the job cycle,
- Preventative maintenance designed in conjunction with the OEM, and
- Project design reviews utilizing human factors analysis.

Key Learnings:

1. Hazards relating to all aspects of the unloading process must be identified, controlled and understood by all personnel involved.
2. Maintenance strategies must incorporate all manufacturers' specifications.
3. All procedures created for the use of specific plant equipment must be completed by competent personnel with in-depth knowledge of the equipment, and in conjunction with the manufacturers' operating manual and specifications.
4. All personnel involved in high-risk activities must be regularly verified as competent to perform those tasks.
5. Critical equipment involved in high-risk tasks should have hard controls installed to prevent assumptions or mistakes, and to prevent the system from progressing in an uncontrolled state.

As a result of this incident and investigation, CSBP has reviewed and revised its ammonia import procedures and practices to help mitigate the risk of similar incidents occurring in the future.

CSBP also shared its lesson learnt presentation with ammonia industry participants through the Australia New Zealand "ANZ" network.

Ammonia Nitriding, Knowledge and Design Considerations

Nitriding of steel due to gaseous ammonia is a severe damage mechanism. This phenomenon is active at high temperature, which in ammonia plants occurs in the synthesis section, especially in the ammonia converter reactor.

Casale has set up a large nitriding analysis campaign. In the last decade samples of materials operated under different pressure and temperature and for different time spans have been tested and analyzed. The experience gained has improved the knowledge of nitriding in this specific application, giving valuable insight on how to predict and control it.

The main results of this research together with the improvement in material selection and design of the affected components will be presented.

L. Redaelli, G. Deodato
Casale

Introduction

Strange as it may seem, the ammonia converter is often forgotten in ammonia plants. The ammonia synthesis converter is the reactor with the longest run between catalyst changes, usually more than ten years but sometimes up to 25 and more. Ammonia catalyst, once reduced, is highly pyrophoric and should not be allowed to come into contact with oxygen. Therefore, any maintenance activity is only possible when the catalyst is replaced and converters should operate between catalyst changes for ten years or more without repairs or internal inspections.

Of course, when the moment of catalyst replacement approaches it is a different story and the converter suddenly jumps up in the priority list. The converter reliability is essential as a plant cannot run without it, and the risk involved in its failure is significant because of the high pressure and flammable gas it contains. Catalyst replacement is the occasion to perform inspection and maintenance, change damaged and aging components or entirely replace the internals and sometime also the relevant pressure vessel. The internals of the converter cannot be inspected beforehand, but intervention shall be decided well in advance of turnaround, when the plant should be kept down for the shortest period possible. Therefore, a clear understanding of the damaging phenomena and their consequences in the ammonia converter is essential. Failure to foresee any possible issue and to provide all needed components could lead to unexpected problems that cannot easily be solved during a turnaround, with unpredictable cost and delays.

A typical example are the internal heat exchangers. Casale experience shows that tubes of these exchangers, which cannot be thick because of the heat exchange function, are particularly subjected to consumption and possible mechanical failure.

Figure 1. Broken tubes inside operated internal exchanger

Exchangers are not the sole components exposed to degradation: in Fig. 2 an internal course that suffered huge deformation is shown.

Figure 2. Deformed course inside an ammonia converter

Not all parts inside the converter are exposed to the same level of consumption since operating conditions vary significantly between different sections of the reactor, causing uneven deterioration of different components. A deep knowledge and capacity to predict the behavior of the different components in relation to the varying operating condition is essential to schedule the required maintenance intervention at catalyst changes, but also to design the critical components and select the construction materials in order to avoid failure and increase their operating life reducing the cost of turnaround.

An accurate material selection during the design reduces the likelihood of some components wearing out significantly faster than others, adopting materials with better characteristics where it is needed the most. This way it is possible to avoid the early replacement of some critical items, like exchangers and hot collectors, during the shut-down for catalyst change. The result is a reduction of the cost and the duration of maintenance activities. To achieve this, several aspects need to be considered since converters are subject to different metallurgical deterioration phenomena, and they have a complicated mechanical design with multiple catalyst beds and internal heat exchangers to improve efficiency.

As explained further in the article, nitriding is certainly the most critical among the causes of deterioration of ammonia converter internals. For this reason, Casale performed research aimed at increasing the knowledge of this phenomenon and improving the capability to predict its development over time.

Operating environment

The ammonia converter operating environment is characterized by an aggressive combination of high pressure and high temperature gas composed of hydrogen, nitrogen and ammonia, which implies the concurrence of hydrogen related damage and nitriding.

To reduce these problems the catalytic bed where the ammonia is generated at high temperature is usually separated from the pressure bearing shell by an internal cartridge (sometimes called “basket”), while the vessel is cooler through a flush by the inlet gas that is low in temperature and ammonia content. This arrangement called “cold wall design" confines the harsher environment inside the internal cartridge.

A brief introduction to the metallurgical phenomena that affect the ammonia converter is required to understand the different choices in the design of ammonia converters, the problems related to these choices and the solution proposed.

As already mentioned, the combination of a high content of hydrogen and ammonia implies the concurrence of hydrogen-related damage and nitriding, exacerbated by high temperature and high pressure.

Hydrogen related damage refers mainly to high temperature hydrogen attack (HTHA) and hydrogen debonding.

High temperature hydrogen attack occurs in hydrogen-rich environments where, under certain conditions of temperature and pressure, carbon and low alloy steels can suffer irreversible damage. Its mechanism is described in internationally recognized standards such as API 941 and it is dealt with in ammonia converter pressure vessels by using the cold wall design and by proper material selection. In this design the converter cartridge and all of its internals are made of austenitic materials that are not affected by HTHA.

Hydrogen debonding affects welding between dissimilar metals, including weld overlays of stainless steels and nickel alloys on ferritic steels. Cracking commonly occurs at the interface between the austenitic weld material and the heterogeneous base metal, due to hydrogen, which has penetrated the metal during fabrication or operation, remaining entrapped up to saturation levels at cooling down cycles. The faster the rate of cooling, the higher the likelihood of entrapped hydrogen causing debonding. In general, stressed heterogenous welds should be avoided, especially when involving thick sections.

Introduction to nitriding

As a general phenomenon, nitriding is the introduction of atomic nitrogen in the surface of a metallic component. Atomic nitrogen forms solid solution and several nitrides with iron, but also nitrides with other elements with an affinity for nitrogen such as chromium. Since atomic nitrogen is required, molecular nitrogen is not a nitriding agent unless it is ionized, but gaseous ammonia mixtures with hydrogen are. Above a certain temperature ammonia decomposes over steel according to the reaction $NH_3 <> [N] + 3/2 H_2$, where [N] represents the nitrogen dissolved in the steel. This reaction occurs on the surface of the steel. Depending on the type of steel, temperature, pressure and gas composition, different types of solid solution and nitrides can form on the surface, creating an external nitride layer. This layer can increase in thickness over time and typically comprises a compound layer and an underlying diffusion zone. The compound layer is richer in nitrogen and harder, while the diffusion zone is softer with fewer nitrides, but overall the nitride layer is much harder than the base metal. This characteristic has been widely used to increase resistance against wear and fatigue of components such as engine cylinders.

While controlled nitriding is a technological process used to improve specific features of steel components, uncontrolled nitriding can be a problem due to its intrinsic characteristics. The nitride layer is hard but also brittle and involves structural modifications that cause volumetric changes.

The penetration rate of this layer will slow down after an initial fast growth since the layer itself acts as a barrier to further diffusion. This layer does not cause any problem until it remains compact and does not crack.

The main characteristic of a hard and brittle material compared to a ductile one is that there is little or no plastic deformation before rupture.

For this reason, in case of stress concentration, there is no plasticization and consequently stress cannot redistribute over a larger area and can easily reach high local peaks. Therefore, a brittle material will more easily reach its rupture limit in areas of stress concentration. When the rupture stress is exceeded, a brittle material will crack.
In a nitriding environment, when cracks appear, additional surface is exposed leading to further penetration of the nitride layer (Fig. 3). The apex of the cracks is subject to high stress concentration, even ten times higher than nominal stress. When nitriding progresses, these high stresses cannot be accommodated by plasticization of the material and the rupture limit is again exceeded leading to further propagation of the crack. This propagation, cycle after cycle, can lead to the component failure.

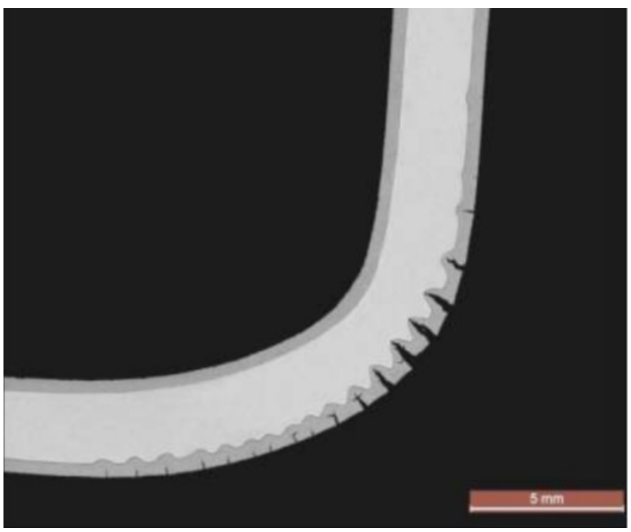

Figure 3. Effect of increasing penetration of nitriding (darker layer) due to cracks in a thin bended plate

Experience shows that components designed to avoid any stress concentration--preventing any abrupt geometrical change, sharp corners, temperature induced peak stress or sharp transitions--can withstand moderate nitriding because the brittle layer remains compact. However, it should be noted that as nitriding generally involves a volume increase in steel, it also generates internal stresses that could lead to cracks even in the absence of external loads.

Nitriding in ammonia converters

In ammonia converters, nitriding will occur to a degree depending on the combination of pressure, temperature, ammonia content and steel composition. Nitriding develops on carbon steel, low alloy steels and on stainless steels, however, on the latter at a much-reduced rate and at higher temperatures.

According to the literature and Casale experience, nitriding of carbon steel and low alloys starts at temperatures above 370-380°C (700-715°F) and becomes significant above 400°C (750°F). As a consequence, carbon steel and low alloys are not recommended in ammonia atmospheres above 370-380°C (700-715°F): instead, austenitic stainless steel or even nickel alloy should be used. This limitation is the main reason, together with hydrogen attack, for the selection of the cold wall design of the ammonia converter where the pressure retaining vessel is cold flushed by the inlet gas and low in ammonia content with an internal stainless steel cartridge enclosing the hot part of the process.

At higher temperature and reduced rates, nitriding also affects austenitic stainless steels, converting the comparatively ductile, moderate strength austenitic matrix to a very hard and brittle magnetic microstructure. It is the most critical material degradation phenomenon for the internals of ammonia converters, affecting the design and limiting the useful life of many components. However, due to the limited industrial application of nitriding on stainless steel and the differences between the controlled nitriding of the industrial process and the long term effects of uncontrolled nitriding in the ammonia synthesis environment, data about the effects of nitriding inside ammonia converters are scarce and difficult to correlate with actual operating conditions. No detailed data are available in the literature and it is not easy to simulate the effects of high temperature and pressure over an exposure time of 10 to 20 years in a laboratory.

Improving the knowledge

Ammonia plants have been around since more than one hundred years and a wide experience in the effects of nitriding on the design of converter internals has been gained. In the continuous effort to develop ever more efficient and reliable technologies, Casale implemented a specific program to review the knowledge of nitriding in the ammonia synthesis environment for the purpose of optimizing the design of critical components. Samples of materials which operated under different pressures and temperatures and for different time spans from ammonia converter components replaced in revamps, were analyzed in laboratories, and mechanically tested over the last decade.

This knowledge supplemented by laboratory testing has provided valuable insight into this phenomenon and how to predict and control it in newly designed components as well as how to assess existing components in order to advise plant owners about the safety of their plant.

As a leader in converter revamping, Casale has modified all types of existing ammonia converters and therefore during this survey samples from different operating conditions and design were collected.

Some numbers from the survey are helpful in understanding the extent of this effort. Of all samples collected, about one hundred were examined in specialized laboratories, for visual analysis, nitriding thickness measurement and chemical composition. The sample with the longest operating life was in service for 45 years, while the one with shortest was in service for about four years. The thickness of samples varied from 2 mm to more than 20 mm. The maximum nitride thickness measured was about 1.6 mm, as expected in the sample with the longest service life. Since the tendency to crack increases with nitride layer thickness, measurements were taken in unaffected areas. Several of these samples were also subjected to tensile testing, a test in which a specimen of the material undergoes traction loads until it breaks, to characterize the material response to elongation or stretching (Fig. 4). In addition, samples of different chemical composition were submitted to a controlled nitriding atmosphere for comparison with real life results. Fig. 5 shows the effect of nitriding in a perforated plate after 20 years in service.

Figure 4. Nitrided sample after traction test. Cracks occurred in the nitrided layer

Figure 5. Effect of nitriding in a perforated plate operated for 20 years

Some of the results of this survey are summarized here. It is understood that these considerations are valid only for operating conditions within the range of the tested samples, as they are based on an empirical analysis, but for practical purposes the operating range represented covers the conditions found in practically all ammonia converters still in operation. For reference, the samples analyzed cover a timespan from four years to 45 years in operation, and a temperature range from 400°C to 540°C (750°F to 1000°F). The ammonia content varied from about 2-3% to 21%, and the absolute pressure was also considered.

Outcomes and considerations

Some of the main outcomes of this research are summarized in the following paragraphs.
In general, it was found that, the nitriding rate (increase of nitride layer thickness versus time)

is initially high, then progressively decreases but does not stop in the timeframe considered. As an indication, the nitriding thickness reached after eight years will take three times as long to double.

Regarding the operating conditions, the survey shows that the rate of nitriding depends markedly on operating temperature, increasing exponentially with operating temperature itself. Nitriding depends less markedly on ammonia but increasing with its content. This increase is less than linear, with nitriding becoming significant above about 5% but with a thickness which does not double even at concentrations as high as 20%. Of course, the higher the absolute pressure the higher the relevant thickness, since the effective parameter is the ammonia partial pressure, which is the product of ammonia concentration and absolute pressure.

The data obtained has been used to establish a correlation which allows the extent of nitriding over time to be predicted, thereby allowing the most suitable design and relevant material thickness to be selected. This correlation improves previous rationalizations that can be found in the literature, thanks to the huge quantity of specific data that covers the complete operating range of the ammonia converter (see Fig. 6).

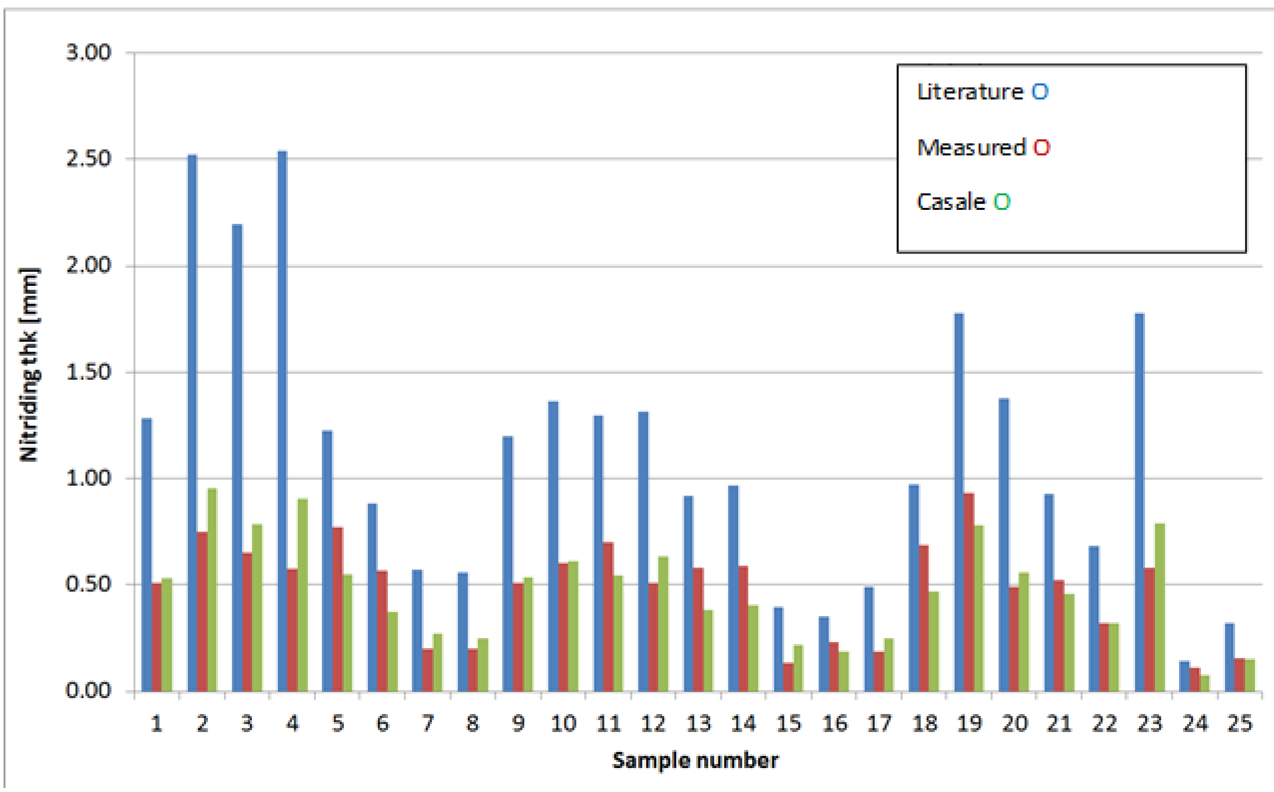

Figure 6. Predicted values of nitriding depth form available literature (Blue) and Casale method (Green) compared to actual values from measured samples. (Red)

Another important issue that has been substantiated by this survey, is the effect of the volumetric change due to nitriding. In stainless steel, the absorption of nitrogen involves an increase in volume in the compound layer that generates stresses due to the geometrical constraints of the unmodified core material. In smooth geometries, when the nitriding layer is small compared to the base material, this effect usually goes unnoticed, but when the thickness of the nitriding layer is high compared to the overall thickness, especially where there are abrupt changes of geometry, cracks will occur in the brittle nitrided layer (see Fig. 7). These cracks will expose the unaffected material, which will be subject to initial fast nitriding of the new material. This phenomenon will lead to a higher nitriding rate due the mechanism of crack progression described previously. For this reason, frequent temperature changes such as in start-up and shutdown, which increase the thermal stress and accelerate the progression of cracks, are much more critical than continuous service at high temperature where the nitriding rate is generally low after some years.

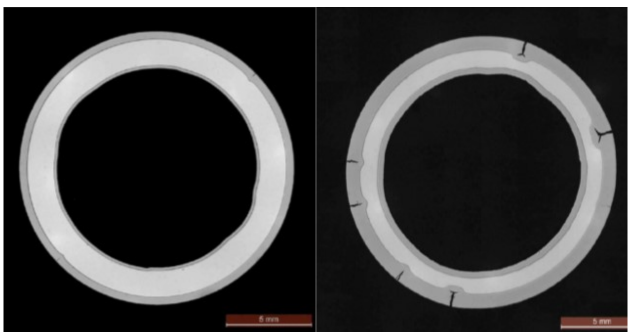

Figure 7. Nitrided sections of an interchanger tube. Cracks start at high nitride thickness

In addition to volume changes, mechanical stresses can also lead to cracking of the nitrided layer. To assess the effects of stresses on the nitrided samples, a series of tension tests were performed on operated samples. As expected, the nitrided layer, which is harder but brittle and therefore cannot accommodate excessive strain by plasticization, will always fail first. This should be taken into account in ammonia converter design. The progress of the cracks in the nitride layer depends on many parameters, including but not limited to the initial geometry of the component and the loading history. Except for some specific well-known situations, predicting the exact status of an operating unit in advance is not straightforward and might lead to inaccurate results. Nevertheless, the knowledge of the brittle behavior of nitride layer and the phenomenon of crack progress, just described, is very important in the material selection, as it will be explained later in the article.

Another point to be noted is that the nitrided layer becomes magnetic and subject to oxidation. While in operation, the atmosphere in the ammonia converter is reducing and this phenomenon is not a problem. However, it should be taken into consideration if the ammonia converter internals are subjected to a long shut down in an unprotected atmosphere during catalyst replacement.

Figure 8. Oxidized surface of an operated internal exchanger

Simulated Nitriding Campaign

It is known that the nitriding rate decreases with increasing nickel content, but it was not possible to address this effect in the correlation by retrieved data only, because all of the samples collected were mainly made of stainless steel grade 304, 316 and 321, which have limited variation of nickel content, or were Inconel, which is virtually immune to nitriding.

To fill this gap of knowledge, Casale set up a cooperation with a long-time ammonia manufacturer who was interested in evaluating the nitriding of some critical component of the newly supplied Converter internals. For this reason, laboratory tests of accelerated nitriding were set to evaluate the behavior of components under accelerated nitriding and to compare different grades of stainless steel.

The campaign involved 8 samples that were subjected to different treatments, ranging from 270 to 1150 hours, and then analyzed in laboratory. Tests were performed in furnace at high temperature used for commercial nitriding of steel, at pressure slightly above the atmospheric in ammonia environment.

It was observed that, in the treatment duration range from approximately 300 to 800 hours, the progress of accelerated nitriding was comparable to that of samples from the operated components taken from the field. The maximum treatment time, equal to 1150 hours, produced a nitriding thickness that would be reached on the majority of internal components of ammonia reactors in much more than 40 years, the maximum for which the calculation method is referenced and well beyond the operating life of a typical set of internal components.

Not only were the tests useful to compare different materials, but also to observe the volume expansion caused by nitriding. Even though establishing a relationship between nitrided thickness and volume expansion is not straightforward, it was observed that the linear expansion is in the range of 12%-18%. This permanent volumetric expansion of nitride layers causes distortions and cracks at bends, corners, and other discontinuities. A key role in the distortions of nitrided components is played by the ratio between nitride layer thickness and that of the base unaffected material. The thicker the nitride layer, the larger the deformation of the sample, the higher the probability of cracks.

As explained in the previous paragraph, the depth and progression of the cracks is depending on stresses and cycles. It should be considered that volumetric expansion of the new nitride layer growing at the tip of the cracks can generate by itself, depending on the geometry, enough stresses for the progression of the crack. Again, this is the case where abrupt changes in geometry are present, such as sharp corners in thin sheets.

