Theory and Operation of Purification Systems

Johnson Matthey
Catalysts

1 Introduction

Purification is an important part of any synthesis gas generation plant, and this is no different for an Ammonia plant. Because of the large volumes of hydrocarbon feedstock processed even small traces of poisons exit the purification system will have a significant cumulative effect on the performance of downstream catalysts. It is therefore extremely important to completely purify the feedstock before it is further processed to achieve the long catalyst lives and hence production runs needed for economic operation. As such the importance of the good operation, monitoring and maintenance of the purification system can not be under-stated.

The purpose of this paper is to,

- Detail some fundamentals about purification chemistry,
- Detail the principles of the operation of purification,
- Discuss some common operating problems.

2 Typical poisons

2.1 Sources and forms of poisons

There are a large variety of poisons that can be found on an Ammonia plant. The following table details some of the typical poisons that can be found.

Table 1. Types of poisons on an ammonia plant

Name	Form	Source	Poisons
Sulphur	H_2S Organic Sulphurs Mercaptans Thiophenes	Feed gas	Primary reformer High Temperature Shift Low Temperature Shift
Chlorine	HCl Organic Chlorides	Feed gas	Zinc Oxide High Temperature Shift Low Temperature Shift
Lead	Lead	Naphtha	Reformer
Arsine	Arsine	Feed gas Vetrocoke	Reformer
Mercury	Organo-mercury Mercury	Feed gas	Reformer
Silica	SiO_2	Inert balls Refractory Steam	High Temperature Shift
Water	Vapour	Synthesis Gas	Ammonia Synthesis
Carbon Oxides	CO and CO_2	Synthesis Gas	Ammonia Synthesis
Oxygenates	Oxygen	Feed gas	Ammonia Synthesis
		Nitrogen purge	Ammonia Synthesis

2.2 Purification stages

There are a number of different purification stages within an ammonia plant; these are the,

- Mercury Guard
- Hydrodesulphurisation
- Chloride Removal
- Sulphur Removal including Zinc Oxide and Ultra-purification
- Methanation

2.3 Purification position

There are a number of locations for the purification of the process gas passing through an ammonia plant. The following table summarises the various locations of the purification steps on an ammonia plant.

Table 2. Locations of purification steps on an ammonia plant

Name	Form	Locations
Sulphur	Organic Sulphurs Mercaptans Thiophenes	Converted to H_2S in HDS and then absorbed on Zinc Oxide
	H_2S	Absorbed on Zinc Oxide
Chlorine	Organic chlorides	Converted to HCl in HDS and then absorbed on Chloride Guard
	HCl	Absorbed on Chloride Guard
Lead	Lead	Absorbed on HDS
Arsine	Arsine	Absorbed on HDS
Mercury	Mercury	Absorbed on Mercury Guard
Silica	SiO_2	Trap on inert layer in top of HTS
Water	Vapour	Remove in knock out pots
Carbon Oxides	CO and CO_2	Remove CO_2 in CO_2 absorber Residual CO_x is methanated in the methanator
Oxygenates	Oxygen	Operating procedures

3 Purification theory

3.1 Chemistry

3.1.1 Mercury removal

Mercury that is present in feed gas can cause catastrophic failures in cryogenic equipment or poisoning of process catalysts as outlined in reference 1. The key reaction in Mercury Removal is,

$$MS + Hg \Rightarrow M_2S + HgS$$

- choice of two materials, effectively pre-sulphided or sulphide in situ
- capacities up to 15 wt% possible,
- equilibrium favours lower temperature.

In terms of catalyst choice, there are two materials that are available, Johnson Matthey **PURASPEC™** 2156 which is pre-sulphided and therefore requires no activation process before entering service and **PURASPEC** 2157 which reacts with the H_2S in the feed gas and therefore becomes active once the bed sees natural gas. Use of these mercury guards allow reduction of mercury contents from 5 μg/Nm³ to less than 0.01 μg/Nm³ with a total capacities up to 15 wt%.

3.1.2 Hydrodesulphurisation

Hydrodesulphurisation (or HDS) is a key step in the purification of feed gases on ammonia plants since it converts organic hydrocarbons to hydrogen sulphide. These organic sulphur compounds will not be absorbed in the zinc oxide bed and therefore must be hydrogenated. The key hydrogenation reactions that occur as follows,

$$CH3SH + H_2 \Rightarrow CH_4 + H_2S$$
$$C_2H_5SH + H_2 \Rightarrow C_2H_6 + H_2S$$

Or more generally,

$$C_nH_{(2n+1)}SH + H_2 => C_nH_{(2n+1)}H + H_2S$$

Also the hydrolisation of COS can occur if present in the feed gas when there is water present, say from hydrogen recycle,

$$COS + H_2O => CO_2 + H_2S$$

Also there is the hydrogenation of organo-chlorides,

$$RCl + H_2 => RH + HCl$$

Johnson Matthey Catalyst recommends the use of **KATALCO**^{TM} 41-6 or **KATALCO** 61-1. The choice of HDS catalyst is dependent on the syngas plant, on methanol plants where the purge gas from the synthesis loop is returned to the desulphuriser the CO and CO_2 levels are small. However on the event of a feed trip high levels of CO_x can enter the HDS catalyst. There is the potential of methanation on the HDS catalyst, NiMo does not promote methanation catalyst therefore would be the preferred choice in methanol plants.

3.1.3 Chloride removal

If chlorides are present in the feedgas it is important that the chlorides are removed in a chloride guard bed since chlorides are a very virulent poison. If the chlorides are present as organo-chlorides, then as noted above, a HDS bed will be required to hydrogenate the organo-chlorides. The reaction for chloride removal is using sodium-alumina composite.

$$2HCl + 2NaAlO_2 => H_2O + 2NaCl + H_2O$$

For this application Johnson Matthey Catalysts recommends the use of **KATALCO** 59-3 which removes chlorides to very low levels.

3.1.4 Sulphur removal in zinc oxide

In order to protect the primary reformer and the low temperature shift catalysts, any hydrogen sulphide in the feed gas has to be removed. Johnson Matthey offers two catalysts for this duty, **KATALCO** 32-4 or **KATALCO** 32-5. The absorption reaction for hydrogen sulphide removal within the zinc oxide is as follows,

$$H_2S + ZnO => H_2O + ZnS$$

3.1.5 Sulphur removal in Ultra-purification

Ultra-purification should be used after the zinc oxide bed in cases where there is a sensitive reformer downstream; this includes pre-reformers and highly stressed reformers. Ultra-purification reduces the sulphur content of the feed gas from typical zinc oxide exit levels of 100 ppb v/v down to 1 ppb v/v. This means that the rate of poisoning of the downstream reformer and also the low temperature shift will be significantly reduced. The absorption reaction for hydrogen sulphide removal within the ultra-purification is as follows,

$$H_2S + CuO => H_2O + CuS$$

For this application, Johnson Matthey recommends the use of **PURASPEC** 2084.

3.2 Low temperature systems – PURASPEC range

At temperatures of less than 300°C, the hydrogenation activity of the standard range of hydrodesulphurisation catalysts is low. Therefore a higher metal loading catalyst i.e.: higher levels of molybdenum and cobalt or nickel have to be used for temperatures between 200-300°C. However, these catalysts must be sulphided before commissioning in order to have sufficient activity at low temperatures. This can be achieved by pre-sulphiding either before installation or post installation.

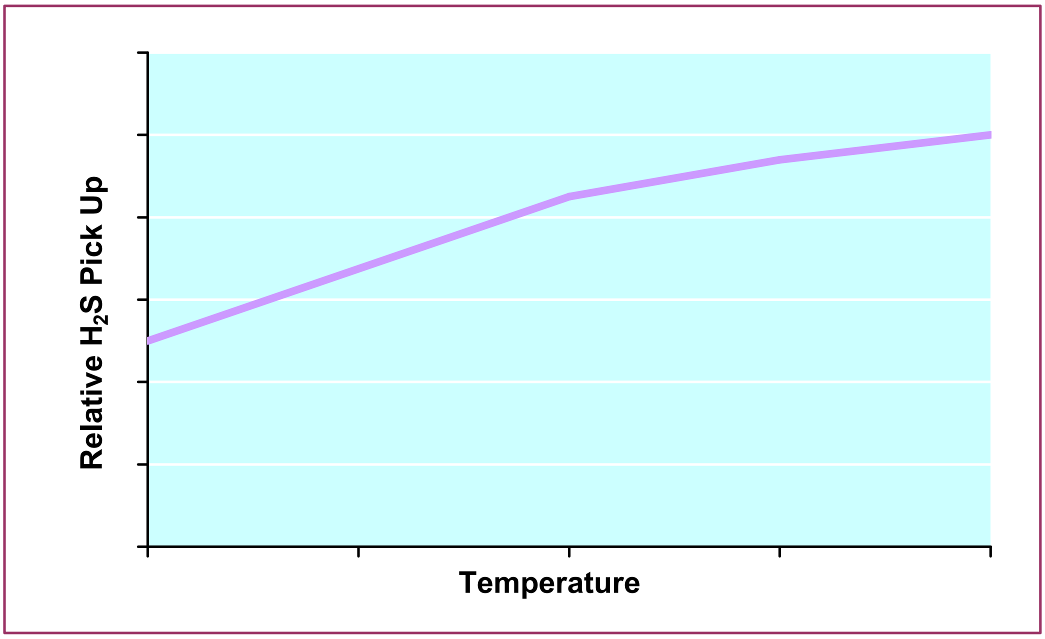
3.3 Optimal pressure

One question that is raised from the above sections is what is the optimal operating pressure? In reality the optimal pressure for purification of the feed gas is defined by the requirements of the overall flowsheet and the other unit operations (both catalytic and non-catalytic).

3.4 Optimal temperature

For the zinc oxide, the higher the operating temperature, the higher the absorption capacity. This is illustrated in the following graph,

Figure 1. Zinc oxide performance against temperature



However, there is an upper limit to the purification operating temperature; at temperatures in excess of 400°C, there is the potential for hydrocarbon cracking in the feed preheat coil. As the temperature inlet the feed pre heat coils increases, so does the potential for hydrocarbon cracking. It is therefore typical that the purification feed is preheated to 400°C.

4 Purification schemes

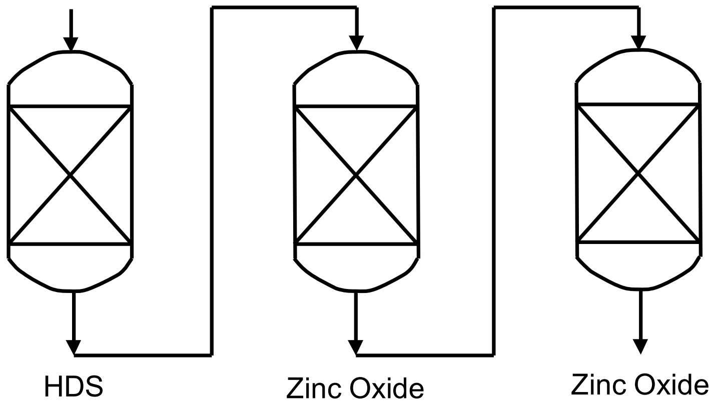
4.1 Introduction

There are a number of schemes that can be used to purify the feed gas; these are detailed in the sections below.

4.1.1 Location of the purification system

The following figure illustrates the typical layout of a conventional purification system within the ammonia flowsheet,

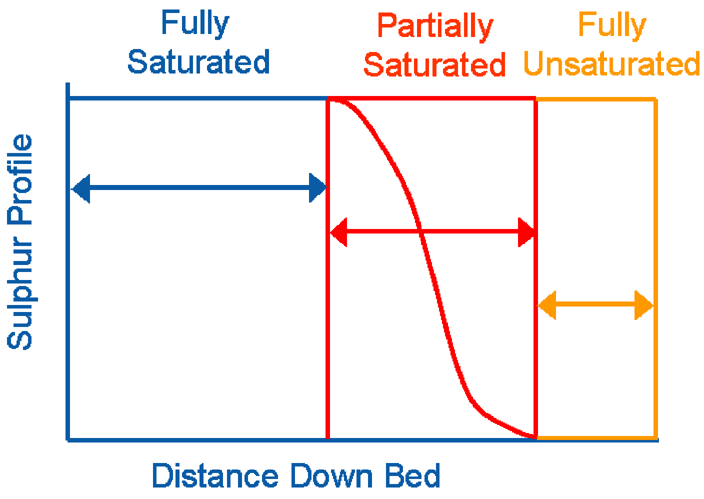
Figure 2. Layout of conventional purification system



4.1.2 Zinc oxide saturation profile

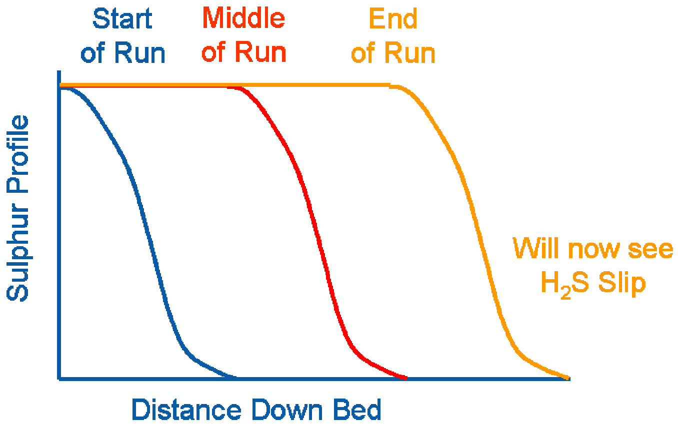
Zinc oxide differs from the other catalysts in the ammonia plant, in that it is not a catalyst but an absorbent. There is therefore an absorption profile within the zinc oxide bed; the following figure illustrates the absorption profile,

Figure 3. Zinc oxide absorption profile



As can be seen there is a fully saturated zone at the leading edge of the bed; a partially saturated zone below this, with the sulphur saturation level dropping from fully saturated to unsaturated. Beneath this zone and the bottom of the bed, there is an unsaturated zone. The following figure illustrates this effect with time on line,

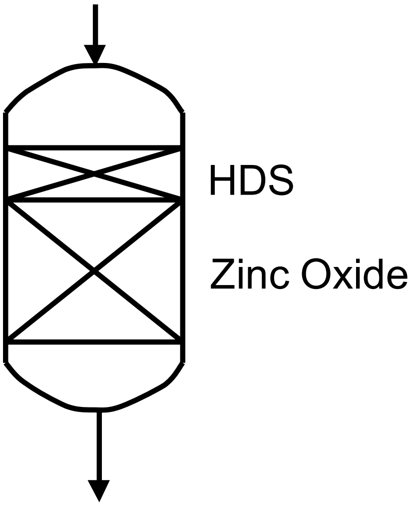
Figure 4. Zinc oxide absorption profile variation with time



4.1.3 Single vessel scheme

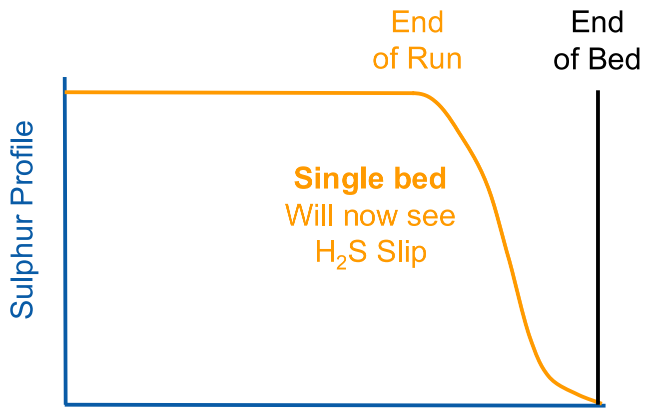
The following scheme is utilised on many modern plants where the sulphur content of the feed gas is very low,

Figure 5. Single vessel scheme



The advantage of this scheme is that only a single vessel is used which minimises the capital expenditure (CAPEX) of the purification section of the plant. Unless the vessel is supplied with specially designed internals, the disadvantage of this scheme is that the HDS catalyst has to be discharged at the same time as the zinc oxide and this increases the operational expenditure (OPEX). If the sulphur content of the feed gas is higher than expected then the zinc oxide will be fully saturated before the design life is achieved and therefore the HDS catalyst will be discharged before it has reached the end of life. A further disadvantage again occurs if the sulphur content of the feed gas is higher than design in that the plant will have to be shut down prematurely which will add additional turn around's. A further disadvantage of this scheme is that the zinc oxide starts to slip sulphur well before the whole bed is fully saturated. Since the bed has to be discharged once sulphur starts to slip to prevent long term damage to the downstream catalysts, this increases the OPEX of such a scheme. The following figure illustrates the point at which the bed starts to slip sulphur,

Figure 6. Single bed saturation profile

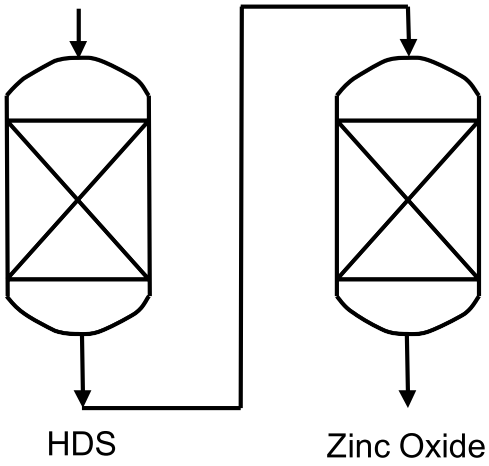


As is clear there is a portion of the zinc oxide bed that is not fully saturated at the bottom of the bed.

4.1.4 Double vessel scheme

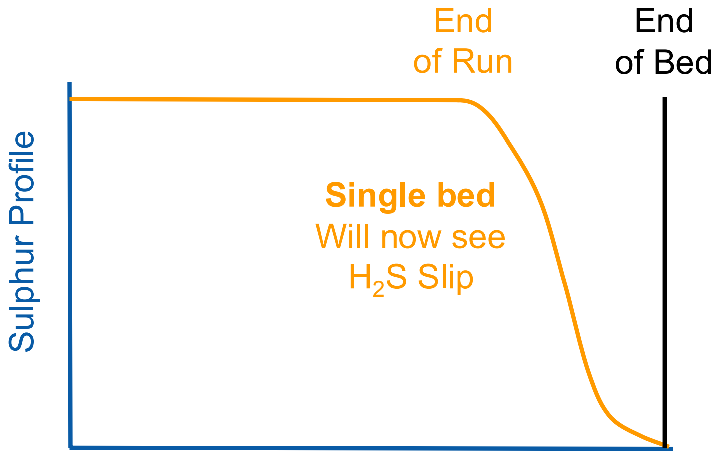
The following scheme is utilised on many plants where the HDS and zinc oxide are in separate vessels,

Figure 7. Double Vessel Scheme



Although this scheme means that the HDS does not have to be discharged when the zinc oxide is discharged (as with the previous scheme), if the sulphur content of the feed gas is higher than design, there will be additional shut downs over and above the expected turn around's. The additional CAPEX of the additional vessel is reflected in a lower OPEX compared to the single vessel scheme. As with the first scheme, once the absorption profile reaches the bottom of the bed, the bed will start to slip sulphur and again this will start to poison downstream catalysts.

Figure 8. Single bed saturation profile



4.1.5 Triple vessel scheme – lead/lag

The following scheme is utilised on many modern plants where the sulphur content of the feed gas is high.

Figure 9. Triple Vessel Scheme – Lead/Lag

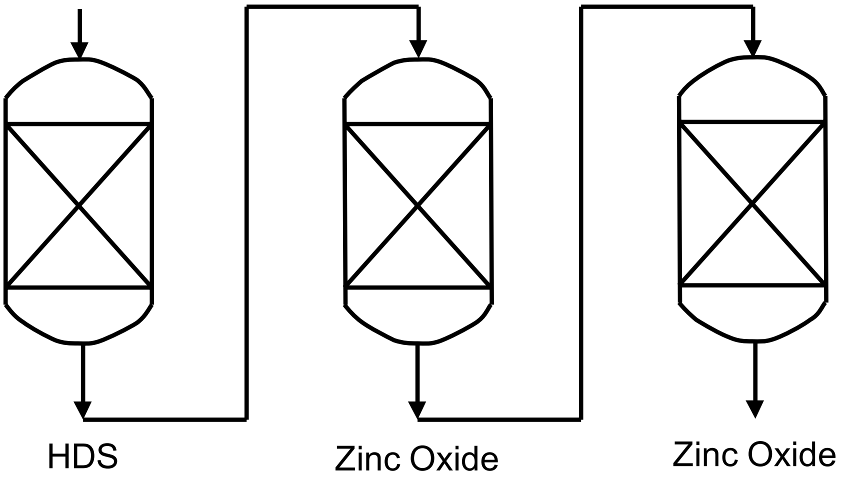
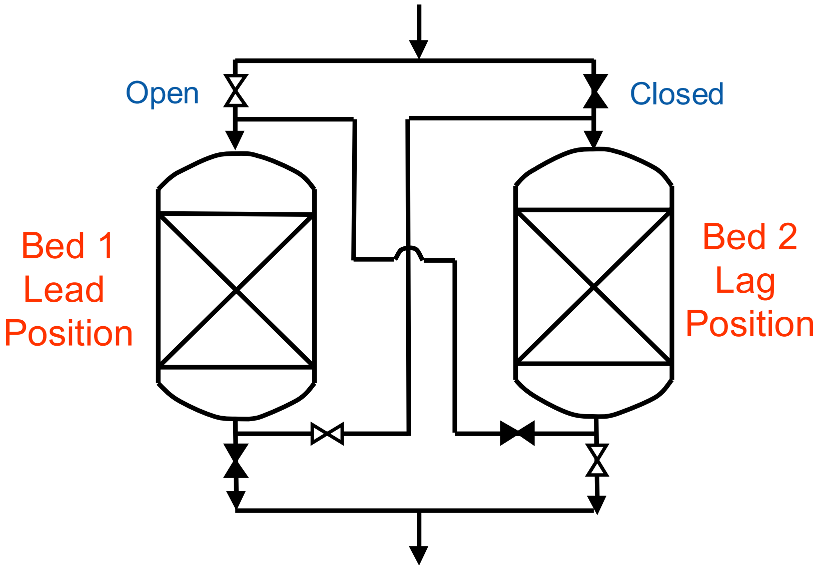
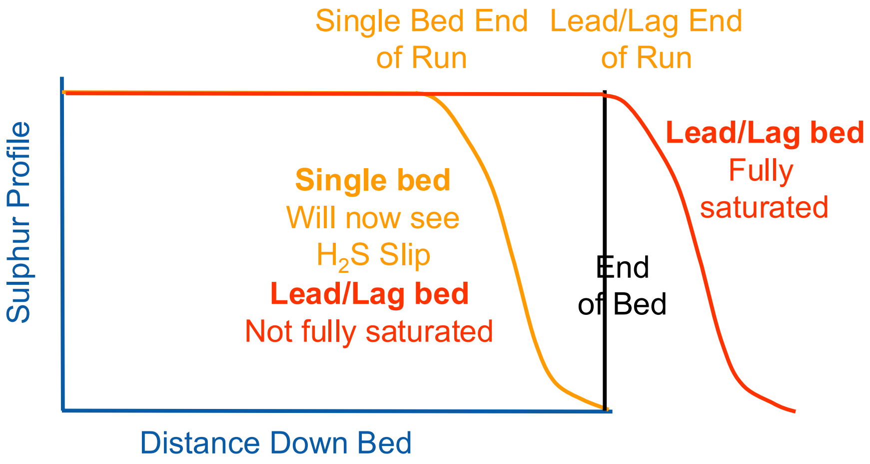


Figure 10. Triple vessel scheme – lead/lag details



The advantage of this scheme is that the zinc oxide beds can be discharged without having to shut down the plant. With this scheme, once the lead bed is fully saturated, then it can be taken out of service and can be discharged and re-loaded with fresh absorbent. This fresh vessel is then brought into service as the lag bed with the partially utilised old lag bed remaining as the lead bed. This additional operational flexibility (reflected in a reduced OPEX), does come with the penalty of an additional vessel over and above the two vessel scheme and therefore increases the CAPEX. A further advantage of this scheme is that the lead bed does not need to be discharged until it is fully saturated as illustrated below,

Figure 11. Triple bed saturation profile



Since the lead bed can be fully saturated before being discharged, the entire sulphur absorption capacity can be utilised; this contrasts markedly with the previous two schemes where the bottom of the bed is not fully utilised. This means that the maximum sulphur absorption capacity of the lead vessel in this scheme is some 12% greater than the schemes detailed above assuming the same type of absorbent is used in both cases.

4.1.6 Other schemes

There are a number of other schemes that are similar to the schemes detailed above, each with its own advantages and disadvantages.

If other poisons are present in the feed gas, then this will have an effect on the layout of the purification scheme.

4.2 Catalyst

There are a number of different types of purification catalyst and adsorbents that are utilised in a syngas plant. The choice of catalyst is dependent on the following factors,

- Type of poisons
- Operating condition
- Purification system design
- Level of purification

Usually the first step in the purification stage will be the hydrogenation of organic poisons (i.e.: organic sulphides or chlorides) this is carried out over a CoMo (cobalt molybdenum) or NiMo (Nickel molybdenum) catalyst.

The second step would be an adsorbent, again depending on the type poisons that are present in the gas. If chlorides are present in the feed gas then a chlorine absorbent (Sodium promoted alumina absorbent) would be used. The chlorine guard would be followed by zinc oxide adsorbent. Again the choice of absorbent is dependent on the factors as described above.

For example in a single bed system the zinc oxide need to have a sharp sulphur adsorption profile so a lower density material would be used than in a lead/lag system a sharp adsorption profile is not important but a higher saturation capacity is more beneficial hence a higher density material is used.

4.2.1 Catalyst types

The following table details the various types of catalyst for each duty defined above,

Table 3. Types of catalyst

Duty	Catalyst Name	Active Species
Mercury Removal	**PURASPEC** 2156/2157	Propriety
Hydrodesulphurisation	**KATALCO** 41-6	Cobalt/Molybdenum
	KATALCO 61-1	Nickel/Molybdenum
Chloride Removal	**KATALCO** 59-3	$NaAlO_2$
H_2S Absorption	**KATALCO** 32-5	Zinc Oxide
	KATALCO 32-4	Zinc Oxide
Ultra-purification	**PURASPEC** 2084	Copper
Methanation	**KATALCO** 11-4	Nickel

4.3 Catalyst loading

Catalyst loading is highly important to ensure good utilisation of the bed. This is particular importance for the zinc oxide bed, since if one part of the bed starts to slip sulphur, then the whole bed has to be discharged. This is further discussed in section 7.3.

5 Control parameters

As noted above, the pressure of purification system is defined by other requirements. The operating temperature of the system is generally defined by the performance of the feed preheat coil and the underlying design philosophy of the plant. As noted above, the temperature should be maximised up to a limit of 400°C. The purification system operating temperature should therefore be optimised to 400°C.

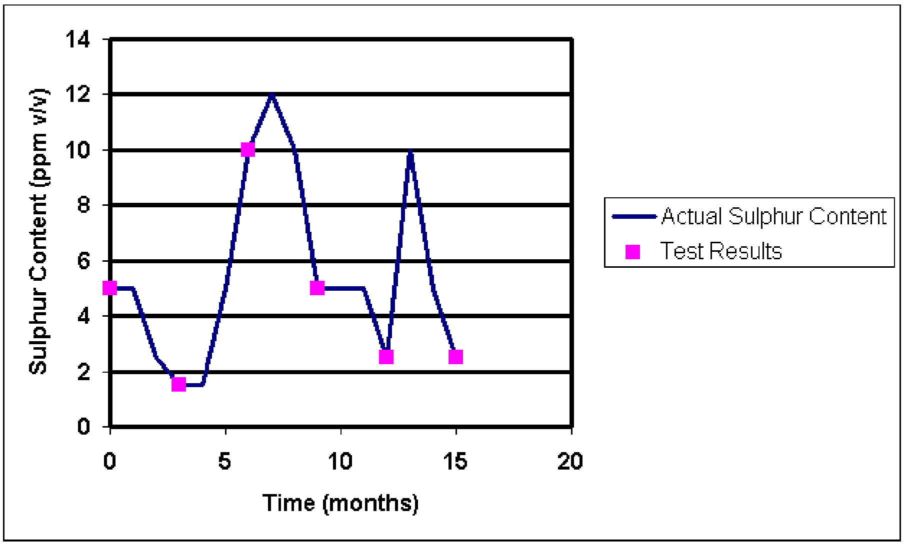
6 Monitoring

6.1 Cumulative sulphur calculation

For zinc oxide, it is possible to determine the cumulative sulphur pick up by measuring the inlet sulphur concentration and multiplying by the coincident feed gas flowrate. This can be compared to the maximum pick up figure and when the cumulative figure approaches the maximum pick up, it can be expected that the zinc oxide will start to slip sulphur.

However, on plants where the total sulphur in the feed is highly variable, then to ensure that this calculation is accurate, the testing frequency of the feed gas has to be increased. Consider the following example; tests for sulphur are conducted every three months and then the average sulphur content is determined by averaging the sulphur content at the start and end of this three month period. This is then multiplied by the total gas flow during this period to generate the total sulphur loading on the zinc oxide bed. The following shows the difference between the actual sulphur levels and those actually seen in the three monthly tests,

Figure 12. Comparison of sulphur inlet zinc oxide



As can be seen this systematic testing does not represent the actual sulphur content of the feed gas since in this example, the testing has missed the peak sulphur levels. In this case, the difference between the actual mass of sulphur passed to the zinc oxide bed and the measured mass of sulphur passed to the zinc oxide bed is 25%. This means that the zinc oxide bed will be utilised 25% quicker than expected. The converse of this effect is also true. Therefore it is important that the frequency of the tests does give a good representation of the actual sulphur content of the feed gas.

If the frequency of the changes in sulphur content increases, then the accuracy of such a calculation becomes less and a less accurate to the point at which the cumulative pick up calculation becomes effectively useless unless the frequency of testing is also increased.

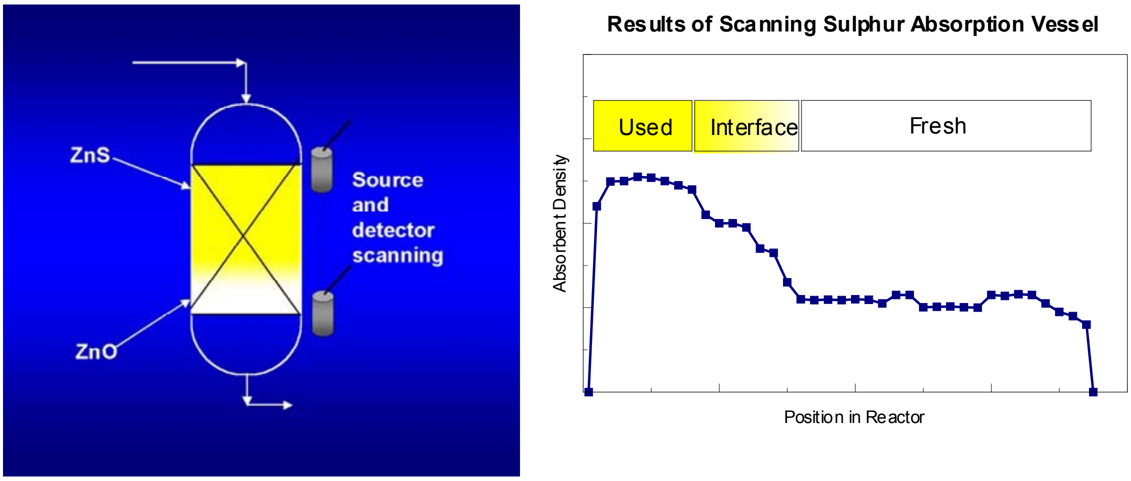
6.2 Sulphur slip

For both HDS and zinc oxide, it is typical to test for sulphur compound slippage from the exit of the bed. For the HDS bed, if any organic sulphur compounds are detected then it can be concluded that the HDS bed has lost activity and is ready for replacement. For the zinc oxide, if hydrogen sulphide is detected outlet of the bed, then for single zinc oxide bed systems, the bed can be deemed as spent and should be replaced. For lead-lag systems, this is not the case, and the bed can be considered as spent when the inlet and outlet hydrogen sulphide are the same; that is to say that there is no pick up of hydrogen sulphide.