The accelerated industrial nitriding environments of the tests cannot be easily compared to that in an actual ammonia converter, and therefore laboratory tests cannot be used directly to predict actual nitriding in operating conditions. However, a relationship could be made comparing the nitriding effect on samples made of materials of grades that have a known behavior in operating conditions versus those of different grades of stainless steel. It has been therefore demonstrated that accelerated nitriding tests are a proven technology to simulate the behavior of metals in ammonia synthesis environment, if a reference sample is used. On this basis, a comparison of different grades of stainless steel in tests was performed.

Material Comparison

From these accelerated tests it has been confirmed that increasing the percentage of nickel has a relevant impact on the nitriding rate. See Fig. 9, where nitriding thickness of samples made with stainless steel grades 321 and 310S are compared. Fig. 10 shows the negligible effect of nitriding on an Inconel 625 wire, which is about 20 times lower than in stainless steel grade 321.

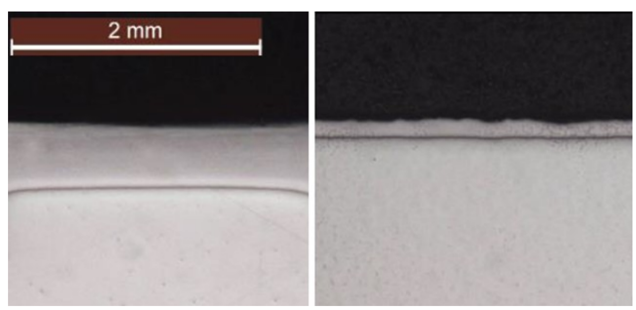

Figure 9. Nitrided layer for a metal sample made with stainless steel grade 321 (on the left) and 310S (on the right), exposed to the same accelerated nitriding treatment

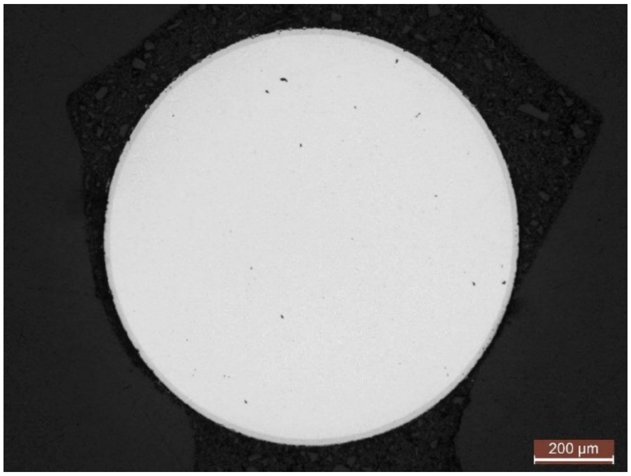

Figure 10. Section of wire of 1 mm diameter made from Inconel 625, subjected to accelerated nitriding treatment

Selecting suitable stainless steel grades for critical components in the ammonia converter allows significant improvement in the mechanical design, increasing reliability and extending operating life.

Of course, the selection should also take into consideration costs and the compatibility of different grades for concerns of welding and thermal expansion. This compatibility with widely used 304 or 321 stainless steel grades is excellent for stainless steel 310S, which has about double the nickel content of 321, while the depth of nitriding thickness of the 310S is less than one third compared to the 321 samples subjected to the same accelerated nitriding treatment.

For this reason, Casale introduced 310S as an improvement for the internal components that are subject to the most severe service conditions, i.e. high temperatures and high ammonia concentration. An example are the tubes of internal exchangers, which are typically made from 304, 316 or 321 steel. They are potentially subjected to the formation of a thick nitride layer, with development of cracks and consequent reduction of the resisting section (see fig. 7). The risks associated to components that are operated in these mechanical conditions are evident from Fig.1, where broken tubes are shown. With the introduction of 310S for the tubes, the formation of nitride layer is significantly reduced and mechanical reliability is greatly improved.

Conclusion

As an ammonia converter catalyst change approaches after many years of operation without internal inspection and maintenance, it is important to anticipate all the activities needed to restore the converter to a fit condition that will permit another trouble free operating cycle.

To effectively define all the needed activities, a deep knowledge of the design of the converter and its damaging phenomena is needed.

Since the most significant deteriorating phenomenon for ammonia converter internals is nitriding, Casale implemented a specific program to review and improve the knowledge of nitriding in the ammonia synthesis environment.

The large amount of data from collected samples and tests have allowed to refine the understanding of the effects of nitriding in the ammonia converter and to establish a correlation which allows the extent of nitriding to be predicted over the years.

All of this knowledge was incorporated in the material selection criteria, improving the design of converters, their reliability and operating life.
Specifically, it has been shown that an improved material selection of critical components could increase their resistance, leading to a higher reliability and a more homogeneous life of the different components, thus limiting the intervention during catalyst changes.

Acknowledgement

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Hydrogen Damage Mechanisms Affecting Assets in the Ammonia & Fertilizer Industry

The focus of this paper is to discuss similarities and differences between hydrogen damage mechanisms that can result in equipment failures and costly downtime in ammonia and fertilizer process equipment. The key factors that cause hydrogen embrittlement (HE), hydrogen-induced cracking (HIC), stress-oriented hydrogen-induced cracking (SOHIC), and high temperature hydrogen attack (HTHA) will be discussed with examples of each.

Daniel J. Benac, P.E., CFEI and Sean Berg, Ph.D., P.E.
Baker Engineering and Risk Consultants, Inc. (BakerRisk®)

Werner Ploumen
OCI Nitrogen

Rob Gommans
Materials & Corrosion Know-How

Ammonia plant equipment operates at elevated temperatures and is exposed to environments such as hydrogen that can potentially result in life-limiting conditions. Ammonia also provides promise as it may provide the source of hydrogen fuel for hydrogen technology. Accommodating increased usage of hydrogen fuel cells using ammonia as the hydrogen source requires increased ammonia production capacity and more global ammonia facilities.[1] Due to increased production and the exposure to hydrogen in process equipment, this increases the potential risk for hydrogen-related damaged to equipment and piping.

Awareness of the hydrogen-related damage mechanisms that can damage equipment is essential in developing the appropriate solution for proper equipment inspection, damage mitigation, and failure prevention. The pertinent damage mechanisms can also provide input for fitness-for-service evaluations as the mechanism and rate of attack needs to be understood to determine the remaining life. For a proper risk-based inspection (RBI) program or during a hazards analysis, the appropriate hydrogen -damaged mechanisms need to be identified so that the probability of failure can be determined in addressing reliability issues.[2]

The following four hydrogen-related damage mechanisms have been observed to affect ammonia equipment, and will be discussed in relation to process variables, process equipment, and materials of construction:

- Hydrogen embrittlement (HE)
- Hydrogen induced cracking (HIC)
- Stress-oriented Hydrogen-induced cracking (SOHIC)
- High temperature hydrogen attack (HTHA)

This paper provides examples and discussion with regard to each type of hydrogen damage mechanism relating to ammonia process parameters, materials of construction and process equipment, and inspection methods and characterization techniques to identify each form of damage. Additionally, useful tips for considering operating envelopes or limits and potential mitigation methods are provided.

Ammonia Equipment Materials of Construction

Most equipment used in the ammonia process production are essentially pressure vessels, piping, and storage tanks whose pressure boundaries are constructed of metallic materials. All materials of construction used in the ammonia industry are susceptible to degradation and various types of damage mechanisms. While it may be possible to select materials of construction that are completely resistant to attack by the process fluids, such an approach can be impractical or cost prohibitive.

Carbon and alloy steels are the most commonly used materials of construction for process equipment in the ammonia industry. These materials offer a suitable combination of strength and ductility and are capable of safely operating in the temperature ranges employed in the ammonia industry. However, carbon and low alloy steels are susceptible to hydrogen damage mechanisms when exposed to a hydrogen environment. Hydrogen may take an atomic (H) or molecular hydrogen (recombined to H_2) form. In either case, only atomic hydrogen (H) diffuses into susceptible alloys such as ferritic steels (C-steel or CrMo alloy steel). The hydrogen molecule (H_2) is too large to diffuse in the steel.

The use of stainless steels in most ammonia plants can reduce susceptibility to hydrogen damage mechanisms. Austenitic stainless steel can also be susceptible if martensite has formed by heavy cold deformation. Titanium sometimes used in equipment has excellent resistance to general corrosion but can form hydrides if in a hydrogen environment.

Comparison of Hydrogen-related Damage Mechanisms for Steel

The hydrogen can be driven into the metal by a corrosion reaction, pressure, partial pressure of hydrogen, temperature, concentration gradient, residual stress, or applied stress in the material. The hydrogen can be in the metal through fabrication, such as in moist welding materials or in a moist welding environment. The microstructure of the material may also influence the location of where the damage may occur. The hardness of a material, weld or heat affected zone is an important factor. There is a hardness limit, often in lower temperature hydrogen damage.

Terminology describing hydrogen-related damage mechanisms can be confusing, inaccurate, or unclear. To identify similarities and help clear up the differences, the four common hydrogen damage mechanisms are described in Table 1. These hydrogen-related damage mechanisms can all occur in Ammonia Process equipment. Table 1 provides an overview and comparison of each type of damage mechanism for steel and alloy steels, including the form the hydrogen takes, description, key parameters, and key mitigation recommendations. This table was compiled for the Ammonia and Fertilizer joint industry program (JIP) by OCI resources collaborating with BakerRisk.[3]

API RP 571 provides general guidance as to the most likely damage mechanisms affecting common alloys used in the refining and petrochemical industry and is intended to introduce the concepts of service-induced deterioration and failure modes. However, as the API standards tend to focus on refining and hydrocarbon processes, the high pressure and temperature conditions in ammonia and methanol production provides a wealth of experience and knowledge base for hydrogen damage mechanisms. This combined experience provides information that can be utilized by plant inspection personnel to assist in identifying likely causes of damage, to assist with the development of inspection strategies, and to help identify monitoring programs to ensure equipment integrity.

Damage Mechanism	Hydrogen Form	Description	Key Parameters	Mitigation Strategies
Hydrogen Embrittlement (HE)	Atomic	Diffusion of hydrogen atoms into steel, which tend to migrate to voids and dislocations, applying pressure to interior of material, and pinning dislocation motion. Results in brittle behavior. Typically occurs at temperatures below 150°C (302°F), following welding, plating, or submerged cathodic protection; when hydrogen is produced; or during elevated temperature service (>200°C) (392°F) when hydrogen cannot diffuse out of steel and is then cooled (shutdown and subsequent startup).	• Strength and hardness • Residual stress • Material microstructure, e.g., heat affected zone • Atomic H-concentration in the steel after charging hydrogen during elevated temperature service.	• Limit steel hardness to <237 HB/HRC 22 or use lower strength steel • Hydrogen bake-out at 204°C (400°F) following weld processes • Allow outgassing of the steel during shutdown, i.e., lower the cooling rate and be aware of Minimum Pressurization Temperature curves.
Blistering and Hydrogen Induced Cracking (HIC)*	Molecular	Exposure to hydrogen environment or wet H_2S (hydrogen produced during formation of FeS). Hydrogen enters in atomic form, but damage occurs after H-atoms recombine to H_2 molecules inside alloy. Blistering and HIC are strongly affected by the presence of inclusions, laminations (both found in "dirty" steels), and internal discontinuities, all of which provide sites for hydrogen accumulation.	• Hardness and strength • Residual stress • Temperature • Corrosion reaction with formation off atomic Hydrogen (such as H_2S) • Low impurities in the steel composition • Surface scales and inhibitors	• Limit steel hardness to below 237 HB/HRC 22 • Use of protective lining in H_2S environment • Chemistry and manufacturing methods can affect susceptibility and can be modified to produce HIC resistant steel (refer to NACE 8X194).
Stress-Oriented Hydrogen Induced Cracking (SOHIC)*	Molecular	Similar to HIC but cracking occurs in a sufficiently high stress field. Blisters or cracks stacked on top of one another and link up through the cross sectional direction (e.g., stair-step cracks).	• Same as HIC • Stress level applied to alloy	• Same as HIC • Lower stress level, if possible • Post-weld heat treatment
High Temperature Hydrogen Attack (HTHA)	Atomic	Diffusion of hydrogen into steel at elevated temperatures((>200°C) (392°F). Hydrogen reacts with carbides at elevated temperatures to form methane gas. Micro voids, grain boundary voids and micro fissures are generated. Buildup of methane pressure can result in blistering, degradation, and fissures within metal.	• Refer to most recent edition of Nelson curves in API RP 941 • Operating temperature • Partial pressure of hydrogen • Material selection	• Monitor pressure, hydrogen partial pressure, and temperatures • Operate with a safety margin, e.g., 28°C (50°F), below the Nelson Curve • Post-weld heat treatment at sufficiently high temperatures that allow stable carbides to form • Use higher alloyed steels

**Note: HIC and SOHIC are mainly related to feedstocks containing H_2S. They can occur in the gas cleaning section where H_2S is removed (i.e., before the "normal" ammonia plant equipment). After the desulfurization vessels, the amount of H_2S is generally too low to cause HIC or SOHIC.*

Table 1. Comparison of Hydrogen-related Damage Mechanisms for Steel

Hydrogen Embrittlement

Hydrogen embrittlement (HE) is the process by which various metals, most importantly high-strength steel, become brittle and fracture following exposure to hydrogen. Hydrogen embrittlement is often the result of unintentional introduction of hydrogen into susceptible metals during forming or finishing operations such as welding and plating.[4]

The mechanism starts with lone hydrogen atoms diffusing through the metal. At high temperatures, the elevated solubility of hydrogen allows hydrogen to diffuse more easily into the metal (or the hydrogen can diffuse in at a low temperature, assisted by a concentration gradient). The hydrogen atoms pin the dislocations in the steel, especially at the tips of cracks and internal defects. This results in limited moveability of the dislocations and brittle behavior of the steel. High-strength and low-alloy steels and nickel and titanium alloys are most susceptible. Also, CrMo steels that have not been properly post-weld heat treated are susceptible. High hardness zones appear due to the formation of bainite or martensite.

During high temperature service the steel can be charged/loaded with hydrogen. When the process is taken out of service, hydrogen may get trapped inside the crystalline structure of the steel, especially for thick-walled components.

Key Parameters and Factors:

- Hydrogen must be present at a critical concentration within the steel and/or alloy.
- Increased risk where equipment temperatures are high, which can increase the solubility of hydrogen in the material.
- The strength level and microstructure of the steel/alloy must be susceptible to embrittlement. High strength steels above 237 HB/22 HRC are particularly sensitive to HE and can suffer delayed cracking before use due to the presence of hydrogen and residual stresses. Steel and welds with hardness of less than 237 HB/22 HRC is not generally considered susceptible to hydrogen embrittlement.
- A stress above the stress threshold for HE must be present from residual stresses and/or applied stresses.
- HE cracking can initiate sub-surface, but in most cases is surface-breaking.
- HE occurs at locations of high residual or tri-axial stresses (notches, restraint) and where the microstructure is conducive, such as in weld HAZs.
- In higher strength steels, cracking is often intergranular (may be transgranular) and can start subsurface.
- Welding – If wet electrodes or high moisture flux weld electrodes are used, hydrogen can be charged into the steel. Improper PWHT or non-post weld heat treated welds in pipes and vessels are susceptible.
- HE is most pronounced at temperatures between ambient to about 150°C (300°F) because the atomic hydrogen can diffuse at the elevated temperature (i.e., the hydrogen is mobile).

Ammonia Equipment Concerns:

- Syngas coolers
- BFW heaters
- Ammonia Equipment:
- Methanation
- Secondary Reformer and Heat Recovery

Mitigation Options:

- Use low hydrogen dry electrodes during welding and preheating methods.
- Bake electroplated steel components at temperatures of 190 to 220°C (375 to

430°F) within a few hours after the electroplating process.

- Use lower strength steels and reduce residual and applied stresses to avoid fracture due to hydrogen embrittlement.
- Apply proper post-weld heat treatment and reduce the hardness below 225-250 HV
- Allow outgassing of the hydrogen out of the steel by applying a proper (slow) cool-down procedure

Hydrogen Embrittlement Examples

Example 1: Syngas Circulation Boiler

Background: A 13CrMo44 (1Cr-0.5 Mo) Connection pipe between the syngas circulation boiler/economizer and the hot cross exchanger leaked after six years in service. Internal cracking and a leakage in the intrados of the pipe bend was determined on the transition of pipe to weld, as well as cracking in the extrados of the bend on the transition of bend to weld, shown in Figure 1. The Syngas, (H_2, N_2, NH_3) temperature was 320-340ºC (608-644ºF) and the pressure 190-215 bar (2.7-3.1 ksi). The hydrogen partial pressure (pH_2) = 115 bar(a) (1.69 ksi)

Findings: The failure mechanism was hydrogen embrittlement: cracking causing a brittle condition. The steel pipe wall was charged with atomic hydrogen during normal operation at high temperature, and the hydrogen got trapped inside of the metal structure as the pipe wall cooled down during shutdown. This led to loss of ductility and brittle behavior of the pipe material.

The hardness of the weld and the heat affected zone are relatively high (> 225 HV) for a hydrogen loaded pipe, which makes the construction vulnerable to hydrogen embrittlement.

The crack initiated on the inner surface along the weld fusion line and had a transgranular character, propagating towards the outer surface, showing many non-oriented hairline cracks and a staggered propagation. This is typical for hydrogen cracking.

The internal stress due to faulty assembly combined with a relatively high hardness and notch effect of the weld (high-low) under the given shutdown process conditions led to brittle cracking.

Most of the spring supports were out of range, which resulted in improper balance of stress under process conditions. No inspection on pipe supports had been conducted.

It appeared that not all the spring supports had been fixed properly while reconstructing the line, resulting in a fitting piece which had incorrect dimensions. Pipe and elbow were lined up using chain hoists before welding to correct for significant misalignment. This led to high internal stress at the weld position.

Mitigation Options:

The following options were considered:

- Create a maintenance program for spring posts and pipe supports, replacing faulty and/or non-readable devices; and performing regular inspections when the spring pot is within its range.
- Review/extend the applicable Engineering Practice along with training and follow-up with regard to the contributing factors for Hydrogen Embrittlement and what measures should be taken concerning the welding process to reduce the risk of Hydrogen Embrittlement. This should also ensure that a designated engineer becomes owner of the entire modification process, supervising all steps of the change when welding in a hydrogen-loaded system becomes necessary, to ensure compliance with all rules.

- Make sure that the correct pressure and heating/cooling procedures for hydrogen loaded systems are applied in all operating procedures. Applicable SOP's need to have specific maximum allowable depressurization rates related to the remaining equipment temperature for each situation based on the specific applicable damage mechanisms.

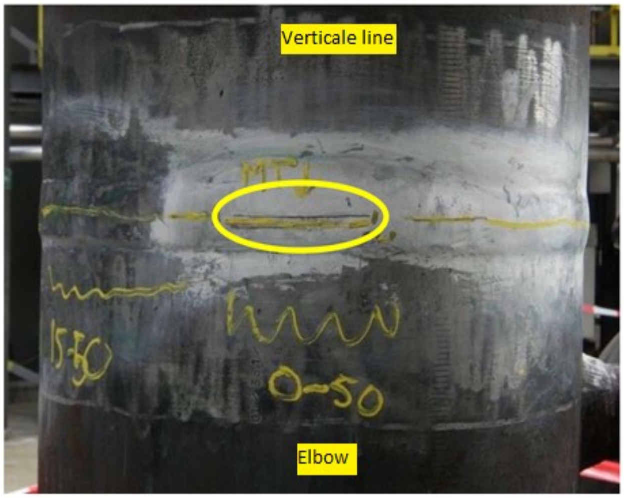


Figure 1. Connection pipe showing the location of cracking at the weld

Example 2: Thermowell Example

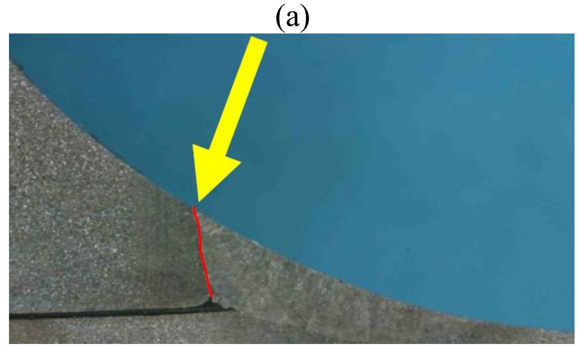
Background: After 48 years of service, a leak was detected in the start-up heater during normal operations because of flames coming out of the line insulation near the thermowell, shown in Figure 2. The Plant was shut down immediately. Syngas leaked through a 30 mm crack in the heat affected zone of the socket weld on the thermowell. The material of the pipe was 10 CrMo 9.10 and the thermowell was 13 CrMo 44. The weld was a mixture of both materials. The normal operating temperature was from 0 to 460ºC (32 to 860°F) and with a pressure of 195 to 215 bar 195-215 bar (2.8-3.1 ksi).

Findings: The crack was of a trans-crystalline character, showing a staggered propagation. The hardness of the material close to the crack was 295 to 380 HV, relatively high but within allowable range. During the 48-year lifetime, Hydrogen-induced cracks formed along the hardest material in the heat affected zone (HAZ) and gradually increased until failure.

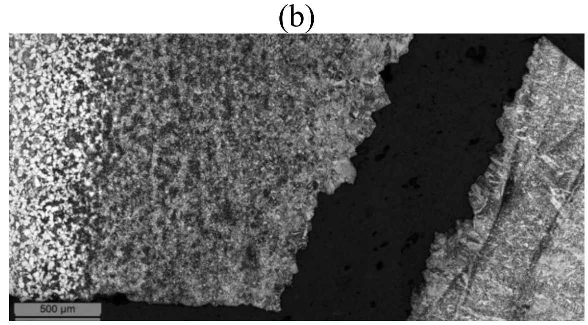
Mitigation Options:

- Post-weld heat treatment for welds in hydrogen loaded systems until the hardness is below 320 HV.
- Review of SOP's to control temperature gradients as much as possible.

(a)



(b)



(c)

Figure 2. (a) Socket welded Thermowell;
(b) Crack in HAZ; and (c) Transgranular cracking

Example 3: Titanium Hydride

Titanium can be very susceptible to titanium hydride formation. Titanium parts that absorbed hydrogen at elevated temperatures can form hydrides upon cooling. These hydrides lead to a decrease in the strain to failure, loss of strength, and ductility. Hydrogen absorbed when present above specification can result in metal embrittlement, hardening, cracking, and spalling due to the formation of hydrides in the metal.