6.3 Zinc oxide scanning

Johnson Matthey Catalysts has developed a new method for directly measuring the quantity of zinc oxide sulphur absorbent that has been consumed. The method builds on experience with **TRACERCO Diagnostics^{TM}** techniques and uses external scanning of the absorber vessel to identify the difference associated with the conversion of zinc oxide to zinc sulphide as illustrated below,

Figure 13. Illustration of the TRACERCO MAXIMISER^{TM} system



The technique allows consumption of the absorbent to be monitored and the remaining life to be predicted, thus ensuring maximum absorbent utilization.

The new scanning method also prevents downstream poisoning if the absorbent has been unexpectedly consumed by slugs of sulphur in the feed.

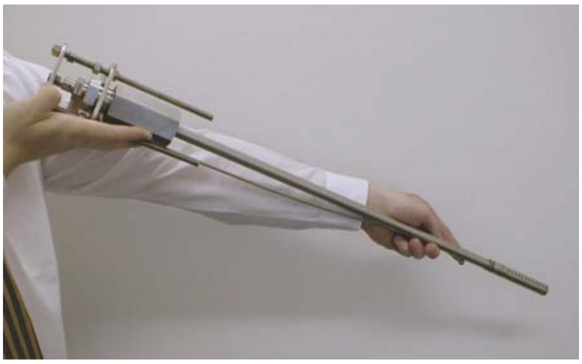
The advantages of this technique are:

- Can monitor performance by external radio-isotope scanning
- This is a direct measurement
- No need for process interruption
- No need for lagging removal
- Rapid scan with quick feedback
- Optimise change out in turnarounds
- Maximise ZnO utilisation

6.4 Catalyst probe

If poisoning of a catalyst bed is found to be a problem, for instance by monitoring of the appearance/tube wall temperature of the primary reformer or increased rate of movement of the low temperature shift, then a rigorous sampling program should be conducted to determine the nature of the poisons. If this does not determine the root cause, for instance, the levels are very low or the laboratory equipment is not sufficiently sensitive enough to determine the type and level of the poison, then a **TRACERCO** Catalyst Probe can be utilised. The probe is illustrated below,

Figure 14. TRACERCO catalyst probe



This probe is inserted through an existing nozzle whilst the plant is one line into the process gas and exposes a selected catalyst to the real process conditions and hence any poisons in that process gas. After exposure for a set period of time, the probe can be removed whilst the plant is on line. Since the probe has been exposed to a large volume of process gas, it will have absorbed a significant amount of poisons that can then be detected. The catalyst tested for the presence of poisons utilising modern laboratory techniques either by the customer or by Johnson Matthey Catalysts.

6.5 Pressure drop

For the HDS catalyst, it is important that the pressure drop across the bed is monitored as a check for carbon formation.

7 Common problems

There are many common problems that can occur within a purification system; below is a brief discussion of some of them. If as an operator you believe that you have a problem, then you should consult your catalyst vendor. Poisons slipping from the purification system can leads to hot bands on the reformer tubes as detailed in reference 2.

7.1 Carbon formation

As noted above, if the feed preheat temperature is too high then the potential for carbon formation in the feed preheat coil and downstream piping increases. At some point, gross carbon formation will occur, and this will cause carbon to be laid down over the HDS bed. This will lead to a high-pressure drop across over the bed and a loss of activity due to coverage of the active metal and this can lead to a short catalyst life.

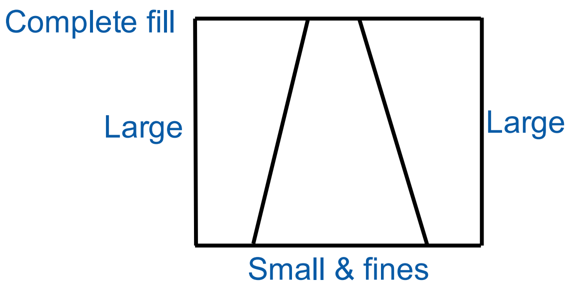
7.2 Loss of hydrogen

For plants where there is organic sulphur compounds in the feed, hydrogen is required to convert the organic sulphur compounds to hydrogen sulphide. If there is a failure of the hydrogen recycle, then these organic sulphur compounds will not be converted, and since they are not absorbed in the zinc oxide, then they will pass to the downstream catalysts and poison them.

7.3 Poor catalyst loading

This is a particular problem in cases where there is a distribution of flows within the bed. When loading the zinc oxide absorbent it is important that the absorbent is loaded such that there is no formation of zones of large and small granules. If for instance the zinc oxide is loaded via a sock which is not moved then zones will be formed since the large granules will tend to flow away from the sock whilst small granules will not flow away from the sock. This effect is illustrated in the next figure,

Figure 15. Large and small granule zones



This can be illustrated with the following example. Assume that the bed is split into two halves with differential voidages; the first half has a high voidage receives 2/3^{rds} of the total flow and the other half has a low voidage receives 1/3rd of the total flow. The following table details the expected life of the entire bed when operating well and also the operation of the two halves of the bed and the effect on the overall performance of the bed,

Table 4. Effect of Flow Mal-distribution on Life within a Zinc Oxide Bed

Name	Units	Good Operation	Zone 1	Zone 2	Overall Operation
Voidage	*n/a*	Expected	High	Low	Variable
Flowrate	*n/a*	Expected	2/3	1/3	Variable
Life	*months*	24	16	36	16

As can be seen the life of the bed is defined by the high flow zone and is significantly reduced by having such a flow mal-distribution within the bed. In this example, the cost of such a mal-distribution will be USD 53,000 per year.

7.4 Channelling

It is also possible to cause gas to channel through the zinc oxide bed due to wetting of the bed and gives an effect as per section 7.3. If zinc oxide is wetted, then it can form a solid cake; this cake has a high resistance to flow and therefore there will be little gas flow through this section of the bed and the life of the zinc oxide bed will be significantly reduced whilst the pressure drop across the bed will rise. Furthermore, the discharge of such material is very difficult and in some cases, the zinc oxide will have to be jack hammered out which can lengthen the absorbent change out and hence the shut down.

7.5 Effect of higher organics

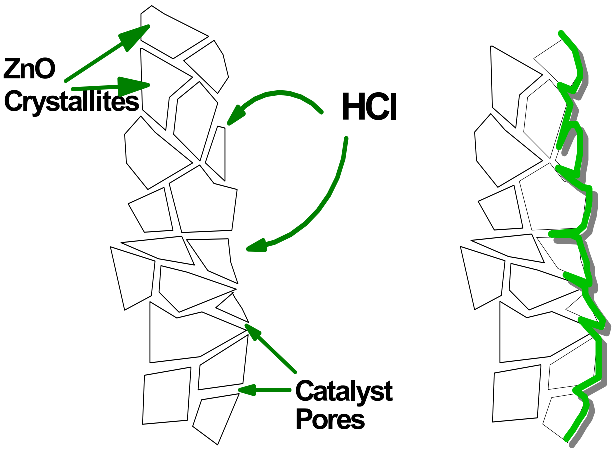
For plants with no HDS catalyst installed, if the feed gas includes high levels of COS or organic sulphur compounds, then these will pass through the zinc oxide and poison the downstream catalysts. Therefore it is important that the feed gas is periodically checked for COS and organic sulphur compounds to ensure that suitable catalysts are installed for the hydrogenation of these species.

7.6 Chloride poisoning of zinc oxide

If there are chlorides present in the feed gas and there is no chloride guard, then there is the potential for chloride poisoning of the zinc oxide. The chloride will block off the pores within the zinc oxide granules and prevent the feed gas, and the sulphur contained in that gas from accessing the inside of the granule.

This in turn reduces the capacity of the zinc oxide bed and will cause premature breakthrough of sulphur and poisoning the primary reformer and low temperature shift. Furthermore, if the chlorides break through the zinc oxide bed, then both of these downstream catalysts will be poisoned by chlorides as well. This is illustrated in the following figure,

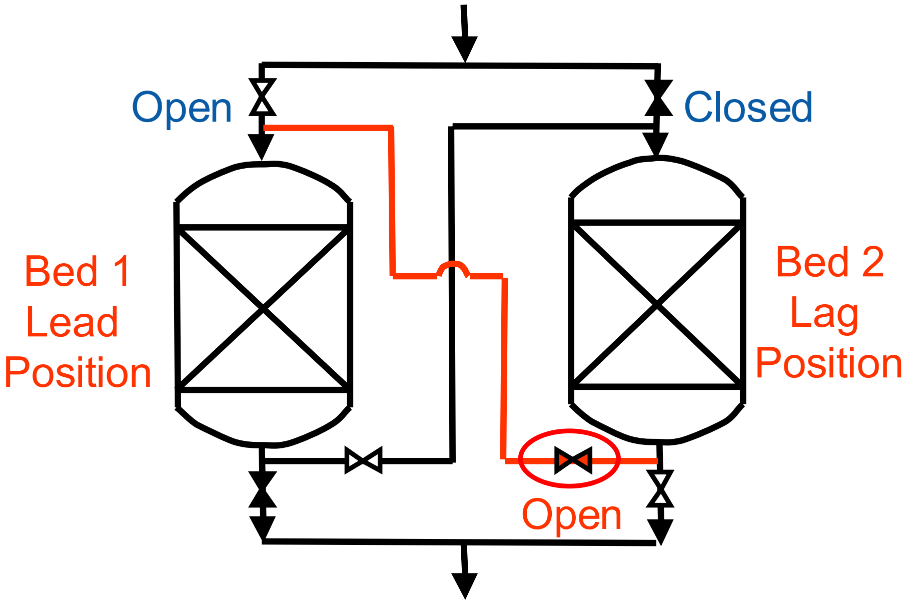
Figure 16. Effect of chlorides on zinc oxide



7.7 Bypassing of zinc oxide

It is possible that in a lead lag system that gas can bypass both beds either via the “bypass” line or the legs of a pressure differential meter; this is illustrated in the figure below,

Figure 17. Bypassing of a zinc oxide



To overcome this problem, when changing over the two beds, all valve positions should be checked thoroughly and the effluent gas from the zinc oxide should be checked for sulphur. A valve locking procedure should be utilised to prevent inadvertent opening or closing of valves during normal operation and hence bypassing of the lag bed (as is illustrated above).

7.8 Problems with sulphur testing

There are a wide range of issues with testing for sulphur compounds in the feed gas which all mean that although the analysis may indicate that there is no sulphur present in the feed gas, there is in reality sulphur in the gas. These problems include,

- **Sample Line Length** – if the sample line is too long (and too large a diameter) then it will take a long time to flush the line with fresh gas. Since the gas in the line has in all likelihood spent a long time in that line, any sulphur can be absorbed into the pipework.

- **Sample Line Metallurgy** – if the sample line is made from carbon steel, then the sulphur will be absorbed into the parent metal which means that a sample taken from the system may not be representative. This is a particular problem if the sample line length is high. This problem can be over come by using stainless steel lines.

- **Sample Bomb Metallurgy** – as with the sample line, if the metallurgy is carbon steel, and the sample is not tested quickly, then the sulphur will be absorbed into the metal and the sample will potentially contain no sulphur. This problem can be over come by using stainless steel bombs or plastic gas sample bags and testing the samples as soon as possible.

8 Conclusions

In conclusion, this paper has illustrated some of the key features of the purification systems, most notably,

- There are many different varieties of catalyst poisons that can be present in the feedstock and the choice of purification catalyst must be suited to the type of impurities.
- The design of the purification system plays an important factor in the choice of purification catalyst, i.e.: lead/lag against single vessel design
- The level of purification required will determine if ultra-purification is required.
- The operating temperature is key, the purification system favours high temperatures, however too high temperatures can lead to carbon lay down in the feed pre-heat coils and the on the HDS catalyst resulting in loss of activity, high PD and inefficient heat transfer or failure of the coils.
- Some systems are designed for low operation so the type and specification of catalyst selected is important to achieve the desired purification levels.
- Uniform catalyst loading is essential to avoid flow gas mal-distribution and channelling in order to utilise the full catalyst volume.
- Monitoring the performance of the purification system is essential to predict the life/capacity of the purification catalyst and avoid poison slip to the down stream catalysts.

9 References

Reference 1	Mercury Removal Technology and its Application P E J Abbott and P Openshaw Johnson Matthey Catalysts ARTC April 2002
Reference 2	Primary Reformers – Theory and Operation Bill Cotton Johnson Matthey Catalysts Gulf Coast Producers Ammonia Conference April 2002

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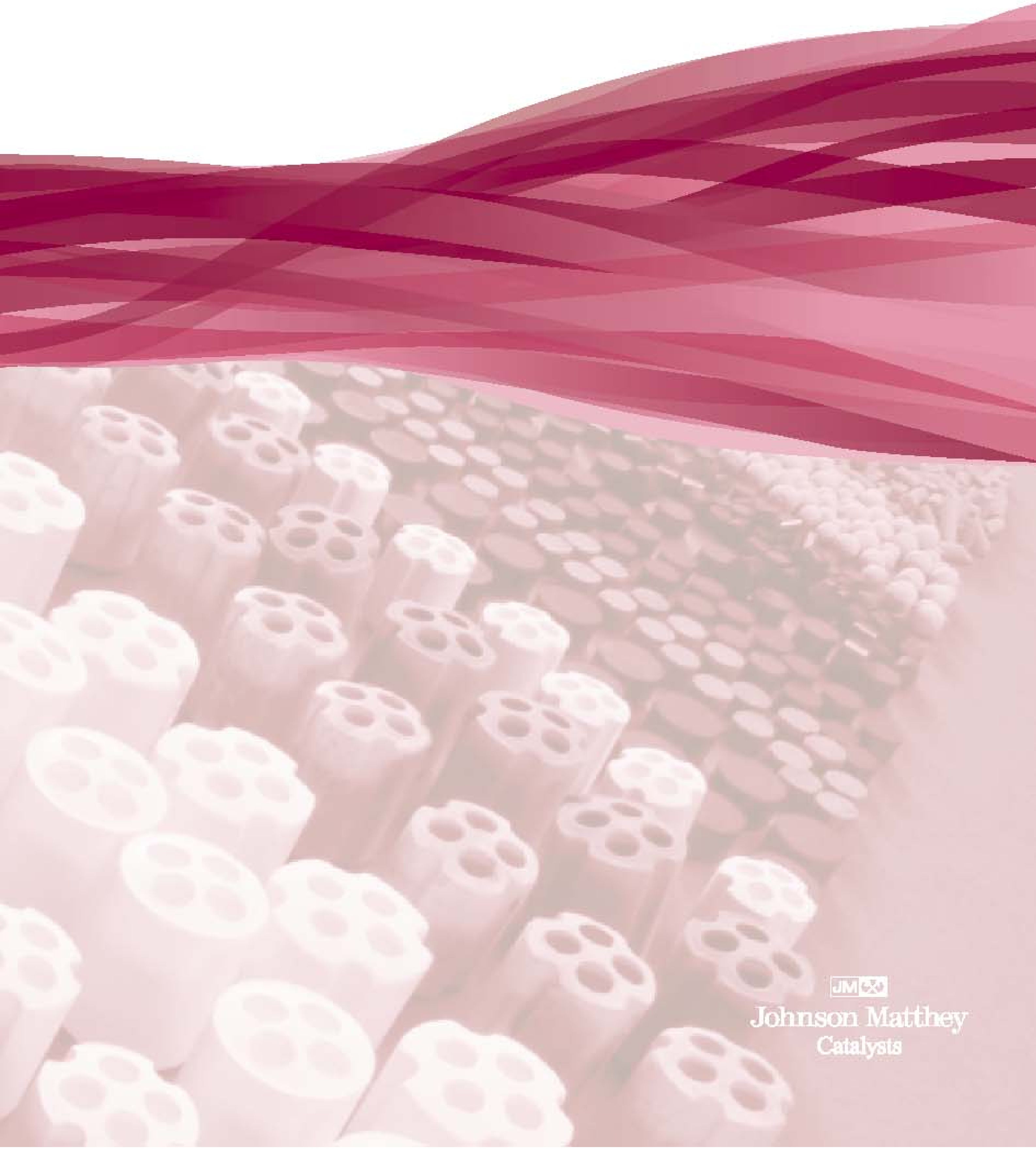
Theory and Operation of Primary Reformers



Johnson Matthey
Catalysts

1 Introduction

The primary reformer is at the heart of any synthesis gas generation plant and as such the importance of the good operation and maintenance of the Primary reformer can not be under-stated.

The purpose of this paper is to,

- Detail some fundamentals about reforming chemistry and equilibrium,
- Detail the theory behind how primary reformers are designed,
- How primary reformers should be operated,
- The key control parameters that the process engineer or plant manager can change on the primary reformer,
- Discuss some common operating problems.

2 Background

2.1 The History of Reforming

The following details the history of reforming in the last 100 years,

1900	Fritz Haber patented a process concept for the production of Ammonia from nitrogen and hydrogen.
1900's	BASF start research on steam reforming.
	First commercial ammonia plant built at Ludwigshafen by BASF.
1930's	First reformers built.
	Raschig ring introduced.
	Standard Oil build steam reformer at Baton Rouge.
1938	First methane-steam (pilot scale) reformer built at Billingham.
	First naphtha-steam reformer built at Heysham.
	Introduction of potash doped naphtha catalyst.
1960's	Introduction of natural gas reforming catalyst.
1970's	Introduction of impregnate gas reforming catalyst.
1980's	Development of compact reformers.
	Development of shaped catalysts.
	Commissioning of Compact Reformer at Severnside, England.
1990's	Development of low pressure drop catalysts.
1994	Commissioning of Compact Reformer at Kitimat, Canada.
1994	Commissioning of Compact Reformer at Melbourne, Australia.

2.2 Terminology

The following details some definitions of terms that are used within this paper,

- **Approach to Equilibrium** – The difference between the real exit temperature from the catalyst and the equilibrium temperature. This is further discussed below.

- **Convection Section** – This is the part of the reformer where heat is recovered from the fluegas into boiler feed water, steam, combustion air and feed gas.

- **Equilibrium Temperature** – the temperature at which a gas with a specified methane slip is at equilibrium.

- **Geometric Surface Area** – This is the surface area per unit volume of the catalyst. This has units of m^2/m^3 (or ft^2/ft^3).

- **Maximum Tube Wall Temperature** – This is the maximum temperature down the tube.

- **Methane Slip** – the percentage of methane exit the reformer. Typically this is stated in dry mol %.

- **Radiant Section** – This is the part of the duct where heat is transferred from the combustion of fuel gas to the process gas.

- **Steam to Carbon Ratio** – This is the ratio of the moles of steam to total moles of organic carbon in the feed gas. Note that ethane is considered to have 2 moles of carbon, propane 3 moles etc. The following equation defines steam to carbon,

$$\mathrm{SC} = \frac{\text{Steam Rate}}{\text{Feed Rate} \times \sum_{1}^{N} n \times C_n H_{2n+2}}$$

- **Steam to Gas Ratio** – This is similar to steam to carbon ratio but is the ratio of the steam rate to the feedrate. Provided that the feedstock composition remains constant, then this ratio does give a true indication of the steam to carbon ratio. However, if the feedstock composition does vary, it is possible to operate at too low a steam to carbon ratio which can lead to carbon deposition.

- **Tube Wall Margin** – This is the difference between the design temperature of the tubes and the actual maximum operating temperature of the tubes.

3 Reforming Theory

3.1 Chemistry

The key reactions that occur in reformers are as follows,

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H = +206\ \text{kJ/kmol}$$

$$C_2H_6 + 2H_2O \leftrightarrow 2CO + 5H_2$$

$$C_3H_8 + 3H_2O \leftrightarrow 3CO + 7H_2$$

And so on. Note that only the methane-steam reaction is reversible. The Water Gas Shift reaction also occurs,

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H = -41\ \text{kJ/kmol}$$

As can be seen the steam reforming reactions are highly endothermic whilst in comparison the water gas shift reaction is mildly exothermic. Combining the Methane-Steam reaction and the Water Gas Shift reaction, the following equation can be derived,

$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$ $\Delta H = +165$ kJ/kmol

3.2 Reaction Kinetics

The reaction rate is defined by the following equation,

$$\frac{dCH_4}{dt} \propto \text{Activity} \times \text{GSA} \times \exp^{[-\Delta E/(R.T)]} \times \frac{P[CH_4]}{P[H_2O]^m} \times (Kp' - Kp)$$

Where,

- Activity is the activity of the catalyst,
- GSA is the geometric surface area of the pellets,
- ΔE is the activation energy for the methane-steam reaction,
- R is the universal gas constant,
- T is the absolute temperature,
- $P[CH_4]$ is the partial pressure of methane,
- $P[H_2O]$ is the partial pressure of water,
- M is a number less than 1 but greater than 0.

To achieve a high reaction rate, methane steam reforming requires a very high temperature (for instance as used in partial oxidation) or with a catalyst and at more moderate temperature. It is typical to use a catalyst that is either coated or impregnated with nickel; however, for some particularly severe duties a more active catalyst is required; in these circumstances a precious metal catalyst is used. From this it can deduced that a high activity and high GSA catalyst is important. Furthermore, high reaction rates are favoured by high temperatures and pressures. The reaction rate equation is very similar for the higher hydrocarbons.

3.3 Equilibrium

Another important parameter is equilibrium; the following equation defines the equilibrium expression for the methane steam reaction,

$$Kp = \frac{P[CH_4].P[H_2O]}{P[H_2]^3.P[CO]}$$

This can be rewritten in a more useful form,

$$P[CH_4] = Kp\frac{P[H_2]^3.P[CO]}{P[H_2O]}$$

Which can be simplified by converting to molar fraction to give,

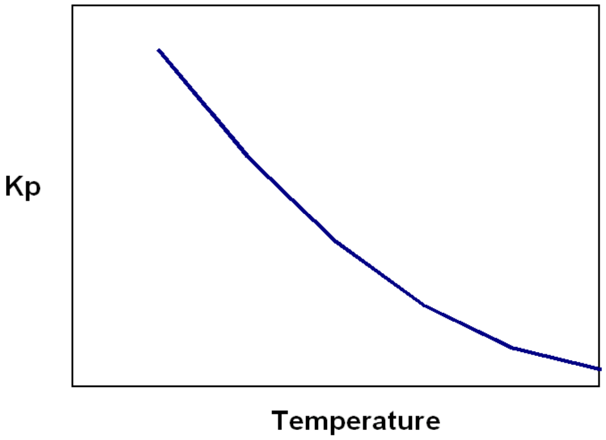
$$[CH_4] = Kp\frac{P^2[H_2]^3.[CO]}{[H_2O]}$$

The key points to note are,

- That increases in pressure will increase the methane slip by a large amount,
- Increasing the steam to carbon ratio will reduce the equilibrium constant and therefore lower the methane slip.
- It should be noted that although a good equilibrium position is favoured by low pressure, a high kinetic rate is favoured by a high pressure.

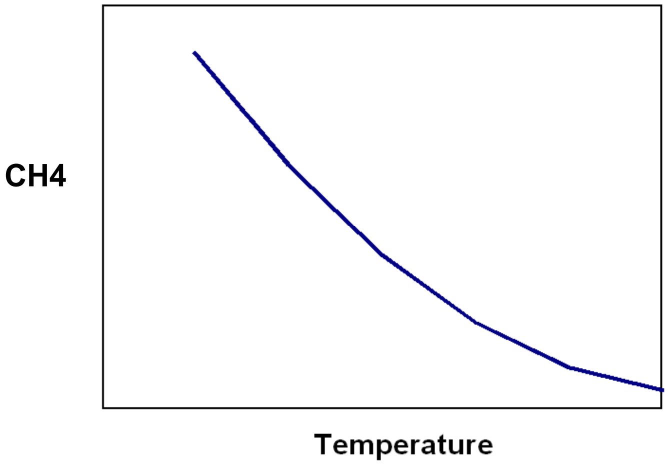
The equilibrium constant, Kp is related to temperature by the following graph,

Figure 1 – Effect of Temperature on Equilibrium Constant



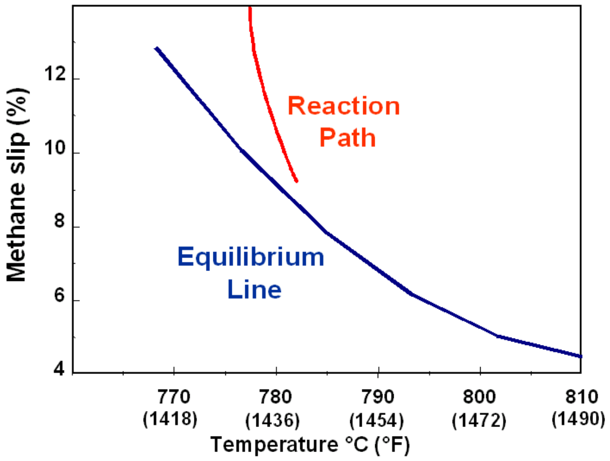
This graph can be linked with the above relationship to derive the following graph which relates temperature and methane slip,

Figure 2- Effect on Temperature on Methane Slip



The following graph illustrates the progress of the reforming reaction with regards to equilibrium for an ammonia reformer,

Figure 3 – Reaction Path and Equilibrium Line



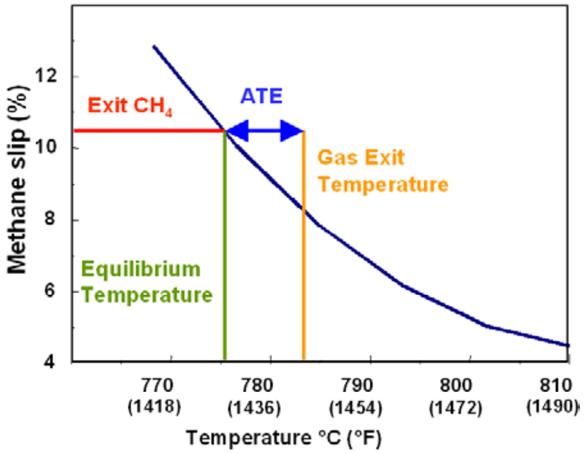
3.4 Approach to Equilibrium

Approach to equilibrium, or as it is commonly known, ATE, is a method of tracking the performance of a reformer with time. Approach to equilibrium is defined as,

ATE = Actual Exit Catalyst Temperature – Equilibrium Temperature

It should be noted that in this equation, the actual exit catalyst temperature is used. This will generally be higher than the observed measured temperature since there will be heat losses between the exit of the tubes and the measurement point[1]. The exception to this rule is Kellogg furnaces with risers installed where the measurement point is at the point where the sub manifolds met the riser and so there is no heat loss. The following figure illustrates the method of determining ATE for an ammonia primary reformer,

Figure 4 – Determination of ATE



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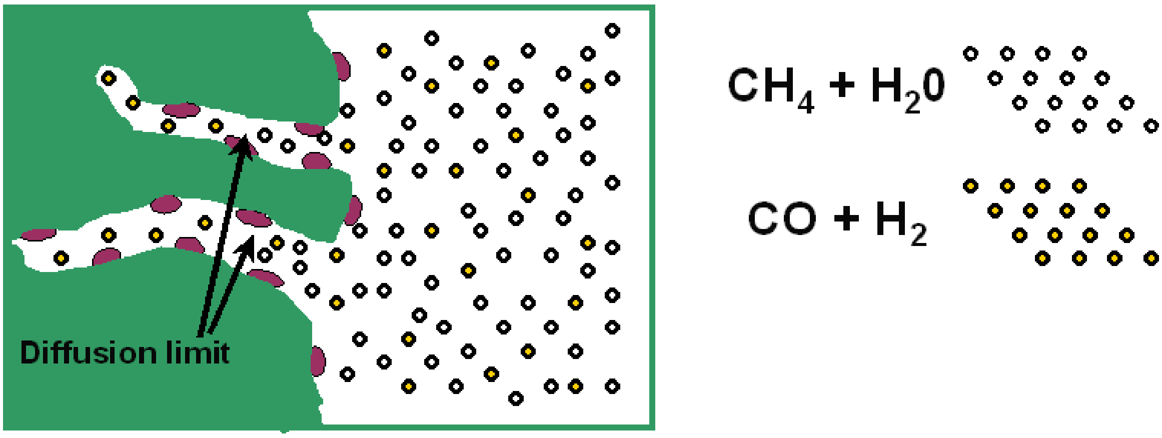
[1] Typically the temperature measurement point is inlet the secondary reformer.

3.5 Diffusion

The effect of diffusion must also be considered. The following figure illustrates the processes that occur around an active surface,

Figure 5 – Diffusion Limitations



There are six key steps in the diffusion of reactants from the bulk gas to the surface of the pellets and then back to the bulk gas,

1. Diffusion through the bulk gas – a fast process
2. Diffusion through the laminar film – a slow process,
3. Absorption on to the surface – a slow process,
4. Reaction on the surface – a fast process,
5. Desorbtion from the surface – a slow process,
6. Diffusion through the laminar layer – a fast process.

Hence the limiting processes are the diffusion through the laminar layer and the absorption/desorbtion from the catalyst surface. From this it can be inferred that the methane steam reaction will only occur on the surface of the catalyst and that the interior of any pellet will not be utilised.

3.6 Application of Le Chateliers Principle

If we apply Le Chateliers principle to the methane-steam reforming reaction, then we find that,

Table 1 – Effect of Operating Parameters

Parameter	**Effect**
Higher Pressure	Increases methane slip as volume of products is greater than volume of reactants
Lower Pressure	Decreases methane slip as volume of products is less than volume of reactants
Higher Temperature	Decreases methane slip since reaction is endothermic
Lower Temperature	Increases methane slip as reaction is endothermic
Higher Steam to Carbon	Decreases methane slip as more reactants available
Lower Steam to Carbon	Increases methane slip as less reactants available

So Le Chateliers principle would indicate that the steam reformer should be operated with the highest possible exit temperature, lowest possible exit pressure and the maximum amount of steam addition.

3.7 Optimal Pressure

One question that is raised from the above sections is what is the optimal operating pressure ?

As can be seen from the above, the reforming reaction requires a high pressure to maximise the reaction rate but a low pressure to obtain a good equilibrium position. In reality there is more to answering this question than equilibrium and kinetics; consideration should be given to,

- The capital cost of the reformer – low pressure means large vessels and pipes which increases the capital cost.
- The operating costs – high pressure will lead to a high methane slip which increases operating costs,
- The requirements of the synthesis loop – to minimise the capital expenditure required for the synthesis gas machine, a balance must be struck between the front end pressure and the loop pressure since this will define the number of stages required for the synthesis machine. The more stages required will increase the CAPEX for the machine.

3.8 Optimal Steam to Carbon Ratio

Again from the above, it is clear that a high steam to carbon ratio gives a favourable equilibrium position and hence a low methane slip. However, this steam has to be raised in the fluegas duct and the waste heat boiler, and therefore operation at high steam to carbon ratio's may not be economic. Furthermore high steam to carbon ratios do increase the size of the pipes, the steam reformer and heat exchangers. Hence there is the classic trade off between the CAPEX and OPEX associated with the plant. It is typical that the steam to carbon ratio is set at between 2.7 and 3.8.

3.9 Summary

The key points to note from the above are,

- The methane steam reaction is highly endothermic and is reversible,
- There is an equilibrium limitation which is sensitive to pressure,
- A high kinetic rate for methane-steam reforming is favoured by high pressures and high temperatures whereas a good equilibrium position is favoured by low pressure and high temperature,
- Diffusion through the laminar layer is the rate controlling step,
- Only the surface of the catalyst is used in the reaction,
- Any methane that is not reacted in the primary reformer will pass to the secondary reformer hence increasing the reaction load on the secondary reformer.

4 Reformer Design

The design of the primary reformer is dictated by the requirements outlined above. These are,

- The reforming reactions are endothermic so a large amount of heat is required,
- The reaction has to be carried out at moderate pressure,

- The maximum reaction rate and best equilibrium position is favoured by high temperatures,
- By using a catalyst, the reaction rate can be promoted such that lower temperatures can be used.

In order to satisfy these conditions, a large heat transfer area is required and this is provided by a large number of small diameter tubes which contain the catalyst. The heat is produced from the combustion of a combination of off gases from the plant and natural gas; this combustion is carried out in a refractory lined casing operating at slightly below atmospheric pressure. The feed, effluent, fuel and combustion systems need to be symmetric to ensure that the operation of the reformer is even such that the heat input to the tubes is even and hence the tube wall temperatures are the same for all tubes.

4.1 Components of the Primary Reformer

The main components of the primary reformer are,

- High alloy (25% nickel/35% chrome plus promoters) tubes of between 3 and 5" diameter,
- Feed header systems for distributing the feed, fuel and combustion air and an collector header system for the effluent from the reformer,
- A system of burners for combustion of the fuel gas,
- A steel casing lined with refractory to contain the combusted gases (fluegas) typically between 900°C and 1050°F and minimise heat losses; typically this is called the radiant section,
- A convection section to recover heat from the hot flue gases.

4.2 Types of Primary Reformer Designs

There are three main types of reformer designs which each have their own specific features,

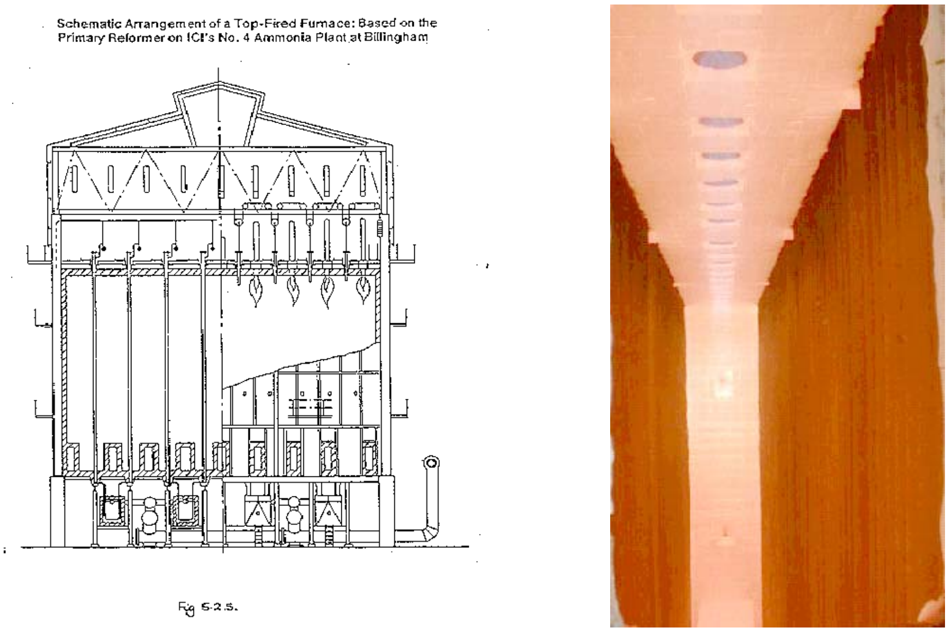
- **Top Fired** – typically offered by M W Kellogg, Krupp Uhde, Davy Process Technology, Toyo and Linde,
- **Terraced Wall** – offered by Foster Wheeler,
- **Side Fired** – offered by Selas, Linde, Chiyoda and Haldor Topsøe.

There are a multitude of other reformer designs, but these are few and far between and therefore will not be discussed in detail in this paper.

4.2.1 Top Fired Furnaces

Top fired furnaces are so called because the burners are situated in the roof of the furnace and the fluegas flows downwards co-currently with the process gas. The tubes are arranged 200-300 mm apart in rows, with between 2,000 and 2,500 mm between the tube rows. A typical design is shown in the figure below,

Figure 6 A/B – Top Fired Designs



The key advantages of this design are,

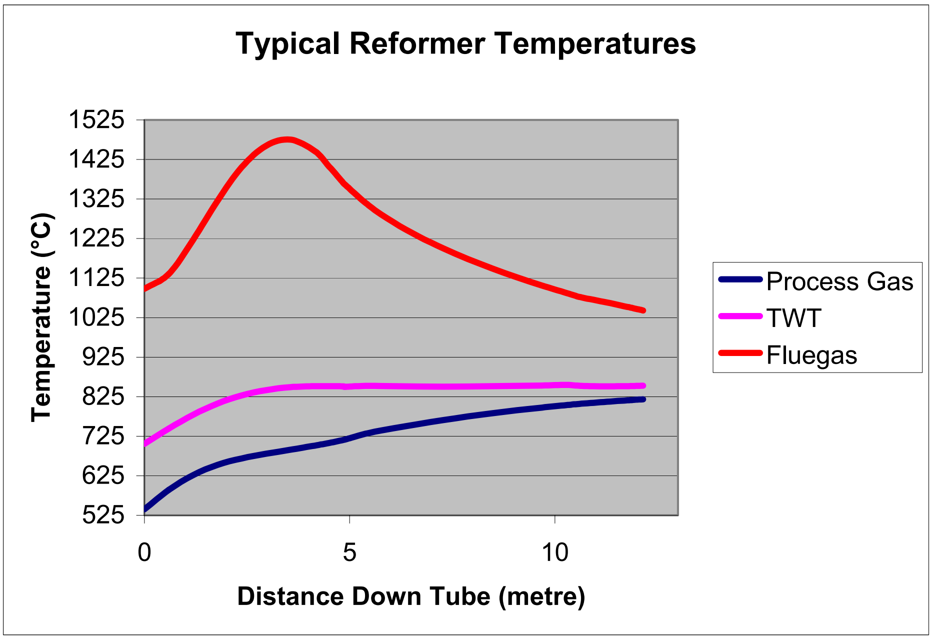
- Small catalyst volume,
- A relative small number of burners,
- Combustion air preheat is simple to install.

The key disadvantages of this design are,

- High heat fluxes at the top of the tubes can lead to carbon formation and hence to hot bands,
- The heat flux down the tube can not be varied,
- Burner control is coarse due to the low number of burners used on top fired reformers.
- A temperature pinch between the fluegas and process gas at the exit of the tubes.

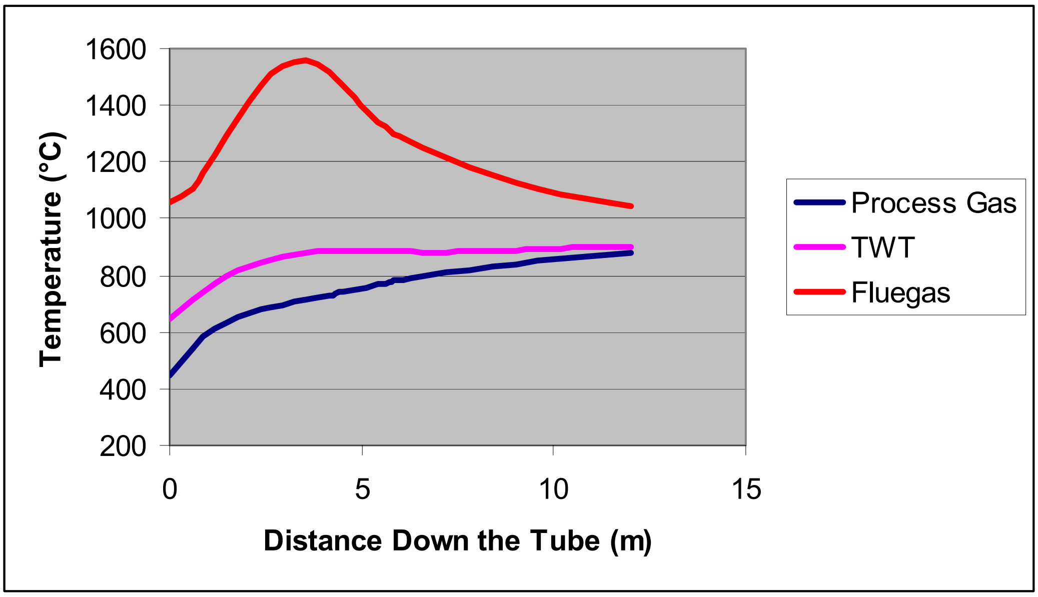
The following graph illustrates typical outside tube wall and process gas temperatures for an ammonia primary reformer,

Figure 7 – Temperature Profiles for an Ammonia Primary Reformer



The following figure illustrates the same temperatures for a methanol primary reformer,

Figure 8 – Temperature Profiles for a Methanol Primary Reformer



4.3 Tube Design

The design of the reformer tubes is absolutely critical in ensuring that the plant will operate successfully. The process of design usually includes the following steps,

- Selection of the tube material,
- Determination of the operating temperature profile,
- Determination of the operating pressure profile,
- Calculation of maximum allowable stress on tube using the Larsen Miller plot,
- Calculation of tube thickness using a hoop stress formula as shown below,

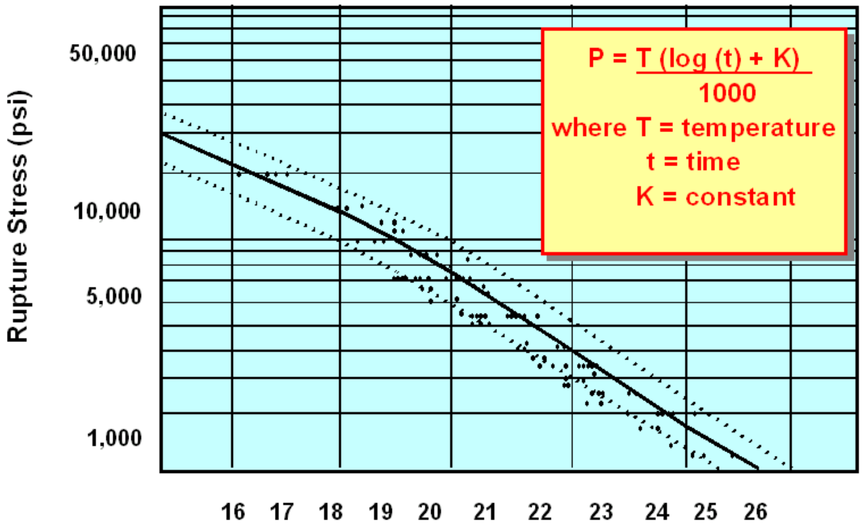
$$\sigma = \frac{\Delta P \times ID}{2t}$$

Where,

- σ is the maximum allowable stress,
- ΔP is the differential pressure,
- ID is the tube inside diameter,
- t is the tube thickness.

The following figure illustrates a typical Larsen-Miller plot,

Figure 9 – Larsen-Miller Plot



Failure to design the tubes correctly will lead to premature tube failure and potential plant shut downs. The following figures illustrate some typical failures, the first is of the parent material and the second of a weld,

Figure 10A/B – Longitudinal Tube Failure

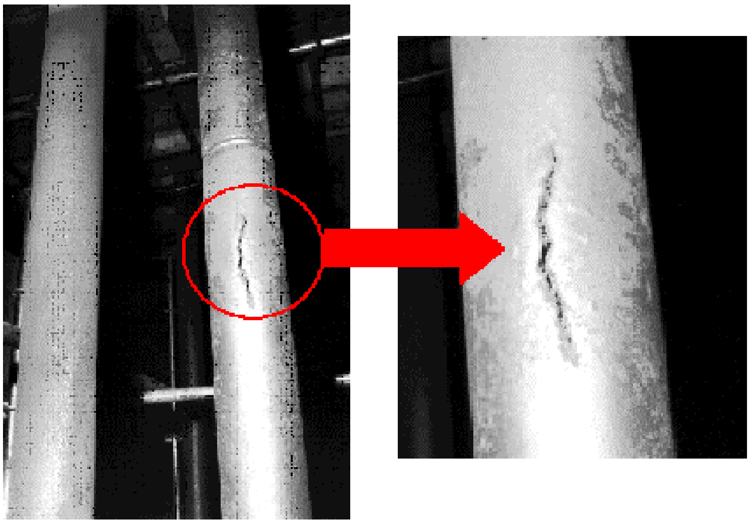
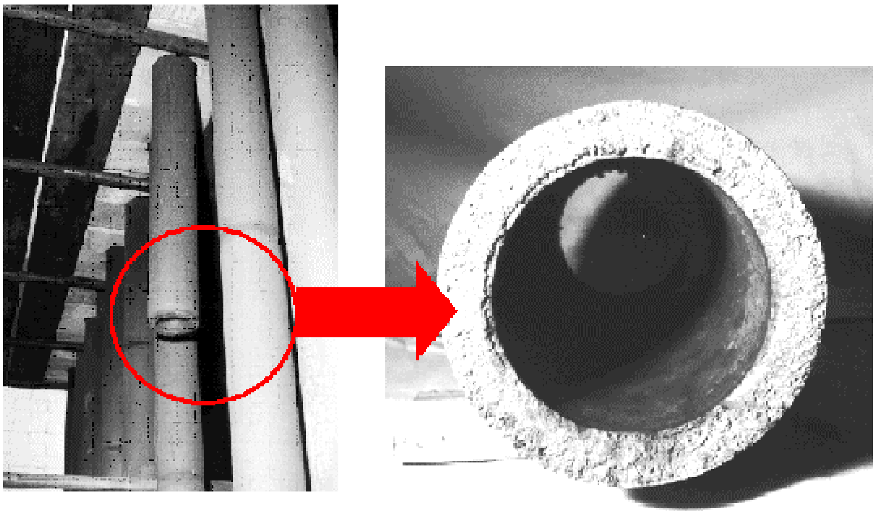


Figure 11A/B – Weld Failure



4.4 Convection Section Design

The convection section is designed to maximize heat recovery from the hot flue gases from the radiant section; typically these gas are between 900 and 1100°C depending on the type of reformer and the operating conditions. Heat is normally recovered into the following streams,

- Boiler feed water for preheating,
- Boiler feed water for steam raising,
- Steam for steam superheating,
- Feed gas for preheating prior to desulphurisation,
- Feed gas and steam for preheating prior to entering the primary reformer,
- Combustion air preheating,

- Fuel gas preheating.

Incorrect design and/or maintenance can lead to poor heat recovery and therefore increased tubeskin temperature in the duct. This can in the worst case, lead to plant rate reductions to prevent tubeskin temperatures exceeding the design value and hence failure of the coils.

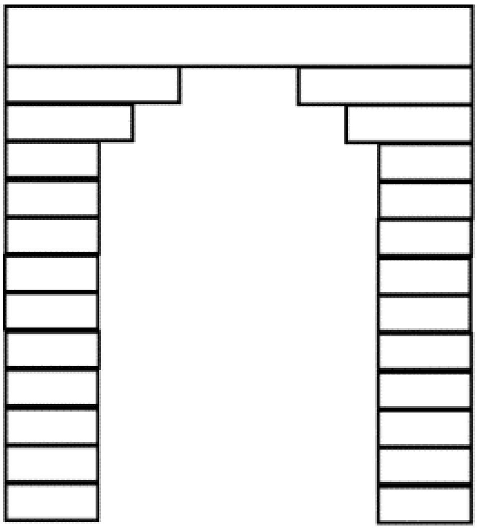
4.5 Header Designs

The design of the feed, fuel, combustion air and effluent headers is very important since poor design can lead to mal distribution either on the process or fluegas side. The fundamental design philosophy is to ensure that as far as possible all headers are symmetrical. Some typical problems that occur if the header designs are not correct are detailed below.

4.6 Coffin Design

In top fired reformers, the flue gases are collected in coffins (sometimes called tunnels); these run between the tube rows and are made from refractory bricks. At various points along the coffins, bricks are left out of the side wall to allow flow of fluegas from the radiant section into the tunnels. The number of holes down the coffin is varied to vary the free area to compensate for the pressure rise down the coffin. A typical design of coffin is shown below,

Figure 12 – Coffin Design



Inappropriate design of the coffin can lead to fluegas mal distribution (see reference 3) or collapsing of the coffins as illustrated below,

Figure 13 – Collapsed Coffin

Some plants have removed the coffins and this has lead to flue gas mal-distribution; this is discussed below.

4.7 Catalyst

The catalyst is also a very important factor in determining the performance of the primary reformer. The key parameters and the things they affect that must be considered when design a catalyst or selecting a catalyst for a primary reformer are,

Table 2 – Catalyst Characteristics

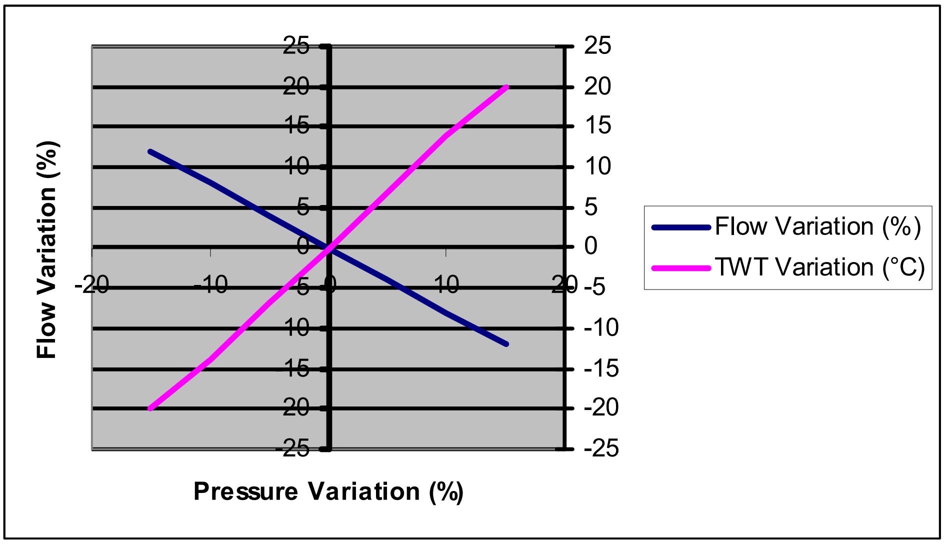
Parameter	**Affects**
Higher activity	Reduces approach to equilibrium Reduces tube wall temperatures Reduces potential for carbon formation
High heat transfer	Reduces tube wall temperatures
Alkali Support	Reduces potential for carbon formation
Shaped catalyst v ring shape	Reduces pressure drop Increases GSA
Increased size	Reduces pressure drop Reduces GSA
Number of holes	Increases GSA Reduces pressure drop Worsens breakage characteristics
Poor breakage characteristics	Increases pressure drop rise
Increased GSA	Reduces approach to equilibrium Reduces tube wall temperatures Reduces potential for carbon formation

These are typical relationships; a poorly designed catalyst may not give the expected performance as defined above.

4.8 Catalyst Loading

The importance of a good catalyst loading can not be understated; if the catalyst is loaded well then the process gas flow through the tubes will be even and the tube wall temperatures will be even. However, if the catalyst loading is poor, the there will be a variability in the resistance to flow through the tubes and this will lead to variations in the process gas flow which will be seen as tube wall temperature variations. The following graph illustrates this effect,

Figure 14 – Effect of Pressure Variation on Flow and TWT



It is strongly recommended that the catalyst is loaded carefully and where possible using a technique such as **UNIDENSE™** which ensures very even loading. Also it is recommended that the tube pressure drops are checked at the following levels,

- Check with no catalyst installed to ensure pigtails are not blocked,
- Check with 50% of the catalyst loaded to ensure that a good loading has been achieved in the bottom half of the tube,
- Check with 100% of the catalyst loaded to ensure that a good loading has been achieved in the top half of the furnace.

If a high pressure drop is seen with no catalyst installed, then a boroscope should be used to check the bottom section of the tube and inlet to the pigtail to see if there is an obvious blockage. If a high pressure drop is seen during catalyst loading, then that tube should be discharged and reloaded with the pressure drops checked again to ensure a good loading. If the pressure drop is too low, then the tube should be vibrated using a soft faced lump hammer to reduce the voidage and again the pressure drop through that tube shall be checked.

5 Control Parameters

The parameters that an operator can vary are,

- Exit reformer temperature,

- Exit reformer pressure,
- Feedstock rate,
- Steam to carbon ratio.

It should be noted that there are other parameters such as the firing splits between different levels of burners in Foster Wheeler and Side Fired furnaces.

5.1 Exit Reformer Temperature

5.1.1 Ammonia Plants

As noted above in the sections above, increasing the exit temperature will reduce the methane slip and thereby reduce the amount of reforming required in the secondary reformer. It is typical that a change in primary reforming methane slip of 1% will reduce the methane slip from the secondary by 0.1%. Hence raising the temperature exit the primary reformer will improve conversion of the feedstock to synthesis gas, thereby raising plant efficiency. The effect of changing the outlet temperature by 18°F (10°C) for an ammonia plant are outlined in the table below,

Table 3 – Effect of Exit Temperature for Ammonia Plants

Name	**Units**	**Base Case**	**Increased Temperature**
Plant Rate	*%*	100	100
Steam to Carbon	*n/a*	2.88	2.88
Outlet Temperature	*°C*	818	828
Methane Slip	*mol %*	12.31	11.37
Pressure Drop	*Bar*	1.33	1.35
Approach to Equilibrium	*°C*	3.1	3.1
Outlet Pressure	*Bara*	40.90	40.90
Maximum Tube Temperature	*°C*	866	875
Minimum Tube Wall Margin	*°C*	25	16
Fluegas Temperature	*°C*	1043	1061
Fluegas Flowrate	*kmol/hr*	12835	13609
Furnace Duty	*MW*	198	206

These changes will require that the following checks are made to ensure that the plant is not operated above design limitations,

- Check that the outlet headers will still be operating below the design temperature.
- Check that the fluegas duct coils will still be operating below the design temperature.
- Check that the fuel gas headers are capable of handling the increased fuel flow rate.
- Check that carbon formation will not become an issue.
- Check that the ID (induced draft) fan is capable of handling the increase fluegas flowrate.
- Check that the FD (forced draft) fan is capable of handling the increase fluegas flowrate.

5.1.2 Methanol Plants

The effect of changing the outlet temperature by 18°F (10°C) for a methanol plant are outlined in the table below (assuming the plant has no secondary reformer installed; if it has a secondary reformer, then the numbers in the table above are more applicable),

Table 4 – Effect of Exit Temperature for Methanol Plants

Name	Units	Base Case	Increased Temperature
Plant Rate	*%*	100	100
Steam to Carbon	*n/a*	3.00	3.00
Outlet Temperature	*°C*	880	890
Methane Slip	*mol %*	1.83	1.54
Pressure Drop	*Bar*	3.19	3.22
Approach to Equilibrium	*°C*	4.8	4.8
Outlet Pressure	*Bara*	15.5	15.5
Maximum Tube Temperature	*°C*	907	917
Minimum Tube Wall Margin	*°C*	41	35
Fluegas Temperature	*°C*	1041	1051
Fluegas Flowrate	*kmol/hr*	22204	22793
Furnace Duty	*MW*	433	441

The same comments apply in terms of the checks that should be made in terms of the plant operability noted above apply to the results above.

5.2 Exit Pressure

5.2.1 Ammonia Plants

Again as seen above in the sections above, by lowering the exit reformer pressure it is possible to reduce the methane slip, again this improves plant efficiency.

The following table illustrates this for an ammonia plant,

Table 5 – Effect of Exit Pressure for Ammonia Plants

Name	Units	Base Case	Increased Pressure
Plant Rate	*%*	100	100
Steam to Carbon	*n/a*	2.88	2.88
Outlet Temperature	*°C*	818	818
Methane Slip	*mol %*	12.31	12.57
Pressure Drop	*Bar*	1.33	1.30
Approach to Equilibrium	*°C*	3.1	3.0
Outlet Pressure	*Bara*	40.90	41.90
Maximum Tube Temperature	*°C*	866	865
Minimum Tube Wall Margin	*°C*	25	23
Fluegas Temperature	*°C*	1043	1041
Fluegas Flowrate	*kmol/hr*	12835	12699
Furnace Duty	*MW*	198	197

The following comments can be drawn from this,

- The tube wall temperature margin and thereby the tube life are decreased since the differential pressure and hence the hoop stress on the plant is increased. In this case, this change in pressure will decrease the tube life by about a year.
- The differential pressure across the synthesis gas machine will be reduced causing either the machine speed/power to be decreased or the loop pressure to be increased.
- The pressure drop through the front end of the plant will also decrease slightly, thereby, again decreasing the speed and power requirement for the synthesis gas machine.

Typically, an increase of 1 bar will decrease the front end pressure drop by about 3%.

5.2.2 Methanol Plants

Again as seen above in the sections above, by lowering the exit reformer pressure it is possible to reduce the methane slip, again this improves plant efficiency. The following table illustrates this for a methanol plant,

Table 6 – Effect of Exit Pressure for Methanol Plants

Name	Units	Base Case	Increased Pressure
Plant Rate	*%*	100	100
Steam to Carbon	*n/a*	3.00	3.00
Outlet Temperature	*°C*	880	880
Methane Slip	*mol %*	1.83	2.00
Pressure Drop	*Bar*	3.19	3.03
Approach to Equilibrium	*°C*	4.8	4.5
Outlet Pressure	*Bara*	15.5	16.5
Maximum Tube Temperature	*°C*	907	907
Minimum Tube Wall Margin	*°C*	41	35
Fluegas Temperature	*°C*	1041	1040
Fluegas Flowrate	*kmol/hr*	22204	22078
Furnace Duty	*MW*	433	431

Again, the same comments as made above apply to a methanol plant when increasing outlet primary reformer pressure.

The converse of the effects noted above are true when reducing the exit pressure.

5.3 Feed Rate Changes

5.3.1 Ammonia Plant

It is also possible to increase or reduce the feed rate to the plant which will alter the operating parameters of the primary reformer. The following table illustrates the effect of a 5% increase in feed and steam rate has on the primary reformer for an ammonia plant,

Table 7 – Effect of Feed Rate for Ammonia Plants

Name	Units	Base Case	Increased Rate
Plant Rate	*%*	100	105
Steam to Carbon	*n/a*	2.88	2.88
Outlet Temperature	*°C*	818	818
Methane Slip	*mol %*	12.31	12.39
Pressure Drop	*Bar*	1.33	1.45
Approach to Equilibrium	*°C*	3.1	3.4
Outlet Pressure	*Bara*	40.90	40.90
Maximum Tube Temperature	*°C*	866	870
Minimum Tube Wall Margin	*°C*	25	21
Fluegas Temperature	*°C*	1043	1057
Fluegas Flowrate	*kmol/hr*	12835	13658
Furnace Duty	*MW*	198	208

Again the reformer and associated equipment should be checked to ensure that there will be no operating problems at this higher rate.

The checks outlined in above should be sufficient to ensure operation is acceptable.

5.3.2 Methanol Plant

The following table illustrates the effect of a 5% increase in feed and steam rate has on the primary reformer for a methanol plant,

Table 8 – Effect of Feed Rate for Methanol Plants

Name	Units	Base Case	Increased Rate
Plant Rate	*%*	100	105
Steam to Carbon	*n/a*	3.00	3.00
Outlet Temperature	*°C*	880	880
Methane Slip	*mol %*	1.83	1.84
Pressure Drop	*Bar*	3.19	3.46
Approach to Equilibrium	*°C*	4.8	5.4
Outlet Pressure	*Bara*	15.5	15.5
Maximum Tube Temperature	*°C*	907	912
Minimum Tube Wall Margin	*°C*	41	35
Fluegas Temperature	*°C*	1041	1054
Fluegas Flowrate	*kmol/hr*	22204	23583
Furnace Duty	*MW*	433	455

Again the reformer and associated equipment should be checked to ensure that there will be no operating problems at this higher rate.

5.4 Reduction in Steam to Carbon Ratio

5.4.1 Ammonia Plant

Steam to carbon ratio can also be changed to reduce the heat load on the primary reformer. Such a change can reduce the pressure drop across the primary reformer and the downstream equipment, thereby allowing for a feed rate increase. The effect of such a change is as outlined in the table below for an ammonia plant,

Table 9 – Effect of Steam to Carbon for Ammonia Plants

Name	**Units**	**Base Case**	**Decreased Steam to Carbon**
Plant Rate	*%*	100	100
Steam to Carbon	*n/a*	2.88	2.78
Outlet Temperature	*°C*	818	818
Methane Slip	*mol %*	12.31	12.81
Pressure Drop	*Bar*	1.33	1.27
Approach to Equilibrium	*°C*	3.1	2.8
Outlet Pressure	*Bara*	40.90	40.90
Maximum Tube Temperature	*°C*	866	864
Minimum Tube Wall Margin	*°C*	25	27
Fluegas Temperature	*°C*	1043	1037
Fluegas Flowrate	*kmol/hr*	12835	12505
Furnace Duty	*MW*	198	195

5.4.2 Methanol Plant

The effect of such a change is as outlined in the table below for a methanol plant,

Table 10 – Effect of Steam to Carbon for Methanol Plants

Name	Units	Base Case	Decreased Steam to Carbon
Plant Rate	*%*	100	100
Steam to Carbon	*n/a*	3.00	2.90
Outlet Temperature	*°C*	880	880
Methane Slip	*mol %*	1.83	1.95
Pressure Drop	*Bar*	3.19	3.07
Approach to Equilibrium	*°C*	4.8	4.4
Outlet Pressure	*Bara*	15.5	15.5
Maximum Tube Temperature	*°C*	907	907
Minimum Tube Wall Margin	*°C*	41	42
Fluegas Temperature	*°C*	1041	1039
Fluegas Flowrate	*kmol/hr*	22204	21965
Furnace Duty	*MW*	433	429

6 Monitoring

6.1 Tube Wall Temperature Measurement

It is recommended that the tube wall temperatures of the reformer are measured on a regular basis to ensure that,

- There are no hot tubes which could fail prematurely,
- There are no cold tubes that will lead to high methane slip,
- There are no signs of hot banding etc.

References 1 and 2 give further details on how best to conduct such tube wall temperature measurements.

If a tube is found to be excessively hot then the fuel rate to the burners around this tube should be reduced to prevent premature tube failure. Conversely if a tube is found to be excessively cool, then the fuel to the surrounding burners should be increased. It is recommended that a tube shoot be conducted at least once a week.

It is recommended that an infra red pyrometer such as a Land 52 or 339 is used. Consideration must be given to the effect of background radiation when using such pyrometers.