Background on the Equipment: The titanium 3Al-2.5V float was in the ammonia unit.[5] The titanium float system is a magnetic level indicator that consists of a chamber and a magnet-equipped titanium float that raises and lowers with the fluid level. Operators reported problems with the float and erroneous level readings to site supervision. The titanium float (shown in Figure 3) was removed for investigation and was found cracked, as shown in Figure 4.

Figure 3. The titanium float

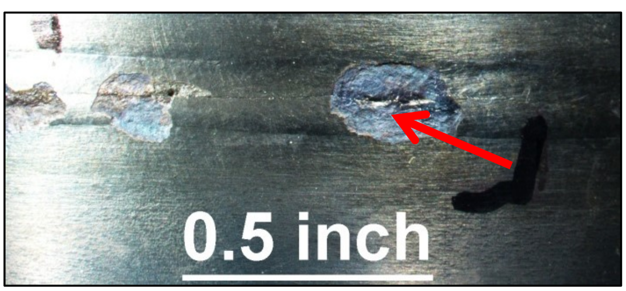


Figure 4. Close-up of the weld showing cracks

The typical operating temperature was 133 °C (271 °F), the typical pressure was 2.8 MPa (400 psig), and the process medium included: Water 10.4%; Hydrogen 54.7%; Nitrogen 18.3%; and CO_2 15.9%.

Findings: Metallurgical analysis determined that the cracking and spalling of the titanium float was due to the excessive pickup of hydrogen, which resulted in the formation of embrittling titanium hydrides.[5] The gas analysis of the weld region showed absorption of excessive amounts of hydrogen at the weld and heat affected zone. The weight percent of hydrogen was as much as 0.479% in the weld compared to 0.015 wt.% in the non-cracked sheet metal.

The most likely source of the hydrogen was from the operation in a hydrogen, steam, and ammonia environment. The areas where the most hydrogen was absorbed were at the weld and weld heat affected zones, likely due to residual stresses. These regions were also harder.

Figure 5 shows the affected weld and HAZ.

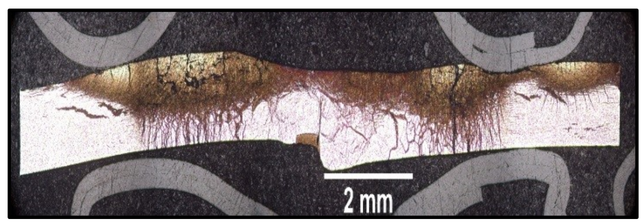


Figure 5. Cross section through the weld and HAZ showing the cracking and hydrides

Mitigation Options:

- Because the titanium absorbed hydrogen, action was taken to include a design change by applying a PTFE (Teflon-like) coating over the titanium float to prevent cracking from occurring. While the manufacturer provided a replacement titanium float with a PTFE coating, this coating may not be protective enough. Other more suitable metals could have been considered for replacement. It is best to keep titanium away from areas with high ammonia concentrations due to titanium's affinity for nitrogen and hydrogen.

HIC and SOHIC

Hydrogen-induced cracking (HIC) and stress-oriented hydrogen induced cracking (SOHIC) are related. Both occur from the presence of hydrogen or from corrosion where hydrogen is liberated and diffuses into the steel, such as with Wet H_2S corrosion. Hydrogen blisters may form as visible surface features or within the material. These blisters may be in arrays. HIC is a potential problem, mostly in low alloy steel weldments, and especially equipment fabricated in the 1960s that has high hardness and/or high levels of impurities and segregations.[6]

SOHIC occurs when these arrays of cracks are stacked on top of one another, usually in the base metal adjacent to the heat affected zone (HAZ).[7] This often occurs at high localized applied or residual stresses.

Key Parameters:

- HIC occurs at locations of high residual or tri-axial stresses (notches, restraint) and where the microstructure is conducive, such as in weld HAZs. Explosion cladding will generate high stresses.
- Hydrogen partial pressure
- Higher hardness alloys or local areas in welds are more susceptible to HIC and SOHIC
- Proper PWHT is required to ensure lower hardness is obtained
- Manual welds made with moisture in the electrodes
- Increasing H_2S potential and temperature increases the available hydrogen. Blistering has been observed between ambient and 150 °C (300 °F).

Ammonia Equipment Concerns:

Some of the equipment below could be susceptible, but the most likely concern for HIC or SOHIC would occur in H2S removal section of the plant.

- Ammonia converter
- Loop waste heat recovery
- Startup Heater Coil
- Shift Converter (moisture in electrodes)
- SynLoop
- Methanation
- High and Low Shift
- Syngas Compression
- Mol Sieves

Mitigation Options:

- Carbon steels should be controlled to keep the weld hardness below 200 HB. Localized areas of hardness above 237 HB can be susceptible.
- Temper or PWHT procedures should be carefully followed and documented. Hardness testing with follow-up PWHT should be performed if hardness levels exceed recommendations.
- Some designers are moving away from Vanadium steels due to difficulty with fabrication.
- Where possible, conduct a furnace stress relief (instead of a local stress relief).
- If necessary, use alloy cladding to protect the steel from the H_2S corrosion.
- Use clean steels, like so-called HIC-resistant steels (NACE 8X194)

High Temperature Hydrogen Attack (HTHA)

High Temperature Hydrogen Attack (HTHA) is a form of degradation caused by hydrogen reacting with carbon to form methane in a high temperature environment.

$$C + 4H \rightarrow CH_4$$

When steel is exposed to hydrogen at elevated temperatures, hydrogen will diffuse into the alloy and react with carbon to form cavities/voids filled with methane.[8]

The methane is trapped in these voids and does not diffuse out of the metal. Over time, more and more methane is formed, forming more cavities at the grain boundaries. These cavities coalesce and form micro-cracks at the grain boundaries, which later will grow into macro-cracks. An example of such fractures can be seen in the microstructure of a pipe weld in Figure 6,[9] which shows a decarburization and fissuring region caused by hydrogen depleting the iron carbides. The cracks lower the rupture ductility and fracture toughness, which may result in brittle fracture. The brittle behavior of the material can result in a catastrophic brittle fracture of the asset [10-12] during startup or shutdown excursions.

Susceptible materials include plain carbon steels, C-½Mo Steels, and other low alloy steels and non-post weld heat treated (PWHT) welds. API RP 941 provides guidance to aid in materials selection for fixed equipment operating in environments with hydrogen partial pressures at elevated temperatures and pressures.[13] This guidance can also be useful to materials engineers and process engineers alike, as knowledge of both process conditions and the materials of construction will provide information on an asset's susceptibility to this particular damage mechanism.

The most obvious equipment concerns are any equipment exceeding normal operating temperatures or operating window limits, specifically carbon and low alloy steel vessels and piping operating at temperatures that are above the API 941 RP Nelson curve values. These exceedances may not occur during normal operation, but during startup, shutdown or upset conditions. Catalyst changes, fouling, and flow irregularities may also produce localized areas in exceedance of the recommended limits. Aging plants should be mindful of API RP 941 Nelson Curve operating point changes and should determine whether process changes or HTHA mitigation strategies may be implemented. HTHA is not a concern in solid stainless steel vessels. API RP 941 recommends not to take credit for the presence of a stainless steel cladding or weld overlay when selecting the base metal for a new vessel.

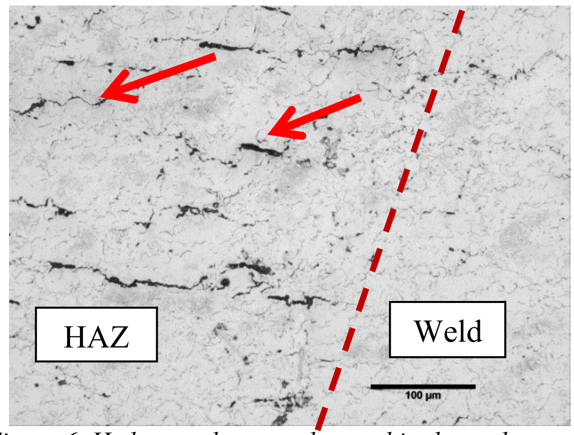


Figure 6. Hydrogen damage observed in the carbon steel line at the heat affected zone (HAZ). Nital etch. (Original magnification: 200x).

Hydrogen content is high in the ammonia process streams, and so it is important to evaluate the potential for HTHA where the temperatures rise above 204°C (400°F) for carbon steel materials. The hydrogen content should be considered on a wet gas basis.

Typical HTHA concerns start with the Shift Unit and equipment through the Ammonia Synloop where temperatures are above 204°C (400°F). However, HTHA may be present in other areas such as secondary reformer pressure shells where refractory failures allow higher shell temperatures. HTHA can also be a concern throughout the ammonia process, including equipment in the following units: Shifts (both high and low shift), Methanation, and SynLoop. SynLoop equipment, particularly converters without furnace stress relief or operating at high temperatures, and startup heater coils are also a vulnerable point for attack. Additionally, hot spots in secondary reformer and waste heat boilers, Mol Sieves, and pressure envelopes where refractory failures occur are also a concern.

Key Parameters:

- Non-post weld heat treated steels are more susceptible.
- Operating temperatures within, e.g., 28°C (50°F) of the API RP 941 curve values make the material more susceptible due to measurement capability.
- Environmental conditions: Hydrogen partial pressure and operating temperatures as susceptibility to attack increases as H_2 partial pressure increases.
- Materials with an inadequate safety factor using the API RP 941Curve.
- Material substitutions with a wrong material or welding rods and equipment that are not inspected by PMI.
- Material substitution can also happen during maintenance activities when, e.g., bends before and after heat exchangers are accidently mixed up (same dimensions, different steel)
- Exceeding normal operating temperatures or operating window limits.
- Refractory-lined vessels or refractory protected nozzles/pipes where refractory has been compromised (hot spots).
- Aging plants that have inadequate information on API RP 941 Nelson Curve changes, especially for C-½Mo steel and non-PWHT'd carbon steel.
- Stainless Steel-lined vessels with the possibility of hydrogen getting behind the liner.
- Carbon Steels and Low Alloy Steels at operating temperatures that are above the API 941 RP Curve values, including processes that stray outside of the target IOW.

Equipment Concerns:

Aging vessels in particular are subject to HTHA and other hydrogen mechanisms because of their years of service, potential operating excursions, and initial materials selection. The methanator is a high temperature vessel that is subject to temperature excursions and is a candidate for HTHA along with the other methanation unit equipment. There have been reports of progressive degradation when HTHA is found in methanators, with the most notable damage on the bottom of the vessel, which experiences higher temperatures. HTHA damage should be monitored, and a Fitness for Service (FFS) considered to ensure integrity is maintained.

SynLoop:

HTHA is a concern, particularly after a retrofit increases the ammonia conversion, which raises the outlet temperatures of the converter and the downstream equipment. Retrofit heat and material balance predictions may underestimate the temperatures for fresh catalyst, resulting in HTHA conditions for existing materials. Sometimes risk is difficult to identify as temperatures can be unknown due to a lack of instrumentation.[9]

Ammonia Equipment Concerns:

- Hydrogen content is high in the ammonia process streams, and so it is important to evaluate for HTHA potential where the temperatures rise above 204°C (400°F) for carbon steel and low alloy materials.
- The hydrogen content should be considered on a wet gas basis, which may reduce the risk susceptibility for equipment prior to process condensate removal at the CO_2 Purification.

- Typical concerns start with the Shift Unit and equipment through the Ammonia SynLoop where temperatures are above 204°C (400°F).
- However, HTHA may be present in other areas such as secondary unit pressure shells due to refractory failure.

Mitigation Options:

One of the most critical ways to mitigate the potential for HTHA is for plant engineering to review plant processes, the design basis or Form U1 Manufacturer's Report which includes the materials of construction, and operating conditions to identify potential HTHA risks with hydrogen-containing equipment. An important component of this includes conducting an engineering review of pressure, hydrogen partial pressure, and temperatures. Operating with safety margins, e.g., 28 °C (50°F) below the API RP 941 Curve, can also provide additional assurance. Engineering should establish integrity operating limits for all vulnerable equipment. Having an active PMI and retro PMI program is also an essential mitigation component.

If possible or feasible, aging plants should consider replacing equipment with higher alloyed material that are less susceptible to HTHA according to the API RP 941 Curve for desired operating conditions. This review should include determining whether welded equipment or piping was post-weld heat treated, and if not known, assume non-post weld heat treated welds and operate at lower temperature and pressures. One may also consider performing PWHT during the next opportunity. Installing temperature indicators at critical locations, to monitor actual temperatures, and performing regular thermography measurements can help to ensure operating windows and limits are not exceeded or can be addressed.

- Review plant to identify potential HTHA risks with hydrogen-containing equipment.
- Perform regular thermography measurements.
- Have an active PMI and retro PMI program.
- Operate within safety margins, e.g., 28 °C (50°F) below the API RP 941 Curve.
- Review quality of past repairs and ensure PWHT practices did not introduce an HTHA risk.
- Determine whether welded equipment or piping is post-weld heat treated. If not known, then assume non-post weld heat treated and operate at lower temperature and pressures. One may also consider performing PWHT during the next opportunity.
- Replace equipment with higher alloyed material that is less susceptible according to the API RP 941 Curve.
- Install temperature indicators at critical locations to monitor actual temperatures.
- Conduct engineering review of pressure, hydrogen partial pressure, and temperatures.
- Set up integrity operating limits for equipment.
- Recheck IOW's in conjunction with process changes where temperatures are affected, such as SynLoop converter retrofits for higher efficiencies.

HTHA Example:

Background: An investigation conducted into a carbon steel effluent cooler header piping rupture, installed in an ammonia converter and synthesis loop, occurred 5 years after a change in operating conditions.[14] The process temperature was increased from 232 to 254 °C (450 to 490 °F), and the operating pressure was decreased from 29.0 MPa (4200 psig) (0.1 MPa (2100 psig) hydrogen partial pressure) to 23.4 MPa (3400 psig) (0.8 MPa (1700 psig) hydrogen partial pressure).

Findings: This process change placed the carbon steel pipe above the API RP 941 Nelson curve temperature for carbon steel at the corresponding hydrogen partial pressure. The piping rupture was found to have a brittle fracture appearance. Failure analysis revealed that HTHA was the damage mechanism that caused the pipe rupture. This example case demonstrates the vulnerability of this portion of the ammonia process if material limits are exceeded and how process changes can create the potential for eventual failure.[14]

Mitigation options considered:

- Conducted Hydrogen damage review of equipment.
- Replaced piping with higher alloy material.

Inspection Methods

For HE, HIC, and SOHIC, some common inspection methods such as those listed below can be used:

- Penetrant testing (PT)
- Magnetic particle testing (MT)
- Wet fluorescent magnetic particle testing (WFMT)
- Ultrasonic testing (UT)
- Radiographic testing (RT)

For volumetric (through wall thickness) HTHA inspections, the previous suggestions found in API RP 941 Annex E will be discontinued and replaced with API RP 586 (in balloting process at this time). It has been demonstrated that the historical methods have been supplanted by more advanced modalities of the Ultrasonic Testing methods found in API 586. These include Advanced Phase Array (using 64 Element Arrays), Total Focusing Method (TFM) or Full Matrix Capture (FMC), Time of Flight Diffraction or a combination of these methods. As always, these methods are strictly dependent on the technique and skill level of the inspector. There is a recognized training and certification program for these methods to qualify and maintain personnel competency.

Inspection methods that can identify potential regions of HTHA are:

- High Sensitivity Wet Fluorescent Magnetic Particle Testing (WFMT)
- Replication of surfaces
- Positive Material Identification (PMI)
- Thermographic temperature surveys

Summary

Hydrogen-related damage mechanisms are present in ammonia producing equipment. Having an understanding of these hydrogen damage mechanisms and how operations or process conditions can affect equipment will help mitigate the occurrence of hydrogen-related damage mechanisms. By making better distinctions between the three main hydrogen-related damage mechanisms, one will better identify and mitigate the damage mechanism.

The main hydrogen related damage mechanisms are:

High-Temperature Hydrogen Attack (HTHA)
Reaction of atomic hydrogen with carbides and formation of methane bubbles. It typically occurs above temperatures of 200°C (400°F).

Hydrogen Blistering, Hydrogen-Induced Cracking (HIC), Stress orientated Hydrogen-Induced Cracking (SOHIC)

Recombination of atomic-H to molecular-H2 at defects/segregations in the steel. It typically occurs in ‘dirty’ steels and with corrosion reactions generating atomic hydrogen.

Hydrogen Embrittlement
Atomic hydrogen hinders dislocation movement in the steel and causes brittle behavior. It typically occurs at temperatures below 150°C (300°F). This can also happen after cool-down when the steel has been charged with hydrogen during high-temperature service.

It is essential that these mechanisms be communicated to plant and management staff and that the preventative actions are implemented; otherwise, the high risks are not mitigated.

Acknowledgements

The shared information from the 2020 Joint Industry Program (JIP) facilitated by BakerRisk has contributed to the content of this paper. The JIP was a successful collaboration between a significant group of Ammonia producers to share materials and corrosion knowledge based on investigations after incidents.

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The First Commercial Reference of Award-Winning AmoMax®-Casale Catalyst at Nutrien

AmoMax-Casale® is a new ammonia synthesis catalyst jointly developed by Casale and Clariant, particularly for use in Casale ammonia converters. AmoMax-Casale® is a customized evolution of the industry-proven, wustite-based catalyst, AmoMax® 10, and is significantly more active. This feature allows a reduction in the loop recycle rate and the loop pressure, which reduces CO2 emissions, and/or allows an increase in ammonia production. The advantages of AmoMax-Casale® catalyst have been recognized through two prestigious awards.

This paper will detail the performance of the first reference of AmoMax-Casale® catalyst in a large-scale ammonia plant at Nutrien Trinidad, now 2 years on-stream. It will also highlight how the performance of this catalyst supported the achievement of the energy-improvement project targets. The variable cost of production was lowered by reducing gas consumption per ton of ammonia. Importantly, this has also improved overall plant sustainability by lowering the CO2 emissions intensity.

Lawrence Sandy
Nutrien, Trinidad

Michelle Anderson
Clariant, Trinidad

Marco Mazzamuto
Casale, Switzerland

Introduction

The 01 ammonia plant is an original M.W. Kellogg design constructed in 1981. In 2006 the plant was revamped to a production capacity of 1750 STPD with installing an S200 Haldor Topsoe designed ammonia converter. In 2019 an Energy Improvement Project (EIP) was implemented with the focus being on improving the efficiency and sustainability of the plant. Casale and Clariant were selected to retrofit the existing converter using advanced technologies in converter design in combination with an innovative new catalyst jointly developed by Clariant and Casale. This first reference of the AmoMax®-Casale ammonia synthesis catalyst was successfully installed and has demonstrated high performance thus far, allowing reduced operating pressure and subsequent lower CO_2 emissions which have exceeded the EIP targets.

Project Feasibility

While conventional fertilizer manufacturing is one of the most important innovations for food and agriculture, it presents unique challenges to reducing emissions. The industry is actively working towards innovative, more sustainable production methods, including low-emission processes powered by renewable energy. Though it will take time for these technologies to scale up and be cost-competitive, there are still ways to improve the emissions intensity of conventional fertilizer production in the short term.

Climate change is the top environmental, social and governance risk identified by Nutrien stakeholders. Nutrien's 2030 Climate Change commitment is at least a 30 per cent reduction in emissions intensity from the baseline year of 2018.

Nutrien has identified ways in which this target can be achieved by energy efficiency improvements, implementing nitrous oxide (N_2O) abatement at its nitric acid production facilities, carbon capture, utilization, and storage (CCUS) at strategically located assets, and cogeneration projects that use natural gas for lower GHG electricity generation and waste heat recovery. Nutrien is also leading the way on the development of clean ammonia, with the Geismar site being evaluated for construction of the world's largest clean ammonia production facility

The Energy Improvement project at the 01 plant was initiated according to Nutrien's sustainability goals. In collaboration with Casale and Clariant, a retrofit was done of the exiting converter with Casale's 3-bed interchanger design specifically installed with Clariant and Casale's innovative ammonia synthesis catalyst, AmoMax®-Casale. This innovative solution was projected to create an energy savings of 0.2 MMBtu/ST and over 6,000 MT/year of CO_2 reduction.

Figure 1. Nutrien 01 and 02 Units in Trinidad

Amomax®-Casale Catalyst

Figure 2. AmoMax® -Casale Catalyst

AmoMax®-Casale ammonia synthesis catalyst is an innovative product developed through the collaboration between Clariant and Casale, using their expertise to make ammonia production more efficient and allow sustainable CO_2 reduction for ammonia producers. This catalyst is based on Clariant's proven and successful AmoMax® 10 wustite-based catalyst with more than 100 references worldwide and is customized specifically for CASALE converters (patent pending) with significantly improved activity compared to state-of-the-art iron-based catalysts. With 30% higher activity than the standard wustite based catalyst available on the market (figure 3), the combination and synergy of this catalyst with the ammonia converter technology provided by CASALE offer a design with exceptional performance in terms of lower synloop operating pressure and higher ammonia conversion.

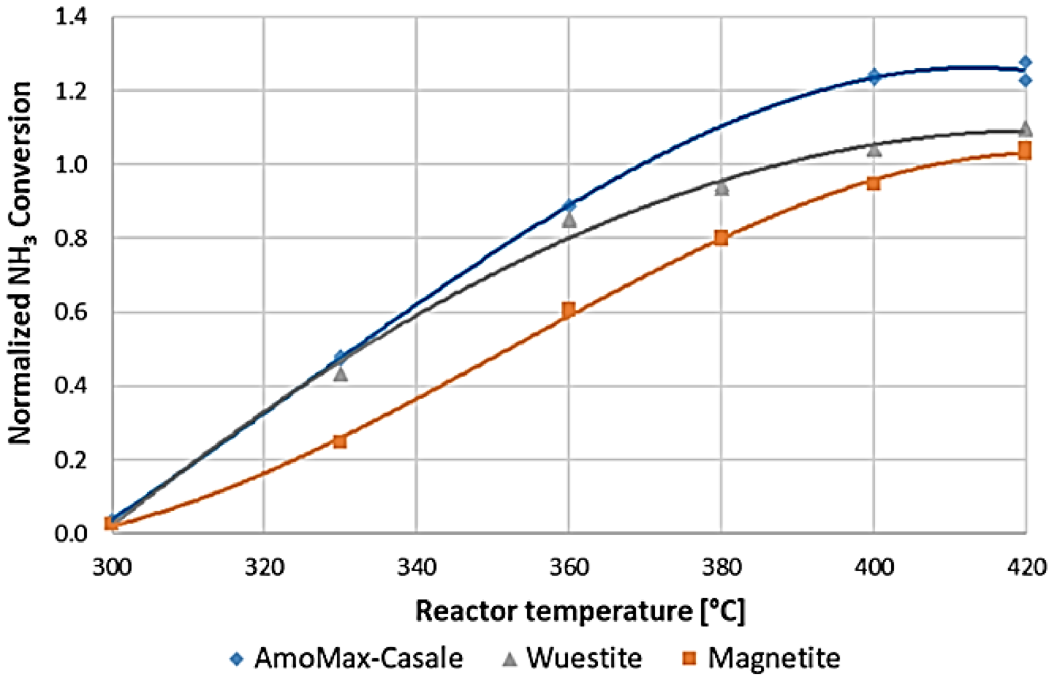

Figure 3. Catalyst Performance Comparison

These benefits are converted into energy savings, lower natural gas consumption or higher production if the limitation to a plant load increase is the synthesis loop[1].