6.2 Tube Visual Appearance

As part of the regular reformer tube shoot, the tubes should be visually inspected in order to detect whether there are,

- Hot bands,
- Giraffe necking,
- Hot tubes.

If a tube is found to be operating hot, then it is recommended that pictures are taken of the affected tube or tubes on a regular basis, typically once a fortnight or a month is sufficient to allow for an objective monitoring of the tubes.

6.3 Refractory Inspection

At the same time as the tube inspection is performed, the refractory should also be inspected to check for bricks moving away from the all and cracks appearing between the bricks. These problems can lead to hot fluegas tracking behind the refractory which will raise the casing temperature which poses a safety hazard and ultimately can lead to the failure of the casing.

Steam lances or water curtains can be used on such hot spots to reduce the temperature of the casing and prevent the damage from spreading.

6.4 Burner Inspection

At the same time as the tube inspection is performed, the burners should also be inspected to check for flame pattern deviations and flame impingement.

6.5 Methane Slip

The methane slip from the primary reformer should be checked every week. This should be recorded along with the following parameters,

- Exit reformer temperature,
- Exit pressure,
- Steam to carbon ratio,
- Plant rate.

This allows for early identification of problems on the reformer before they become too severe. By collecting the other key process parameters it is easy to check whether a rise in methane slip can be attributable to a change in a process parameter.

6.6 Pressure Drop

Pressure drop should also be recorded on a regular basis to ensure that early identification of excessive breakage or carbon formation is possible. If the plant rate is changing then the pressure drop should be normalised for changes in feed rate and also steam rate.

7 Common Problems

There are many common problems that can occur on a steam reformer; below is a brief discussion of some of them. If as an operator you believe that you have a problem, then you should consult your catalyst vendor.

7.1 Poisoning

Poisoning of reformer catalyst is more common than most operators expect; this is because there are many ways of poisoning the catalyst and the detection of poison can be very difficult. Common poisons include,

- Sulphur in the form of H_2S, COS or simple mercaptans,
- Chlorides,
- Phosphates,
- Arsenic,
- Vanadium.

Poisoning causes deactivation of the catalyst by covering the nickel crystallites and blocking off access for the reactants in the process gas. This reduction in the local rate of reaction causes the tube wall temperatures to rise and hot bands eventually form.

Once the inside tube wall temperatures rise high enough, the rate of carbon deposition exceeds the rate of carbon removal and carbon laydown starts.

This reduces the inside wall heat transfer, covers the nickel crystallites, hence reducing the catalyst activity and increases the resistance to flow through the tube and hence the flow through the tube is reduced. All of these lead to an increase in the tube wall temperatures which increases the rate of carbon formation.

Eventually the tube wall temperature rise such that the plant rate or the primary reformer firing has to be reduced.

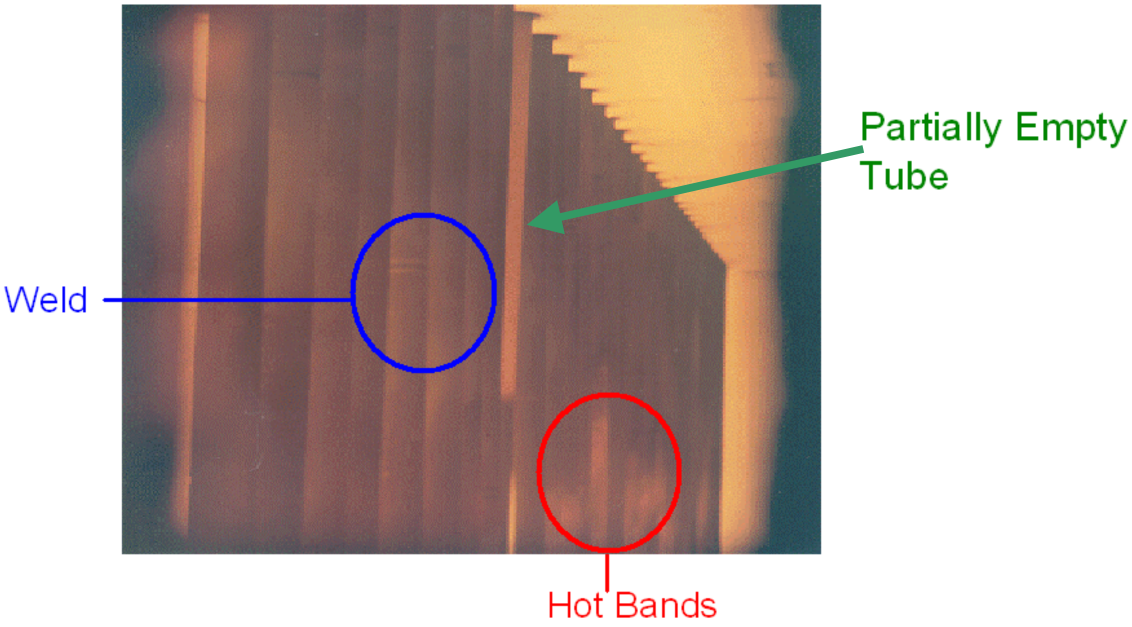
7.2 Carbon Formation

Carbon formation occurs when,

- The catalyst activity is low due to old age or poisoning,
- The feed gas composition has become heavy,
- The steam to carbon ratio has been too low.

It is typified by the formation of hot bands about one third of the way down the tubes in a top fired reformer as illustrated in the next picture,

Figure 15 – Hot Bands in Primary Reformers



Light carbon formation caused by operation at steam to carbon ratios just below the design figure. Once carbon lay down has occurred, then there are some temporary measures to limit the rate of carbon formation; these include,

- Operation at elevated steam to carbon ratios,
- Increased hydrogen recycle.

However, this is a temporary measure and rarely will such actions removed carbon that has been laid down.

To ensure complete removal of carbon, then a steam out should be conducted; this process should follow these guidelines,

1. The steam rate shall be set at a minimum of 50% of the design steam rate.
2. The reformer exit temperature shall be as high as possible and shall be in excess of 700°C.

3. The steam out shall be performed for at least 12 hours.
4. The gas exit the reformer shall be tested for methane and carbon dioxide; it should be noted that there will be little carbon monoxide since the water gas shift reaction favours the formation of carbon dioxide. The results of the test shall be trended as a measure of the progress of the steaming.
5. The exit reformer gases shall also be tested for hydrogen sulphide. An alternate is to test the process condensate for sulphites and hydrogen sulphide (in some cases a small test is adequate for detecting this).
6. If the gas sample is taken down stream of the process condensate knock out pot, the nitrogen shall be added at the mixing tee to act as a carrier gas.

Johnson Matthey Catalysts can provide a more detailed procedure on request.

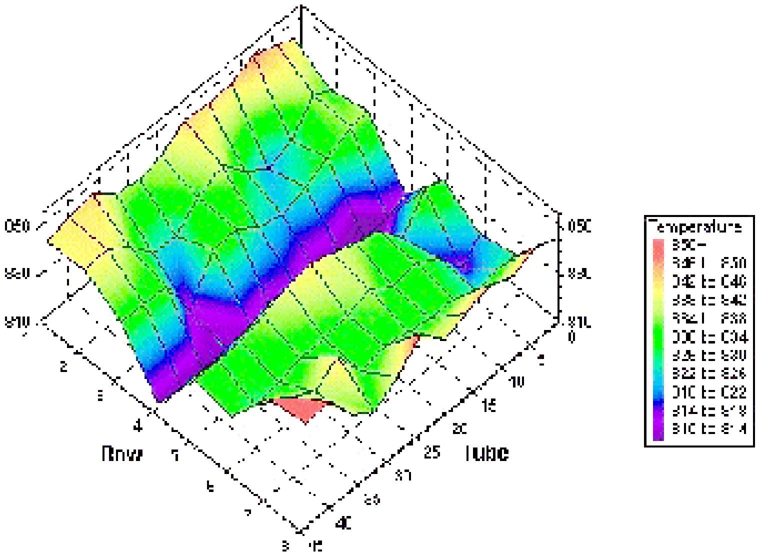
In some cases, such as carbon lay down which occurs during a transient, a steam out may not be sufficiently aggressive enough to remove the carbon. If this occurs, then an air burn can be considered and if this fails then the catalyst may have to be drilled out.

Carbon formation should not be a problem on Foster Wheeler or Side Fired furnaces during normal operation; however, during transients such as start up and shut down, it is possible to operate at low steam to carbon ratios and have gross carbon formation.

7.3 Poor Catalyst Loading

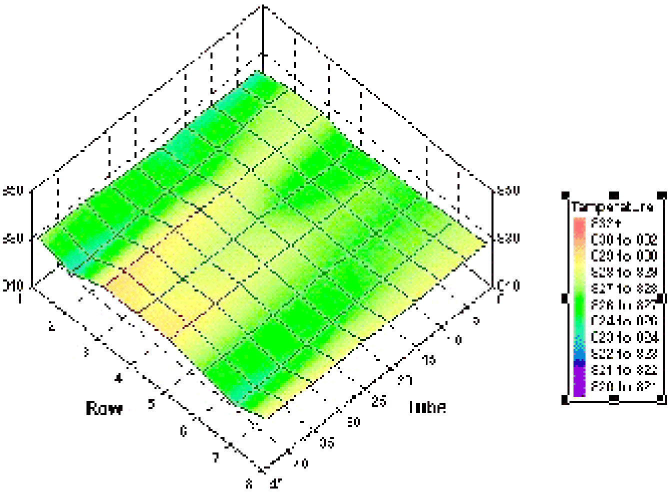
Ensuring a good catalyst loading is fundamental in ensuring efficient operation of the primary reformer. Any deviations in resistance to flow through the tubes will result in differential flows between tubes and this in turn will lead to tube wall temperature differences as illustrated below,

Figure 16 – Poor Catalyst Loading



A good catalyst loading will cause even process gas distribution and hence even tube wall temperature distribution.

Figure 17 – Good Catalyst Loading



7.4 Flame Impingement

Flame impingement occurs when the burner is mis-aligned or is damaged, causing the flame to deviate from the vertical and to impinge on the tube. This causes local overheating, reducing the life of the tube/tube failure and potentially can lead to carbon formation. If a burner is found to be defective, then it is possible to remove it from service whilst the reformer is on line, rectify the problem and reinstate the burner.

7.5 Mal-distribution

There are a number of causes of mal-distribution with in a primary reformer, due to poor design of the,

- Fuel headers,
- Combustion air ducting,
- Process feed headers,
- Exit headers,
- Coffins/outer lane.

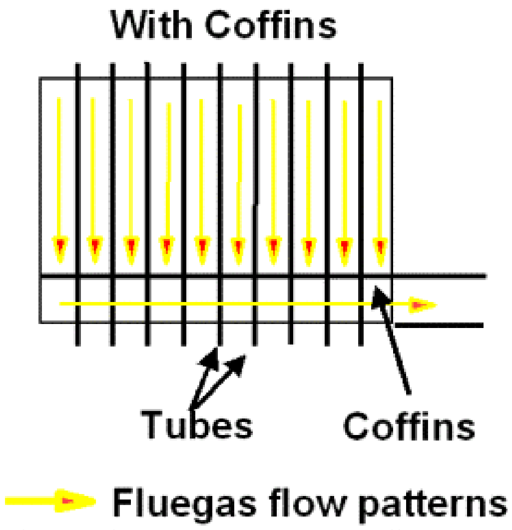
The effect of these are very similar in that they will induce some form of mal-distribution, either on the process gas side or the flue gas side of the reformer. Such mal distribution will commonly be highlighted by,

- High tube wall temperature spreads,
- High exit temperature spreads,
- Higher than expected methane slips,
- Higher than expected ATE's.

7.6 Coffin Removal

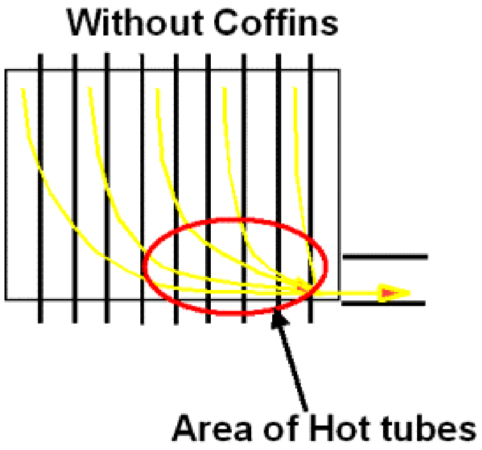
A number of plants have removed the coffins from the radiant section of the box because of either a high pressure drop through the poses a limit to the plant rate or repair issues associated with damage to the coffins. The figure to the right shows the fluegas flow patterns with coffins installed – as is clear the fluegas in passing down the furnace in plug flow.

Figure 18 – Flow Patterns with Coffin Installed



The following figures shows that fluegas flow patterns with the coffins removed. As is clear there is a significant mal distribution of gas and much of that gas is flowing preferentially towards the fluegas extraction end.

Figure 19 – Flow Patterns with Coffin Installed



The overall effect of this is to increase the tube temperatures at the fluegas extraction end of the furnace,

Figure 20 – Effect on TWT

7.7 After-Burning

After-burning is caused by incomplete combustion in the top of the furnace which allows fuel to move down until it mixes with oxygen, at which point the fuel combusts giving the classic observation of flames licking around the tubes in the bottom half of the furnace. To resolve this problem, additional combustion air needs to be supplied to the area affected by the after-burning. Checks should be made for CO and O_2 in the fluegas to ensure that the problem is resolved.

7.8 Poor Combustion Air Header Design

During a routine reformer survey of a world scale Methanol customer's primary reformer, it was noted that there was severe after burning was occurring in the centre of the radiant box. After-burning is caused by incomplete combustion in the top of the furnace which allows fuel to move down until it mixes with oxygen, at which point the fuel combusts giving the classic observation of flames licking around the tubes in the bottom half of the furnace. It was noted that no after burning was seen in the outer lanes. It was noticed that the oxygen measurement exit the radiant box was at 1.5%; this was rechecked and confirmed by the plant operator. It was also noted that the fluegas fan was operating at its maximum speed and that the box pressure was close to being positive. Inspection of the duct found that the combustion air system design was symmetrical and that this could not be the cause of the problem.

On inspection of this system it was clear that there was insufficient pressure differential between the duct and the box to force enough air through to the centre of the furnace. This caused there to be a lack of combustion air in the centre of the furnace, and hence there was incomplete combustion and fuel passed into the bottom half of the furnace. The outer lanes of burners had an excess of air, and therefore there was a high excess oxygen content in the fluegas. Some of this excess oxygen then mixed with the excess fuel in the centre of the furnace and this resulted in the after burning noted.

7.9 Start Up

During start up it is normal to circulate nitrogen through the reformer to acts as a heat up medium. Once the temperature of the exit headers of the reformer exceeds the dew point of water by 15-20°C, then steam can be introduced and nitrogen can be backed out of the process. This prevents condensation of water in the reformer tubes which will lead to catalyst damage.

8 Trouble Shooting

The following is a brief list of some common problems, the cause of these problems and the actions that should be taken to minimise or eliminate their effect. As noted above, you should consult you catalyst vendor.

Problem	Cause	Actions
Hot bands	Poisoning of the catalyst.	Reduce localised firing. Steam catalyst.
	Operation at low steam to carbon.	Steam catalyst.
	Aged catalyst.	Replace catalyst. Steaming can help remove carbon temporarily.
	Localised overheating.	Reduce localised firing. Check burners.
	Incorrect catalyst loading.	Check that potash doped catalyst loaded at inlet to tube. Replace as required.
Excessive Pressure Drop	General catalyst breakage.	Reduce plant rate. Replace catalyst (all or a portion).
	Carbon formation due to low to steam carbon operation or poisoning.	Reduce localised firing. Steam catalyst.
	Catalyst breakage at inlet to tubes.	Check design of inlet to tube for jet impingement on catalyst. Check if there is water droplet carry over. Check is water can be carried over on a trip or start up. Check if condensate can form in dead legs or low points during a shut down.
	Catalyst breakage at outlet of tubes.	Check if there has been water ingress into the bottom of the tube.
	Water leaching support material and causing formation	Clean the inside of the tubes with brushes or frapper to prevent a in reduction inside

	of cement.	heat transfer coefficient.
Hot Tube	Low catalyst voidage due to breakage or over vibration on loading.	Replace catalyst in affected tubes.
Hot Patch	Flame impingement.	Reduce localised firing. Check burners.
	Localised over firing.	Reduce localised firing. Check burners.
Shimmering on Tube	Flame impingement.	Reduce localised firing. Check burners.
Hot Spots[2]	Localised low voidage.	Reload affected tube.
Hot Patch at Top of Tube	Settling of catalyst.	Reload or top up affected tubes.
	Poor reduction of catalyst at top of tube.	Add hydrogen to reformer feed to reduce this catalyst.
Tube Failure	Flame Impingement.	Repair burner and either nip or change tube.
	Localised overheating.	Nip or change tube. Check burners.
	Excessive creep.	Nip of change tube. Check other tubes for excessive creep.
	Catastrophic cracking.	Nip or change tube. Check for water ingress.
	General overheating – burn down.	Replace tubes and review operating procedures.
	Localised overheating at bottom of tube.	Nip of change tube and check for tunnel port effect. Install high heat transfer/activity catalyst.
Catalyst Changed Colour	Catalyst is blue/green or blue-green.	Catalyst has been overheated.
Collapsed Tunnel	Poor design.	Repair next turn around. Check bottom of tubes for excessive temperatures.
Cracking of Tube Tops	Stress corrosion cracking.	Lag tube tops to prevent condensation and vapourisation.

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[2] This is a small patch on the tube that appears hotter than the rest of the tube. As such it differs from a hot band.

Cracking of Tube Bottoms	Stress corrosion cracking.	Check design of tube outlet. Redesign to eliminate cold zones.
Bowed Tubes	Excessive firing from one side. Poor tensioning.	Reduce firing. Review and redesign tension system.
Pigtail Failure	Failure by creep. Failure by cracking.	Replace pigtail. Replace pigtail. Check for excessive stress on pigtail.
Fluegas Maldistribution	Flame impingement, high ATE's.	Use dry powder or K_2CO_3 to check for flow patterns. Check design of outer lanes, burners and coffins. Modify reformer design as appropriate.
Camel Hump Effect[3]	High peak temperatures below fluegas fans.	Introduce more pressure drop in duct.
Afterburning	Localised burning on tubes near bottom of box.	Insufficient combustion air supplied to some burners. Increase combustion air to these burners.
High O_2 Levels at Stack	Too much excess air in box. Poor tube to casing seal. High air leakage into convection/radiant sections. Large air leakage in combustion air preheater.	Reduce combustion air rate to reformer. Repair existing or install new sealing system. Check for air leaks and repair. Check heat balance and O_2 inlet/outlet air preheater and repair.
High Duct Temperatures	Fouling of duct coils.	Clean coils. Check excess air levels. Repair refractory where damaged.
Hot Refractory Casing	Damage to refractory. Failure of anchors.	Use steam lance or water to cool casing. Repair at shut down. Use steam lance or water to cool casing. Repair at shut down.

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[3] Foster Wheeler Furnaces only.

9 Conclusions

In conclusion, this paper has illustrated some of the key features of steam reformers, most notably,

- The under lying principles of the chemistry, equilibrium and diffusion that affect the reforming process,
- The requirements of the process and how this affects the design of the reformer,
- The main three reformer types,
- The typical parameters that a process engineer/plant manager can control,
- Typical parameters that should be monitored,
- Some typical problems that can occur,
- Some guidelines on trouble shooting these common problems.

10 References

Reference 1 Tube Wall Temperature Measurement in Steam Reformers
B J Cromarty and S C Beedle
Johnson Matthey Catalysts
AICHE Ammonia Plant Safety
1993

Reference 2 Modern Techniques for Optimisation of Primary Reformer Operation
P W Farnell
Johnson Matthey Catalysts

For further information on Johnson Matthey Catalysts, contact your local sales office or visit our website at www.jmcatalysts.com

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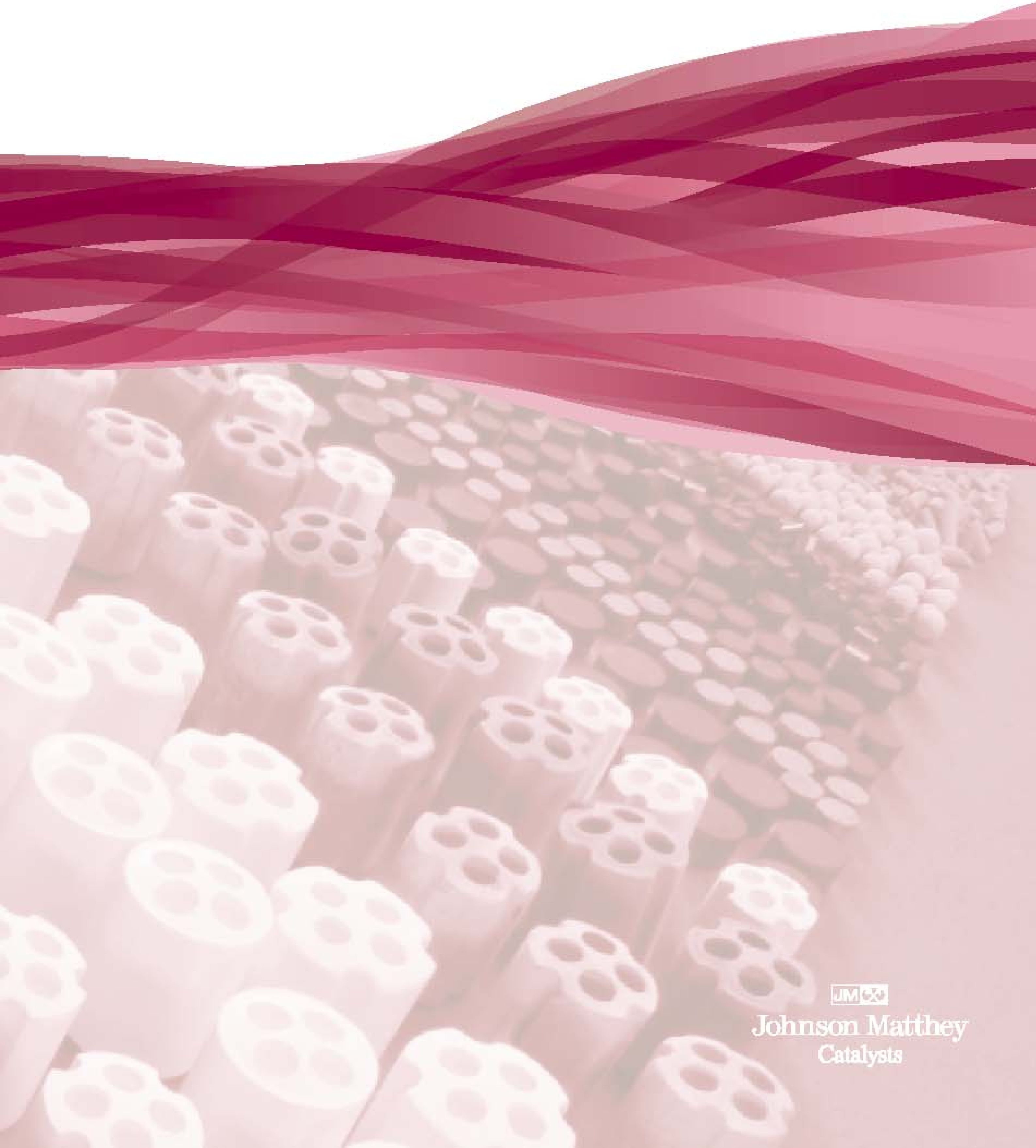
Theory and Operation of Secondary Reformers



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1 Introduction

The secondary reformer is at the heart of any ammonia plant and almost rivals the primary reformer in terms of complexity of design and operation. Furthermore, secondary reformers are becoming more common on large scale methanol plants to minimise the size of the primary reformer and on some hydrogen plants. The secondary reformer is an integral part of the synthesis gas generation section of a conventional ammonia plant and allows for minimisation of methane slip and the introduction of nitrogen to allow for the production of ammonia. This paper will highlight the key features of the design of secondary reformers and the developments that Johnson Matthey Catalysts has made for both the catalyst and the burner gun. As part of the development of the Johnson Matthey Catalysts burner, the High Intensity Ring Burner, Computational Fluid Dynamic's (CFD) has been used extensively in order to prove the design and modifications to the original design. Case studies are presented to illustrate the changes that can be made to a secondary reformer to improve the performance.

Failure of one of the components of the secondary reformer can have disastrous consequences for plant occupacity. Given that a typical ammonia plant loses around US$150,000 per day whilst shut down and that a shut-down to effect repairs to a secondary reformer takes at least seven days due to the time to cool and re-heat the vessel, the cost of a problem will be in excess of US$1,000,000. For a methanol plant, the costs are very similar.

2 Key components

A number of key components are included in the secondary reformer,

- The burner gun,
- The mixing or combustion volume,
- The catalyst.

2.1 Process description

The figures below illustrates the typical design and layout of a secondary reformer. The secondary reformer consists of a refractory lined carbon steel vessel with inlets for the primary reformer effluent and the oxidant whether this be air (Ammonia) or oxygen (Methanol and Hydrogen), and a single outlet for transferring the effluent to the waste heat boiler. A burner gun is situated within the neck of the secondary reformer, which ensures even distribution of the oxidant through out the cross section of the vessel.

Figure 2. Ammonia secondary

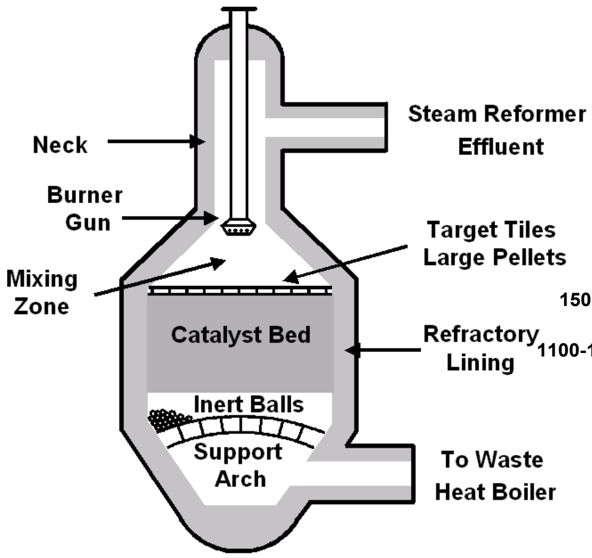
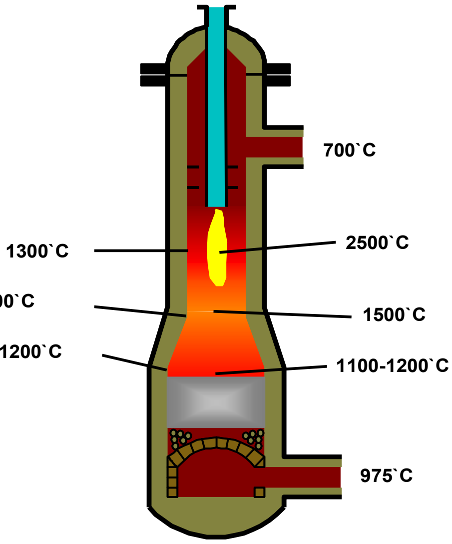


Figure 2. Methanol secondary



Below the burner gun there is a space, called either the combustion or mixing zone, where the mixing of the primary reformer effluent and oxidant, and subsequent combustion, occurs. Within this zone the rate of combustion of the primary reformer effluent is controlled by the mixing of the fuel and oxidant. The rate of mixing is determined by the turbulence created by the differential momentum of the primary effluent and oxidant. It is important that the gas leaving the combustion zone is evenly mixed, such that the variation in flow, temperature and composition entering the catalyst bed is minimized to ensure good catalyst utilization.

The gas from this zone then passes to the catalyst bed. The bed is normally covered with a layer of target tiles, alumina lumps or large catalyst pellets such as **KATALCO^{TM}** 23-8E. The catalyst bed rests on a layer of inert balls or lumps that in turn sit on a support arch; the support arch collects the effluent from the secondary reformer catalyst bed before being passed to the waste heat boiler.

2.2 Poor performance of secondary reformers

2.2.1 Example of poor performance

There are a number of causes of problems that can affect secondary reformers and the performance of this unit operation. Any problem within the secondary reformer will be highlighted by a high approach to equilibrium. This is independent of the root cause of the problem, whether the it is due to poor burner gun design or failure, insufficient mixing volume or poor catalyst performance. The following generic theoretical example illustrates this by assuming that there is a problem associated with the burner gun such that half of the secondary reformer receives 20% more air than design and that the other half receives 20% less air than design. The results of simulation of this theoretical analysis for an ammonia plant are detailed in the table below,

Table 1. Effect of mal-distribution

Parameter	**Units**	**Poor Mixing**			**Good Mixing**
		-20% Air	+20% Air	Average	
Exit Temperature	°C	902	1034	971	957
Methane Slip	mol %	1.89	0.13	0.97	0.62
Approach to Equilibrium	°C	10	10	53	10

As can be seen from the analysis in table 1, poor distribution of the air leads to an increase in the methane slip exit the secondary reformer of 0.35 mol %. This equates to US$750,000 per year in lost production.

A similar effect will be seen on a methanol plant if the burner gun does not perform as well as expected.

2.2.2 Burner gun

There are two key problems associated with the burner gun; firstly, poor design and installation of the burner gun in the secondary reformer and secondly failure of the burner gun whilst in service. Poor design of the burner gun can lead to poor gas mixing within the mixing zone. This in turn leads to poor gas distribution at the inlet to the catalyst bed, not only in terms of poor gas flow distribution inlet the bed, but also in terms of mal-distribution of temperature and composition. For example, poor burner gun design can cause the following problems,

- Poor distribution of process air into the combustion zone as highlighted in the table above,
- Zones of high temperature inlet the catalyst bed and also associated low temperatures inlet the catalyst bed. Such zones will also have different gas compositions inlet the bed,

- Zones of high and low flows inlet the bed; this leads to localised variations in space velocity which in turn leads to variation in methane slip exit the catalyst bed, which will cause the observed approach to equilibrium to be higher than expected.

The design of the burner gun is inherently linked to the geometry of the mixing zone since it is critical to ensure that the high temperature flame zone is maintained at a suitable distance away from the refractory wall to prevent damage to the refractory. There is also a requirement that a flow of the relatively cool process gas passes between the flame region and the vessel wall. The combination of good design in these areas ensures that the refractory operates at low temperature and therefore retains its integrity.

Poor installation of the burner gun can lead to the burner gun being installed off centre within the neck of the secondary reformer. This leads to a variation of process air flow within the combustion zone of the secondary reformer and hence to variations in composition, flow and temperature inlet the catalyst bed. In the worst case, the high temperature portion of the jet from the burner gun can impact on the refractory and lead to refractory damage and potential vessel failure.

Catastrophic failure of the secondary reformer burner gun causes problems similar to those outlined for poor installation of the burner gun. However, the problems occur much more rapidly and the potential for refractory and subsequent vessel failure is much greater. For methanol plants, failure of the burner gun is even worse than for an ammonia plant since as oxygen is used as the oxidant and therefore the flame temperatures are much higher. Therefore any impaction of the jet on the refractory will lead to very fast damage to the refractory.

Changing the burner gun to a design that provides enhanced mixing can solve any problems associated with the burner gun and insufficient combustion volume.

2.2.3 Insufficient combustion volume

Early secondary reformers were designed with a combustion chamber from which the combusted gases were passed to the catalyst containing vessel ensuring that the combusted gases were well mixed prior to entering the catalyst. On modern secondary reformers, the mixing/ combustion zone is an integral part of the secondary reformer vessel (as illustrated in the figures above) and therefore the design of the mixing volume is more critical in determining the performance of the secondary reformer.

Furthermore, the required size of the combustion volume is inherently linked to the burner gun design. Burner guns that provide short mixing distances clearly require a smaller combustion volume whilst burner guns that provide longer mixing distances will require a larger combustion volume. Insufficient combustion volume leads to the same problems as outlined above for burner gun problems.

The volume of the mixing zone is directly linked to the installed catalyst bed volume, therefore care must be taken to design the correct catalyst loaded volume and to ensure this volume is loaded into the secondary reformer. As such, problems associated with insufficient combustion volume can be solved by either changing to a burner gun design that provides enhanced mixing within a shorter distance or installing a high activity catalyst which allows for a reduction in catalyst volume.

2.2.4 Catalyst

The third key component of the secondary reformer is the catalyst. The catalyst is often blamed for poor secondary reformer performance. In reality, however, the secondary reformer catalyst is very robust and exhibits a very stable activity. Unless the catalyst is at its end of life, the catalyst will not be the root cause of any secondary reformer problem. In the vast majority of cases, a low nickel content catalyst is suitable for use in secondary reformers. However, in some cases, precious metal catalysts may be required in the leading edge of the catalyst bed where the process gas temperatures are at their highest.

2.2.5 Summary

In summary, the vast majority of problems associated with secondary reformers are due to combustion problems leading to inadequate mixing and variable temperature, gas composition and flow inlet the catalyst bed. Such problems are rarely linked to insufficient catalyst activity, with the one exception of plants that have been up-rated significantly. Johnson Matthey recommends the use of **KATALCO** 23-8Q with a layer of **KATALCO** 23-8EQ as a heat shield.

2.2.6 Oxygen blown secondary reformers

Many of the issues already discussed also apply to oxygen blown secondary reformers that are increasingly being used on methanol and hydrogen plants. The one key difference between air blown and oxygen blown secondary reformers is that the process gas temperatures are much higher with oxygen since there is no nitrogen to act as a diluent. A consequence of these higher temperatures is that when there is a problem with the burner gun and the hot gases impact on the refractory, the refractory will fail more rapidly. A second problem is associated with the lower mass flow of oxygen. Since the mixing process between the oxidant and process gas is determined by the relative momentum of the two streams, the oxygen must leave the burner gun at higher velocity.

The gas in the combustion zone is sufficiently hot that it can vaporize both the nickel on the catalyst and the catalyst support. As the gas passes down through the catalyst bed, the temperature drops and eventually there will be condensation of the nickel/catalyst support resulting in a localized increase in the resistance to flow. This will cause a change in gas flow and mixing patterns within the mixing zone and can lead to an increased probability of refractory overheating.

These factors mean that the design of an oxygen burner gun is even more critical than for an air burner.

3 Computational fluid dynamics

3.1 Introduction to computational fluid dynamics

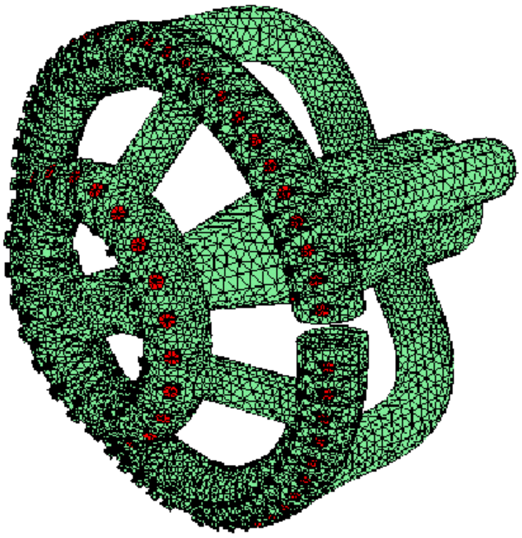
Computational Fluid Dynamics (CFD) allows simulation of highly complex fluid flow problems by using the Navier-Stokes equations (these are fundamental equations of fluid flow governing the conservation of momentum and mass). These standard models can then be linked to models that define turbulence, the effects of heat transfer, whether convective or radiative, mixing of different fluids, pressure drop and reactions such as combustion.

Given the above capabilities, CFD is ideally suited to modelling of secondary reformers.

3.2 Application of computational fluid dynamics

The first stage of using CFD for modelling a unit operation is to ensure that a full representative set of plant data is collected. This data should then be checked for consistency and accuracy using an appropriate model such as Johnson Matthey Catalyst CATPER or PERFORM models.

Figure 3. Burner gun mesh



The next stage is to generate a mesh that represents the geometry to be modelled; this mesh includes the physical boundaries such as inlets, outlets, vessel walls and any vessel internals. Within the physical constraints, there are a large number of cells that can be defined as empty, solid or porous; the latter can be used to model catalyst beds. The solid cells can be used to represent the vessel walls and vessel internals. This is illustrated to the right for the Johnson Matthey Catalysts High Intensity Ring Burner.

Within this mesh, the values of velocity, temperature, pressure and concentration within each cell depend solely upon the values of those properties within the neighbouring cells. The flows are specified at all the inlets to the mesh and from these, the program calculates the values for each property for all of the cells within the mesh.

The final stage is to run the model and ensure that the results seem sensible, utilizing good engineering judgement and comparison to other similar situations. If possible, the results of the CFD simulation should be compared to any observations made on the plant such as catalyst bed disturbance and damage to either the burner gun or refractory.

3.3 Application to secondary reformers

CFD is highly suitable for application to modelling secondary reformers; however, there are some unique problems that must be fully understood. Firstly, the oxidant is injected at very high velocity (100 m/s) into a slower moving stream of process gas (15 m/s) which means that the mixing is highly turbulent. Further complications are that,

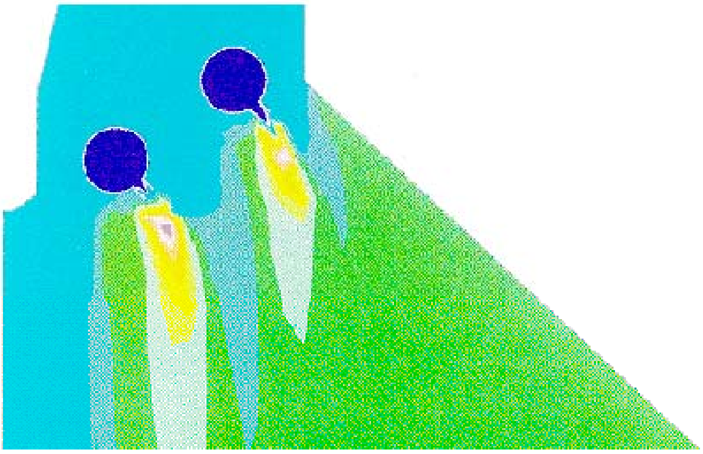
- The air density is higher than the process gas density,
- When these two streams are mixed together there will be combustion,
- Under the temperatures and pressures prevalent in secondary reformers, the products of combustion are not carbon dioxide and water but a variety of intermediate products.

Johnson Matthey Catalysts has developed the standard models available in commercial packages to allow for successful modelling of secondary reformers. This was originally developed for the burner gun used in the secondary reformer of the Johnson Matthey Catalysts LCM methanol process. As noted previously for oxygen burners, the design of the burner is critical and the safety issues are of paramount importance and require the use of CFD as a design tool.

3.3.1 Results of model for high intensity ring burner

The following figure illustrates the results of a CFD simulation of the Johnson Matthey Catalysts High Intensity Ring Burner; in this case, the temperatures in the combustion section are illustrated,

Figure 4. Temperature plot for a ring burner



4 Development of the Johnson Matthey Catalysts high intensity ring burner

The Johnson Matthey burner used on ammonia plants is called the High Intensity Ring Burner and as the name suggests, the burner provides a short highly intense flame with the actual burner consisting of concentric annular rings. The following figure illustrates the present design of the Johnson Matthey Catalysts High Intensity Ring Burner,

Figure 5A/B. Johnson Matthey ring burners

Burner Gun for
Large Diameter
Secondary Reformers

Burner Gun for
Small Diameter
Secondary Reformers

When considering the large diameter ring burner gun above, each ring is fed from the central pipe via a set of symmetrical feed pipes. As can be seen in the figure above the rings that comprise the burner heads are symmetrical so that the feed from the central feed pipe is evenly distributed within the ring. The rings themselves are broken up into sections, again to ensure even distribution of the air to the nozzles.

There are a large number of nozzles (typically 150) on the underside of the burner gun and these provide short flames that ensures that the combustion occurs high up within the mixing zone and therefore make sure that there is no flame impingement on the bed or the refractory. Above the burner is a can assembly with two drilled plates to ensure that the process gas flows evenly to the burner gun.

5 Catalyst development

As with the Johnson Matthey Catalysts High Intensity Ring Burner, the **KATALCO** range of secondary reforming catalyst has also been undergoing development to allow operators to improve the performance of their secondary reformers. The latest development offered by Johnson Matthey Catalysts is the **KATALCO** Quadralobe catalyst which offers a 20% increase in activity with no penalty in terms of pressure drop. Since the activity of **KATALCO** Quadralobe catalyst is higher, the installed catalyst volume can be reduced giving a reduction in pressure drop whilst maintaining the approach to equilibrium.

Figure 6. Quadralobe catalyst

The table below details the potential reduction in catalyst volumes that are achievable when changing the installed catalyst from a generic ring type to the **KATALCO** 4-hole and Quadralobe.

Table 2. Effect of KATALCO catalyst shape and size on loaded volume

Parameter	Units	Base Case Ring	4-Hole	4-Hole Mini	Quadralobe Mini
Catalyst Volume	*m³*	35	21.60	18.4	14.8
Approach	*°C*	6	6	6	6
Methane Slip	*mol %*	0.23	0.23	0.23	0.23

It should be noted that there are other limitations that must be taken into account when reducing the catalyst volume and these must be checked. Alternatively the full catalyst volume can be installed and this allows for a reduction in methane slip as illustrated in table 3,

Table 3. Reduction in CH_4 slip with KATALCO secondary reforming catalysts

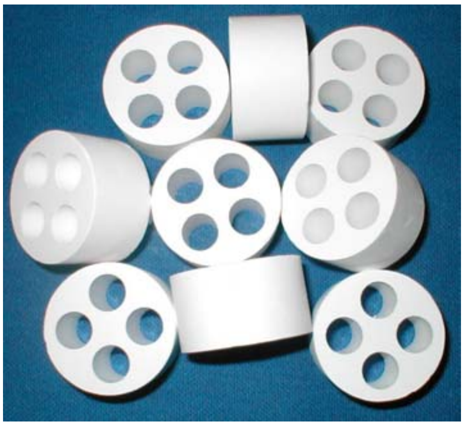
Parameter	Units	Base Case Ring	4 Hole	4 Hole Mini	Quadralobe Mini
Catalyst Volume	*m³*	35	35	35	35
Approach	*°C*	6	3	2	1
Methane Slip	*mol %*	0.23	0.22	0.21	0.20

Such a change will increase production to the value of US$75,000 per annum. If the methane slip is higher, then the reduction in slip and consequent increase in production will be even greater.

5.1 Heat shields

Historically many secondary reformers have a heat shield on top of the catalyst bed; this heat shield consists of either target tiles or alumina lumps. However, Johnson Matthey Catalysts has introduced a large 4-hole pellet, **KATALCO** 23-8E and a similar quadralobe shape, **KATALCO** 23-8EQ which can be placed on top of the catalyst bed and acts as a heat shield whilst providing some activity for the steam reforming reactions.

Figure 7. KATALCO 23-8E

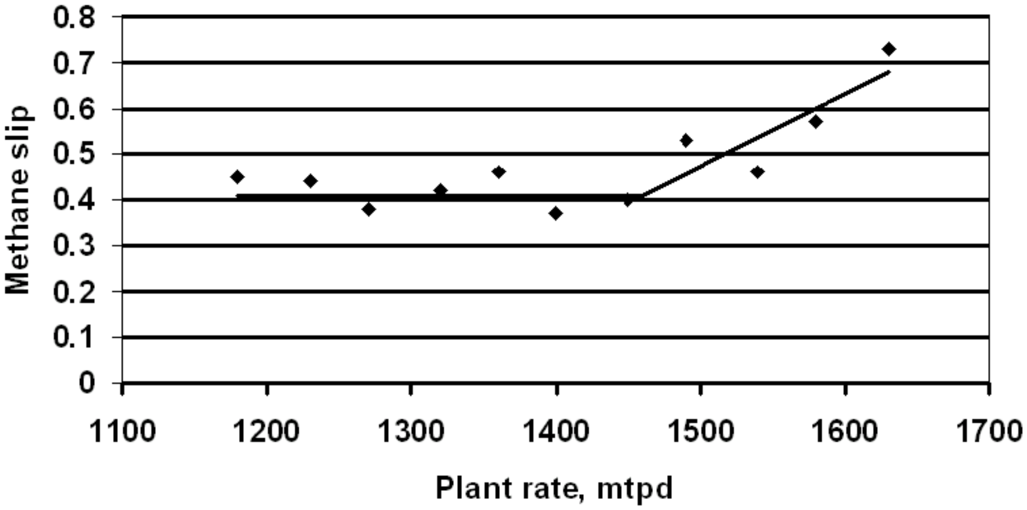


6 Case studies

6.1 Case study 1

This North American ammonia plant had been up-rated from 1040 mtpd to 1620 mtpd without significant problems. However, when the plant rate was increased above 1450 mtpd, the methane slip rose appreciably as highlighted below.

Figure 8. Variation in methane slip with plant rate

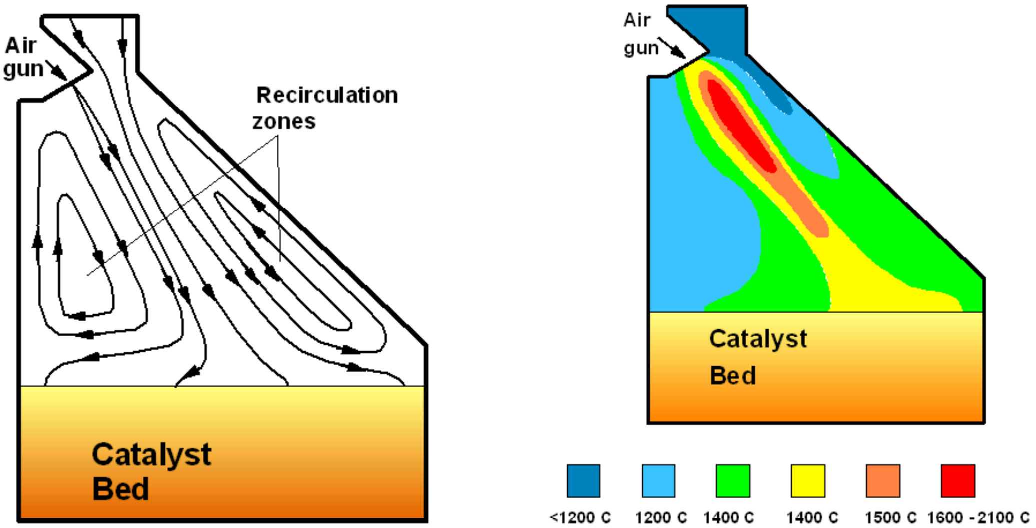


Further plant rate increases were feasible but the performance of the secondary reformer posed a significant economic limit. Detailed analysis of the secondary reformer had determined that,

- There was sufficient catalyst activity to achieve a close ATE,
- The burner gun had been inspected and found to be in good condition and the had been used in many other reformers very successfully.

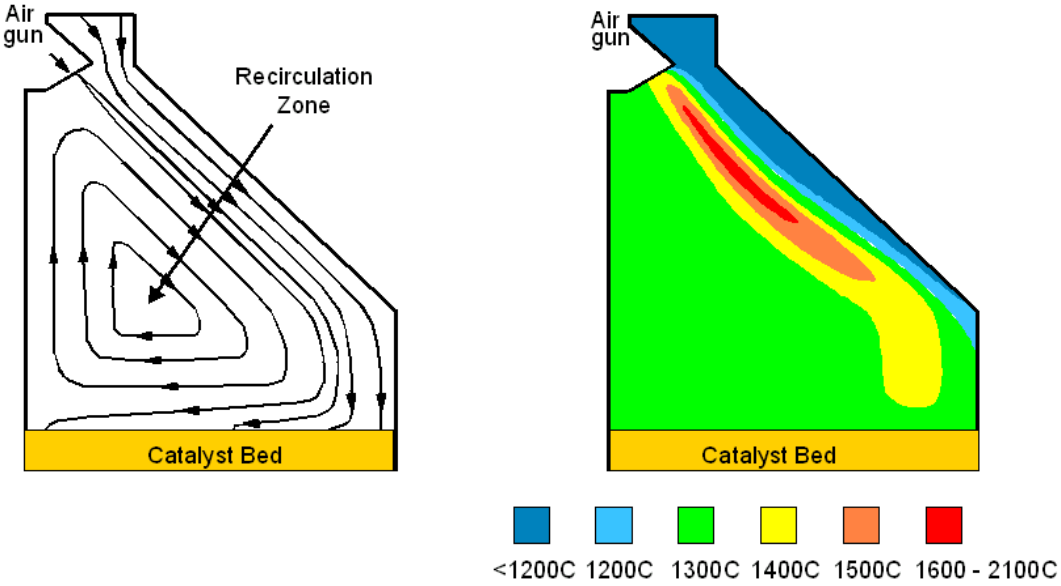
From this it was concluded that there was a limitation in the mixing volume within the secondary reformer at the higher plant rates. In order to fully understand the problem, CFD was used to model the mixing zone within the secondary. The results of this simulation are presented in the figure below. The figure to the left details the flow patterns predicted by the model; as can be seen there is a high velocity jet with two low velocity re-circulation zones to either side. The figure to the right shows the temperature profile within the mixing zone. As can be seen there is a high temperature core where the combustion is occurring, however, this hot gas does not have sufficient time to mix and a portion of the catalyst bed is exposed to high temperature gas. This has two consequences, firstly the catalyst in this zone is sintered rapidly and secondly the catalyst bed sees a wide variation in feed gas conditions, which leads to poor utilization of the catalyst bed.

Figure 9A/B. Streamlines and temperature plots



In order to solve this problem, it was decided to increase the mixing volume by installing a high Geometric Surface Area (GSA) catalyst – **KATALCO** 23-8. Since the GSA of this catalyst is higher than the installed ring catalyst, the overall activity was maintained whilst reducing the catalyst volume, which in turn increased the mixing volume. The results of the CFD simulation of this new situation is shown below,

Figure 10A/B. Modified streamline and temperature plots



As can be seen, the flow inlet the catalyst bed is even with no zones of high velocity. The vessel wall is protected by a region of relatively cool process gas ensuring that there is no refractory damage. The temperature profile shows that there is no hot gas near the refractory, again ensuring that the refractory will not fail prematurely. Moreover, the temperature profile inlet the bed is very even and this coupled with the even flow distribution ensures that the catalyst will be fully utilized.

Overall, the new design of the reformer will be significantly better than the original design and allowed the plant rate to be increased in excess of 1650 mtpd.

6.2 Case study 2

In many cases, reducing the installed catalyst volume will still not improve the performance of the secondary reformer sufficiently. In this case the installed burner does not give sufficient mixing performance. In this case study, the secondary reformer was of a similar design to that in case study 1, except there was less distance between the tip of the burner gun and the surface of the catalyst bed, which exposed the catalyst to excessive temperatures.

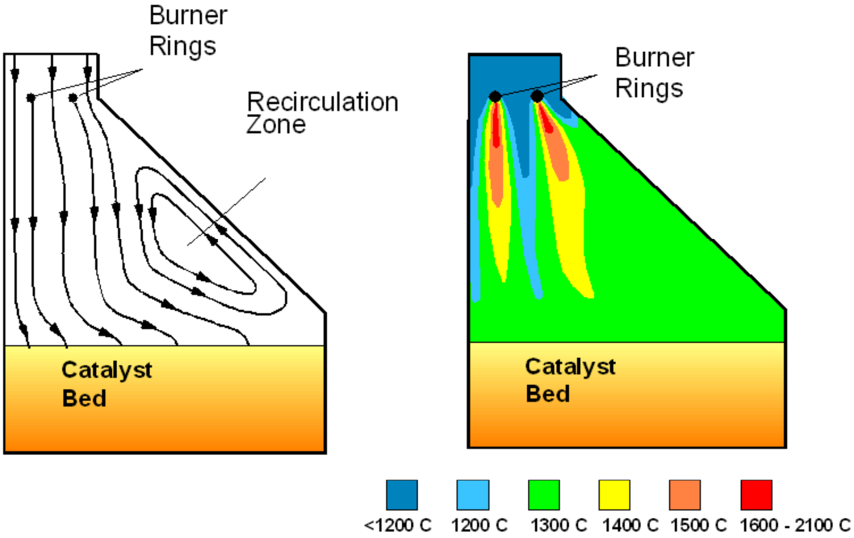
In order to determine the performance of the secondary reformer, CFD was used to model the secondary reformer with the Johnson Matthey Catalysts High Intensity Ring Burner installed as illustrated below.

Figure 11. Johnson Matthey Catalysts burner gun

As noted previously, the design of this burner gun introduces the oxidant through a large number of points and therefore less distance is required to achieve good mixing.

The results of the CFD study are shown the figure below.

Figure 12A/B. CFD Streamlines and temperature plots for the Johnson Matthey ring burner



As can be seen the Johnson Matthey Catalysts High Intensity Burner Gun has produced a single re-circulation zone next to the vessel wall that will ensure that the refractory wall remains cool. Furthermore this ensures that there is excellent mixing between the oxidant and primary reformer effluent. The temperature plot illustrates the temperature inlet the catalyst bed is very even and that there high temperature zone is contained in the upper portion of the mixing zone.

7 Conclusions

This paper has illustrated the importance of the three key components of the secondary reformer: the burner gun, the mixing zone and the catalyst, and the importance of the correct design has been stressed. It has been shown that the majority of operating problems within secondary reformers are due to poor burner design or insufficient mixing volume. It has been illustrated that the costs associated with problems within the secondary reformer can lead to significant plant down time, loss of production and hence profitability.

The development of the Johnson Matthey Catalysts high intensity ring burner has been discussed and the potential options for use have been shown. The options for improvements using the **KATALCO** catalysts have been highlighted.

The use of Computation Fluid Dynamics have been illustrated in the design, optimization and troubleshooting of secondary reformers.

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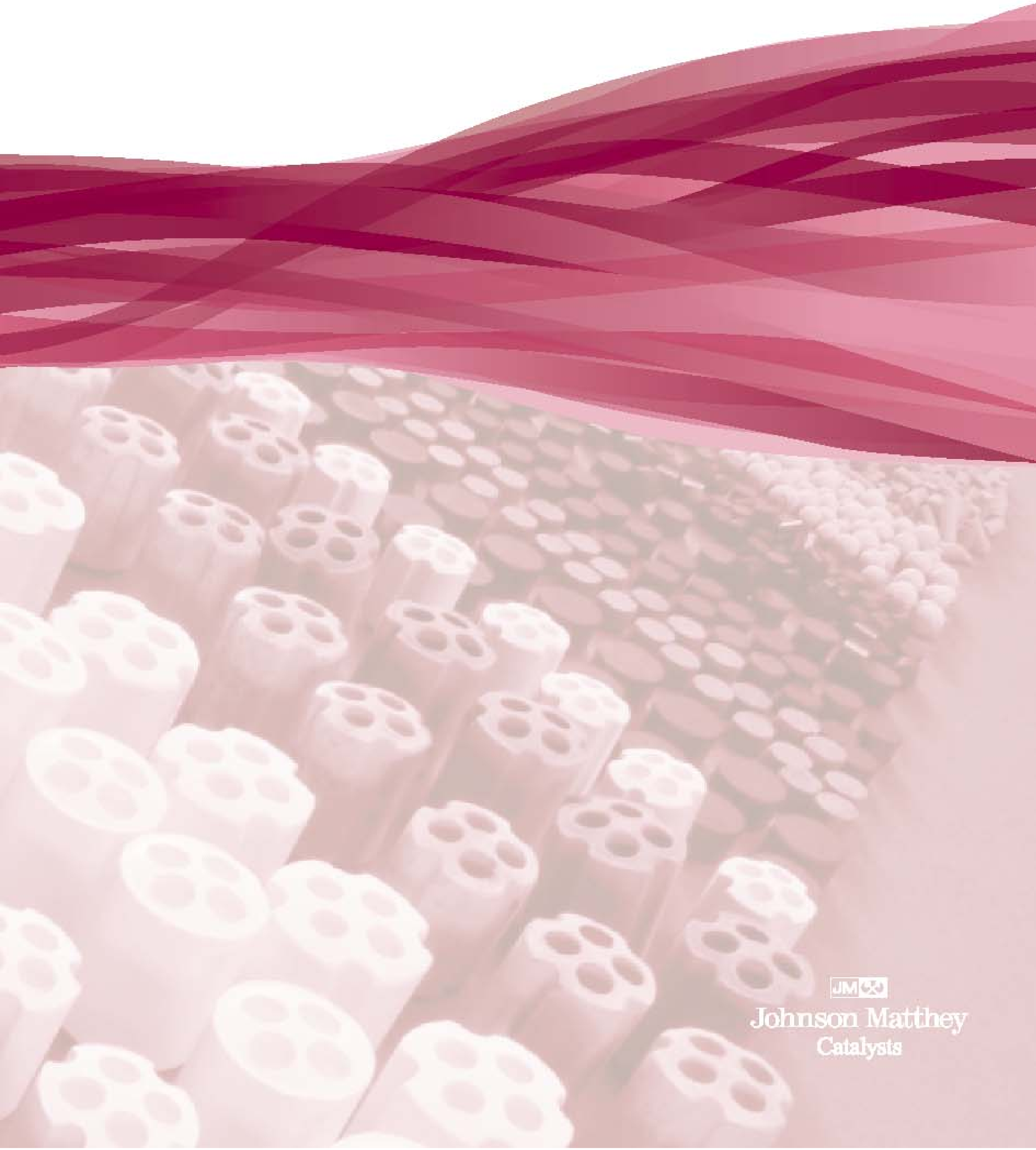
Theory and Operation of Shift Catalysts



Johnson Matthey
Catalysts

1 Introduction

The water gas shift reaction is an essential step in modern ammonia plants. Efficient and reliable shift conversion is required to ensure that the highest yield of hydrogen can be obtained from the reformed hydrocarbons. Hence good performance of the shift catalyst and attainment of equilibrium CO slip from the catalyst system is critical to the efficient and economic operation of the plant to maximise the hydrogen production from the plant.

In most ammonia plants the shift conversion is carried out in two stages. Usually, a high temperature shift (HTS) catalyst is used as the first stage and typically converts over 80% of the CO. A low temperature shift catalyst (LTS) then converts the majority of the remaining CO.

As well as maximising the hydrogen production, the water gas shift reaction also maximises the CO_2 production from an ammonia plant. This has added benefits:

- Carbon oxides, both carbon monoxide and carbon dioxide (CO_x) are a poison to the ammonia synthesis catalyst and therefore must be removed
- CO is converted to CO_2 for easier removal in the CO_2 removal system
- CO_2 is an essential component for the Urea plant

The purpose of this paper is to,

- Detail some fundamentals about water gas shift chemistry and equilibrium,
- How the high and low temperature shifts catalysts should be operated,
- The key control parameters that the operator can change within the shift section of the plant,
- Discuss some common operating problems.

,

2 Basic theory

The water gas shift reaction has always been an integral part of the ammonia plant flowsheet. It provides the most effective and economic way of removing CO from the reformer product gases by converting it to CO_2. A liquid scrubbing system easily removes the CO_2.

The reaction is described by equation below, in which CO reacts with steam over a suitable catalyst to generate CO_2 and hydrogen.

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad \Delta H = -\ 41.1\ kJ/Kmol$$

This equation is equally applicable for each catalyst type in the shift section: HTS and LTS. The reaction is moderately exothermic and is reversible, hence the higher the temperature the lower the equilibrium conversion. Pressure has no influence on the equilibrium position, as equal moles of gases are present on each side of the equilibrium. Increasing the steam level to the reactor will push the equilibrium position in the forward direction. Hence excess steam and low temperatures give maximum equilibrium conversion.

2.1 Equilibrium

Equilibrium is an important parameter; the following equation defines the equilibrium expression for the water gas shift reaction,

$$\mathrm{Kp} = \frac{\mathrm{P}[\mathrm{CO}].\mathrm{P}[\mathrm{H_2O}]}{\mathrm{P}[\mathrm{H_2}].\mathrm{P}[\mathrm{CO_2}]}$$

This can be rewritten in a more useful form,

$$\mathrm{P}[\mathrm{CO}] = \mathrm{Kp}\frac{\mathrm{P}[\mathrm{H_2}].\mathrm{P}[\mathrm{CO_2}]}{\mathrm{P}[\mathrm{H_2O}]}$$

Which can be simplified by converting to molar fraction to give,

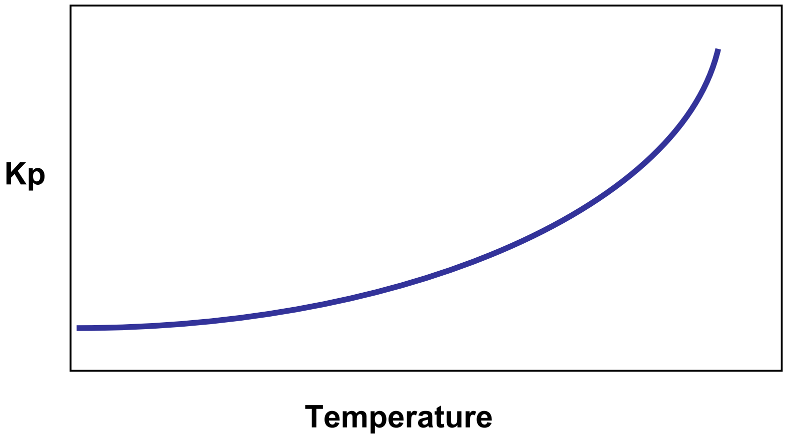
$$[\mathrm{CO}] = \mathrm{Kp}\frac{[\mathrm{H_2}].[\mathrm{CO}]}{[\mathrm{H_2O}]}$$

The key points to note are,

- That pressure will have no effect on the shift reaction,
- Increasing the steam to carbon ratio will reduce the equilibrium constant and therefore lower the CO slip and give higher potential hydrogen.
- The reaction equilibrium is favoured by low temperatures.