In addition to the high activity, the AmoMax®-Casale catalyst shows higher poison resistance than the reference wustite-based catalyst. Figure 4 shows the comparative performance of AmoMax®-Casale at different oxygen concentrations in the feed at different temperatures

For the 01 plant EIP project, Casale and Clariant provided the specific technology to achieve the project goals. The ammonia converter was revamped with a 3-bed CASALE design in which the AmoMax®-Casale catalyst was strategically installed in the third bed of the converter, where the benefit of its high activity produced the highest impact considering the lower operating temperature and kinetic limitations. This bed represents 72% of the total catalyst volume of the converter. For bed one, pre-reduced AmoMax® 10 RS was installed, and for bed two, the oxide form of AmoMax® 10 was installed.

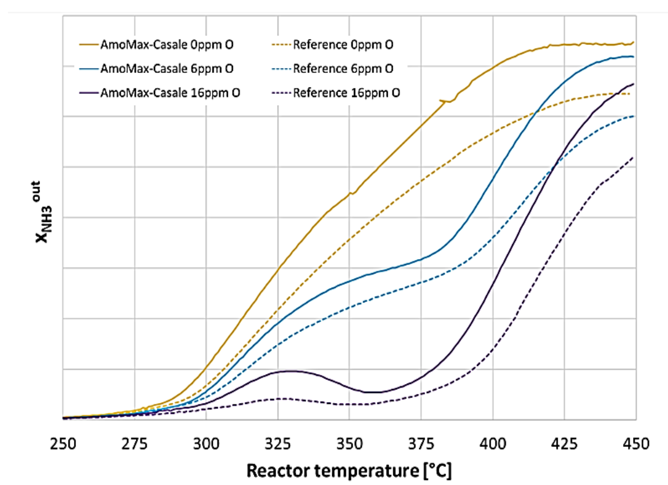

Figure 4. Poisons Resistance Comparison

[1] Recognizing this achievement, Clariant and Casale have won two prestigious awards: the Swiss Chemical Society's Sandmeyer Award 2021 and the ICIS Innovation Award 2020 for "Process with Best benefit to the Environment and Sustainability".

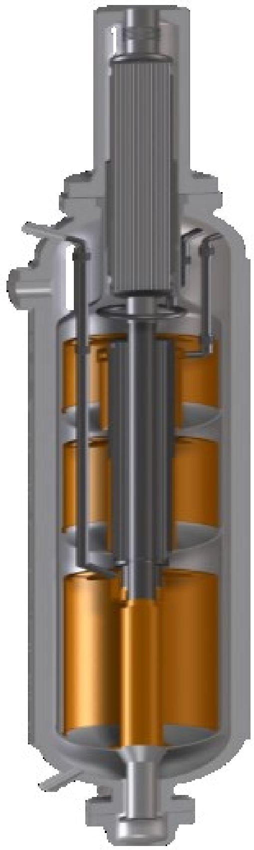

Figure 4: Casale Converter

Energy Improvement Project – Phase 1

The 01 Plant turnaround commenced on October 19th, 2019 and ammonia production was established on January 2nd, 2020. Nutrien, Clariant, Casale and JVIC collaborated to ensure that all parties were involved to ensure a successful installation for the basket and catalyst installation. JVIC was contracted for mechanical work and to perform the catalyst loading completed in 11 days.

The importance of successful loading and reducing the ammonia synthesis catalyst is imperative to ensure optimum converter performance. Clariant and Casale incorporated the use of specialty equipment with on-site technical experts to support these procedures.

Before the start of the shutdown, the new AmoMax®-Casale catalyst was screened, and the total fines were deemed low at less than 0.05% by weight. Clariant effectively screens catalysts before shipment to its customers. Thus, screening at the plant site is usually not necessary. However, in this case, the screening was done to remove any dust generated in transportation and as a precaution for this new product.

Casale's dense loading equipment and procedure for bottleneck type converters were used to get even density throughout the beds. Outages were regularly taken to calculate layer densities and monitor bed levelness by carefully weighing and tallying the catalyst loaded. Adjustments were made to the equipment to control the loading rate as necessary especially as the bed level increased up to the top section of each bed. All catalyst beds, including the AmoMax®-Casale 3rd bed, final density within expected range.

In preparation for the reduction, once again the Nutrien, Casale and Clariant team worked together to prepare for a successful reduction. Moisture liberated by the reduction process is cautiously monitored and the reduction rate controlled to prevent high water concentrations which have the potential of causing permanent damage to the catalyst. With traditional moisture measuring methods with long turnaround times for results, the reduction time could be longer than necessary as well as sudden increases in water concentration could go unnoticed for some time resulting in catalyst damage.

At the 01 plant, Clariant installed its portable ActiSafE™ moisture analyzer to monitor the reduction progress and achieve a safe reduction for optimum catalyst performance. This latest technology simultaneously measures water vapour and ammonia during the reduction by utilizing an NDIR (non-dispersive infrared) method continuously. This allowed for effective monitoring of the reduction with only occasional check-samples performed by the site's analytical laboratory.

Figure 5. Clariant ActiSafE™

The reduction commenced on Christmas Day December 25th. There were three (3) interruptions that occurred during the reduction. The first occurred early in the heat-up stage when high LEL was detected around the start-up heater burners. This was quickly resolved and heat up resumed. The second interruption was observed at the inlet sampling point of the converter. Lubricant oil poses a poisoning risk to the catalyst as it can effectively cover and block active sites and chemically poison the catalyst with contaminants such as sulphur in the oil. The oil level was closely monitored but remained stable, which confirmed the absence of a continuous leak. The third interruption occurred following the complete reduction of beds 1 and 2 and during the bed 3 reduction. The bed 1 temperature suddenly dropped, attributed to a moisture/ammonia carry-over event. Following this interruption, the reduction resumed, and it was observed that the exotherms in beds 1 and 2 gradually increased over time. All three interruptions had the potential to affect the activity and life of catalyst.

Plant Performance

The start of run evaluation of the 01 plant following the 2019 turnaround was done with some identified limitations in the front end of the plant. Nevertheless, some comparison is tabulated below pre and post turnaround at the same feedgas rates:

Conditions	Before Revamp	After Revamp	Change
Life	MOR	SOR	
Production (STPD)	1776	1788	+12 stpd
Syngas Compressor Discharge Pressure (psig)	2206	2039	7.5% lower
Inerts (mol%)	11.5	16.7	45% higher
Exit NH3 (mol%)	13.9	13.8	Same

Table 1. Key Performance Data

At the same plant feedgas rate, the synloop operating loop pressure was 167 psig lower, and production was 12 stpd more ammonia despite the 45% higher level of inerts in the loop caused by the frontend limitations. The performance was deemed exceptional especially considering the interruptions experienced.

A couple of years after the reactor revamping and catalyst activation, additional analysis was undertaken to understand if the catalyst could maintain its performance over time.

	Before Revamp	After Revamp	Change
Life	3 years before revamp	2 years after activation	
Production (STPD)	1754	1754	
Syngas Compressor Discharge Pressure (psig)	2215	1972	11% lower
Inerts (mol%)	9.6	10.9	14% higher
Exit NH3 (mol%)	12.9	14.3	11% higher

Table 2. Performance Data after Two (2) Years

As shown on Table 2, the comparison was carried out at the same plant rate and the recorded operating data shows that the improved performance has been maintained over 2 years.

With the lower operating loop pressure, significant energy savings were realized on the Steam Turbine for the Synthesis/Refrigeration Compression Train (103JT) estimated at 0.15 MMBtu/ST. This equates to approximately $500,000/year of cost savings at an assumed natural gas price of $5/MMBtu and a reduction in CO_2 emissions of 4,700 MT/year.

Due to continued front-end limitations and fluctuating feedgas rates due to gas supply curtailments, from SOR to the time of writing this report, the full benefit of the converter revamp could not be quantified. It is estimated that with the reduced inerts, reduced recycle flow, and optimization of the AmoMax®-Casale bed 3, further energy savings and production can be achieved. Nutrien's planned shutdown in 2022 is expected to address these limitations and complete Phase 11 of the EIP. This will allow the full potential of the revamp and AmoMax®-Casale catalyst to be realized.

Conclusion

The combined technologies and technical support from Casale and Clariant provided a relatively easy to implement an innovative solution for Nutrien Trinidad to incrementally improve the 01 plant's sustainability performance by reducing the plant's energy consumption and its CO_2 emission intensity. This first reference of the award-winning AmoMax®-Casale ammonia synthesis catalyst successfully demonstrates its value for a greener and less energy-consuming process for industrial-scale ammonia plants.

Acknowledgement

The authors wish to acknowledge the contributions of Nutrien's management, technical, operations, and maintenance teams. The commitment of these teams and partnership with Clariant and Casale were invaluable.

DISCLAIMER

This presentation is intended for educational purposes only and does not replace independent professional judgement. Statements of fact and expressions of opinion are those of the participants individually and, unless expressly stated to the contrary, are not the position of Nutrien, its directors, officers, employees, or agents. Nutrien does not endorse or approve and assumes no responsibility for the content, accuracy or completeness of the information presented

Challenges in Flange Excellence Management - Pitfalls during Re-Commissioning

During March-May of 2021, in the Grand Quevilly Ammonia Plant Turn Around, modifications were performed at the bottom fitting connection of the Synthesis Reactor. This modification was to avoid recurring leaks observed since 2009. At each start-up and shutdown during depressurization and re-pressurization, leaks would form at the low temperature of the synthesis loop. During each event, there was a risk of Hydrogen leaks and an explosive atmosphere in the lower part of the reactor was possible. The result was a potentially dangerous operating situation and restricted work in the area.

In early July 2021, while executing the start-up procedures, the synthesis section tripped, and a leakage and a fire at the synthesis reactor bottom occurred. The synthesis loop was depressurized, and the fire was immediately controlled and extinguished by the plant's emergency response team.

This paper aims to evaluate the pitfalls and areas of improvement during the design phase, work execution and re- Commissioning after this incident. A multidisciplinary team performed a complete incident investigation; the main damage was found in electrical cables and non-metallic components.

A thorough investigation was done to identify all critical success factors for the whole arrangement across all technical disciplines involved. After the incident, all repair activities were followed-up in strong and excellent collaboration with site personnel, vendor's assistance and Borealis Nitro group experts to achieve the required quality assembly. The technical documentation was reviewed to assure the quality of the repair; the surface sealing at the bottom flange was corrected by machining, and the new assembly was performed under close supervision and using an agreed procedure. As mitigation actions, new leak detection sensors and an improved nitrogen blanketing (Fire Extinguish) system were installed. After repair, a tightness verification test was done with nitrogen at 100 bar with satisfactory results.

Militza Lobaton, Laurent Steinmetz, Sarah Palmer, David Chazallet
Borealis Chimie SAS – Usine Grand Quevilly

Introduction

Plant de-/re-commissioning is a complex and comprehensive work process involving many interfaces and stakeholders.

The use of a standardized work process for daily maintenance, turnarounds, and projects will reduce process safety risks and operational risks. At the same time, it will increase work effectiveness and efficiency, ensure alignment between the different stakeholders, including interfaces and define/clarify the roles and responsibilities.

In combination with the execution of the work, the properly planned and managed ~~de~~-/re-Commissioning phase enables the restart of the production unit in time and reduces the process safety risk significantly.

In early July 2021, while executing the start-up procedures after Turnaround, the synthesis section tripped, and leakage at the synthesis reactor bottom occurred. Consequently, a fire broke out, which was immediately controlled by depressurizing the synthesis loop and extinguished by the plant's emergency response team.

Turnaround Synthesis Reactor Modifications and Incident

In the March-May 2021 Turnaround at the Borealis Grand Quevilly Ammonia Plant in France, modifications were performed at the bottom fitting connection of the Synthesis Reactor. Those modifications were to avoid the recurring leaks observed since 2009 at each start-up and shutdown during depressurization and re-pressurization at a low temperature of the synthesis loop. At each time, there was a risk of Hydrogen leaks forming an explosive atmosphere in the lower part of the reactor, resulting in potentially dangerous operating situations and restricted work in the area.

In 2015, the finite element evaluation indicated a problem of differential expansion, which leads to over tension in the bolts when the temperature rises. The gasket and its environment are subjected to excessive compression pressure, which is partially released by plastic deformation without causing any leakage at the time, but when the temperature decreases, the pressure on the seal becomes insufficient and may leak.

To solve the differential expansion indicated, a new solution using low alloy bolts (Superbolts®) combined with spring/elastic washers was implemented in the bottom fitting of the Synthesis Reactor.

This technique is normally used for higher temperature amplitudes. It consists of a stack of conical washers between the flange and the nut, creating a "spring" of strong stiffness capable of absorbing a few tenths of a millimeter of differential expansion without big load variation.[1]

Despite the modifications and introduction of Superbolts® on the reactor's bottom flange, a leak occurred once again in early July 2021. While executing the start-up procedures, consequently, a fire broke out which was immediately controlled and extinguished by the plant's emergency response team.

Immediately after the incident, an interdisciplinary investigation team consisting of local and corporate experts was formed to perform a thorough root cause analysis.

TAG	K-1501
Function	Synthesis Reactor
Fluid	Synthesis Gas
Manufacturer	Creusot Loire
Fabrication Year	1977
Const. Code	ASME Code Section VIII Div. 1+SNCT Code 1977
Material	1,3 Mo DV + SS 321
Design Conditions	Body: 288 Bar (28800 kPa / 4177 psi) / 300 °C (572 °F) Bottom: 288 Bar (28800 kPa / 4177 psi) / 450°C (842 °F)
Operational Conditions	213 Bar (21300 kPa) / 300°C (572°F)

Table 1. Synthesis Reactor Characteristics.

Figure 1. View of Synthesis Reactor

Figure 2. Modification implemented in Bottom Flange of the Synthesis Reactor – Superbolts® and spring washers.

De- and Recommissioning Process in Borealis

The following steps are the most important in the sequence of activities of a TA[2]:

- Planning
- Decommissioning
- Execution and Pre-commissioning
- Mechanical Completion
- Commissioning
- Start-up

In Borealis, the De- / Re-Commissioning steps are indicated in Figure 3 [3].

There are five phases with Four Milestones:

- Unit Operational / Planning and Preparation.
- Milestone – Ready for Commissioning.
- De-commissioning.
- Milestone – Ready for Execution.
- Execution and Pre-commissioning.
- Milestone – Mechanical Completion.
- Re-Commissioning.
- Milestone – Ready for Start-up.
- Startup.

The sequence of steps and the analysis of the main pitfalls that occurred during this particular incident are in the next section of this article.

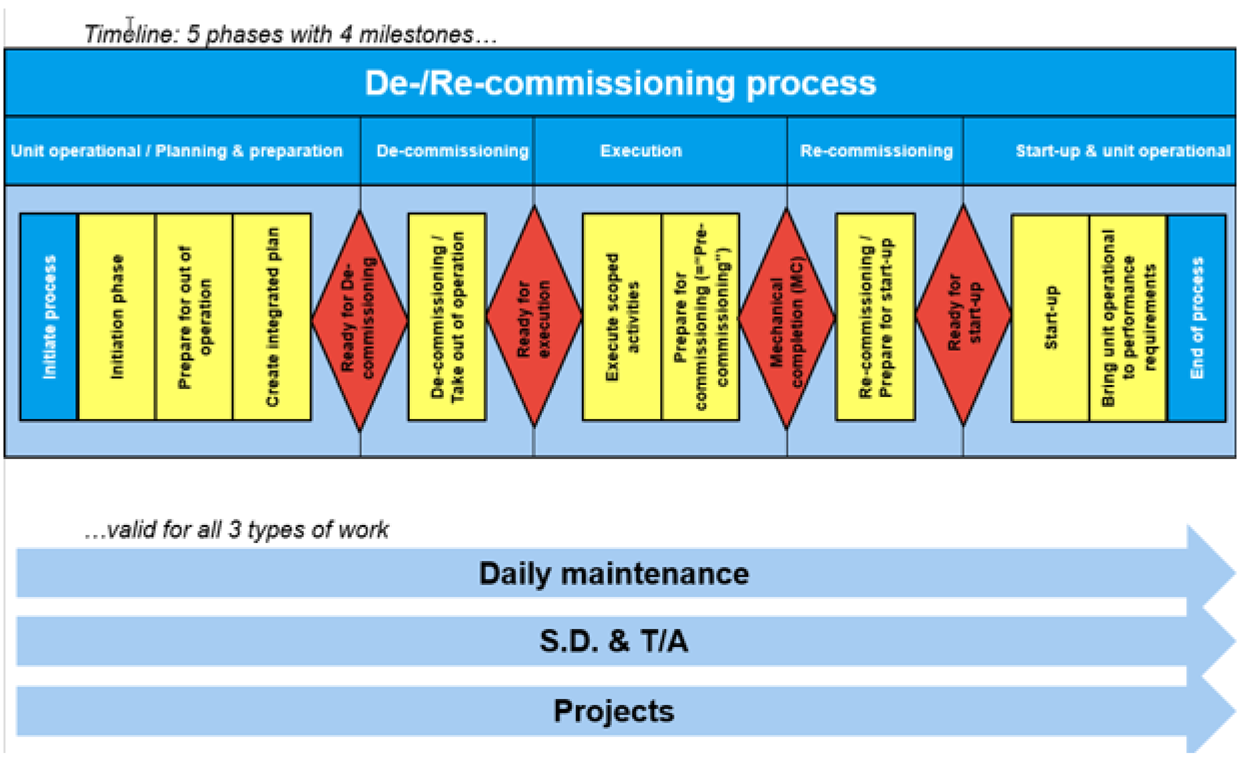

Figure 3. Borealis De- / Re-Commissioning Steps.

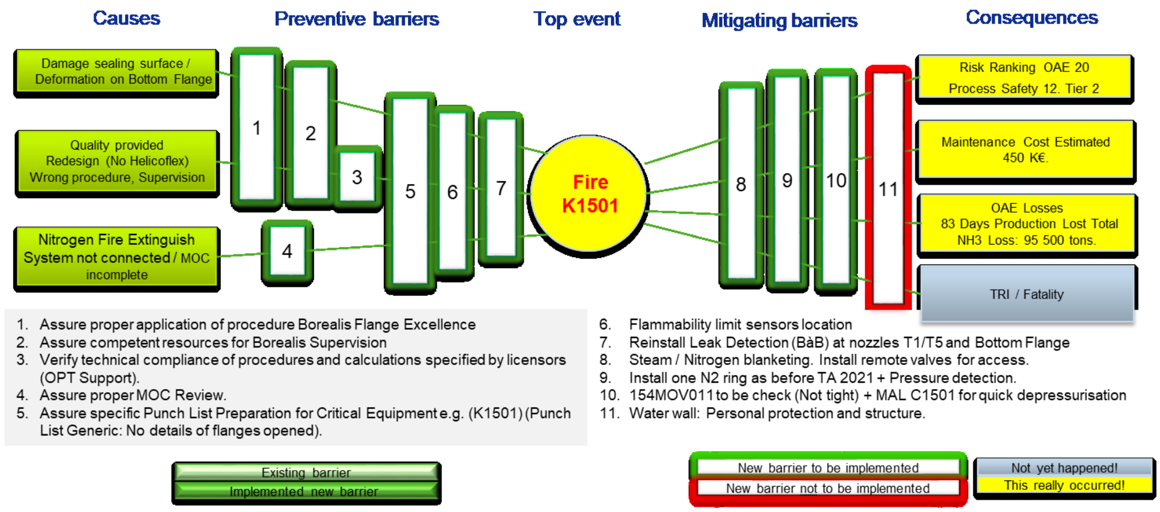

Figure 4. Bow Tie Showing Main Root Causes of Failure.

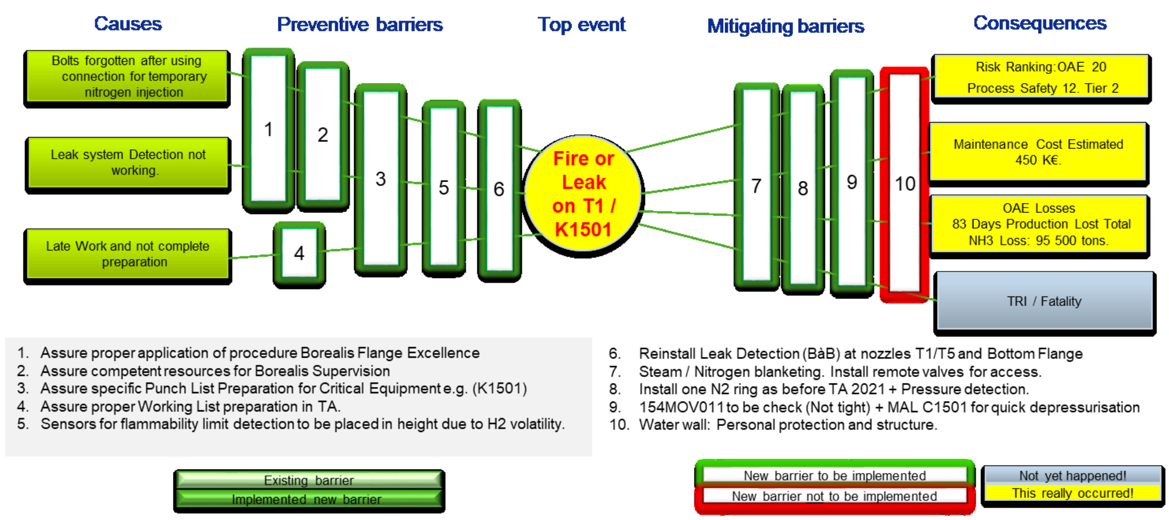

Figure 5. Bow Tie Showing Main Root Causes of Failure.

Unit Operational / Planning and Preparation

While the unit is still operational, this phase comprises of scoping of the work, setting-up organization, preparing for out of operation and creating an integrated plan (for de-commissioning, execution, commissioning, and start-up).

The incident investigation identified Lack of Borealis personnel for Project Management and supervision as one of the main root causes. This limited the depth of the technical scope review, and only the local team evaluated the procedures without involving the Static Equipment Experts, which resulted in loss of internal ownership. In addition, key evaluations requested in the minutes of a meeting before the Purchase Order award, were not included in the final Purchase Order text, and the final proposed procedure was submitted late in the planning of the Turnaround.

Another cause identified was the incomplete Management of Change (MOC). The removal of the ""Helicoflex" ®" gasket type, which secures the function of the leak detection system, was not considered in the MOC process. ""In French this system is called ""Bulle à Bulle"" or BàB, consists of tubing connecting the collection point to a beaker containing glycol water (see Figure 6).

In addition, the nitrogen Blanketing (Fire Extinguish) System was not reconnected after assembly of the bottom flange arrangement resulting in a further escalation of the incident.

Considering the investigation findings, a clear lack of proper flange identification was indicated as another main element leading to the incident and the consequential escalation.

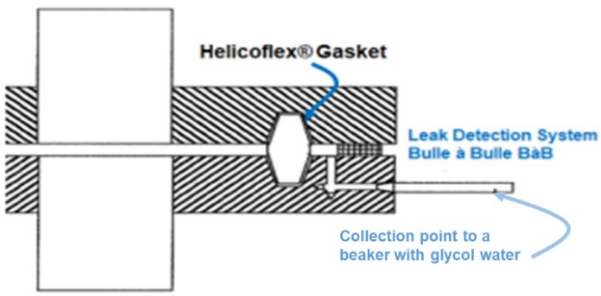

Figure 6. Leak Detection System Schema

Ready for De - Commissioning – Milestone

One of the early success milestones is the Preparation review to verify the whole planning and preparation phase. The following aspects are typically verified:

- Scoping finalized, management and communication plan exists.
- Risk assessment, HSE plan and MOC done.
- De-commissioning plan ready.
- Execution plan ready.
- Re-commissioning plan ready.
- Start-up plan ready.
- An integrated plan exists.

In the list, the issues related to management, communication and MOC were not identified as milestones.

As per the root-cause analysis, the communication deficiencies concerning the MOC were identified as one of the major contributors.

De-commissioning

In this phase, the unit is prepared for safe work execution by taking it out of operations. The main activities are:

- Taking the unit out of operation, de-energizing, emptying.
- Purging, flushing, steaming
- Inertization / Blanketing with Nitrogen
- Isolation from the process - blinding, blocking & bleeding, locking-out & tagging out.
- Field checks and verification.

Also in this phase, the lack of proper flange identification (Identified in the Unit Operational / Planning and Preparation phase), does not allow proper flange tagging in the De-commissioning phase.

Ready for Execution - Milestone

This milestone represents the formal approval to start a safe work execution by verifying all required actions before. (Normally Work Permit).

During the investigation, no deviations were found in relation to this work sequence.

Execution and Pre-commissioning

In this phase, the scoped work is executed, including quality checks and activities to prepare for commissioning. The main activities are:

- Scope execution activities:
    - Opening of lines and vessels for work (e.g., manholes).
    - Visual inspection, cleaning.
    - Execution of maintenance, repairs, and project work.
    - Pressure testing and inspections (legal).
    - Quality checks, including vendor and contractors.

- Punch list items clarified and agreed. Punch items classes:
  - Punch points Class AX – to be completed before DAC (Discipline Acceptance Certificate).
  - Punch Points Class A – to be completed before Mechanical Completion (MC) acceptance and re-commissioning can start.
  - Punch Points Class B – to be completed before start-up (RFSU).
  - Punch Point Class C – to be completed before closing of the work.
  - Punch Point Class D – to be carried out after closing.
- Safety reviews – MOC, HS5, PSSR (Pre Start Up Safety Review).

- Prepare for commissioning / (" Pre-commissioning ").
  - ""Dry"" tests, e.g., loop checks, valve movements, rotating direction tests, cold alignments. Special care has to be taken if early utilities (energy) are needed for these tests (e.g. electricity to test the rotation direction of an installed pump).
  - Hydro checks and leak checks (e.g., tubes of heat exchangers).
  - Cleaning, blowing, packing and internal installation.
  - Lubricants, oils, cooling media etc.
  - Granted discipline approvals
  - Punch lists
  - Master set of red-marked as-built documents (as required by the MOC process) are available for Operations and the Re-commissioning team (e.g., P&IDs and interlock descriptions in the control room, E&I hardware documentation, etc.).
- All lines and vessels closed. Flange tightening must be done carefully and following the Borealis maintenance best practices (Flange Excellence Protocol).

In this phase, the lack of ownership and absence of direct Borealis supervision for all steps (despite two external levels of supervision), affected the execution of the work.

The procedures for assembly were not adapted and lacked proper communication in the field. For example, in connection with the Borealis Flange Excellence procedure, [4] the flange's, inspection before reassembly, were not carried out, and the surface defects were noticed after the leakage. In addition, insufficient supervision during tightening was identified (four eyes verification), and improperly low torque was applied.

With the incomplete MOC, no Leak Detection System was installed (No Helicoflex Gasket), and the Nitrogen Blanketing ***(***Fire Extinguish***)*** System was not re-connected.

Furthermore, the punch list used for this activity was generic and not sufficient for the complexity of the modification; therefore, the quality checks needed in this phase were deficient.

Mechanical Completion - Milestone

Mechanical Completion is a critical key milestone to verify that the execution phase has been fully accomplished according to specifications, quality has been checked and deviations have been punch listed. Formal approval reflected in Mechanical completion check records is required to document that mechanical completion has been reached.

Even though the formal approval for mechanical completion was signed, due to the pitfalls mentioned above, some flange connections were not assembled correctly, and the Borealis Flange Excellence Protocol was not followed. Therefore, the mechanical completion was not fully achieved.

Re - Commissioning

Recommissioning is the phase where the unit prepares for safe start-up, the energy introduced, and punch list items corrected. The main activities are:

- Check if all work is mechanically complete, and all stakeholders sign the Mechanical Completion Certificate.
- Check if MOC is required.
- Execution of re-commissioning activities.
  - Final system flushing, purging, drying
  - Leak testing of the system/unit.
  - Process Isolation re-instated. All blinds, locks, and tags have to be systematically removed and signed off in the related documents (e.g. blind list, tag list, lock management system) to ensure that the installation is ready to be started-up.
  - Utilities put in service (energy introduced).
  - Flare and process chemicals ready to use. If needed for start-up preparation some process chemicals can already be introduced (e.g., feed tanks filled, washing media, catalyst beds/batches equipped, etc.)
  - ""In-situ"" functional tests. Functional testing of control loops, interlocks and sequences and rotating equipment run-in and dynamic tests.
  - Inertization (nitrogen or other). If it is needed for start-up preparation to remove oxygen from inside equipment (e.g., to prevent a flammable atmosphere) it is important to apply specific, locally defined inertization procedures (e.g., verification of oxygen/media maximum concentration, used pressure, duration, number of repetitions and needed measurements and devices)
  - Finalize punch list Items.
  - Interlock bypasses (hard/software) removed.
  - For S.D. and TA and for projects: safeguard that all clamps are removed (and the causative leak is repaired) in the decommissioned part and the follow-up register of installed temporary leak repairs is updated.
  - Re-instatement as per PID and other relevant documents. Hoses, end caps, status of drains/vents, LO/LC valve positions checked.
  - Passive and active safety systems are checked and operational (e.g., gas detectors, cameras, firefighting installations, etc..….).
- Ready for Start-Up safety check. A final check is executed in the field, confirming readiness for the start-up.
- Organizational readiness is safeguarded (setting up the team for success): all operators are sufficiently trained (Temporary) start-up documentation is available in the control room and Sufficient staff ready for action is available or organized for on call Start-up.

In this case, the activities described before recommissioning were partially executed.

First, the punch lists prepared for the Turnaround were generic and do not indicate the particularities of the Synthesis section and the changes done in the reactor bottom fitting.

The first tightness check with soaping was performed at 5 bars (500 kPa / 72.52 psi) at nitrogen grid pressure and the final tightness test of the synthesis section was performed with nitrogen at 100 bars (10000 kPa / 1450.38 psi). Unfortunately, the production personnel at site were not able to detect leakages because they were relying upon the Leak Detection System (BAB) that was not connected properly (Missing Helicoflex Gasket).

Ready for Start Up – Milestone

Ready for Start-Up is an important milestone to verify that activities related to re-commissioning has been accomplished and it is safe to introduce the process media and start-up of the unit. The formal approval of this milestone achievement is critical and is a mandatory requirement. In Turnarounds, the formal approval of the milestone is done by the operator responsible with the document Ready For Start-Up Certificate (RFSUC).

The (RFSUC) includes agreed actions from PSSR and HS 5 completed for projects.

The investigation clearly identifies that the Ready for start-up milestone was not accomplished because the previous critical milestones were not achieved in the work sequence. As the different stages of the De- and Re- commissioning process only partly or without sufficient level of detail,, a leak could occur, and ultimately, the incident escalation ended up in a fire.

Startup

As a result, the incident arises during the Start Start-Up procedures, producing the fire.

After the incident, all repair activities were followed-up in strong collaboration with site personnel, vendor's assistance and corporate group experts to achieve the required quality assembly. To ensure the repair quality, the technical documentation was reviewed, the surface sealing at the bottom flange was corrected by machining, and the new assembly was performed under close supervision using an agreed procedure. As mitigation actions, new leak detection sensors were installed, and the nitrogen blanketing (fire extinguisher) system was put back in operation. After repairs, a tightness verification test was done with nitrogen at 100 bar with satisfactory results.

Figure 7. Repair activities in Synthesis Reactor

Conclusions

Plant De-Re-commissioning is an interdisciplinary & comprehensive process with many stakeholders and interfaces that requires detailed and appropriate preparation and progress follow up.

The involvement of competent and experienced personnel with sound plant-specific know-how is needed for high-level HSE and technical review from design, purchasing, planning and all the phases of De-Re-commissioning.

Sufficient and competent personnel need to be assured to guarantee in-time proper work preparation and execution.

It is important to keep internal ownership in all the sequence of tasks required for successful de-recommissioning activities.

Depending on the complexity of the project, detailed and not generic Punch List need to be prepared.

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Pre-Commissioning, Commissioning, Start-up and Operating Experience of a Mega Ammonia Plant in Saudi Arabia

The process concept of a dual-pressure ammonia plant as invented by thyssenkrupp Uhde (tk Uhde) is well known to be the leading concept to achieve production capacities exceeding one million tons per year of ammonia in a single train. Four dual-pressure plants have been successfully commissioned in the last 16 years, contributing to about 2.5% of the world's annual ammonia production.

With the most recent sister plant of Ma'aden III, located at Ras Al-Khair in Saudi Arabia, a new chapter has been added to the story of the success of thyssenkrupp Uhde ammonia technology.

Although it is the fifth reference of mega plant, every project has its peculiarities. This text gives a project overview, focusing on pre-commissioning, commissioning, and start-up, including a presentation of the new loading process for ammonia synthesis catalyst. It also explores problems encountered during these phases and the lessons learned.

Dr. Bernd Mielke, Omer Yousif
thyssenkrupp Uhde

Metab Motlaq Alsolamy
Ma'aden Fertilizer Company

Introduction

This paper shares a project overview and two incidents which took place during the pre-commissioning and commissioning phase of the Saudi Arabian Mining Company (Ma'aden) Ammonia III project. The Ma'aden Ammonia III plant came on-stream successfully in March 2022. The plant is based on thyssenkrupp Uhde's 'dual pressure' technology [1] and is located in Ras Al Khair on the eastern coast of Saudi Arabia. The Ma'aden Ammonia III plant uses natural gas as a feedstock. The plant's nameplate capacity is 3,300 MTPD (3,638 STPD) of refrigerated ammonia with >99.8 wt.% purity.

Case Study 1: An unexpected oxidation and temperature increase of pre-reduced Once-Through (OT) Ammonia Converter catalyst took place during the pneumatic test of the ammonia synthesis section.

Case Study 2: During the commissioning phase, a moisture analyzer upstream of the OT Ammonia converter and downstream of a temperature swing drying unit showed cyclic readings based on day/night ambient temperature differences.

The root cause and lessons learned from both incidents are described below.

Project Overview

The Ma'aden Ammonia III Project, owned by Ma'aden Fertilizer Company (MFC) is a follow-on plant from the Ma'aden I and II Ammonia plants, commissioned in 2011 and 2016. These three 3,300 MTPD (3,638 STPD) ammonia plants at Ras Al- Khair (RAK) located in the eastern province of Saudi Arabia, are part of an industrial complex to produce di-ammonium phosphate (DAP) for the global fertilizer market. The new Ammonia III plant is integrated and interconnected with the existing facilities of Ammonia I and II plants and will share common utilities and export facilities.

The Ma'aden Ammonia III project was led by the main EPC contractor Daelim. The ammonia plant is based on the thyssenkrupp Uhde's 'dual pressure' design as used in the Ma'aden I and II Ammonia plants. Johnson Matthey has supplied all of the process catalysts for all three Ma'aden ammonia plants.

Figure 1. World scale thyssenkrupp Uhde 3,300 MTPD (3,638 STPD) ammonia plant

The project was awarded with an effective date of 1st November 2018 to Daelim Industrial Co. Ltd for the execution of the project as lump sum EPC contract, for 38 months to the time of completion, and engineering was started immediately in the Seoul, South Korea offices. Key project milestones are described in Table 1 below:

Milestone	Number of months from contract award date
Mechanical completion	34
First Ammonia production	37
Take over	42

Table 1. Key project milestones

The engineering planned duration was 22 months from the contract award date, and the execution strategy was to complete as early as possible, taking advantage of the fact was a similar unit to Ammonia II. Engineering achieved completion on 15th August 2020, 21.5 months after the effective date.

The EPC contractor also executed procurement activities from their offices in Seoul, South Korea. The contractor identified all the equipment that required early procurement and this was considered critical to the successful completion of the project. Particular attention was focused on placement of the long lead order to expedite the work to meet the project schedule. All purchase orders were placed as planned by February 2020, except for catalyst and chemicals, which were intentionally postponed to avoid unnecessary storage at site and increase the safety risks associated with it. Despite difficulties during the COVID-19 pandemic, in which various countries in Europe, as well as Asia (where key vendors were located), were shut down and manufacturing and delivery were disrupted, the project was barely affected by this, and procurement did not result in a delay.

Construction of infrastructure needs was commenced immediately after the contract award, with the site preparation work and the construction of temporary facilities. The project required extensive foundation work, which commenced in May 2019 to avoid any impact on other early civil activities. Some of the milestones were completed with small delays due to the impact of the COVID-19 pandemic, mainly due to manpower availability, as travel was heavily restricted to and from KSA.

Pre-commissioning activities commenced during the 24th month and supported the power energization, which was safely achieved on the 26th month. The NG line and Aux. Boiler were started up on the 30th month, only 1 month after baseline plan. This timely achievement allowed the project to commence steam blowing activities, considered part of the main critical path.

1st Production of Ammonia was achieved on the 10th of February 2022. After completion of catalyst reduction of the three ammonia converters, all ammonia plant process units were online by the 10th of March 2022.

Pre-Commissioning Phase Case Study

Exothermic excursion during the pneumatic test of Once-Through (OT) ammonia converter

After completion of catalyst loading with pre-reduced catalyst and boxing up of the OT ammonia converter, a pneumatic test of the Once Through Synthesis section was scheduled to take place on November 5th, 2021, at a test pressure of 149 bar g (2161 psig).

An external mobile N_2 generation unit was provided, and the test started at 03:00. During the late morning, a strong exothermic excursion was noticed in the upper part of the first bed of the OT reactor. Maximum temperatures reached 335 °C (635 °F) before stopping the pressurization and purging with plant-supplied N_2. The purge resulted in a reduction in temperature to around 155 °C (311 °F) on 15:30, November 6th, 2021.

At the time of stopping the pressurization, the loop had reached 15 bar g (217 psig).

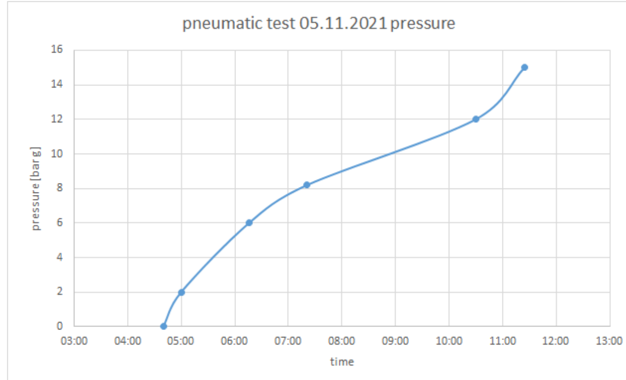

Figure 2. Pressure Profile

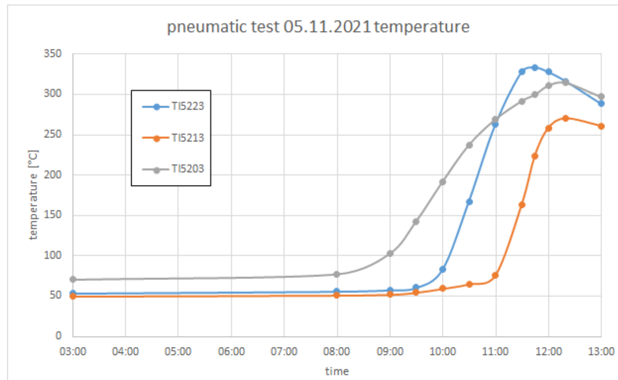

Figure 3. Temperature Profile

At 08:00, a temperature indicator in the upper bed of the OT converter, TI5203, showed a marked increase in temperature. At that point, the indication of TI5203 had already increased by 6.7 °C (12 °F) from the value at 03:00 when pressurization was started.

The temperature increase accelerated for some time. At 09:30, the indicator TI5223 showed an increase in temperature too, which accelerated much more quickly. Lastly, TI5213 began showing increased temperatures from 09:30, which began to run off at 11:00.

The maximum temperatures reached were high, 333.5 °C (632 °F) for TI5223, 270.0 °C (518 °F) for TI5213 and 314.5 °C (598 °F) for TI5203.

At around 11:30, the pressurization was stopped, and the OT Converter was purged with high purity nitrogen from the nitrogen header line. Nitrogen purging reduced the temperature, which reached around 170 °C (338 °F) on November 6th, 2021 at 07:30, and 150 °C (302 °F) at 15:00.

The graph in Figure 3 only shows the temperature trends for the upper sensors in the first bed of the OT converter. The lower sensors did not show a marked increase in temperature. This may indicate a localized event that took place in the upper part of the bed for most of its circumference, nevertheless did not reach the lower part of the bed.

Nitrogen generation

The nitrogen used for the pressurization of the loop was generated on-site in a unit using membrane separation technology. Membrane units do not reach sufficiently high purities of nitrogen. The nameplate of the unit on-site states a purity of 95 %. Upon questioning, the unit operator stated a possible purity of 99 %, which, in his word, was reached during the pneumatic test.

Possible causes

The oxidation of the catalyst caused the rapid increase in temperature. Because of its strong exotherm and slow heat transfer to the surrounding bed, the reaction is self-accelerating, resulting in an almost exponential increase in temperature. Due to the sudden generation of heat and its local entrapment within the bed, it is possible that much higher temperatures than shown by the indicators were developed locally. The pre-reduced catalyst is reverted to its oxidized state during the reaction.

Other causes, like a change of temperature caused by a change in pressure according to the Law of Amontons, are not likely. This relation is valid only for isochoric conditions and constant molar count, which is not given during the filling of the OT loop with nitrogen. No such change was observed during the initial stages of compression.

The underlying cause of the excursion is twofold. First, while the OT reactor was purged with nitrogen, the rest of the loop was still filled with air from the construction phase.

Second, the mobile air separation unit provided nitrogen of insufficient purity, which contained a much higher amount of oxygen than previously specified.

The oxygen from these two sources came into contact with the pre-reduced catalyst. The oxidation reaction did not start to accelerate until 08:00 at TI5203 strongly and even later for the other two temperature indicators, as the reaction rate is dependent on the partial pressure of oxygen, which is increased by oxygen intake into the loop and rising system pressure.

After a localized start, the oxygenation, which is strongly exothermic, produced much heat, some of which was transported to the surrounding catalyst, some was retained, and served to accelerate the reaction further.

Possible consequences for the catalyst

The oxidation of the synthesis catalyst is at least partially reversible. Due to sintering, there is a chance of a loss of activity, leading to a reduced active surface and incomplete reduction of the oxidized catalyst.

There is a chance the loss of catalytic activity is so slight it cannot be detected during normal operation. On the other hand, it is possible the bed suffered serious damage, up to not being able to reach its intended production rate. In the early days of operating the plant, this may not be noticeable, as the fresh catalyst is highly active and could mask the damage.

The probability of these two outcomes and the actual damage the catalyst suffered cannot be determined at this point.

Path forward after the incident

The following three options were identified after consulting the catalyst vendor Johnson Matthey as possible path forward scenarios:

Option 1 is to go with the second load of pre-reduced catalyst. Because of its unstable nature, pre-reduced catalyst cannot be transported by air freight and must be transported by ship. While there is catalyst available at present from the catalyst vendor, a tentative delivery time is 45 days to site from the day of placing the order. During reduction, the pre-reduced catalyst will be fully reduced within about 12 hours and provide heat for the reduction of the lower beds.

Option 2 is to change the catalyst load to an oxygenated catalyst, which can be transported by air freight and have a tentative delivery schedule of 10 days. At that time, the availability of oxygenated catalyst was unclear and under discussion with the catalyst vendor. During the first start-up the oxygenated catalyst will take approximately 4 days to fully reduce the first bed. However, due to its much shorter delivery time, it allows for a much earlier box-up of the synthesis loop and start-up of the reformer.

Option 3 is to borrow catalyst from a neighboring plant and utilize the excess catalyst at hand. There is a stock of oxidized catalyst leftover from loading the OT converter and loop converters. Further catalyst stock was available in-store at the AMP-I neighboring plant.