The last point is highlighted by the following graph which shows how the equilibrium constant, Kp, is related to temperature,

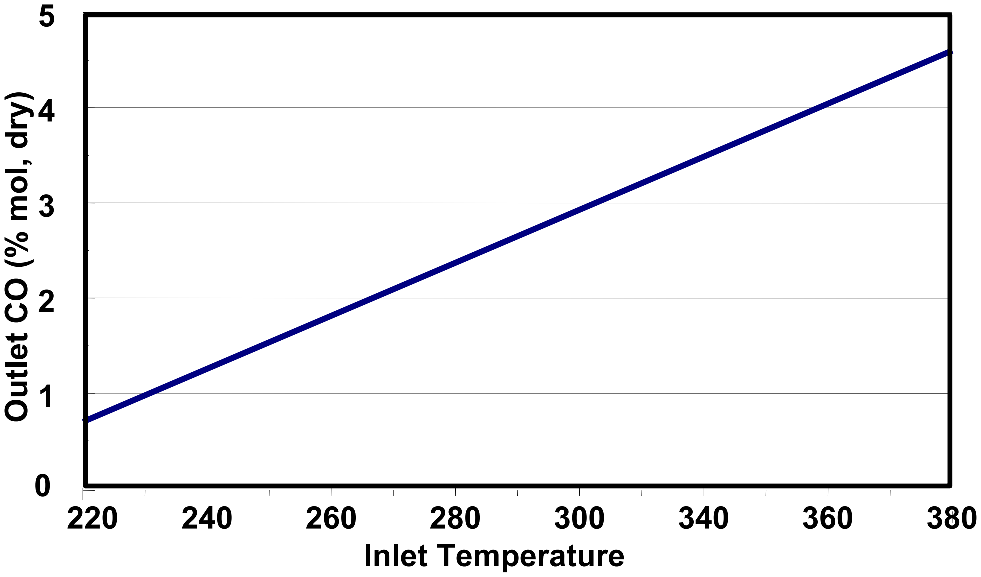
Figure 1 – Effect of temperature on equilibrium constant



Under adiabatic conditions, conversion in a single bed is thermodynamically limited; the heat of reaction increases the operating temperature, which restricts the extent of conversion that can be achieved.

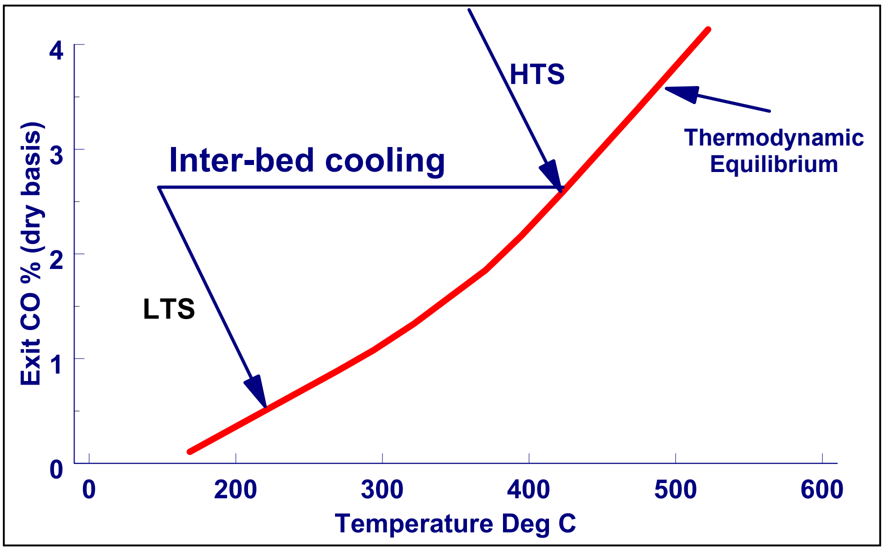
Typical CO levels from the exit of a shift reactor catalyst on a ammonia plant are given in the figure below.

Figure 2- Effect of Inlet Temperature on Outlet CO



This limitation is typically overcome with a two stages system with a suitable form of inter-bed cooling as illustrated in the figure below.

Figure 3 – Typical final CO concentration form a two stage system



The bulk of the conversion is carried out across the HTS catalyst, in which typically 80% or more of the CO is converted to CO_2. The HTS is followed by a low temperature shift (LTS) catalytic stage.

This catalyst allows the water gas shift reaction to proceed at low temperatures, usually limited only by the dew point temperature at the inlet. The CO level at the exit of the LTS bed can usually be reduced to around 0.1 – 0.3% by operation at low temperatures

2.2 Reaction kinetics

The reaction kinetics for the water gas shift reaction can be described as:

$$\frac{dCO}{dt} \propto \text{Activity} \times \text{GSA} \times \exp^{[-\Delta E/(R.T)]} \times \frac{P[CO]}{P[H_2O]} \times (Kp' - Kp)$$

Where,

- Activity is the activity of the catalyst,
- GSA is the geometric surface area of the pellets,
- ΔE is the activation energy for the water-gas shift reaction,
- R is the universal gas constant,
- T is the absolute temperature,
- P[CO] is the partial pressure of carbon monoxide,
- P[H_2O] is the partial pressure of water.

A simplified way of defining the reaction kinetics for the water gas shift reaction would be to consider the following equation:

Reaction Rate = Rate Constant x Driving Force

- The driving force is dependent on equilibrium and the closer the reaction is to equilibrium the lower the driving force.
- The rate constant is dependent on the catalyst, its activity and the operating temperature, i.e.: the higher the catalyst activity and/or temperature the higher the reaction rate.

Hence, the actual conversion is a balance between reaction kinetics on the catalyst and thermodynamic equilibrium and could ‘increase’ with temperature.

2.3 Approach to equilibrium

Approach to equilibrium, or as it is commonly known, ATE, is a method of tracking the performance of a shift bed with time.

The ATE is defined at the exit of the of the catalyst bed is the difference between the gas temperature at the exit of the catalyst bed and the equilibrium temperature corresponding to the gas composition, i.e. Approach to equilibrium is defined as,

ATE = Actual Exit Catalyst Temperature – Equilibrium Temperature

To calculate the ATE:

- Measure the actual catalyst bed exit temperature T_m
- Calculate the value of water gas shift equilibrium constant, Kp

$$\mathrm{Kp} = \frac{[\mathrm{H_2}].[\mathrm{CO}]}{[\mathrm{CO}].[\mathrm{H_2O}]}$$

- Find the temperature (T_{eq}) that corresponds to Kp (from equilibrium tables), this is the equilibrium temperature of the water gas shift reaction.
- Calculate ATE = $T_m - T_{eq}$

3 Shift catalysts

The HTS catalyst is comprised of iron oxide, with a chromium oxide stabilising agent to reduce the rate of sintering of the active iron crystallites at high temperatures. More recently, copper has been added to the formulation to increase the activity per unit bed volume and to provide protection against catalyst over-reduction at low steam-to-gas ratios. Typical operating temperatures for an HTS catalyst are between 310-460° C and at this temperature a new catalyst charge should be able to reduce the CO level at the reactor exit close to the equilibrium level of the process conditions, usually in the range 2-3 mol%. At these temperatures iron has sufficient activity to deliver the required performance.

The LTS catalyst is composed of a mixture of copper oxide, zinc oxide and alumina. At typical LTS operating temperatures, the HTS exit gases must be cooled before entry into the LTS reactor and this is usually accomplished by a heat exchanger to typically 180 - 190° C. The LTS catalyst will reduce the residual CO level at the reactor exit close to the equilibrium level of the process conditions, usually in the range 0.1 – 0.3 mol%.

The catalyst is a very important factor in determining the performance of the shift vessels. The key parameters and the things they affect that must be considered when designing a catalyst or selecting a catalyst for a shift duty are,

Table 1 – Catalyst parameter and affects

Parameter	Affects
Higher activity	Reduces CO Slip Reduces approach to equilibrium Increase Hydrogen production
Increased size	Increases voidage →Reduces pressure drop Reduces GSA →Reduces activity
Increased Catalyst Strength	More robust Catalyst Reduces breakage →Reduces PD increase rise

4 High temperature shift catalyst

4.1 Catalyst parameter

The catalyst parameters for **KATALCO™** 71-5 are as follows

Table 2 – HTS catalyst parameters

Form	Pellets
Production Method	Pelleting (patented Non sulphate route)
Size	8.5 mm diameter 4.9 mm length
Fe_2O_3	88 wt%
Cr_2O_3	9 wt%
CuO	2.6 wt%

Virtually all HTS catalysts are in the form of pellets of $Fe_2O_3/Cr_2O_3/CuO$, with a small level of residual impurities from the manufacturing process, primarily sulphur (production specification <0.025 wt%, typically < 0.01 wt% for 71-5). The active phase of iron oxide is magnetite, Fe_3O_4, and so the catalyst must be reduced to the fully activate the catalyst. The reduction of an HTS charge normally occurs at the same time as the reduction of the reforming catalyst, as both process gas and steam are needed for a controlled reduction to occur. The equilibrium point is controlled by the $H_2O/H_2$and the CO_2/CO ratios. It is important to have steam present as a part of the reduction process as it moderates the reduction effect. Otherwise, the catalyst would over-reduce to metallic iron. It can be shown that if the H_2O/H_2 ratio exceeds 0.18 at 400° C then the desired magnetite is the stable phase. Similarly, the CO_2/CO ratio should exceed 1.16 at 400° C to prevent the reduction of Fe_3O_4 to metallic iron.
The reduction process is given in equations below:

$$3Fe_2O_3 + H_2 \Leftrightarrow 2Fe_3O_4 + H_2O$$

$$3Fe_2O_3 + CO \Leftrightarrow 2Fe_3O_4 + CO_2$$

The hydrogen reduction is slightly exothermic and the CO reduction slightly endothermic, so the overall reduction of Fe_2O_3 is basically thermo-neutral.

The CuO is reduced to metallic copper. This is an exothermic reaction, but the exotherm is only approximately 12° C per 1% CuO. The equations below show this reduction:

$$CuO + H_2 \Leftrightarrow Cu + H_2O$$

$$CuO + CO \Leftrightarrow Cu + CO_2$$

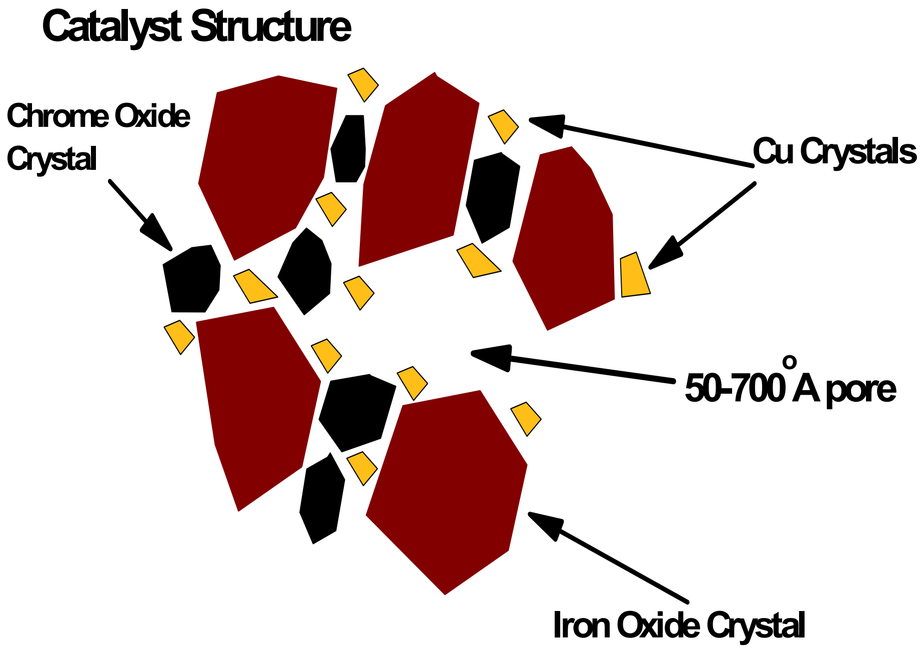
4.2 HTS catalyst requirments

For a good HTS catalyst the requirements would be,

- Good dispersion of the Cr_2O_3, because this provides the catalyst with,
  - High strength needed for process upsets like wetting
  - High thermal stability (long life) - Produces “amorphous” type structure reducing sintering rate of Cu and Fe crystals
  - Little CrO_3 (**KATALCO** 71-5 has typically <400 ppmw)
- Good dispersion of CuO, because,
  - Small crystals give high activity (Surface area)
  - Prevention of sintering
- Uniformly distributed, small crystals of iron oxide
  - High activity due to higher surface area

An effective catalyst also needs large pores for rapid diffusion and small pores for high surface area and activity, **KATALCO** 71-5 has been designed specifically with all the above characteristics as illustrated below.

Figure 4 – Catalyst structure



4.3 Reduction procedure for HTS catalyst

a Purge the reactor free of air with inert gas.

b If possible, heat the catalyst bed with dry gas until the process gas condensation temperature is exceeded. Alternatively, heat the catalyst with process gas and allow the effluent gas to go to the vent. Pressurisation to system pressure can be carried out at any time during the reduction. The process gas and steam flow combined should give a space velocity of approximately 200 h^{-1} – 1000 h^{-1}.

c Raise the catalyst temperature to 300° C at up to 50° C per hour. Reduction begins around 150° C.

d The CO shift reaction will begin around 300 – 320° C and the observed temperature rise will depend upon the inlet CO content and steam-to-gas ratio. The inlet gas must contain less than 15% CO (wet basis) because the maximum allowable temperature at this stage is 500° C.

e Raise the inlet temperature to at least 370° C and hold for several hours. This allows any residual sulfur from the manufacturing process to be converted into H_2S and driven off. This temperature should be held until the sulfur level has reduced to a low enough level that it will not poison the downstream LTS catalyst, if applicable. The desulphurisation period should be only 4 hours from the first introduction of gas. It is usual to bring the catalyst on line without the need of a special desulphurisation step. It may be prudent to check the sulphur levels in the outlet stream before bringing the LTS on line.

f Adjust the bed inlet temperature and process gas rate to operating values. The catalyst is now fully activated and the process gas can now be passed forward to the next step.

4.4 Normal operation

An HTS catalyst charge is fairly easy to operate once it has been brought on-line. Typically, the catalyst should be operated at the lowest possible temperature consistent with minimum CO slip.

Over time, the activity will fall slowly as the iron crystallites coalesce and the active surface area falls. It is usually necessary to periodically adjust the inlet temperature to compensate for the decrease in activity.

The decrease in performance is seen by the total temperature exotherm across the bed, which falls relative to the new catalyst exotherm, and eventually the CO slip exit the HTS bed rises to a level that necessitates changeout of the catalyst bed, as the improved conversion with a new charge justifies the cost of replacement.

An example of a typical HTS temperature profile is given in the figure below.

Figure 5 – Temperature profile for normal 'die-off' – thermal sintering

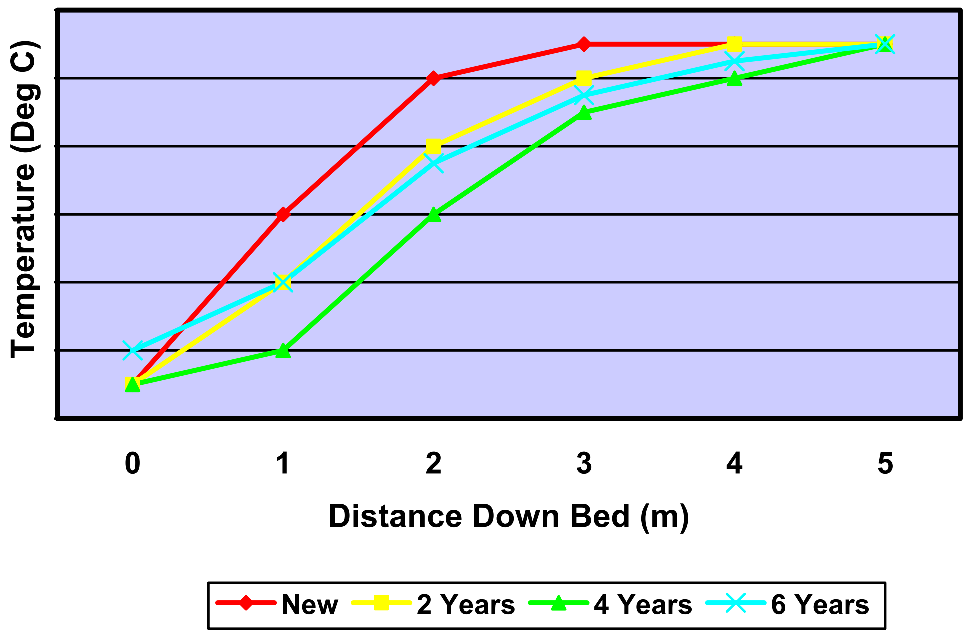


Figure 6 - Temperature profile for unusual ‘die-off’ – poisoning/fouling

4.5 Control parameters

The parameters that an operator can vary are,

- Steam to gas ratio.
- Inlet temperature,

Table 3 – Effect of steam to gas ratio

Name	Units	Base Case	Steam:Gas Ratio
Catalyst Age	*years*	0	0
Inlet Steam:gas ratio	*n/a*	0.475	0.500
Inlet Temperature	°C	370	370
Exit Temperature	°C	442.7	442.5
Exit CO Slip	*(dry)mol %*	3.29	3.13
Approach to Equilibrium	°C	0.0	0.0

The table shows that at start of life the catalyst is operating at equilibrium and the effect of increasing the steam to gas ratio is to reduce the CO slip, however, the effect of increasing the inlet temperature when the bed is operating at equilibrium would be the reverse i.e.: CO slip would increase since the shift reaction is favoured by low temperatures as demonstrated in the table below,

Table 4 – Effect of increased temperature

Name	Units	Base Case	Increased Temperature

Catalyst Age	*years*	0	0
Inlet Steam:gas ratio	*n/a*	0.475	0.475
Inlet Temperature	*°C*	370	380
Exit Temperature	*°C*	442.7	451.1
Exit CO Slip	*(dry)mol %*	3.29	3.48
Approach to Equilibrium	*°C*	0.0	0.0

4.6 Common problems in HTS

There are many common problems that can occur within the shift section; below is a brief discussion of some of them. If as an operator you believe that you have a problem, then you should consult your catalyst vendor.

4.6.1 Poisoning

Sulphur, in the form of H_2S, can combine with the iron oxide to form iron sulphide, depending on the level of H_2S in the feed. This is only significant when high level of sulphur is present in the feed gas. For a high constant level of H_2S (>200 ppm), the equilibrium allows iron sulphide to form at normal HTS operating temperatures. The effect is to lower the activity by approximately half. Occasional high sulphur excursions could also cause a reduction in activity, but it is found that if the sulphur level drops again to a low level, the sulphur is tripped off the catalyst to form H_2S again, as the equilibrium becomes unfavourable. Frequent cycling between high and low levels of sulphur can lead to weakening of the catalyst pellets due to structural changes in the catalyst and eventual break-up of pellets resulting in high-pressure drop through the bed. The other major poison is chlorides, but these are rarely seen at high enough levels to cause problems. The effects of chlorides is the formation of $FeCl_2$ and consequent loss of catalyst activity. The most likely source is from chlorinated solvents that are used for degreasing items during turnarounds.

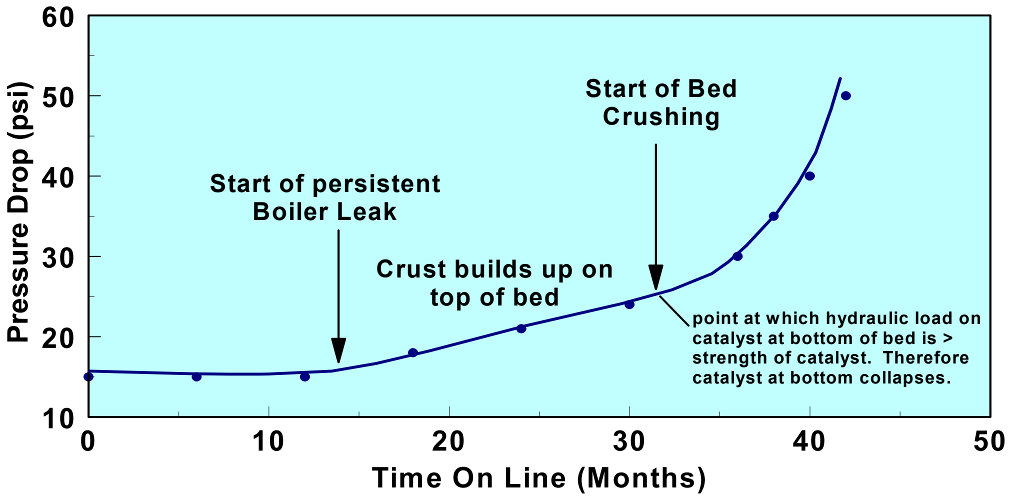
4.6.2 Condensation or boiler leaks

Wetting of the HTS catalyst as a result of condensing of steam or waste heat boiler leaks can cause a number of problem, these are:

- Reduction in the catalyst strength.
- Agglomeration of the HTS catalyst leading to problems when discharging the catalyst.
- The thermal shock from wetting and then rapid evaporation of water within the pores of the catalyst can cause catastrophic failure resulting in excessive catalyst breakage and rapid pressure drop rise through the catalyst bed.
- Contamination of the catalyst with boiler solids resulting in the blocking of active sites and consequently loss of catalyst activity
- Boiler solids will plate out on the HTS catalyst and form a ‘cake’ on the catalyst. This can lead to high-pressure drop and the potential for flow mal-distribution.

The following graph illustrates the effect of boiler solids on HTS catalyst pressure drop:

Figure 7 – Effect of boiler solids on HTS PD



4.6.3 Low steam to gas ratio

On operating at lower steam-to-gas ratios, problems can be seen with the HTS catalyst. With lower steam levels, the gases passing across the HTS catalyst act as stronger reducing agents as the equilibrium swings to higher CO concentrations exit the reformer and hence over-reduction of the Fe_3O_4 to metallic iron can occur. The over-reduction leads to crystallite changes within the catalyst that can lead to physical degradation and weakening of the pellets. It tends to produce a larger molecule, this starts to form fissures and cracks on the outside of the pellets and it become very fragile and breaks down very quickly

The metallic iron forms iron carbide in combination with CO. Iron carbide is a catalyst for the Fischer Tropsch reaction also promotes side reactions, such as the Fischer-Tropsch synthesis of hydrocarbons, which again waste valuable hydrogen. The over-reduction path is seen below,

$$Fe_3O_4 + 4H_2 \Leftrightarrow 3Fe + 4H_2O$$

The Fischer-Tropsch reaction equation:

$$CO + nH_2 \Leftrightarrow CH_4, C_2H_4, C_2H_6, \ldots.$$

CO disproportionation

$$2CO \Rightarrow C + CO_2$$

CO disproportionation will result in carbon lay down on the catalyst, this results in the physical poisoning of the catalyst, the catalyst is weakened by the growth of carbon within the pores. Hence if HTS catalyst is over-reduced, then there will be a significant loss in strength of the catalyst and in the worst case, the catalyst will fall to bits. This will increase the pressure drop across the bed and can lead to flow mal-distribution.

With modern catalysts with copper doping, this is less of a problem. The Cu increases the activity of the HTS catalyst significantly, reducing the CO level down rapidly to a safe level both on the top of the catalyst bed and on the surface of the catalyst pellets themselves. Hence the likelihood of over-reduction is minimised.

5 Low temperature shift catalyst

5.1 Catalyst parameters

The catalyst parameters for **KATALCO** 83-3 and 83-3X are as follows

Table 5 – LTS catalyst parameters

Catalyst	83-3X	83-3
Form	Pellets	Pellets
Production Method	Pelleting	Pelleting
Size	5.2 mm diameter 3.0 mm length	5.2 mm diameter 3.0 mm length
CuO	51.0 wt%	51.0 wt%
ZnO	31.0 wt%	31.0 wt%
Promoters	-	1.0%
Al_2O_3	balance	2.6 wt%

LTS catalysts are formulated as pellets of $CuO/ZnO/Al_2O_3$. The active phase is metallic copper, formed when the LTS catalyst is reduced. The zinc oxide and alumina act as a support for the copper crystallites, both against sintering, hence minimising the rate of activity loss as well as physically providing strength in the pellet itself. The zinc oxide has a self-guarding effect – it adsorbs the poisons in the process gases, protecting the active copper from deactivation by poisoning.

The reduction reaction is as follows,

$$CuO + H_2 \Leftrightarrow Cu + H_2O \qquad \Delta H = -80 \text{ kJ/Kmol}$$

The reaction is extremely exothermic and therefore must be conducted in the presence of an inert gas (usually N_2), using low concentrations of H_2 either in a circulating or once through system.

5.2 LTS catalyst requirments

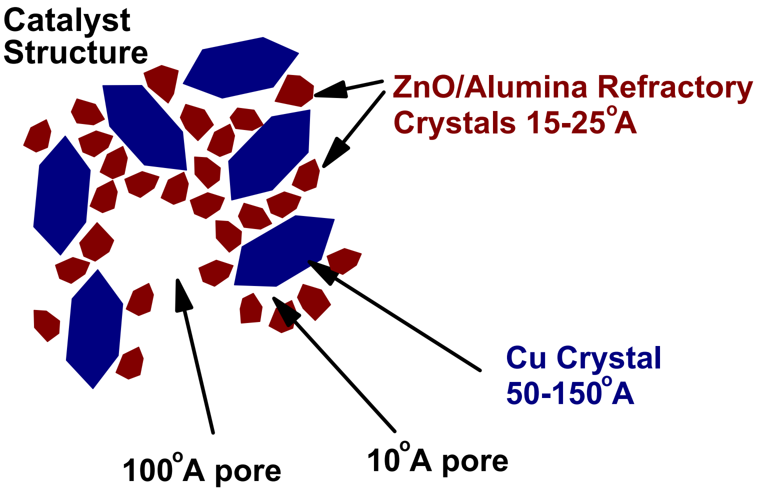
For a good LTS catalyst the requirements would be:

- Good dispersion of the Cu crystallites, within the alumina structure because this provides the catalyst with,
    - High shift activity
    - High strength needed for process upsets like wetting
    - High thermal stability (long life) – Cu crystallites resist from sintering
    - Protection against poisons in the gas stream
- Good dispersion of ZnO/Alumina refractory crystallites, because they provide,
    - High Strength
    - Prevention of Cu crystallites from sintering
    - ZnO provides sink for sulphur and chloride poisons
- Increasing Cu content yields,

- Higher activity
- Lower stability
- Lower strength

An effective catalyst needs a formulation that provides a balance between thermal stability and activity. **KATALCO** 83-3 has been designed specifically with all the above characteristics as illustrated below.

Figure 8 – LTS catalyst structure



5.3 Reduction procedure for HTS catalyst

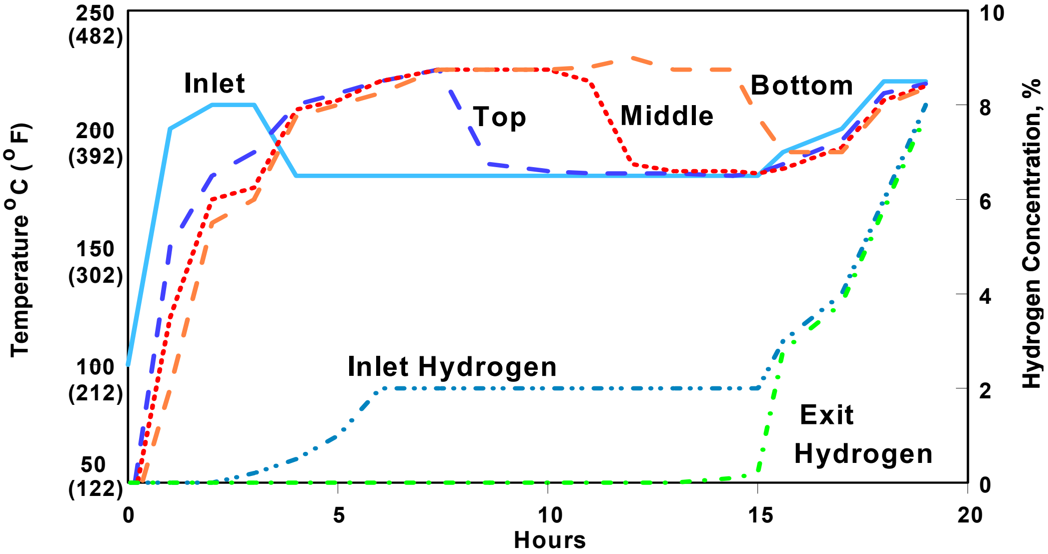
The reduction of an LTS catalyst is different from an HTS catalyst. In the case of an LTS catalyst, the exotherm associated with the reduction is so large that the temperature would cause the catalyst to completely sinter if it were allowed to happen in an uncontrolled manner. This deactivates the catalyst to such an extent that it is useless and would have to be changed. In order to achieve the maximum activity from a charge of LTS catalyst, it is important to control the reduction to ensure that the catalyst is not subjected to high temperatures.

High initial activity comes from the size of the copper crystallites that are part of the formulation of an LTS catalyst: the smaller the crystallites, the more active the catalyst.

The reduction itself is normally carried out using a small concentration of hydrogen (typically 2% to start) in an inert carrier gas, such as nitrogen or methane. The hydrogen dilution needs to be accurately monitored into the carrier stream. An excess of hydrogen will give a larger exotherm and could lead to catalyst damage. The gas needs to be free from poisons, such as sulphur and chlorides, and free from trace amounts of oxygen. Either a once-through or a recycle system can be used to carry out the reduction, depending on local preferences, or plant piping.

The key indication of the progress of an LTS reduction is the movement of the exotherm through the bed. It is vital that the thermocouples are checked prior to the start of the reduction for accuracy. An LTS reactor will normally have several thermocouples down the depth of the bed, as well as thermocouples on the inlet and exit. An example of the progress of an LTS reduction is given in figure below:

Figure 9 – LTS reduction profile



The reduction process also causes the LTS catalyst to shrink, usually by around 10% of its volume. This is due to the crystal structure reorganising and "relaxing" back into a new structure. The flow through an LTS bed during reduction should be uniform to ensure an even reduction.

An example of a typical LTS reduction schedule is given below,

1. Purge the converter free of oxygen with an inert gas. If natural gas is to be used as the carrier gas, then normal safety procedures for gas/air systems should be followed.

2. Check that all associated pipework is free of water, then establish a flow of carrier gas (nitrogen or natural gas) at a space velocity of 250 hrs^{-1} or higher. The reduction is more quickly completed at higher space velocities.

3. On most plants the reduction may be carried out at any convenient pressure, though a higher pressure is normally better. In a circulating system a higher pressure is normally preferred as it allows a higher flow to be achieved in the system, a higher partial pressure of hydrogen help the reduction

4. Heat the catalyst at a rate of not greater than 50° C/hr. During the heat up, while the bed temperatures are below 120° C, the hydrogen injection valve should be checked and calibrated over the range 0.5% - 2% hydrogen inlet the converter. This should be done quickly and the valve isolated between injections.

5. When at least one-third of the bed is at 180° C, establish a hydrogen flow aiming for not greater than 1% H_2 at this stage. When gas analysis confirms the hydrogen concentration and the exotherm is stable, the hydrogen concentration may be raised to approximately 2% in stages. THIS MUST BE DONE WITH CAUTION AND ONLY IF THE CATALYST TEMPERATURES ARE AT A SAFE LEVEL AND THE ENTIRE SYSTEM IS STABLE.

6. The maximum bed temperature during reduction should be limited to 230° C. In any situation, if a bed temperature reaches 250° C then the inlet hydrogen should be reduced to less than 1%.
7. When an elevated hydrogen concentration consistent with a safe temperature is established, the reduction should be allowed to continue until the exit gas analysis indicates a rising hydrogen concentration. When the inlet and exit hydrogen concentrations differ by less than 0.5%, the inlet hydrogen should be raised above 5% in stages. The bed temperatures should be watched closely after each hydrogen adjustment.
8. The entire bed should be raised to 200° C. It is recommended that the bed be "soaked" in the high hydrogen concentration for at least two hours.
9. The reduction can be considered complete when the entire bed is at 200° C or greater and the inlet and exit hydrogen concentrations differ by no more than 0.2%.
10. The catalyst can now be put into service.