The commissioning team has decided to proceed with Option 3 because it offers the fastest resolution of the issue.

Rectification and lessons learned

Based on the possible damage to the catalyst, it was decided to replace the catalyst with a new charge.

For pneumatic test activities, liquid nitrogen with an evaporator unit was used to fill the loop as its purity typically is very high (99.99%).

The loop was purged thoroughly to remove residual oxygen within the piping and equipment. A sample was taken to determine the residual oxygen content.

Unloading and loading of catalyst in 1st bed of OT converter

A catalyst loading/unloading contracting company was contacted for the safe execution of the related activities. thyssenkrupp Uhde personnel were involved in the execution of the job to make sure that the job was done as per the required methodology, following all the safety precautions.

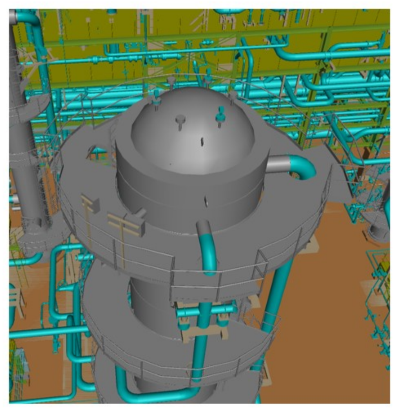

Figure 4. Ammonia OT Converter

Safety precaution highlights related to catalyst unloading handling of pre-reduced catalyst:

- Catalyst is active and starts to oxidize immediately in contact with oxygen. Hence blanketing with nitrogen from the bottom of the converter is required during the opening of the converter and unloading of the catalyst
- Catalyst temperature must be monitored during the catalyst unloading period
- Basic PPE (coverall, safety helmet, safety shoes, safety goggles, ear plugs) were required before entry into the site

- During all work, a safety warden was always present
- Safety precautions were taken during confined space entry under nitrogen (using BA set up, fall arrestor, safety rope and continuous monitoring of gas level was maintained using gas detectors)
- All the BA technicians had experience and underwent proper training with certifications during their work period
- All rescue items were kept ready (keeping medical oxygen and SCABA at location)
- Safety talks were given at each shift and following the safety rules laid out by the client
- Working at heights, safety precaution (safety harness to be worn)
- Proper signalman/flagman were there during any vehicle movement at site (crane /forklift and truck)
- Area barricading and certified lifting belts were utilized during lifting activities
- Safety precautions were taken while carrying out blinding and de-blinding activities and carrying out bolt torqueing (using proper gloves, finger saver, permissible limits per the torque value for the flanges to be followed, etc.)

Steps involved in the opening of OT converter top cover

For unloading the catalyst, the converter pressure vessel cover and bed covers needed to be removed.

- This included cutting of the lip seal gasket from the top cover, removal of thermowells and finally lifting of the converter cover
- After removing the converter top cover, a temporary cover was installed to keep the nitrogen blanketing intact and avoid air ingress (Refer to Figure 6)
- One thermocouple was inserted and temperature transmitters were connected to DCS for temperature monitoring during catalyst unloading/loading
- Cutting of internal piping and removal of cartridge cover bolts

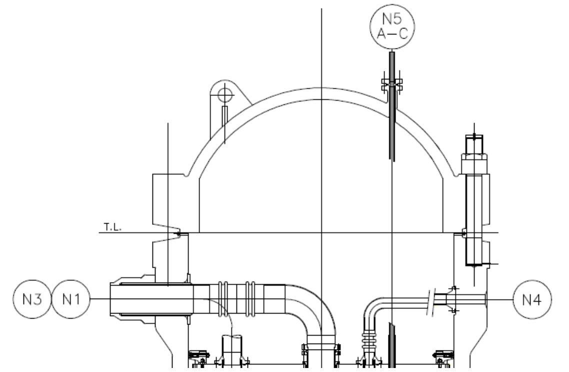

Figure 5. Ammonia OT converter top cover arrangement

Figure 6. Temporary converter cover

- Lifting of cartridge cover after loosening all bolts

Steps involved in unloading the pre-reduced catalyst

- Initial gas and temperature tests were carried out and to ensure a safe condition to perform the work
- Unloading of the catalyst by a vacuum truck. The unloaded catalyst was then collected in the vacuum truck filled with water ensuring the catalyst was not exposed to air at any point
- The unloaded catalyst was then transported to a designated place where it was dumped from the vacuum truck. Refer to Figure 7. While dumping, the catalyst was sprinkled with more water
- The bed was then vacuum cleaned, and video inspected

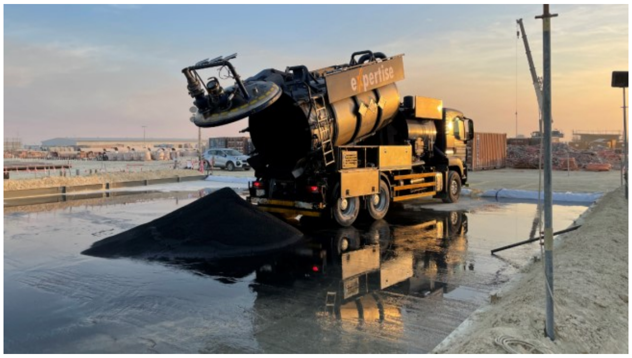

Figure 7. Vacuum truck unloading pre-reduced catalyst in a designated area

Figure 9. Loading hopper on top of converter

Catalyst loading with thyssenkrupp Uhde dense loading method

Conventional loading of ammonia synthesis catalyst by vibration is a very safe method to reach the required bulk density, but it is time-consuming. An alternative loading method is the Dense Loading method used by thyssenkrupp Uhde to provide higher density and faster loading times.

The advantages of this proprietary thyssenkrupp Uhde method was a significantly higher loading rate and, potentially, a higher bulk density. With this technique, each particle is given enough time for random fall in the ideal position and void space can be avoided. The single distribution of the particles over the whole cross-sectional area of each reactor bed enables a maximum loading rate to be achieved. No compacting by vibration after filling is necessary as dense loading is a continuous loading method.

Figure 8. Time consuming filling of catalyst in layers of 30 cm (12 inch) via hose and vibrator

Figure 10. Catalyst distribution cone inside the catalyst bed (patented by thyssenkrupp Uhde)

thyssenkrupp Uhde had successfully utilized the dense loading technique during the pre-commissioning phase of the Ammonia III project for catalyst loading of all three ammonia converters to increase loading efficiency and save time. This method uses multiple catalyst distribution cones of patented design, which are arranged above the catalyst bed in a circular way (see Figure 10). For filling, the catalyst was stored in a hopper located at the top of the converter with connections to each catalyst distribution cone via a unique distribution device.

The desired uniform catalyst densities were achieved with less effort and in a shorter period. Compared to the conventional catalyst loading method (see Figure 8), the catalyst loading was shortened by 3-4 times.

The upper catalyst bed (1st bed) loading with oxidized catalyst JM KATALCO 74-1A in the Ammonia Ma'aden III plant took place in the first half of December 2021. Due to its oxidized nature, the handling of the catalyst was easier to manage compared to the handling of pre-reduced catalyst.

Commissioning Phase Case Study

Mysterious false readings from synthesis gas moisture analyzer

In the Ammonia Ma'aden III plant, a synthesis gas drying unit was installed between the stages of the synthesis gas compressor. In this drying unit, the makeup synthesis gas is passed through molecular sieves to remove the remaining water vapor before the gas is introduced into the ammonia converter.

According to the ammonia catalyst supplier's operating procedure, the water content of the gas entering the converter should be kept as low as possible to avoid catalyst deactivation or damage. Typically, the desired value in this application is less than 1 ppmv moisture.

During the recent commissioning, the synthesis drying unit was put online. At the same time, the moisture analyzer reading downstream of the drying unit was swinging with an amplitude of up to 200 ppmv. This created severe doubts about feeding the synthesis gas into the ammonia converter. Calibration of the moisture analyzer was done, but the periodically high readings remained unchanged.

On the 4th day of having the synthesis drying unit online, a pattern in the moisture reading was noticed. A peak in moisture reading was observed daily at noon, which coincides with the highest ambient temperatures.

An effect on the moisture reading due to high levels of solar radiation was determined. Sunshades were installed and the analyzer box was continuously purged with plant air which would act as a coolant.

With this arrangement, the moisture reading became stable. The team was then able to proceed with the commissioning of the ammonia converter without any fear of deactivating the catalyst. The team later learned that this cyclic effect is defined by the so-called "Diurnal Effect" and is typical for analyzer systems that are in outdoor locations. Refer to Figure 11.

This effect is a real moisture change in the process sample system, associated process piping and vessels.

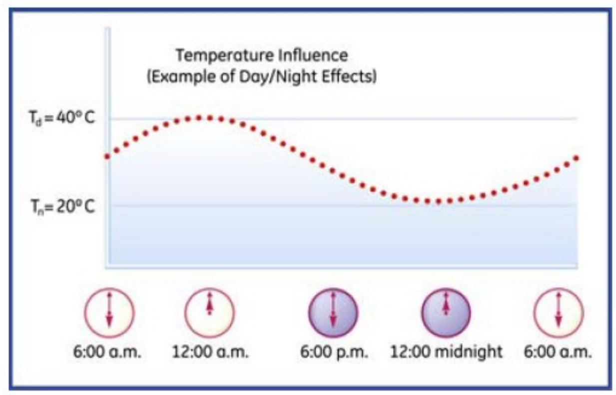

Figure 11. Diurnal effect of moisture analyzer

The polar nature of the water molecule allows for it to adsorb to all surfaces with a full or partial ionic charge like iron oxides on the inside of process piping or equipment. The equilibrium of the adsorption depends on the temperature.

Due to lower temperatures during nighttime, water molecules are adsorbed onto the inner pipe wall in equilibrium. This adsorbed water leaves the pipe wall during heating up at daytime and enters the gas sampling system.
The moisture analyzer reading was influenced by the swinging ambient temperature within the analyzer box. As soon as this temperature in the analyzer box was stabilized by plant air purging, no more fluctuations were observed any more.

The team has learned from this incident that environmental conditions could influence the moisture analyzer reading, and an appropriate arrangement should be considered to avoid analyzer box temperature fluctuation.

Summary

Ma'aden Fertilizer Company chose thyssenkrupp Uhde's 'dual pressure' technology for the Ammonia plant III as used in the earlier Ma'aden I and II Ammonia plants. The Ammonia III plant was started successfully and its energy consumption, production, product quality and emissions parameters were within specification. The team spirit and interactions between the Owner, Contractor and Licensor were the main contributors to the success of this project.

The gained experience during the Ma'aden Ammonia III project demonstrates that an effective pre-commissioning phase, together with an agile approach to coping with unplanned unexpected circumstances, would result in a smooth and time-saving commissioning phase.

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New Steel with High Resistance to Metal Dusting

Metal dusting, a type of corrosion resulting from catastrophic carburization of steels, is a prominent cause of damage for materials used at high temperature in ammonia and methane reformer plants. For preventing metal dusting, a new steel (25Ni-20Cr-3Cu-Si, Nb) has been developed. This steel shows no metal dusting in mild and moderate carburization environment. This excellent resistance is attributed to the hybrid-suppression technique, which is based on the formation of protective scales and the reduction of reactivity with CO gas. The HAZ (Heat Affected Zone) of this new steel also shows higher resistance to stress relaxation cracking than that of 800H after aging treatment without PWHT (Post Weld Heat Treatment).

Masaki Ueyama
NIPPON STEEL NORTH AMERICA

Yuya Matsuda, Shogo Aota, Takahiro Osuki
NIPPON STEEL CORPORATION

Introduction

Metal dusting is a type of corrosion resulting from catastrophic carburization of steels and alloys that occurs in carburizing environment. It is a prominent cause of corrosion damage for high temperature materials used in ammonia, methanol, dimethyl ether and gas-to-liquids production plants [1-4]. It is often encountered when steels and alloys are exposed in carbon-bearing gas mixtures including CO, H_2, CO_2 and H_2O. Once the metal dusting occurs on the metal surface, a pit like wastage continues to grow during exposure to the carbon-bearing gases at intermediate temperatures. This catastrophic wastage from metal dusting is a more severe problem than carburization because it seriously decreases service life of the materials.

It is known that nickel alloys including aluminum like UNS N06601 form protective oxide scale at high temperature to prevent metal dusting. However, aluminum containing alloy shows embrittlement due to gamma prime phase precipitation after long time exposure at high temperature.

Therefore, new steel with high resistance to metal dusting and good ductility has been developed through a hybrid-suppression technique utilizing silicon and copper; i.e. formation of protective oxide scales and reduction of reactivity with CO gas in syngas environments [5]. As illustrated in Figure 1, protective oxide scales such as Cr_2O_3 and SiO_2 function as a barrier against CO attack during a certain period. A solid solution of copper in the metal matrix plays a role of the surfactant-mediated resistance on the metal surface where any defects of the oxide scale occurred. In the meantime, the healing of the protective oxide scale can be accomplished successfully, resulting in lack of a pitting nucleation.

In this study, we conducted the Charpy impact test using various specimens and the laboratory metal dusting test.

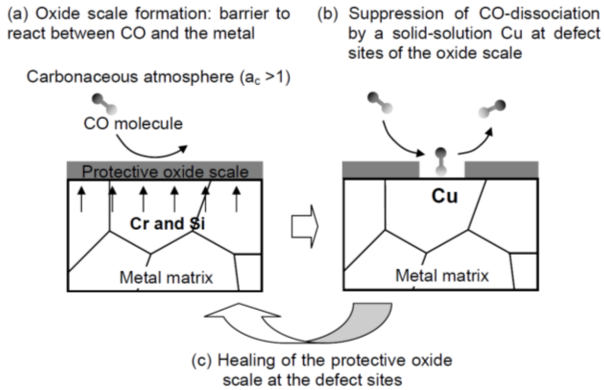


Figure 1. Hybrid technique against metal dusting [5]

Experimental

Charpy impact test

Toughness of the new steel and Alloy 693[6], a nickel base metal dusting resistant alloy containing 3%Al bearing Ni-base metal dusting resistant alloy, were evaluated by Charpy impact test. The chemical composition of them are listed in Table 1. The ingots of the alloy were made in a small-scale vacuum furnace. This was hot forged and hot rolled to plates of thickness 12 mm. After annealing at 1150 °C in air, these plates were cold rolled to a thickness 8.4 mm and then subjected to solution heat treatment at 1180 °C.

(mass%)

	C	Si	Mn	Cu	Ni+Co	Cr	Al	Other
New Steel	0.07	1.0	0.8	3.0	25.1	20.0	0.07	-
Alloy 693[6]	0.02	0.3	-	-	59.6	30.1	3.0	Nb

Table 1. Chemical compositions for impact test

Then, these plates were subjected to aging heat treatment in the atmosphere at 600 to 1000 °C for 1000 and 3000 hours respectively. After that half size of Charpy impact test specimens (5mm thick with 2mm V notch) were taken from aged plates. Then Charpy impact test was performed at 0 deg. C based on ASTM E23.

Metal dusting test

The new steel and three existing alloys were evaluated. Their chemical compositions are listed in Table 2. The ingots of the alloys were made in a small-scale vacuum furnace. These were hot forged and hot rolled to plates of thickness 12 mm. After annealing at 1150 °C in air, these plates were cold rolled to a thickness 8.4 mm and then subjected to solution heat treatment at 1180 °C.

Coupon specimens were cut from the tubes or sheets to 3 x 15 x 20 mm, and a small hole of 2 mm ϕ was drilled in them for support. Their surface was polished with No. 600. A metal dusting test was conducted in a horizontal reaction chamber. The reaction gas composition of 45%CO, 42.5%H_2, 6.5%CO_2 and 6%H_2O (in vol.%), which gives the carbon activity (Eq. (3)) of 5 (without graphite precipitation) and oxygen partial pressure of 1.04 x 10^{-24} MPa at 650 °C obtained from the Eq. (1) and (2), respectively, was chosen to simulate the actual reforming plants.

$$CO + H_2 = C + H_2O \qquad (1)$$

$$2H_2O = 2H_2 + O_2 \qquad (2)$$

$$a = \frac{\left(P \times \frac{m_{CO}}{100}\right)\left(P \times \frac{m_{H2}}{100}\right)}{\left(P \times \frac{m_{CO2}}{100}\right)} \times K \qquad (3)$$

P; Total Pressure
m_X; Mole Fraction
K; Equilibrium Constant

The cycling heating test consisted of heating at 650 °C for 50 hours and cooling down to 100 °C in 5 hours, followed by holding temperature at 100ºC for 0.5 hour. After maximum 10 cycles (corresponds to 500 h heating), the test specimens were cooled down to room temperature. The coke on each specimen was removed by ultrasonic cleaning in acetone, and then metallographic cross section of the specimen surface was investigated using an optical microscope.

(mass%)

	C	Si	Mn	Cu	Ni+Co	Cr	Al	Other
New Steel	0.07	1.0	0.8	3.0	25.1	20.0	0.07	-
Alloy 800H	0.07	0.4	-	0.1	30.5	19.8	0.5	0.5Ti
Alloy 601	0.02	0.4	-	-	60.0	23.0	1.4	-
Alloy 690	0.02	0.3	-	-	59.6	29.9	-	-

Table 2. Chemical compositions for metal dusting test

Results and Discussion

Charpy impact test using aging specimens

Figures 2 and 3 shows the Charpy impact value of the new steel and Alloy 693[6] after aging heat treatment. It has been confirmed that the toughness after aging of the new steel is superior to that of Alloy 693.

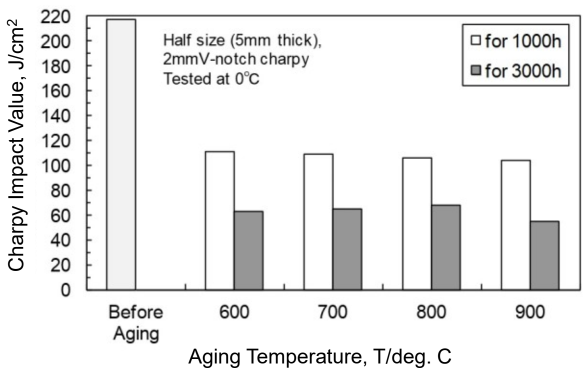


Figure 2. Charpy impact value of new steel after aging

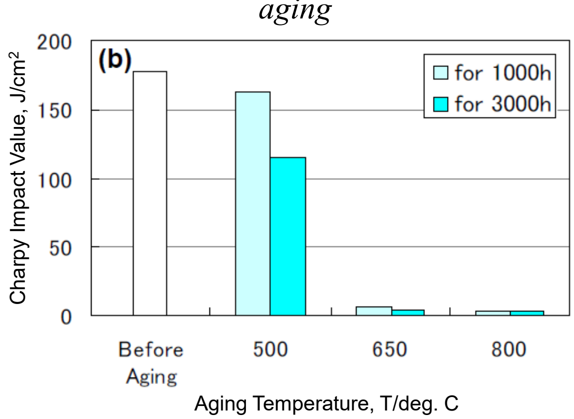


Figure 3. Charpy impact value of alloy 693 after aging [6]

Metal dusting test

Figure 4 shows the appearance of specimens after the test and Figure 5 shows the microstructure of specimens after the test.

The specimens of the new steel had no pit after 500 h corresponding to 10 cycles of the cyclic heating test. On the other hand, Alloy 800H had pits on their surface.

These results demonstrate that the hybrid-suppression technique of the new steel is reliable to prevent metal dusting.