5.3.1 Points to note

- Carrier Gas
  Desulphurised natural gas and nitrogen are acceptable. Ideally the carrier gas is free of hydrogen and oxygen. In the event of contamination, levels should be:

  Hydrogen not greater than 0.5%
  Oxygennot greater than 0.1%

  (Note: 0.1% oxygen consumes 0.2% hydrogen and produces an exotherm of 17° C in nitrogen.)

- Hydrogen Source
  The hydrogen should be free of sulphur and chlorides. Carbon monoxide in the hydrogen is acceptable but the additional associated temperature rise must be allowed for.

- Temperature Control
  There must be an adequate mechanism for inlet gas temperature control and as an absolute minimum thermocouples at the inlet and exit of the catalyst bed. Preferably, for use not only during the reduction but also for performance monitoring throughout the life of the catalyst, thermocouples should be spaced throughout the catalyst bed.

- Sample Points
  Gas sample points must be available inlet and exit the bed.

- Pressure Control
  The system must have an adequate mechanism for pressure control. Wild pressure fluctuations might otherwise result in unacceptable surges of hydrogen flow to the catalyst.

- Cooling/Condensing/Catchpot
  Re-circulating systems must have a mechanism for controlled removal of the water reduction.

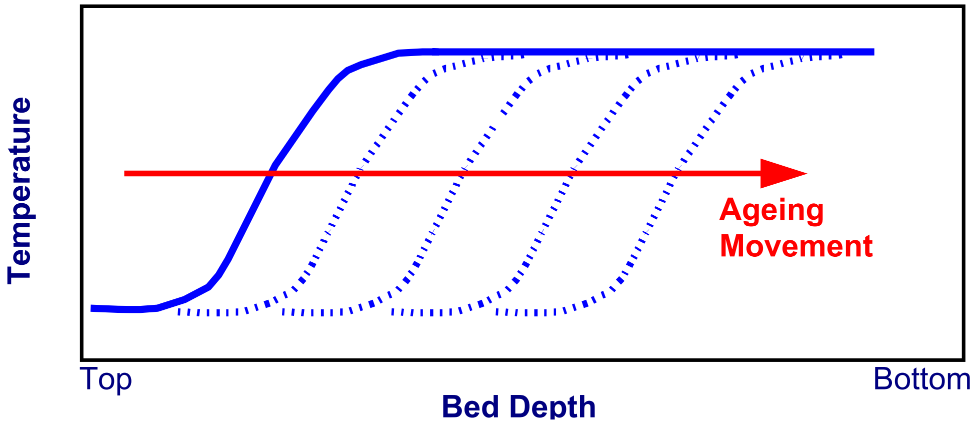
- Contingencies

With natural gas as the carrier in the event of an excessively high temperature (above 290° C), additional hydrogen can be produced by the thermal cracking of the gas. Should, for whatever reason, an excessive temperature rise occur, the natural gas must be isolated and the contents of the reactor purged and cooled with nitrogen. In the event of a temperature runaway, the vessel pressure should be reduced to minimise any chance of vessel damage. Again, in the event of thermal runaway, if possible the heat should be vented by reverse flow to avoid damage to hitherto unaffected catalyst.

5.4 Normal operation

As with HTS catalysts, LTS catalysts should be operated at as low an inlet temperature as possible, consistent with minimum CO slip. LTS catalysts are capable of operating effectively at lower temperatures – the activity of copper for the water gas shift reaction is sufficient to drive the reaction to an equilibrium CO slip of 0.1 to 0.3% exit the LTS bed, dependent on process conditions. The lower limit on the inlet temperature is usually determined by the condensation temperature. It is known that water is detrimental to the performance of LTS catalysts, as it can significantly reduce the activity. Practically, the dew point (condensation point) limit means that modern LTS catalysts are operated at an inlet temperature approximately 15 - 20° C above the dew point. The catalyst volume in an LTS reactor is determined by the life the plant needs for a given CO slip. At start of run, the CO is converted to its equilibrium level in the top of the bed and most of the bed is unused. This is seen by a large exotherm between the inlet thermocouple and thermocouples placed near the top of the bed. As the catalyst near the top of the bed starts to deactivate, more of the load is taken up by catalyst further down the bed and hence the exotherm profile moves down the bed. An example of a typical exotherm movement through an LTS bed as a function of life is given in the diagram below.

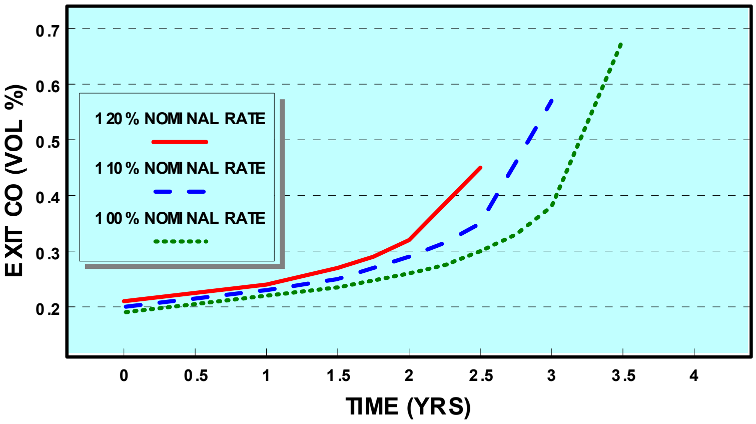
Figure 10 – Typical temperature profile of LTS catalyst



The deactivation is due to a combination of thermal sintering and poisoning by trace components, particularly sulphur and chlorides. However, for a constant poisons level, the rate of deactivation is constant and hence the rate of profile movement is easily calculable. This is used to determine the active life of the catalyst and to guide when change-out of the catalyst should occur. Once the exotherm has reached the bottom of the bed, change-out should be imminent, as the CO slip will start to rise to unacceptable levels within a relatively short time (days or weeks). With a poisons-free process gas, and in the absence of condensation on the catalyst, an LTS charge could be expected to last several years. Practically, exchanger leakages or inadequate quench water evaporation and the effect of trace poisons will usually limit the life of a bed of LTS catalysts to between 3-4 years.

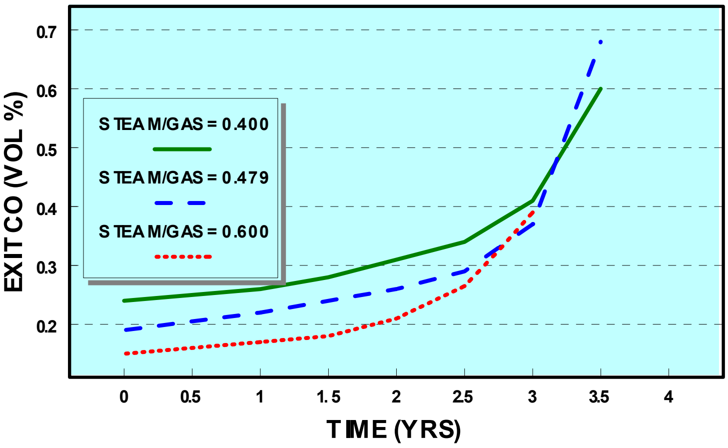
The key parameters to monitor the life of an LTS bed are temperatures, by charting the height of the exotherm and its movement through the bed, and the CO slip. The temperature of the bed may need to be optimised as time goes on to maintain adequate reaction. Increases in process flow rates, whether due to de-bottlenecking or due to lowering the steam ratio, are usually easily handled by an LTS catalyst as shown below.

Figure 11 – Performance of LTS reactor at increased throughput



The activity of the catalyst is so high that the effect on the shape of the exotherm is small – it may lean a little flatter. However, the rate of poisoning may increase, as a greater quantity of poison per unit time are passing across the catalyst and so the rate of profile movement may increase a little too. The combined effect will be to reduce the life of the catalyst in some way, proportional to the rate increase. A lower steam to carbon ratio does not affect the performance of the catalyst – copper catalysts have no Fischer-Tropsch activity – it will only increase the CO slip. The diagram below shows the impact of steam to gas ratio inlet the LTS reactor

Figure 12 – Performance of LTS reactor at different steam to gas ratios



Quite often poisoning is an intermittent effect, brought about by either a failure in the purification system, or by a change in the feedstock. With LTS catalysts, the effect of poisons is usually cumulative and activity cannot normally be recovered by removal of the poison source. As the catalyst ages, it is usual to modestly increase the inlet temperature to the LTS reactor. This minimises the CO content in the exit gas throughout the catalyst life. The graphs below shows the impact of operating at a given fixed inlet temperature throughout the catalyst life and also shows how the inlet temperature is increased to minimise the CO content in the exit gas throughout life.

Figure 13 - Effect of catalyst ageing at fixed LTS inlet temperature

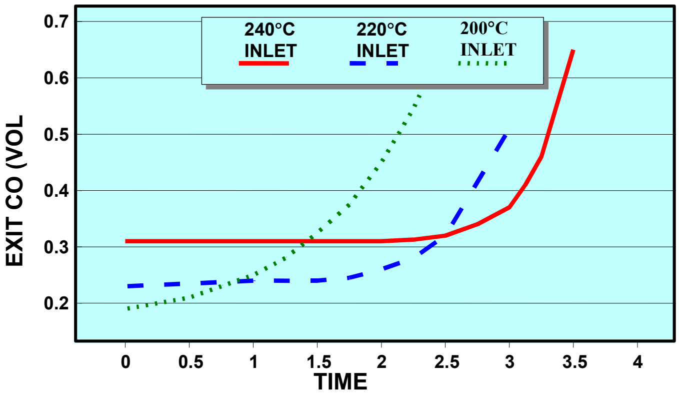
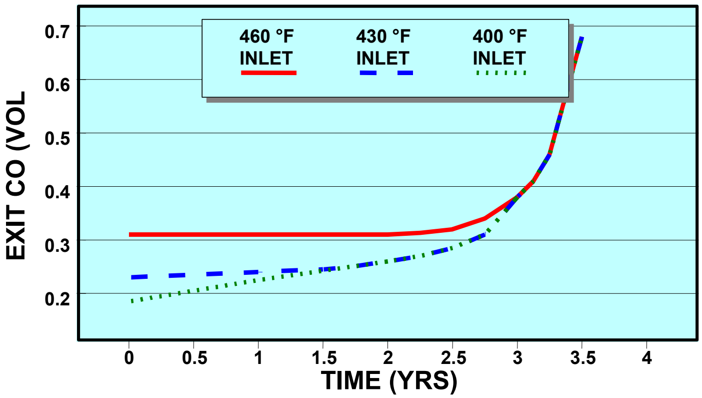


Figure 14 - Effect of catalyst ageing with optimised LTS inlet temperature



AT START OF RUN, INLET
THEN ADJUSTED DURING REMAINDER

5.5 Control parameters

As with the HTS the parameters that an operator can vary are for the LTS catalyst are,

- Steam to gas ratio.
- Inlet temperature.

Table 6 – Effect of steam to gas ratio on LTS performance

Name	**Units**	**Base Case**	**Steam:Gas Ratio**
Catalyst Age	*Years*	0	0
Inlet Steam:gas ratio		0.344	0.365
Inlet Temperature	*°C*	198	198
Exit Temperature	*°C*	223.2	221.5
Exit CO Slip	*(dry)mol %*	0.258	0.233
Approach to Equilibrium	*°C*	0.0	0.0

The table shows that at start of life the catalyst is operating at equilibrium and the effect of increasing the steam to gas ratio is to reduce the CO slip, however the effect of increasing the inlet temperature when the bed is operating equilibrium would be the reverse i.e. CO slip would increase since the shift reaction is favoured by low temperatures. For the purpose of demonstration, say the main LTS catalyst was operated for 6 years, and the guard bed was spent, hence with no shift activity. Hence the catalyst would be operating at a significant ATE, and hence the effect of increasing the inlet temperature from 198° C to 208° C is given in the table below:

Table 7 – Effect of temperature on LTS performance

Name	**Units**	**Base Case**	**Increased Temperature**
Catalyst Age	*Years*	6	6
Inlet Steam:gas ratio		0.344	0.344
Inlet Temperature	*°C*	198.0	208
Exit Temperature	*°C*	222.1	232.8
Exit CO Slip	*(dry)mol %*	0.398	0.325
Approach to Equilibrium	*°C*	26.5	3.6

As we can see from the table above, an increase in the inlet temperature of 10° C will result in the reduction of CO slip by 0.73 mol% to 0.32 mol% and the ATE is reduced to 3.6° C.

5.6 Common problems in LTS

There are many common problems that can occur within the shift section; below is a brief discussion of some of them. If as an operator you believe that you have a problem, then you should consult your catalyst vendor.

5.6.1 Poisons

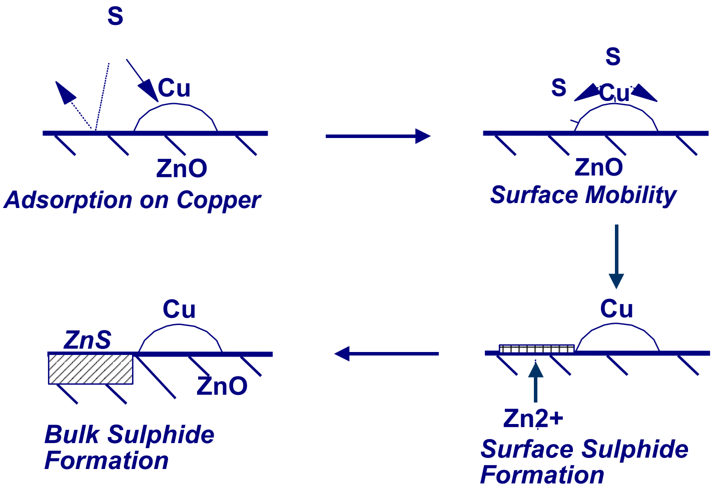
Ammonia plants can use a variety of feedstocks into the front end and with these feedstocks come a variety of poisons that have to be removed before reaching the LTS reactor. Also, the effect of condensation on the catalysts needs to be avoided. Both factors need to be considered, as both can have a significant effect on the life of an LTS charge. It is also possible to form methanol and other trace oxygenates over LTS catalysts and hence conditions have to be controlled to minimise their production. The two most virulent poisons for an LTS charge are sulphur and chlorides. They can reach the LTS catalyst through the feedstock, or as non-volatile components in steam, or even in quench water if this is used. Their effect is the major source of deactivation of an LTS catalyst. High surface coverage is often seen of both sulphur and chlorides on discharged samples, normally above 1% at the top of the bed. The high mobility of halides promotes sintering, so even trace levels can have a significant effect on LTS catalyst activity.

Sulphur is normally present in the feed stream as hydrogen sulphide, or perhaps as organic sulphur compounds. The level of sulphur in the feed to the LTS reactor should be less than 0.1 ppm. Sulphur reacts with the copper to form copper sulphide, a stable component that does not remove from the copper even if the source of sulphur contamination is removed. Hence, it is important to minimise the level of sulphur coming through to the LTS by maintaining an effective desulphurisation system. The use of zinc oxide in the LTS formulation performs a self-guarding measure for the copper. Zinc oxide is much more effective at trapping sulphur. The mechanisms for sulphur adsorption are shown by equations below: and described in the diagram

$$2Cu + H_2S \rightarrow Cu_2S + H_2$$

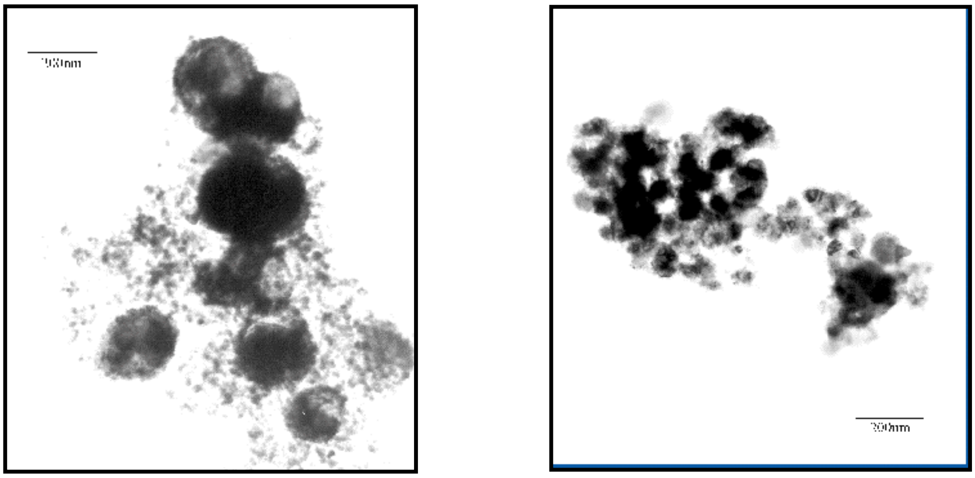
$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Figure 15 – Sulphur poisoning



Chlorides combine with both copper and zinc oxide to form stable chloride salts. The low melting point of copper chloride allows them to move about the catalyst surfaces and act as a virulent sintering agent, decreasing the active copper surface area irreversibly. The photos below show the size comparison between chlorided and non-chlorided LTS catalyst. As can be seen the effect of sintering results in much larger crystals forming.

Figure 16A/B – Effect of chloride poisons



Chlorided LTS **Non-chlorided LTS**

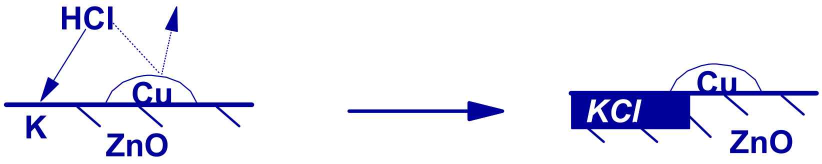
The levels of chlorides in the feed to the LTS reactor should be as low as possible and certainly less than 5 ppbv. The mechanisms are given in equations below:

$$2Cu + 2HCl \rightarrow 2CuCl + H_2$$

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O$$

To minimise the effect of chloride poisoning the 83-3X variant should be used the caesium and potassium promotes have the highest driving force for chloride compared to copper. Hence the Cs and K protect the Cu/ZnO lattice by preferentially reacting with and trapping the chlorine poison. This is illustrated in the diagram below,

Figure 17 – Effect of chlorides on LTS catalysts



Adsorption on Potassium ***Bulk Chloride Formation***

The level of chlorides entering an LTS reactor is usually so low as to be below the level of detection, so actively monitoring for chlorides is very difficult. Practically, only after discharge of an LTS charge can chloride levels be determined. However, prudent precautions can be taken: an alumina guard bed in the purification train can be added to adsorb chlorides. The feedstock sources to the ammonia plant reformer also need to be checked to ensure they are free from chlorides, particularly if some or all of the feed is refinery off-gas that may have organic chlorides trapped in it. Once again, the zinc oxide component can provide from measure of self-guarding against chloride poisoning.

5.6.2 Effect of water

The presence of excess steam in the LTS reactor drives the water gas shift equilibrium to minimise the CO slip. However, if the LTS catalyst is operated at too low a temperature, there is a danger that water might condense on the catalyst, leading to permanent deactivation. This is a particular danger during the start-up of a fresh charge of LTS catalyst and it is recommended that the catalyst bed is heated up to at least 15-20° C above the dew point before process gas is added.

Other sources of water could be from upstream exchanger leaks, in which cooling water passes directly into the process gas to the LTS catalyst or from quench systems that are not functioning properly. The water physically impacts the catalyst and evaporates, causing the pellets to break and giving a pressure drop increase. Also, the water may contain solids and contaminants, which will plate out on the catalyst surfaces, covering the active copper sites. The water will also dissolve soluble poisons already on the catalyst bed, washing them deep into the catalyst bed and hence increasing the affected depth of the bed. Both reasons will accelerate change-out of the catalyst. Any leaks should be attended to as soon as they are detected and quick action will minimise the effect on catalyst performance.

5.6.3 Methanol formation

The formulation of an LTS catalyst is designed to be selective for the water gas shift reaction and to minimise other reactions. LTS catalysts contain a significant amount of copper and at the conditions that the LTS converter operates it is possible to form several hundred ppm of methanol and lesser quantities of other oxygenates. The reaction for Methanol Formation is:

$$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$$

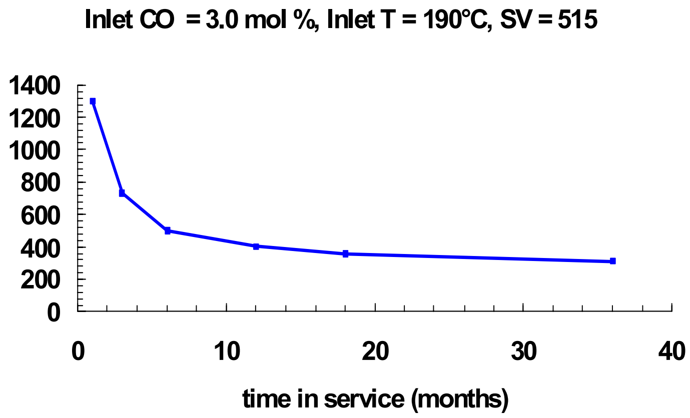
- Methanol increases with
  - High Temperatures
  - High inlet CO levels - increases LTS temperature rise
  - Low S:C ratio
  - Low space velocity / catalyst bed volume

Methanol may be a problem for,

- Effect quality of CO_2
- Quality of process condensate – Environmental legislation

Methanol production decreases rapidly in the first few months of LTS catalyst operation as shown in the diagram below,

Figure 18 – Change in methanol with time



Methanol can be reduced by 20 – 30% by optimising the operating conditions,

- Reduce inlet temperature (check for dew point)
- Maximise HTS CO conversion to minimise LTS temperature rise

Where methanol formation may be more problematic, use of modified LTS catalysts (such as **KATALCO** 83-3X) can substantially reduced the methanol make.

- Use of potassium in the catalyst can reduce the methanol make by up to 50%
- Caesium and potassium modified LTS Catalyst (**KATALCO** 83-3X) can also be used to reduce methanol levels to less than 10% compared with that of conventional catalysts.

6 Monitoring

6.1 CO slip

The CO slip from both the high and low temperature shifts should be checked every week. This should be recorded along with the following parameters,

- Temperature profile,
- Exit pressure,
- Steam to gas ratio,
- Plant rate.

This allows for early identification of problems on the shift vessels before they become too severe. By collecting the other key process parameters it is easy to check whether a rise in CO slip can be attributable to a change in a process parameter.

6.2 Pressure drop

Pressure drop should also be recorded on a regular basis to ensure that early identification of catalyst fouling or break-up. If the plant rate is changing then the pressure drop should be normalised for changes in feed rate and also steam rate.

For further information on Johnson Matthey Catalysts, contact your local sales office or visit our website at www.jmcatalysts.com

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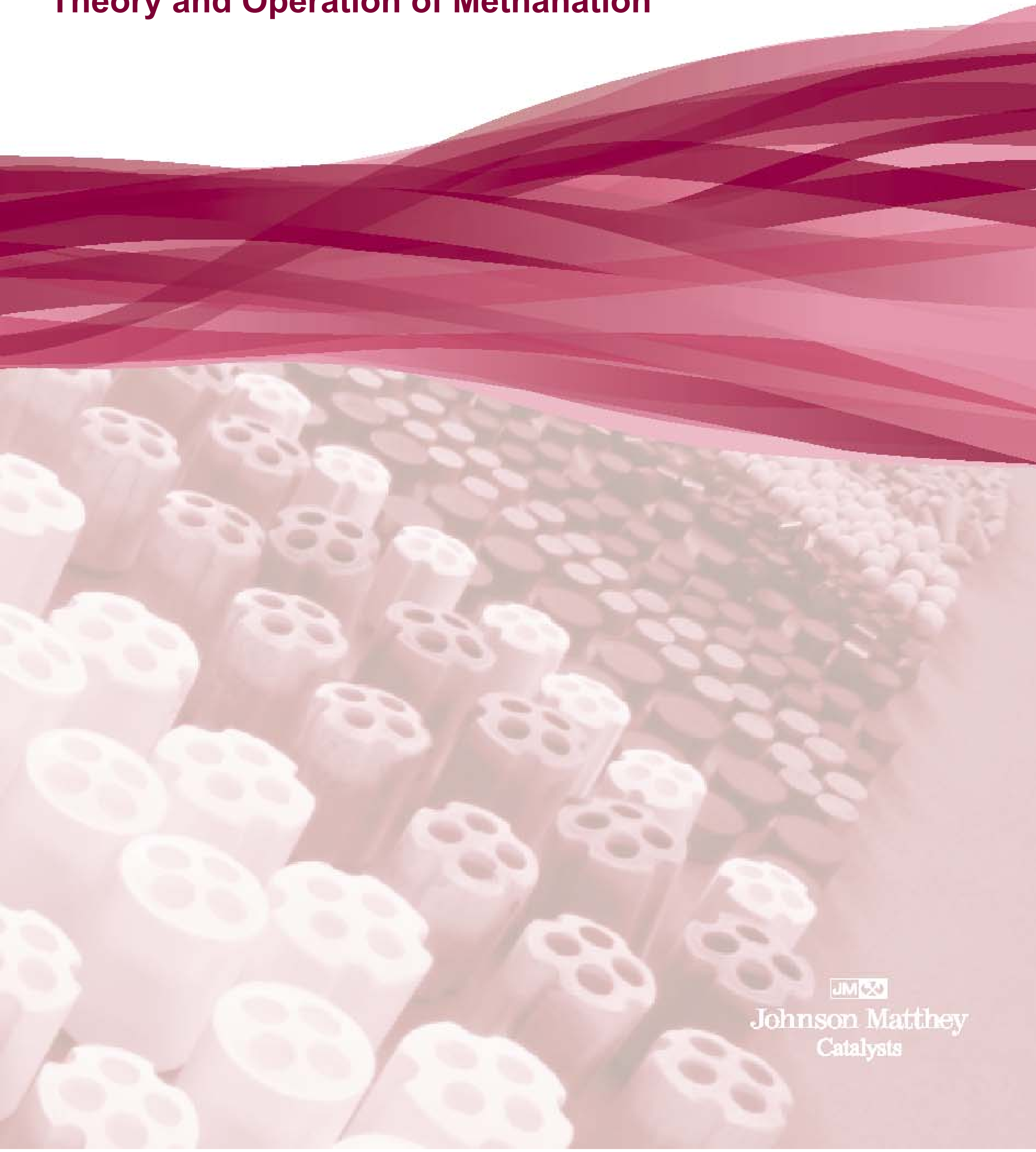
Theory and Operation of Methanation



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1 Introduction

Methanation is an often overlooked part of any ammonia plant due to the well known long lives and robust nature of the catalyst. Even given this, the importance of the good operation, monitoring and maintenance of the methanation catalysts should not be overlooked.

The purpose of this paper is to,

- Detail some fundamentals about the chemistry of the methanation reaction,
- Detail the principles of the operation of methanation,
- Discuss some common operating problems.

2 Methanation theory

2.1 Chemistry

The following reaction details the reaction that converts nitrogen and hydrogen to ammonia,

$$CO + 3H_2 \Leftrightarrow CH_4 + H_2O \qquad \Delta H = -206 \text{ kJ/kmol}$$

$$CO_2 + 4H_2 \Leftrightarrow CH_4 + 2H_2O \qquad \Delta H = -165 \text{ kJ/kmol}$$

2.2 Optimal pressure

The operating pressure of the methanation is defined by other process parameters such as the pressure drop through the various front end unit operations and the performance of the synthesis gas machine.

2.3 Optimal temperature

The optimum operating temperature is a function of the CO and CO_2 entering the methanator and the exit temperature achieved from the methanator.

If the CO and CO_2 inlet the methanator rises, then the exotherm across the bed will rise and therefore the exit temperature will rise. There is therefore an opportunity to reduce the inlet temperature whilst maintaining low levels of carbon oxides exit the methanator.

2.4 Catalyst choice

Johnson Matthey Catalysts recommends the use of **KATALCO**^{TM} 11-4R over 11-4. **KATALCO** 11-4R is a pre-reduced methanation catalyst and allows for a much faster methanator start up.

3 Poisons

Methanation catalysts are not usually deactivated by thermal sintering and the principle reason for any loss of activity is poisoning. Sulphur compounds will poison a methanation catalyst but they are not usually present in the process gas since the LTS will pick up the poisons, but if the LTS is bypassed then this can be a problem. The poisons that are most likely to affect the methanation catalyst under normal operating conditions are those arising from the CO2 removal systems. Carry over of a small amount of liquid into the methanator is not serious, however, large volumes of liquid can have serious consequences, particularly if the liquid if there is sulphur or arsenic present because irreversible loss of activity.

Table 1 – Methanation poisons from CO_2 removal systems

Process	Chemical	Effect
Benfield	Aqueous potassium carbonate	Block pores of catalyst by evaporation of K_2CO_3 solution
Vetrocoke	Aqueous potassium carbonate and arsenious oxide	Block pores of catalyst by evaporation of K_2CO_3 solution As_2O_3 is also a poison – 0.5% of As on he catalyst will reduce activity by 50%
Benfield DEA	Aqueous potassium carbonate with 3% di-ethanolamine	Block pores of catalyst by evaporation of K_2CO_3 solution – DEA is harmless
Sulphinol	Sulpholane, water and di-2-propanolamine	Sulpholane will decompose and cause sulphur poisoning
MEA, DEA	Mono- or di-ethanolamine in aqueous solution	None
MDEA	Aqueous solution of Methyl-di-ethanolamine and activators	None
Rectisol	Methanol	None
Catacarb	Aqueous potassium carbonate with borate additive	Block pores of catalyst by evaporation of K_2CO_3 solution
Selexol	Dimethyl ether of polyethylene glycol	None

When only potassium carbonate or organic solvents are used, the effect are less important, potassium carbonate blocks the catalyst pores and can only be removed by washing with water to restore performance.

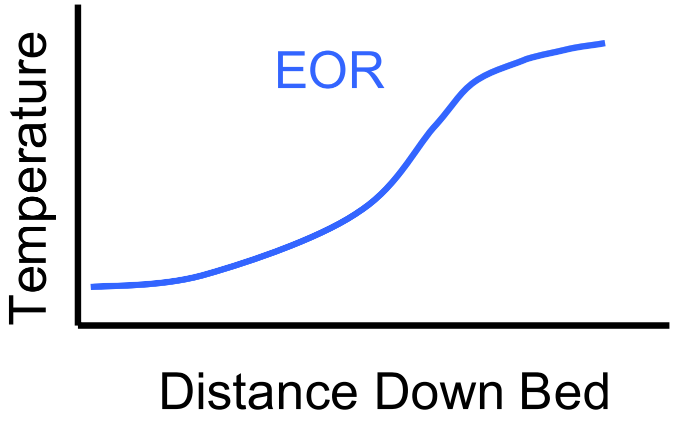
4 Control parameters

The key control parameters are detailed above in sections 2.2 and 2.3.