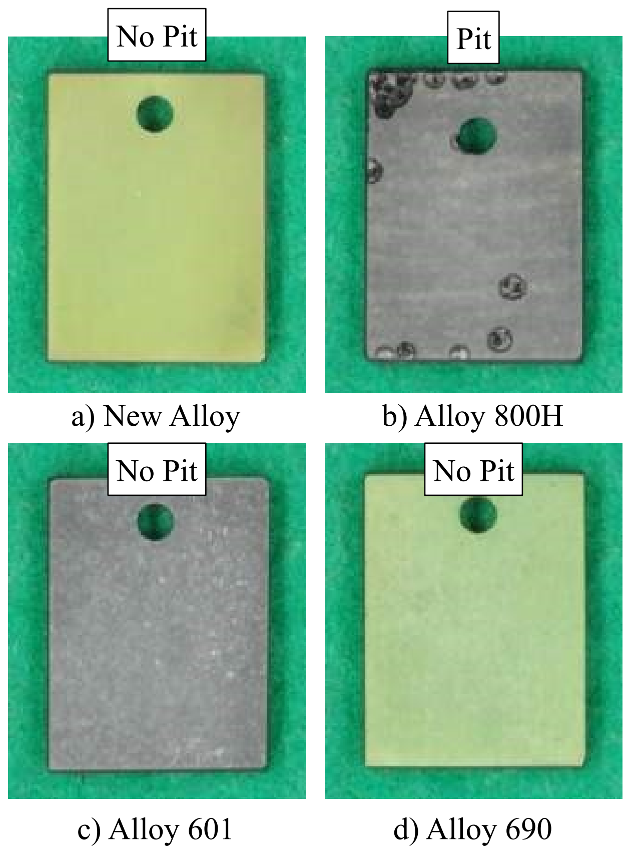
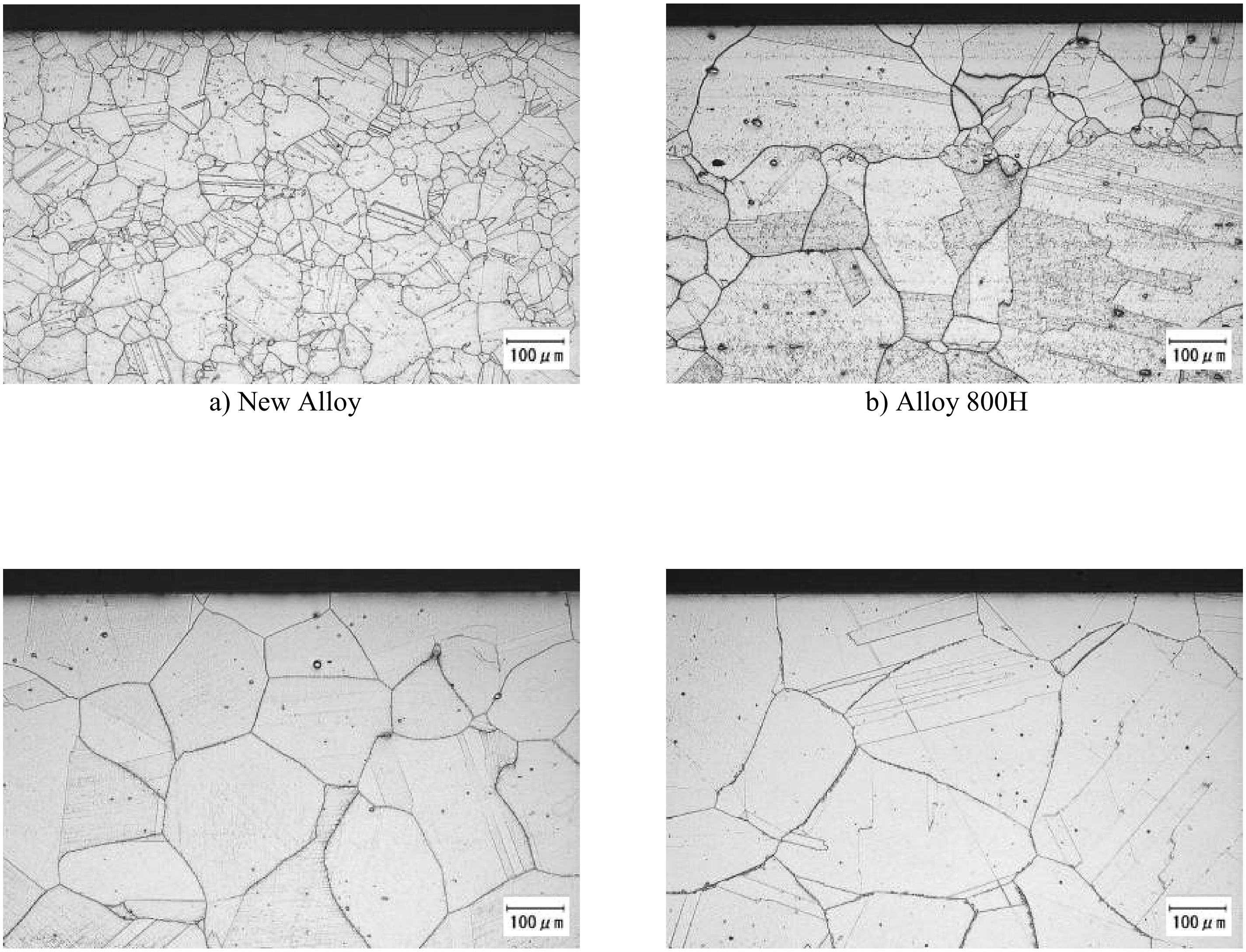


Figure 4. Appearance of specimens after metal dusting test



a) New Alloy

b) Alloy 800H

c) Alloy 601

d) Alloy 690

Figure 5. Microstructure of specimens after metal dusting test

Conclusions

Toughness after aging treatment of the new steel had been investigated. In addition, long-term tests were conducted for several alloys including the new steel to evaluate the metal dusting behavior upon cyclic heating and cooling.
Obtained results are as follows:

1. The new steel has superior toughness after aging to Al bearing Ni-base alloys (Alloy 693).
2. The new steel has better resistance to metal dusting than alloy 800H.
3. The hybrid-suppression technique, a new concept for prevention of metal dusting, is based on the formation of protective oxide scales and the reduction of reactivity with CO gas in syngas environments. The test results have proven that the novel technique holds great promise in a variety of severe carburizing environments.

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Comparative Analysis of Hazard and Operability Study (HAZOP) and Systems Theoretic Process Analysis (STPA)

The objective of the study described in this paper was to evaluate and compare STPA with the standard HAZOP method commonly used for Process Hazard Analysis (PHA). Both methods were applied by independent and qualified expert teams to discover flaws in a real system. Neither team had any preexisting knowledge of flaws before applying the methods. The system contained real flaws that led to adverse events during the operation of the system. The outcomes and recommendations of HAZOP and STPA are compared to determine what differences exist, if any, and identify whether critical gaps exist for modern process industry applications. The HAZOP and STPA results are also compared to the corrective actions produced after the hazardous and costly incident during operation. The STPA method was found to capture hazardous human and automation related behaviors that were missed by HAZOP, and STPA generated critical recommendations missed by HAZOP that would have prevented the real adverse events. The STPA results anticipated the causes and corrective actions that were otherwise only discovered after the hazardous and costly event during system operation.

Faisal Jamal, Kamran Arif, Arooba Arooj
Corporate HSE & Technical Services, Fatima Group, Pakistan

Dr. John P. Thomas
Engineering Systems Lab, Massachusetts Institute of Technology (MIT), USA

Introduction

Major incidents involving hazardous chemicals that are toxic, reactive, explosive, or flammable continue to occur throughout the process industries despite the use of standard methods to prevent such incidents. Investigations identify proximal causes and produce corrective actions to address weaknesses that were discovered only after significant losses occurred. Rarely does the investigation go far enough to ask why the hazard analysis failed to identify the weaknesses or failed to implement effective corrective actions before the system was put into operation. Do standard hazard analysis methods like HAZOP have critical weaknesses that overlook certain types of causes or interactions? Can alternative methods like STPA produce more effective results given the same information before an incident? This paper compares HAZOP and STPA, including empirical results from two expert teams that applied each method.

Background

Overview of Preventable Incidents

Major incidents have been happening for decades. A 1974 incident in Flixborough, Lincolnshire, England [1] resulted in 28 deaths and 36 injuries. A 1984 incident in Bhopal, India [2] resulted in more than 2,000 deaths. A 1989 incident at Phillips Petroleum Company, Pasadena, USA [3] resulted in 23 deaths and 314 injuries. A 1990 incident at BASF, Cincinnati, USA [4], resulted in 1 death and 71 injuries. A 1991 incident at

IMC, Sterlington, USA [5], resulted in 8 deaths and 120 injuries. A 2005 explosion at Texas City Refinery, USA [6] resulted in 15 deaths and 180 injuries. A 2010 incident on the Deepwater Horizon, USA [7] resulted in 11 deaths and the largest marine oil spill in history. A 1976 Ammonia loading line rupture at Swedish Fertilizer Company [8], resulted in 2 deaths. Meanwhile, many more minor incidents continue to occur in the process industries.

This study evaluates gaps in the popular HAZOP-based hazard analysis as performed by professional teams on real applications and compares the results to STPA-based hazard analysis also performed by professionals on real applications. The results are compared to real loss events experienced during operation of the system that were unknown to both teams.

Hazard and Operability Study (HAZOP)

HAZOP is one of the most utilized Process Hazard Analysis (PHA) techniques and is an important element of OSHA Process Safety Management (PSM). HAZOP plays a pivotal role in identification, evaluation and control of all possible hazards involved in the oil & gas and petrochemical process industry which may lead to catastrophic events such as loss of primary containment, fire, explosion, injuries and / or environmental excursions.

The HAZOP technique was introduced in the 1963. Later, it was further developed by ICI and Chemical Industries Association in the early 1970s, however the technique only started to be more widely used within the chemical process industry after the Flixborough disaster in 1974. Over time, the importance of risk management and the acceptance of HAZOP grew throughout the chemical industry. HAZOP eventually became a global standard with IEC 61882 [9].

HAZOP is based on the idea that risk events are caused by deviations from design or operating intent. Deviations are identified by using guide words such as “more”, “less”, or “reverse” flow. This approach can help stimulate the imagination of team members when exploring potential deviations. The HAZOP technique has been useful in the process industries to identify potential hazards and causes and to identify necessary mitigations to prevent them.

A number of HAZOP modifications have been proposed in the literature, but none of these have led to widespread industry adoption to the extent HAZOP has. Modifications include Computer HAZOP (CHAZOP) [10], Safety Culture Hazard and Operability (SCHAZOP) [11], Human HAZOP [12], and Programmable Electronic System HAZOP (P.E.S. HAZOP) [13].

System Theoretic Process Analysis (STPA)

System Theoretic Accident Model and Process (STAMP) is a novel accident causality model based on systems theory and systems thinking [14]. It integrates into engineering analysis the causal factors in our increasingly complex systems such as software, human-decision making and human factors, new technology, social and organizational design, and safety culture. System Theoretic Process Analysis (STPA) is a hazard analysis method based on the STAMP model.

STPA has been adopted on a wide range of applications across several industries including nuclear power [15], nuclear weapons [16], oil & gas [17], aviation [18], automotive and autonomous vehicles [19], and others to control new hazards caused by complex software, incorrect engineering assumptions, unsafe automated behaviors, human interactions, and dysfunctional interactions between systems.

STPA considers component failures and deviations from design intent, but also considers unsafe behaviors that match the design intent with or without a deviation. Examples include components that correctly satisfy all requirements (but the requirements are incomplete or incorrect), components individually work as designed but collectively interact in unsafe ways, humans that follow defined rules and procedures (but the rules and procedures are incomplete or incorrect), or a flawed design or operating intent that is based on incorrect assumptions about the system or the environment. STPA anticipates losses that are caused by unsafe *interactions* of system components with or without a deviation.

Organizations that have adopted STPA report several advantages over traditional hazard/risk analysis techniques including:

1. Capability to analyze very complex systems in less time
2. “Unknown unknowns” that were previously only found in operations can be identified in the development process and either eliminated or mitigated.
3. Ability to begin earlier in concept development to assist in identifying safety requirements and constraints. These can then be used to
   a) Design safety (and security) into the system architecture
   b) Eliminate costly rework involved when design flaws are identified late in development or during operations.
4. Maintaining complete traceability from requirements to all system artifacts, enhancing system maintainability and evolution.
5. Coverage of software behaviors and human operators in one unified analysis. Neither is analyzed in isolation, ensuring a more comprehensive analysis that considers environmental and contextual factors that lead to losses.
6. STPA provides a common easy-to-understand format that documents system functionality that is often missing or difficult to find in large, complex systems.
7. STPA can be easily integrated into the system engineering process and into model-based system engineering.

<u>Comparison Methodology</u>

This study compares results from HAZOP and STPA performed on a real complex application by qualified professionals.

A real fertilizer plant application with both automated and human controls was selected. The application was analyzed by a qualified HAZOP team before commissioning and operation. However, an incident occurred on the HAZOP-ed application.

STPA was performed on the same system to identify the weaknesses. Each team included qualified method experts with appropriate training and over a decade of industry experience applying the selected method.

The application contained weaknesses and flaws that were recognized after it was put into operation. Both analysis teams were blind to the weaknesses and the operational events, with no knowledge of either when they performed the hazard analysis. Both teams were limited to general design information available before the application was put into operation.

<u>Case Study Selection</u>

A study of fertilizer plants and past incidents was conducted to understand the types of causes that have not been adequately prevented by HAZOP in the past and to help select a candidate application to evaluate the differences between HAZOP and STPA.

Fertilizer plant incidents published in American Institute of Chemical Engineers (AIChE) Technical Manuals and other sources were surveyed to identify past incidents. A study of 30 years of incidents revealed that the underlying causes of were directly or indirectly linked with gaps in the HAZOP exercise. A summary of a few of the reported events is provided in Table 1 below.

SN	Incidents	Year	Root cause
1	Failure of Level Bridle in Benfield Service	2016	Mechanical overload due to localized internal corrosion as per the Materials analysis. The process safety review however looked at the lack of the HAZOP to identify the presence of the corrosive liquid in the bridle.
2	Explosion of an aqueous Ammonia scrubber tank	2010	Explosion of a trapped hydrogen/air mixture which had accumulated in dead pockets of the aqueous ammonia scrubber tank. Incomplete/inaccurate HAZOP did not address this risk.
3	Foaming of Catacarb™ CO_2 Removal System leads to Methanator Runaway Reaction and Expander Fire Incident	2015	Methods for analyzing Suspended solids misguided the operational staff. No built in Expander Trip Logic upon closure of Methanator inlet valve caused no seal gas availability and process gas ingress into Expander Oil Console caused fire incident.
4	Catastrophic Explosion in the CO_2 Removal Unit of an Ammonia Plant	2015	Reverse flow of amine solution due to absence of check valves resulted in explosion.
5	Explosion of a Benfield Solution Storage Tank	1985	Hydrogen gas entered the Benfield solution storage tank combining with sufficient oxygen and was ignited by a static charge causing complete destruction of the tank.
6	Failure of Methanator Feed Effluent Exchanger Tubes due to Benfield Solution Carry over from CO_2 Absorber	2014	Absorber Demisters design failure. Low load operation resulting in bypassing of demisters. The gas washing system of Absorber KOD not in continuous service.
7	Failure of Semi-Lean Catacarb Pump due to Reverse flow	2004	Reverse flow of process gas resulting in the reverse rotation of the pump leading to catastrophic failure of pump and driver.
8	Case Study of CO_2 Removal System Problems/Failures	1999	Casing vanes of hydraulic turbines were found to be eroded due to wrong location of valve.
9	Explosion of Hydrogen in a Pipeline for CO_2	2001	Hydrogen enriched gas had entered the pipeline, nitrogen purge had not been effective, air had leaked into the line and formed an explosive mixture, and the mixture had ignited.
10	Failure of NG compressor train	2002	Install an additional trip valve at the inlet steam line of turbine. Also recommended detailed HAZOP of turbomachinery.

Table 1: Summary of Various Reported Events involving HAZOP-ed Processes [20]

HAZOP is popular but not perfect and costly incidents still happen in HAZOP-ed processes. Common HAZOP limitations identified from these events include limited consideration of automation behavior, human factors and interactions between subsystems, components, or nodes.

Comparative Analysis: HAZOP & STPA

A case study was selected based on a real system at Fatima Fertilizer Limited (FFL). Health, Safety and Environment (HSE) is the high priority of our operations. FFL is a Guinness World Records title holder setting a new standard of safe operations with more than 66 million safe man-hours as of 31 March 2022 - the highest in the global fertilizer industry. The team is committed to continuous improvement and innovation in the HSE performance. Thus, FFL was selected as an ideal candidate to provide the resources needed to compare HAZOP and STPA on a real system.

CO_2 removal system with automated and human controls was selected to share the findings of the comparative analysis in this paper. FFL met all industry standard practices for conducting the

HAZOP study as a part of detailed engineering and implementation of the recommendations.

History of FFL Ammonia Plant

The FFL Ammonia plant operating at Sadiqabad, Pakistan was designed by CF Braun & Co. Alhambra California (purifier technology) and built in 1967. This Plant was initially operated by Exxon. It was later bought by Kemira in 1985 and kept the same operational philosophy with exemplary service factor. This plant was shut down in 2000 for business reasons. FFL relocated it from the Netherlands to Pakistan in 2007 and started successful production in 2010.

Description of CO_2 Removal System

CO_2 removal is a vital process (Figure 1) in Ammonia manufacturing as CO_2 present in raw Syn Gas is a poison for Ammonia synthesis catalyst. In the FFL plant CO2 is removed by absorption in potassium carbonate solution (~30% by weight) in proprietary Catacarb^{TM} process. The absorber tower consists of two packed sections. In the lower section, the gas is scrubbed with semi-lean Catacarb solution. In the upper section, lean solution is used to remove CO_2. Process Gas is distributed beneath the bottom packed beds. The lean and semi-lean Catacarb streams are sprayed into the tower over the packed beds. Purified Gas flows from the top of the tower to a knockout drum (KOD) and the carried-over liquid is drained from the bottom of the KOD to the drain system for recovery via a level controller. Purified Gas from the top of the KOD is sent to the Methanator to further remove the oxides to ppm level in Ammonia synthesis gas. Rich Catacarb solution from the hydraulic turbine flows into the top section of the CO_2 stripper. The regeneration of Catacarb solution also takes place in two stages with semi-lean solution being pumped out halfway down the stripper and the lean solution from the base. In the stripper tower, the rich Catacarb solution is stripped by depressurization and by heating with steam vapors generated by reboilers at the base of the tower. The rich solution passes through a hydraulic turbine to partially recover pumping power for the semi-lean pump which pumps the semi-lean solution from middle section of the stripper to midway up the absorber column. The lean solution is pumped from bottom of the stripper tower to the top of the absorber column

Incident Description [21]

On 29th August 2012, Ammonia plant was in restart phase after 10 days of planned shutdown. Various problems were encountered including foaming in Catacarb causing excessive and repeated solution carryover to Methanator. On 3rd September, Methanator temperature increased beyond the trip limit of 806°F (430°C) but Methanator trip logic did not actuate automatically due to its built-in selector switch option on DCS HMI (Human Machine Interface), provision of selecting 1oo4 is provided in build in design for logic actuation. Once it was observed that temperature reached to 960°F (516°C), Methanator inlet valve HV-25 was immediately closed by operators, cutting downstream seal gas flow towards the Expander. The inlet valve HV-25 was designed to close automatically in emergency situations. In addition, there was no built-in Expander Trip Logic to respond in the event of closure of Methanator inlet valve HV-25, which resulted in no seal gas flow and process gas ingress into Expander Oil Console. Cold box Expander process gas broke through from HP drain to oil console causing console over pressurization and resulted in hydrogen fire. Issues were resolved one by one by taking appropriate engineering controls and operational measures. Production resumed on 15th September 2012.

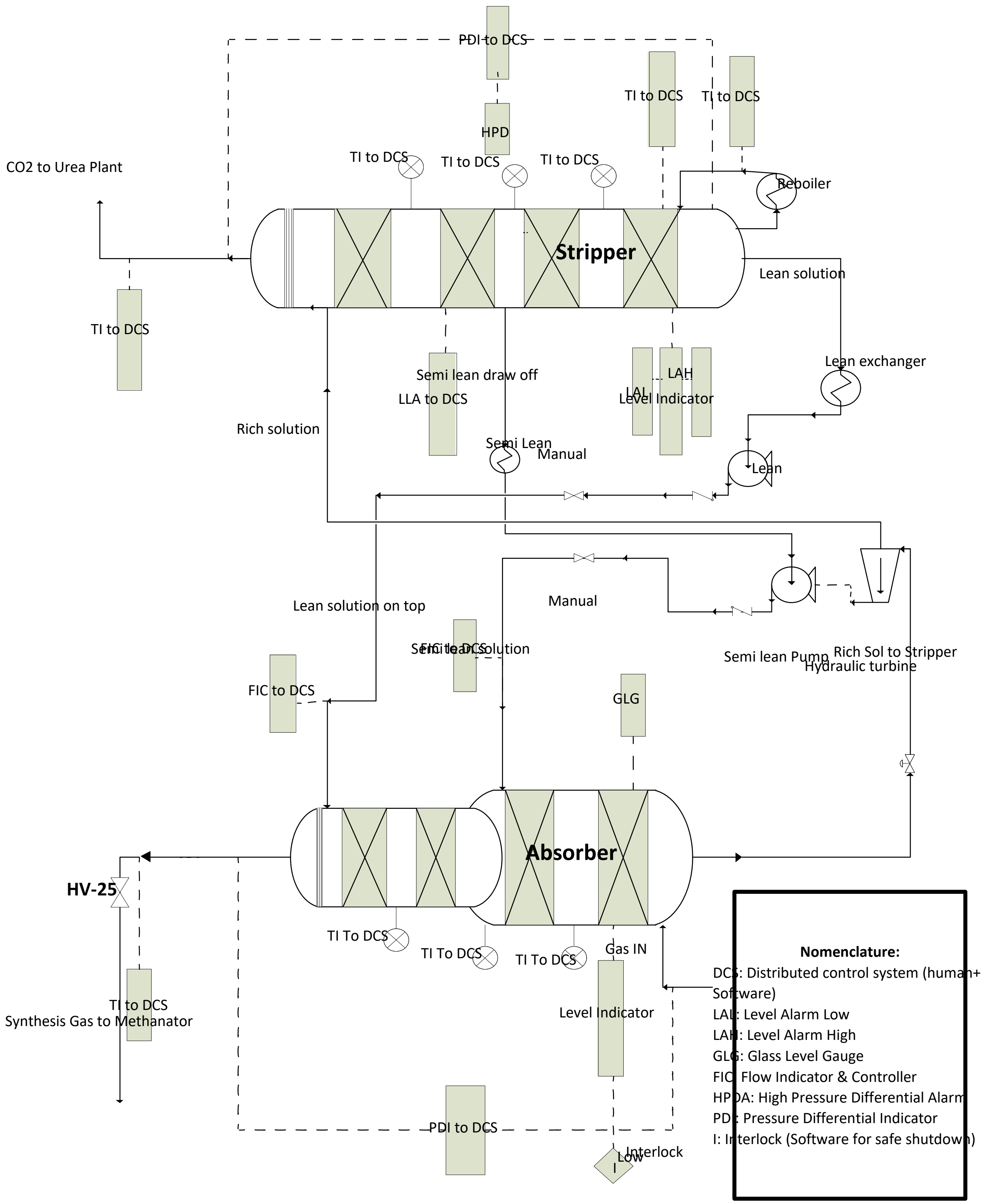

Figure 1: Catacarb™ CO2 Removal System

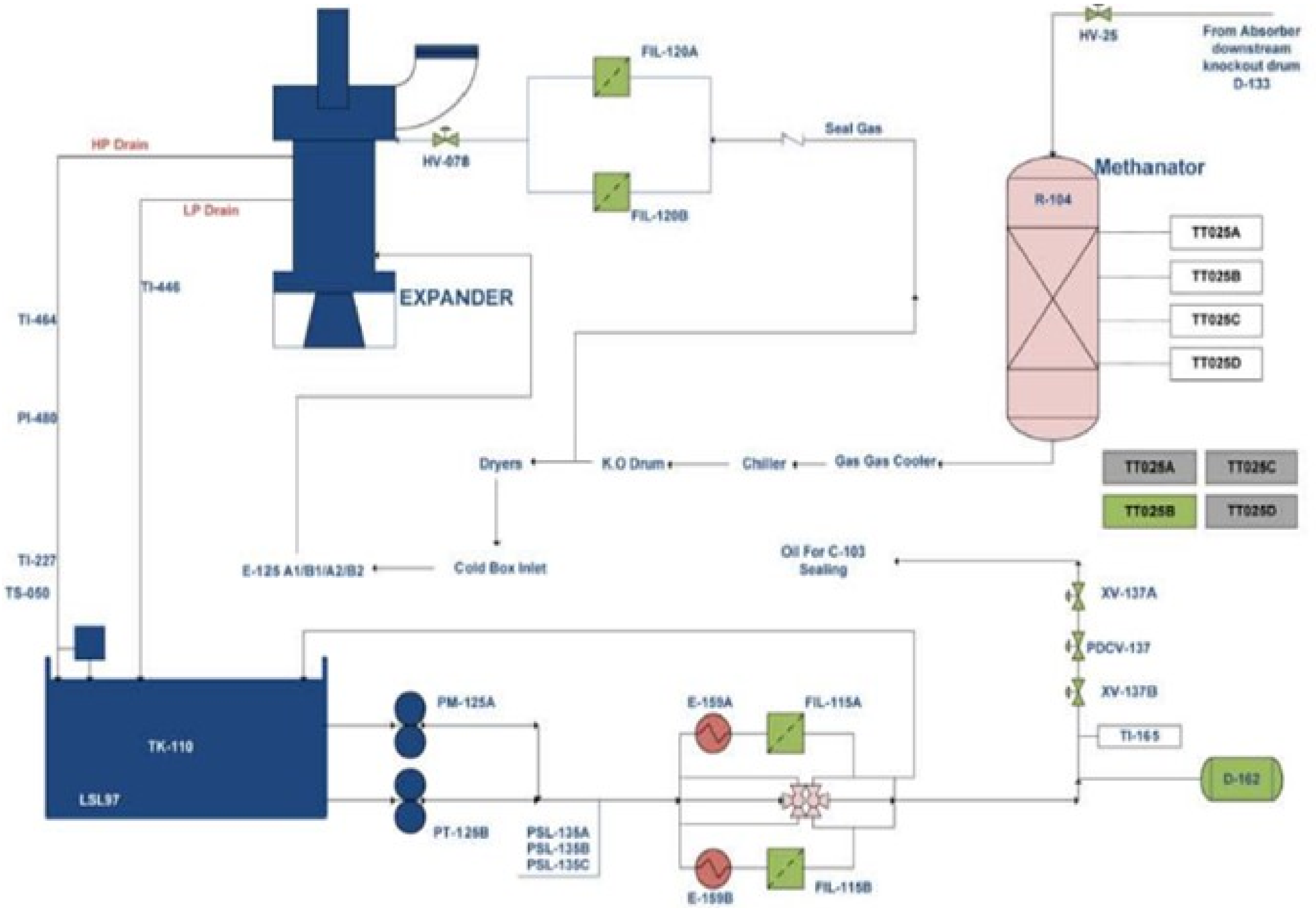

Figure 2: Methanator selector Switches and discontinuation of seal gas flow

HAZOP Summary:

The HAZOP study was performed following industry standard recommended practices, and was led by HAZOP facilitators with decades of expert professional HAZOP experience. The HAZOP team was a multi-disciplinary team that was experienced and fully qualified to perform HAZOP. All HAZOP results were independently reviewed to identify possible gaps or omissions.

The HAZOP did produce useful insights about potential hazards that must be mitigated. Total 436 action were generated with the majority related to interlocks, alarms, control actions and procedural control. “No Flow” and many other conditions were analyzed, as is standard practice. The team used a rigorous methodology, including additional LOPA-style methodology. However, a comparison of the HAZOP results and the actual operating experience, which was not available to the HAZOP team, showed that the HAZOP did not identify the missing requirements of seal gas supply valve cutoff during Methanator tripping that contributed to the hydrogen fire.

The original HAZOP could be updated after the event using hindsight knowledge of the costly new flaws that were discovered during operation. Although that is true, the fact remains that the original team—who did not have the benefit of hindsight knowledge—were unable to catch the flaws involving the interactions between physical components, digital I&C behaviors, and human interactions.

Once the flaw is understood, Hindsight Bias [22] makes the flaw seem more obvious than it was without hindsight. Hindsight Bias creates overconfidence that that particular flaw should have been caught or that it would have been caught if only we had been on that team. To avoid the bias, we need to rely on empirical data rather than guesses about whether it could have been theoretically identified. We did not evaluate whether HAZOP teams could identify this flaw with hindsight knowledge of the flaw. We evaluated whether qualified teams with no hindsight knowledge of the flaw could reliably and consistently discover these flaws using HAZOP. The fact is that teams of fully qualified professionals did not identify these flaws despite decades of experience in HAZOP, the plant, and the chemical processes involved, despite a rigorous state-of-the-art HAZOP methodology, independent reviews, and an additional LOPA-style methodology.

As discussed earlier, this is not the first flaw that has been missed by HAZOP in the process industries and it will not be the last. The authors decided to perform an empirical comparison between HAZOP and alternative methods when performed by teams with no hindsight knowledge of flaws in the system.

<u>STPA Summary:</u>

With the growing adoption of STPA in the process industries to analyze interactions between physical, digital, and human components [15, 17], the authors selected STPA for an empirical comparison using the same system and qualified STPA practitioners. A limited STPA was applied on the same system without knowing the incident that happened, the root causes, or the necessary corrective actions to address the hidden weaknesses in the system.

<u>STPA is performed in four steps: [23]</u>

1. Define the purpose of the analysis, including the losses to prevent. Note that STPA is not limited to explosions or loss of life. STPA can be used to prevent other losses such as loss of production.
2. Model the control structure, which identifies the feedback control loops.
3. Identify Unsafe Control Actions (UCAs) that will lead to a hazard.
4. Identify scenarios that explain why those unsafe behaviors and decisions would occur.

Defining the purpose of the analysis is the first step. What kinds of losses will the analysis aim to prevent? Will STPA be applied only to traditional safety goals like preventing loss of human life or will it be applied more broadly to security, privacy, performance, and other system properties? What is the system to be analyzed and what is the system boundary? These and other Fundamental questions are addressed during this step.

The second step is to build a model of the system called a control structure. A control structure captures functional relationships and interactions by modeling the system as a set of feedback control loops. The control structure usually begins at a very abstract level and is iteratively refined to capture more detail about the system.

The third step is to analyze control actions in the control structure to examine how they could lead to the losses defined in the first step. These unsafe control actions are used to create functional requirements and constraints for the system.

The fourth step identifies the reasons why unsafe control might occur in the system. Scenarios are created to explain:

a) How incorrect feedback, inadequate requirements, design errors, parameter deviations, component failures, and other factors could cause unsafe control actions and ultimately lead to losses.
b) How safe control actions might be provided but not followed or executed properly, leading to a loss.

Once scenarios are identified, they can be used to create additional requirements, identify mitigations, drive the architecture, make design recommendations and new design decisions (if STPA is used during development), evaluate/revisit existing design decisions and identify gaps (if STPA is used after the design is finished), define test cases and create test plans, develop leading indicators of risk, and for other uses as described the STPA handbook.

The following summarizes a portion of the STPA results.

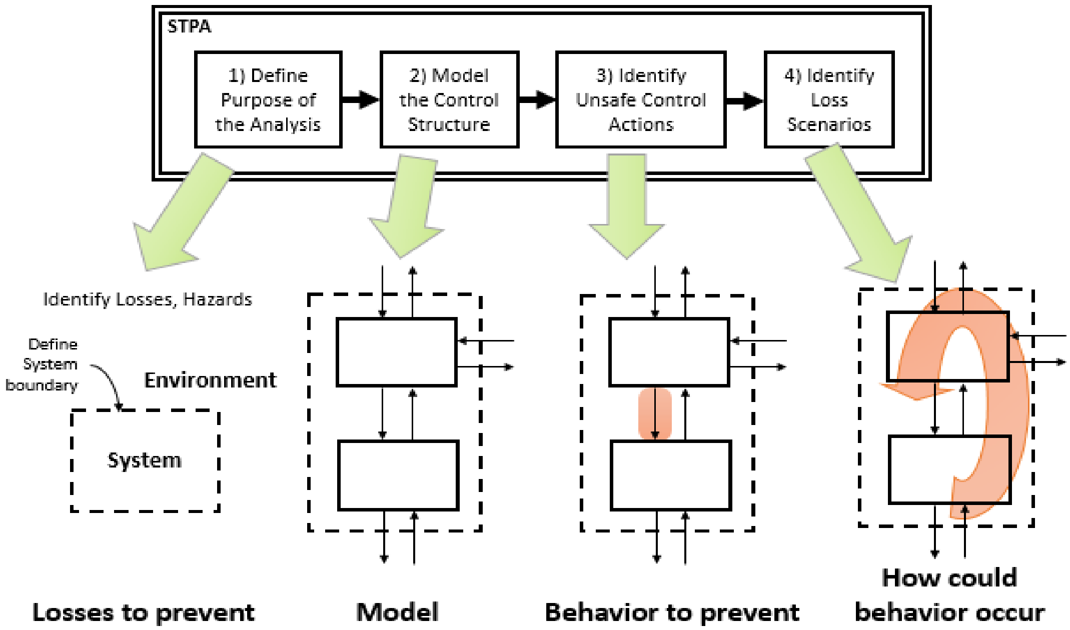

Figure 3: The four steps of STPA from the STPA Handbook

STPA identified the following losses:
L1: Loss of life or injury
L2: Equipment damage
L3: Environmental contamination
L4: Loss of production

Next, STPA identifies high-level system hazards. A system hazard is an overall system state that will lead to losses in a worst-case environment. STPA identified the following hazards for the overall Ammonia Plant Production (APP):
SH-1: APP physically injures people (rupture, fire, etc.) [L1,L2,L3,L4]
SH-2: APP equipment is operated beyond limits [L1,L2,L3,L4]
SH-3: APP releases toxic chemicals into the environment [L3,L4]
SH-4: APP unable to produce sufficient product or high-quality product [L4]

The second step of STPA is to model the control structure. The control structure identifies the controls that oversee and supervise the physical controlled processes—including human, automated, and other controllers—as well as the specific control actions (downward arrows) that can be used to execute control over the controlled processes. The control structure also identified feedback information (upward arrows) that can be used by controllers to inform decision-making and select appropriate control actions. Figure 4 shows an example of a simplified control structure for this application.

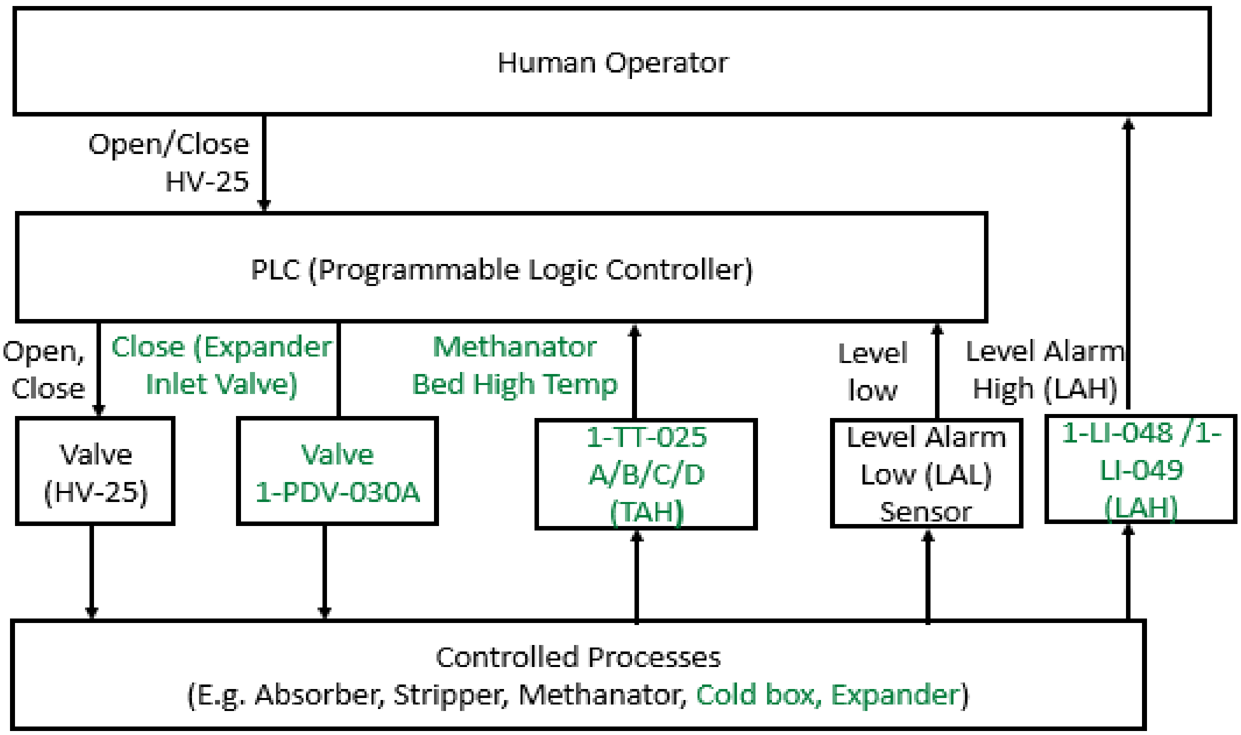

Figure 4: Example of a Simplified Control Structure

The third step of STPA identifies control actions that are unsafe. These Unsafe Control Actions (UCAs) specify a control action as well as a context in which that control action is unsafe, meaning it is a cause of one or more system hazards in the first step. UCAs are identified for all controllers in the control structure, including both automated and human controllers. No assumption is made that the automation is designed correctly or that human procedures exist and are specified correctly. In other words, UCAs are do not identify deviations from a specified requirement or design intent that is assumed to be perfect. UCAs may describe behavior that is required, that is not required, that is intended, or that is not intended.

For example, "UCA-1: PLC does not provide Close HV-25 Command when actual liquid level is high in the Absorber" is unsafe because leaving HV-25 open when liquid level is high will lead to entrainment of Catacarb solution. UCA-1 does not assume that a requirement or a design intent already exists for the PLC to provide the Close HV-25 Command in this condition. The UCAs can be compared to the design intent and the requirements in a later step to identify missing, incomplete, incorrect, conflicting, or unsafe requirements, assumptions, and design intentions.

Tables 2 and 3 identify additional UCAs for both the automated and human controllers in Figure 4.

Source Controller: PLC				
Control Action	**Not providing causes hazard**	**Providing causes hazard**	**Too early, too late, out of order**	**Stopped too soon, applied too long**
Close HV-25 Cmd	UCA-1: PLC does not provide Close HV-25 Cmd when actual liquid level is high in the Absorber. [SH-2, SH-3, SH-4]	UCA-2: PLC provides Close HV-25 Cmd when actual liquid level is absorber is normal (cause Methanator trip). [SH-4] UCA-3: PLC provides Close HV-25 Cmd while expander remains in service (causes low seal gas flow to expander which will eventually result in fire) [SH-1,SH-2,SH-4]	UCA-4: PLC provides Close HV-25 Cmd too early when liquid level is high (trip set point) [SH-4] UCA 5: PLC provides Close HV-25 Cmd too late when liquid level in absorber is high (causes solution carryover to Methanator causing run away of reaction which will lead to Methanator vessel failure) SH-1,SH-2,SH-4]	UCA-6: PLC continues providing Close HV-25 Cmd too long after liquid level is normal (will prevent startup when issue is resolved) UCA-7: PLC stops providing Close HV-25 Cmd too soon before valve has fully closed UCA-8: PLC stops providing Close HV-25 Cmd too soon before liquid level in absorber has returned to normal
Open HV-25 Cmd	NA	NA	NA	NA

Table 2: STPA Unsafe Control Actions for the PLC

Source Controller: Operator				
Control Action	**Not providing causes hazard**	**Providing causes hazard**	**Too early, too late, out of order**	**Stopped too soon, applied too long**
Close HV-25 Cmd	UCA-9: Operator does not provide Close HV-25 Cmd when actual liquid level is high in the Absorber (due to malfunctioning of level indicator or excessive foaming) [SH-2, SH-3, SH-4]	UCA-10: Operator provides Close HV-25 Cmd when actual liquid level is absorber is normal (cause Methanator trip). [SH-4] UCA-11: Operator provides Close HV-25 Cmd while expander remains in service (causes low seal gas flow to expander which will eventually result in fire) [SH-1,SH-2,SH-4]	UCA-12: Operator provides Close HV-25 Cmd too early when liquid level is high (trip set point) [SH-4] UCA 13: Operator provides Close HV-25 Cmd too late when liquid level in absorber is high (causes solution carryover to Methanator causing run away of reaction which will lead to Methanator vessel failure) SH-1,SH-2,SH-4]	UCA-14: Operator continues providing Close HV-25 Cmd too long after liquid level is normal (will prevent startup when issue is resolved) UCA-15: Operator stops providing Close HV-25 Cmd too soon before valve has fully closed UCA-16: Operator stops providing Close HV-25 Cmd too soon before liquid level in absorber has returned to normal
Open HV-25 Cmd	UCA-17: Operator does not provide Open HV-25 Cmd during startup [SH-3, SH-4]	UCA-18: Operator provides Open HV-25 Cmd when liquid level is high [SH-2, SH-4]	UCA 19: Operator provides Open HV-25 Cmd too soon during startup (causes quick pressurization of Methanator will result leakage, catalyst damage etc.)[SH-1, SH-2, SH-3, SH-4] UCA 20: Operator provides Open HV-25 too late during startup [SH-2, SH-4] UCA 22: Operator provide Open HV-25 Cmd too soon during startup which cause high CO2 slippage enter Methanator and will cause temperature run away. [SH-1, SH-2, SH-3, SH-4]	UCA-21: Operator continues providing Open HV-25 Cmd too long when liquid level is high [SH-2, SH-4] UCA-22: Operator stops providing Open HV-25 Cmd too soon before vent is completely shifted downstream during startup

Table 3: STPA Unsafe Control Actions for the Human Operator

Once the UCAs are identified, STPA can generate PLC requirements and human procedures that are necessary to prevent the UCAs. For example, these two requirements were generated by STPA:

R-1.1: PLC shall be designed to provide Close HV-25 Command when actual liquid level is above X in the absorber [UCA-1]

R-1.2: PLC shall be designed to receive feedback that indicates when actual liquid level is above X in the absorber [UCA-1]

The fourth step of STPA is to build scenarios that explain why unsafe decisions and unsafe behaviors will occur in the system. The STPA Handbook contains detailed guidance about the types of scenarios that can be constructed and how to construct them.

The following two scenarios were among those identified by STPA.

UCA-3: PLC provides Close HV-25 Command while expander remains in service *(causes low seal gas flow to expander which will eventually result in fire)* [SH-1, SH-2, SH-4]

Why? PLC Control Algorithm #1: The PLC control algorithm has no logic or design intent to trip the expander in case of low seal gas pressure/flow as a result of HV-25 closure. This condition is missing from the requirements and the PLC logic.

Solution: Add requirement R-CA.1: DCS logic shall provide automatic Expander Trip Command when HV-25 is closed.

UCA-23: Operator does not manually trip Expander C-103 when HV-25 is closed *(causes low seal gas flow to expander which will eventually result in fire)* [SH-1, SH-2, SH-4]

Following are some possible reasons that can lead to inappropriate actions:

Why? Human Decision-making #1: The operator has no training or operational procedure to trip the expander in case of HV-25 closure. (Missing procedure, inadequate training for this procedure, conflicts with experience, etc.)

Why? Human Belief #1: The operator believes (correctly) that downstream alarms require attention, causing the operator to forget to trip the expander

Why? Human Belief #2: The operator believes (incorrectly) that the expander is already tripped automatically and does not need to be manually tripped

Why? Human Feedback #1: The HMI design has no alert or warning to indicate that HV-25 is closed without an expander trip (fire danger).

Why? Human Feedback #2: The RPM (Revolutions per minute) signal is not visible to the operator on DCS by design, so the operator is not able to determine the hazardous state of the system

Why? Human Feedback #3: The operator receives incorrect pressure reading for seal gas

Solutions:

- Add an alert or warning to indicate when a fire danger exists due to HV-25 closed without an expander trip.
- Automatic tripping of expander in case of I-006 (Methanator trip logic) actuation

Comparison Results and Discussion

Both HAZOP and STPA produced useful insights about potential causes of hazards and losses. Common results related to physical behaviors, failures, and deviations in the controlled processes were identified by both methods, such as a valve blockage or failure. The most significant difference is that the HAZOP results—performed by expert practitioners and with comprehensive reviews—did not adequately consider:

- Weaknesses in the intended design of the automation
- Missing logic or unsafe logic in automated controllers
- Safety-critical functionality missing from the design
- Missing feedback information to enable safe decision-making by controllers
- Interactions between multiple controllers
- Incorrect operational assumptions made by human operators, especially assumptions about the automation
- Inconsistent automation that will cause human operator confusion, like automatic mode changes or an automatic trip function that works in almost every possible case except one
- Gaps in human procedures or training
- Assumptions about human operator behaviors that were not validated
- Potentially conflicting commands from multiple controllers, such as a condition that simultaneously triggers an automated downstream trip and a manual human command to open a valve
- Common causes that defeat assumptions about redundancy and independence

STPA produced new scenarios not found by HAZOP that considered both human and automated decision-making, including decisions and beliefs that may appear reasonable at the time given the information available and other contextual factors.

STPA produced safety-critical requirements and recommendations that were missed by HAZOP, including effective low-cost solutions. In this study STPA was applied after the design was created and implemented, but most of the STPA results could have been obtained much earlier in the development process before flawed logic and flawed procedures were implemented.

The HAZOP and STPA results were compared to real operational incidents and losses that were unknown to the teams when the analysis was performed. None of the causes of the real incidents were found in the HAZOP results, although that is not too surprising because a full HAZOP was already performed on the system before it went into operation as a standard practice. The HAZOP results missed all of the safety-critical weaknesses and corrective actions that were discovered after the system was put into operation.

The STPA scenarios included the actual scenarios that caused losses in operation, especially the human and automation behaviors that were not foreseen by the original developers. The STPA results, which were produced from a general system description with no knowledge of the actual weaknesses and operational incidents, matched the corrective actions from the real incidents that were within the scope of the STPA effort. The STPA effort also produced additional corrective actions that were not found in the root cause analysis but would have prevented the incidents.

Limitations

This study was subject to a number of limitations. The STPA team was less than half the size of the HAZOP team. The time allocated to perform STPA was less than half that of HAZOP. The HAZOP team consisted of many domain experts who were fluent in the detailed design and operation of the system, while the STPA team had less familiarity with the system. The STPA team did have the ability to ask specific questions about the system if the questions were generated by the analysis. All information and answers were limited to materials available before the operation of the system and the incidents that occurred.

Conclusion

Although the popular HAZOP method was shown to provide useful insights, the HAZOP method is not perfect even when performed by expert practitioners with multiple reviews and in compliance with industry standards. HAZOP was found to overlook important causes related to new technology, human behavior, and interactions between non-failed components operated as designed. The STPA method was found to address the gaps that were empirically observed in the HAZOP method, including identification of real scenarios and real corrective actions that otherwise were not discovered by HAZOP until hazardous and costly losses occurred during operation.

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