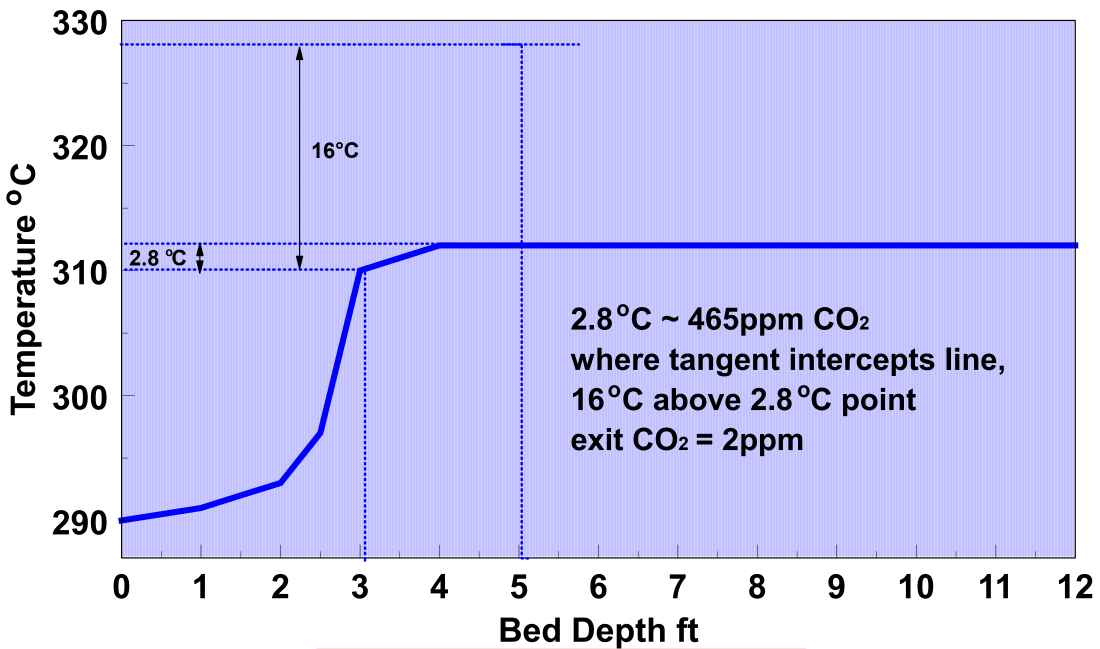
5 Monitoring

5.1 Temperature profile

The temperature profile across the methanator should be monitored and tracked in order to determine whether the catalyst is nearing end of life. If the profile is found to be close to the end of the bed, as illustrated, then it is time for the catalyst to be discharged. The key to determining this is whether there is a flat portion at the end of the bed; if there is then the bed still has some residual life; if not then the bed is close to the end of life the catalyst is ready for discharge and replacement.

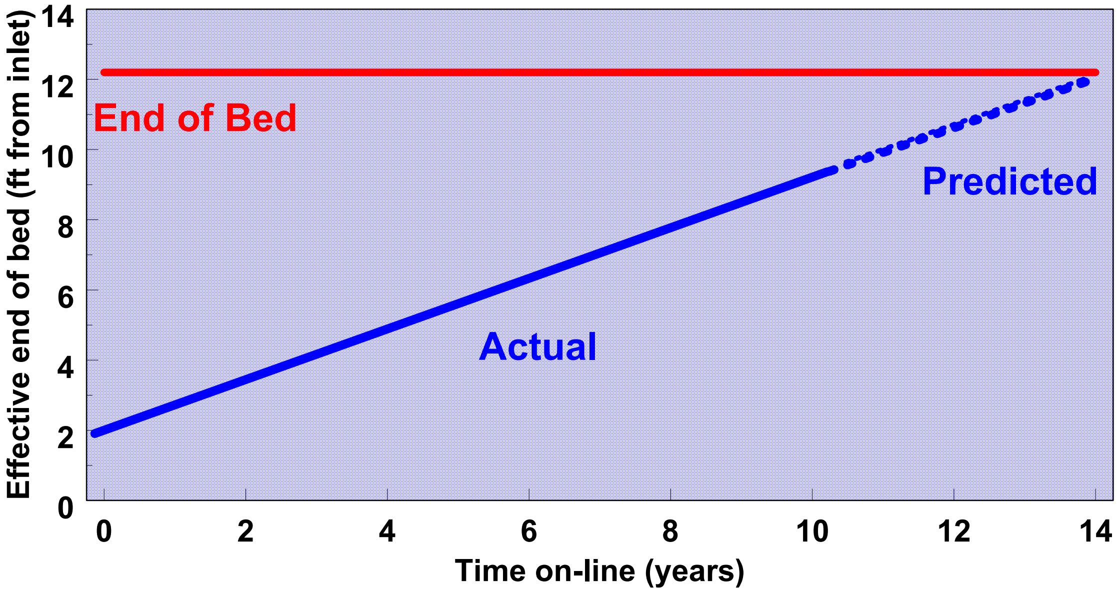


It is also possible to determine the residual life of the methanator by monitoring the movement of the end point of the profile as illustrated below,



Plot end of active catalyst bed as function of time

Once the end point of the profile has been determined, a plot of the end point against time can be constructed and then trended forward as illustrated below to determine the end of life,



5.2 Pressure drop

The pressure drop should be monitored in order to check whether there has been a carry over from the CO_2 removal system or excessive breakage.

5.3 Carbon oxide slippage

The carbon oxides levels exit the bed should be checked to determine if the bed is close to the end of life; if the carbon oxide levels are rising then this indicates that the bed is at end of life. This should be coupled with monitoring of the temperature profile through the bed.

6 Common problems

6.1 Carry over of CO_2 removal system liquor

As detailed above, CO_2 removal liquid can affect the performance of the methanator. It is possible to reverse this by washing with water little or no reduction in catalyst activity or increase in pressure drop. A procedure is available from Johnson Matthey Catalysts on request.

6.2 Bypassing of the LTS

If the LTS is bypassed or fails to perform adequately, then the carbon oxides inlet the methanator will rise. This will cause a significant rise in the exotherm across the bed and hence the exit temperature. Although this can lead to sintering of the methanation catalyst, excursions for a short period of time can be accepted with little or no effect on the activity of the methanation catalyst.

6.3 Failure of the CO_2 removal system

If the CO_2 scrubber fails such that there is a large increase of carbon dioxide passing to the methanator, then the exotherm across the bed will increase and so will the exit temperature. Although this can lead to sintering of the methanation catalyst, excursions for a short period of time can be accepted with little or no effect on the activity of the methanation catalyst.

6.4 Sulphur poisoning

This is not usually an issue but in the case where the LTS is being passed, then the normal sulphur protection offered by the LTS catalyst is not available and this can lead to poisoning of the methanation catalyst if sulphur is present in the reformed gas.

7 Conclusions

In conclusion, this paper has illustrated some of the key features of the ammonia synthesis loop, most notably,

- The fundamentals of methanation,
- The key control parameters,
- The common problems that can occur.

For further information on Johnson Matthey Catalysts, contact your local sales office or visit our website at www.jmcatalysts.com

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Ammonia Synthesis Theory and Operation

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1 Introduction

Ammonia Synthesis is an important part of any ammonia plant. As such the importance of the good operation, monitoring and maintenance of the ammonia synthesis loop can not be under-stated.

The purpose of this paper is to,

- Detail some fundamentals about the chemistry of ammonia synthesis,
- Detail the principles of the operation of ammonia synthesis,
- Discuss some common operating problems.

2 Ammonia synthesis theory

2.1 Chemistry

The following reaction details the reaction that converts nitrogen and hydrogen to ammonia,

$3H_2 + N_2 \Leftrightarrow 2NH_3$ $\Delta H = -52.1$ kJ/kmol

2.2 Optimal pressure

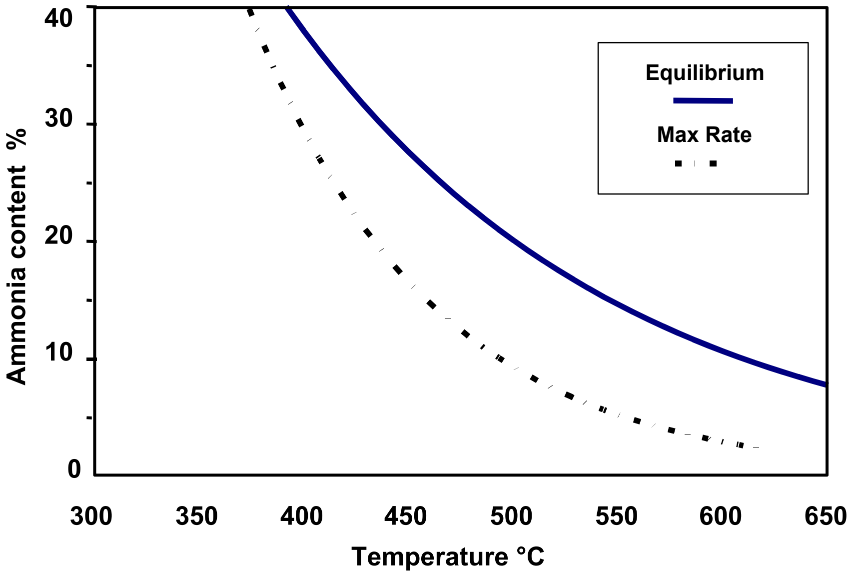
Since there is a large volume decrease associated with the synthesis of ammonia (4 volumes to 2 volumes), the synthesis reaction is favoured by high pressures.

Older ammonia plants required pressures between 300 and 600 bara, however with modern catalysts and converter designs, the synthesis loop pressure has been reduced to 100-300 bara. Furthermore, the Johnson Matthey Catalysts AMV and LCA process operate at an even lower pressure, typically 80 - 100 bara.

2.3 Optimal temperature

An analysis of the thermodynamics equilibrium for the synthesis reaction shows that the highest possible yield is achieved at the lowest possible temperature as illustrated in the figure below,

Figure 1 – Maximum rate line



However, balanced against this is the reaction rate, which is related to the operating temperature by a classic expression as below,

$$\frac{d[NH3]}{dt} \propto \exp\left[\frac{-\Delta E}{R \times T}\right]$$

So at high temperature, the reaction rate of ammonia synthesis will be high whilst at low temperatures, the reaction rate will be lower.

Considering both factors above, there is a balance between the equilibrium and reaction kinetics. The operating temperature range for synthesis catalyst is 350 – 520°C, constrained by kinetics at low temperature and sintering at high temperature. There is a limited temperature range between the minimum strike temperature of synthesis catalyst and the equilibrium temperature required for a high conversion per pass. To satisfy these temperature constraints it is necessary to cool the converter, and various cooling arrangements are used.

- Addition of cold quench gas,
- Transfer of heat from the catalyst bed to colder feed gas,
- Cooling between beds by transfer of heat within heat exchangers to a medium such as steam.

3 Poisons

The most common poison for ammonia synthesis catalysts is oxygen in the form of oxygenated compounds such as water, carbon monoxide and carbon dioxide. Under ammonia synthesis conditions, oxygenates are converted to water and this is considered to be the active poison.

Carbon oxides should be converted in the methanation stage of the front end of the plant, and excessively high carbon oxides are only a problem if the methanator fails to perform correctly.

Water should be removed in the knock out pots prior to the carbon dioxide removal system and between stages of the synthesis gas machine.

Poisoning of ammonia synthesis catalysts can be either temporary or permanent.

3.1 Temporary poisoning

Loss of activity from exposure to oxygen compounds is normally reversible provided that the partial pressure of the oxygenate is low and the period of exposure has been restricted to a few days. Under these circumstances the catalyst can normally be reactivated by following a reduction procedure. Some permanent damage is likely to take place even during temporary poisoning due to thermal sintering and reorganization of the iron surface. However, this is not normally seen as a loss in production.

3.2 Permanent poisoning

Exposure to oxygenates for several weeks normally results in permanent deactivation of the ammonia synthesis catalyst. Activity does not completely recover when pure synthesis gas is re-introduced or the catalyst is re-reduced. When the reduced catalyst is exposed to moderate partial pressures of water vapour, partial and reversible surface oxidation takes place. However, the transient oxidic phases do not contain alumina in solid solution. Hence during re-reduction there is no support-precursor phase present to prevent sintering of the iron crystallites. It is also thought that this oxidation/ reduction mechanism could result in the reorganisation of the crystal faces, decreasing the population of the highly active Fe(111) faces.

Other compounds will affect the catalyst irreversibly. These poisons include sulphur, chlorine, arsenic and phosphorous. Sulphur remains on the catalyst surface as bulk iron sulphide. Catalysts in operating plants that have lost activity as a result of poisoning have been found to contain less than 0.1% sulphur. Chlorine compounds are also severe poisons because the metal chlorides are relatively volatile and their transient formation can lead to irreversible sintering and hence loss of activity.

In addition to chemical poisoning of the iron surface, ammonia synthesis catalysts are also susceptible to loss of activity due to the physical covering of the active sites by an otherwise inert material. Compressor lubrication oil leaking into the process will result in cracking of the hydrocarbons to form carbon, which will act as a physical barrier. This poisoning can be partly reversible provided that the problem is recognized quickly, however permanent damage sometimes occurs.

4 Catalyst

4.1 Promoters

Ammonia synthesis catalysts have been traditionally been based on magnetite along with a range of specialised promoters. It is the addition of these promoters that gives the difference between the various commercially available ammonia synthesis catalysts and this is illustrated below,

Table 1 – Catalyst composition

Parameter	**Units**	**35-4/S6-10**	**74-1**
Magnetite	%	94	94.5
K_2O	%	0.5	0.6
CaO	%	2.5	1.5
Al_2O_3	%	3.0	2.1
SiO_2	%	n/a	<0.2
MgO	%	n/a	n/a
Co	%	n/a	1.0

It is these promoters that define the initial activity and stability of the catalyst.

4.1.1 Effect of promoters

There are a range of promoters that are added to magnetite catalyst; the effects of these promoters are as detailed below,

- **Alumina (Al_2O_3)** – This functions are a structural promoter, enabling the production and preparation of an open and porous structure. During the initial catalyst activation, reduction starts on the outside of the irregular particles, and the dissolved alumina separates out of the solid solution within the pores forming between the iron crystallites. This minimises further crystallite growth during the catalyst reduction and future operation.
- **Potash (K_2O)** – This component is an electronic promoter, functioning by considerably increasing the intrinsic activity if the high surface area iron particle produced on reduction.
- **Calcium Oxide (CaO)** – This promoter (as well as other basic promoters), react with silica impurities in the raw materials to form glassy silicates, which themselves can enhance the

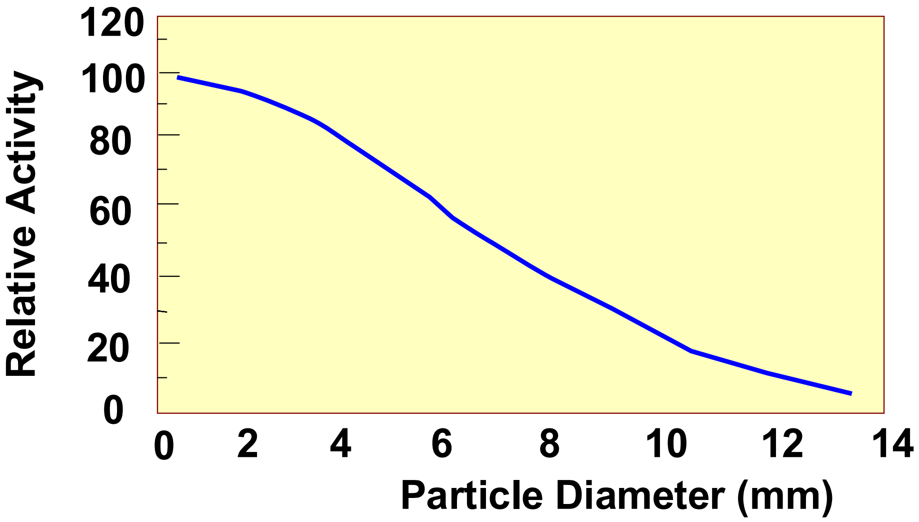
thermal stability of the reduced iron. The main benefit is to minimise any neutralisation of the potash promoter which would reduce it effectiveness.

There is a considerable interaction between the many components of the catalyst which can radically affect both the initial reducibility and level of initial activity and long term activity stability. A through understanding of these interactions is vital in order to optimise the performance of the catalyst.

4.2 Catalyst size

A key feature of all ammonia synthesis catalysts is that there is a diffusion limitation. The catalyst size is important since the smaller the catalyst pellet, the higher the surface area per unit volume and hence there is more surface area within the converter to catalyse the ammonia synthesis reaction. The following figure illustrates the effect of size on catalyst activity.

Figure 2 – Effect of catalyst size on activity



However, if a smaller catalyst size is used to maximise the activity if the catalyst, then this will increase the pressure drop across a bed. Therefore, in order to offset this effect, modern practice is to use radial (or axial-radial) flow through the catalyst beds.

Due to the unique manufacturing route that is used to produce ammonia synthesis catalyst, there is no set catalyst size, but rather a set of size ranges. The industry accepted ranges are detailed in the table below,

Table 2 – Effect – size ranges

Size Grade	Size Range
Units	mm
A	1.5-3.0
B	3.0-4.5
C	3.0-6.0
D	6.0-10.0
G	14.0-20.0

5 Converter schemes

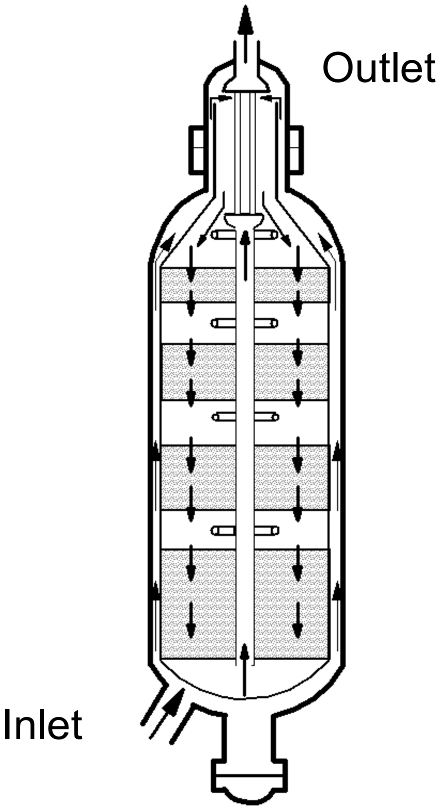
As noted above, the exothermic nature of the ammonia synthesis reaction, the effect of catalyst size, contractor choice and the option for retrofits have defined the nature of the various converter designs that have been historically available and presently available. The various converter types include,

- The Kellogg Axial Quench Converter design,
- The Kellogg horizontal Converter,
- The Johnson Matthey Catalysts Quench Cooled Converter
- The Johnson Matthey Catalysts Tube Cooled Converter (and similar TVA converters),
- Axial radial designs as offered by Ammonia Casale,
- Haldor Topsøe Radial Flow Converter,
- Uhde Radial Flow Converters.

5.1 Kellogg quench type converter

The following illustrates a Kellogg Quench Converter with 4 axial flow beds and inter-bed cooling by addition of quench gas,

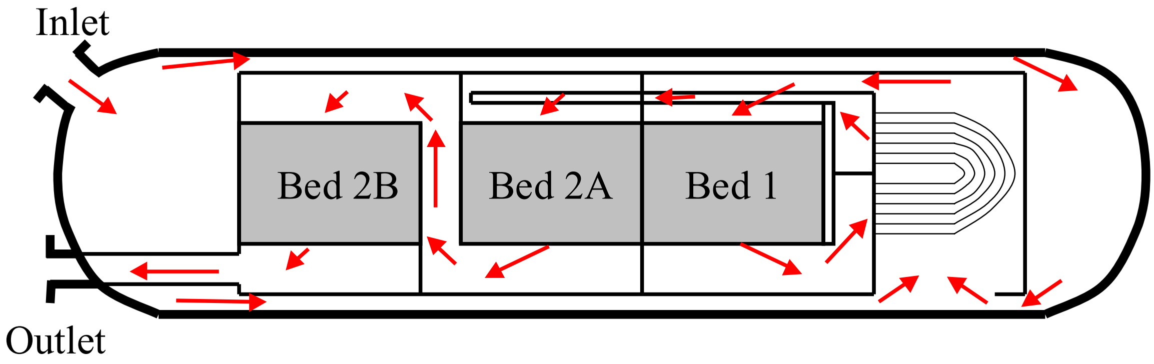
Figure 3 – Kellogg quench converter



5.2 Kellogg horizontal converter

The following figure illustrates the Kellogg Horizontal Converter, This design uses downward flow in beds installed in a horizontal pressure shell. The objective is the same as in radial flow designs, i.e. low pressure drop with small catalyst particles,

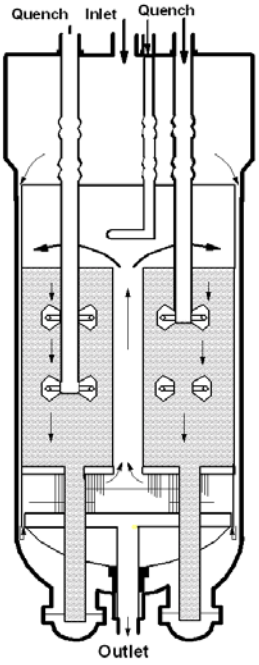
Figure 4 – Kellogg horizontal converter



5.3 Johnson Matthey quench cooled converter

The following figure illustrates the Johnson Matthey Quench Cooled Converter. The ‘lozenge quench’ system was designed to simplify catalyst loading and discharge.

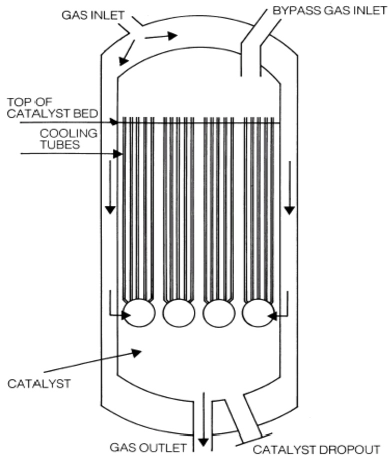
Figure 5 – Johnson Matthey quench



5.4 Johnson Matthey tube cooled converter

The following figure illustrates the Johnson Matthey Tube Cooled Converter as used in LCA ammonia plants. An adiabatic section is included at the exit of the catalyst bed to optimise the temperature profile,

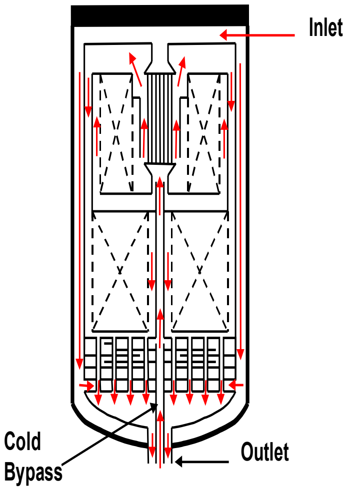
Figure 6 – Johnson Matthey Catalysts TCC



5.5 Haldor Topsøe radial flow converter

Haldor Topsøe's radial flow converters have been installed in a range of configurations, e.g. S-100 2-bed with quench cooling, S-200 2-bed with interchanger cooling and S-300 3-bed with interchanger cooling. The following figure illustrates a S-200 design,

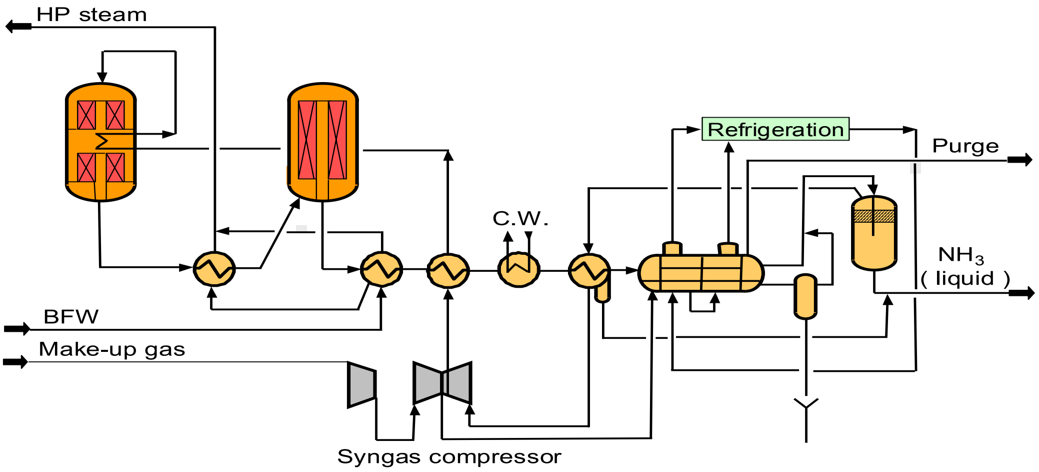
Figure 7 – Haldor Topsøe S-200



5.6 Uhde's three bed radial flow converter

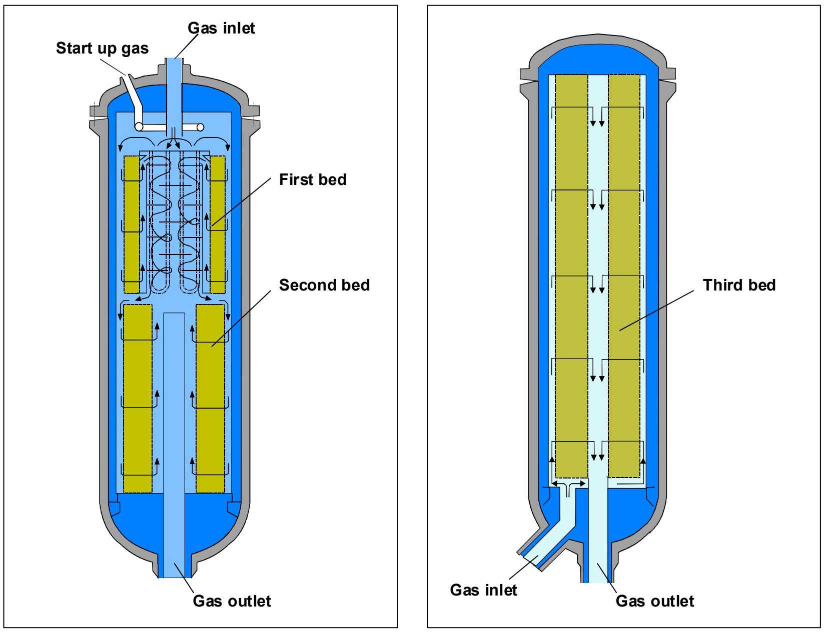
Uhde's radial flow converter technology is available in a range of configurations to suit the application. The following figure illustrates the loop lay out for an Uhde three bed radial flow converter in a large-scale, high conversion per pass application,

Figure 8 – Uhde ammonia loop flowsheet



The following illustrates the design of the first double bed converter and the design of the third and final bed converter,

Figure 9A/B – Uhde converters



6 Control parameters

On initial inspection, there would appear to be a large number of control parameters including,

- Loop pressure,
- Gas composition,
- Circulation rate,
- For temperature control within the converter, the quench rates and / or bypass valve positions.

However, in reality, ammonia synthesis loops are very stable and do not require constant attention. The principal control parameters are as follows:

6.1 Loop pressure

Loop pressure increases as the inert level in the synthesis loop increases. The pressure is controlled by varying the loop purge rate; some plants use cascade control with the purge flow setpoint re-set by the pressure, in many cases a simple flow controller is adequate with manual control of the setpoint. Loop pressure tends to increase slowly with time because of an increase in methane from the front-end and because of loss of activity of the synthesis catalyst.

6.2 Gas composition

As mentioned above, the methane content of the make-up gas tends to increase slowly as a result of catalyst die-off. The other main variable in the circulating gas composition is the H_2:N_2 ratio. This depends on the air rate to the secondary reformer, and is usually controlled manually although some plants do have automatic control of H_2:N_2 ratio. The optimum ratio is believed to be around 2.8 under most conditions, although the effect on loop performance is small over quite a wide range.

6.3 Circulation rate

The circulation rate is not a control parameter since on the majority of plants, the synthesis gas machine and circulator are on the same shaft and therefore the speed and hence the circulation rate is determined by the speed of the synthesis gas machine. However, some compressors have guide vanes on the circulator to give independent control of the compression and circulation duties. When guide vanes are fitted, they are usually controlled manually.

6.3.1 Converter temperature control.

For quench based converters, the quench flows to the individual beds can be varied in order to optimise the temperature profile through the converter. Control of quench flow rates is usually manual (by HICs) because the rate of die-off of ammonia synthesis catalyst is very slow. The inlet temperature to the first catalyst bed is a particularly sensitive control parameter and in some plants this temperature is on automatic control (by varying the bypass flow) because this stabilises the operation of the entire converter.

For converters with inter bed cooling by heat exchangers, the bed temperatures are controlled by heat exchanger bypasses rather than by quench flow rates.

7 Monitoring

7.1 Production rate

The ammonia production rate should be monitored as an overview check on the performance of the plant as a whole. Reduction in the production rate indicates that there is the potential for a problem in one of the upstream unit operations.

7.2 Loop pressure

The loop pressure should be monitored as this is a good general indication of a loss of efficiency in the synthesis loop. An increase in loop pressure may be caused by many factors including high inerts concentration, loss of catalyst activity or low circulation rate. Further investigation will be required to identify the problem.

7.3 Gas composition.

The circulating gas composition should be monitored for inerts concentration and for hydrogen to nitrogen ratio. The exit composition should be monitored for ammonia because this is a good indicator of converter performance.

7.4 Pressure drop

The pressure drop across the converter should also be monitored to determine if there is attrition of the catalyst or failure of the internals within the converter basket. Note that a reduction in pressure drop may indicate a reduction in flowrate through the converter, e.g. because of a partial bypass due to an internal leak.

7.5 Converter temperature profile

The temperature profile within the converter should be monitored in order to ensure that the ammonia production rate is maximised. Furthermore, if there is a leak within the loop interchanger, this will be reflected in a heat imbalance within the converter and hence an unusual temperature profile within the converter.

8 Common problems

Modern ammonia synthesis loops are generally very reliable, although there are many problems that can occur; below is a brief discussion of some of the more common problems. If as an operator you believe that you have a problem, then you should consult your catalyst vendor.

8.1 Poisons

As noted above, oxygenates are the most frequent form of poisons for the synthesis catalyst. Common sources are carbon oxides from a poorly performing methanator (or from a leaking methanator interchanger), water from carryover in the make-up gas separators, or oxygen from impure nitrogen during a plant overhaul. The first indication of a poisoning problem is usually a reduction in converter performance as indicated by a high loop pressure or low conversion to ammonia.

Note that in extreme circumstances, e.g. ingress of air during an overhaul, oxidation of ammonia synthesis catalyst can generate an exotherm of up to 1600°C.

8.2 Leaks

Internal leaks sometimes occur in synthesis loops; these can be in the loop interchangers, in the converter internal interchangers, or in expansion bellows.
In many cases, Johnson Matthey Catalysts can identify leaks from evaluation of operating data, and **TRACERCO™** techniques can be used to confirm the leak.

Loop boilers and steam preheaters normally run at a lower pressure than the loop so leaks lead to hydrogen/nitrogen in the steam rather than water on the synthesis catalyst. During shut-downs there is the potential for the driving force to be the other way resulting in deactivation/oxidation of the synthesis catalyst due to the ingress of water into the synthesis loop.

9 Conclusions

In conclusion, this paper has illustrated some of the key features of the ammonia synthesis loop, most notably,

- The fundamentals of ammonia synthesis,
- The key control parameters,
- The common problems that can occur.

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