



Chemical Cleaning

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1. Introduction



Instruction

- During construction and operation of the boiler, the scale is formed.
 - ▷ Construction : grease, oil, debris, rust, mill scale
 - ▷ Operation : hard scale
 - ※ scale → overheating the tubes → rupture
- The scale must be removed by chemicals or steam blowing
- Chemicals
 - ▷ Alkaline solvent : Remove oil substance
 - ▷ Acid solvent : Remove scale and rust
- Steam blowing : Steam lines(superheater, reheater)



Purpose of Cleaning



- **Ensure safe and normal operation**
- **Recover heat efficiency**

- 1) Remove the deposits and scales**
- 2) Recover heat efficiency**
- 3) Prevent overheating or corrosion**
- 4) Inspect surfaces of the boiler tubes**



Cleaning effect



- **Recover heat efficiency**
 - ✂ It is difficult to calculate the heat efficiency rise of the boiler by chemical cleaning
- **⇒ A preventive character**
(Ensuring safe and normal operation)



Cleaning Chemicals

o Kinds of the chemicals for chemical cleaning

Main agents	Inorganic acids	• Hydrochloric acid • Phosphoric acid, Hydrofluoric acid, • Nitric acid, Sulfuric acid
	Organic acids	• Citric acid, Glycolic acid, • Formic acid, Malic acid, • Oxalic acid, Gluconic acid
	Chelating agents	• EDTA(ethylenediamine tetraacetic acid)
	Alkali agents	• Ammonia, Sodium hydroxide, • Sodium carbonate, • Sodium phosphate, Hydrazine
Aids		• Acid inhibitor, Reducing agents, • Copper dissolved agents, • Copper dissolved sequestering agents, • Dissolution accelerators, Wetting agents



Cleaning Chemicals (Inorganic Acid)

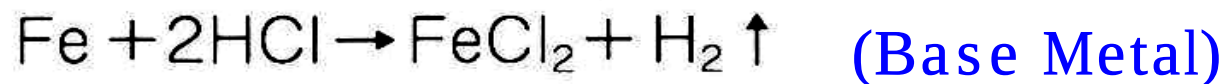
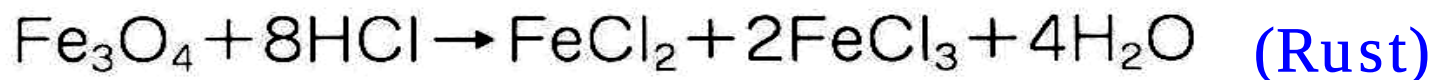


■ Inorganic Acid

1) Hydrochloric acid (HCl)

- In Past, Widely used for chemical cleaning
- Having a strong dissolving power (high solubilities)
- Used in the low temperature (to 60 °C)

<Reaction formula>



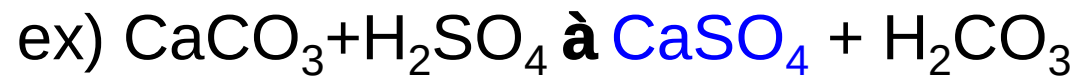


Cleaning Chemicals (Inorganic Acid)



2) Sulfuric acid (H_2SO_4)

- Highly reactive (Exothermic reaction)
- Generates a large amount of heat when diluted
- Dangerous chemical requiring careful handling
- Not used for the removal of scale containing a large amount of calcium



hard scale



Cleaning Chemicals (Inorganic Acid)



3) Phosphoric acid (H_3PO_4)

- **Relatively low corrosive action**
(anti-corrosive phosphate coatings)
- **Relatively high price**
- **Low solubility of the salts**
- frequently used for
 - cleaning of equipment or
 - for metal surface treatment prior to painting.



Cleaning Chemicals (Inorganic Acid)



4) Nitric acid (H_2NO_3)

- Highly reactive and high solubility of salts
- Passivizes stainless steel or aluminum
- Strong corrosive action to mild steel

5) Hydrofluoric acid (HF)

- Large solubility(silica, glass)
- Difficult to handle
- Extremely corrosive
- Strong toxicity



Cleaning Chemicals (Organic Acid)

Organic acids

Used extensively for cleaning of recent new Boiler

Chemicals	Structure formula
Citric Acid	$ \begin{array}{c} \text{CH}_2\text{—COOH} \\ \\ \text{OH—C—COOH} \\ \\ \text{CH}_2\text{—COOH} \end{array} $
Hydroxly Acetic Acid	$ \begin{array}{c} \text{OH—CH}_2\text{—C—OH} \\ \\ \text{O} \end{array} $
Formic Acid	$ \begin{array}{c} \text{H—C—OH} \\ \\ \text{O} \end{array} $



Cleaning Chemicals (Organic Acid)



1) Citric acid

- Relatively large solubilities(in other organic acids)
- Not readily precipitating iron hydroxides
- The iron salt of citric acid tends to precipitate(concentrations of about 4,900 ppm)
- Usually heated to 80-100°C
- Easy to handle, The low solubility of calcium salt



Cleaning Chemicals (Organic Acid)



2) Glycolic acid (hydroxyacetic acid) and formic acid

- The most widely used
- Used in cleaning at relatively high temperatures (80-100°C)
- Readily decomposed and become harmless (if they have to remain in the boiler)
- Used with other organic acids



Cleaning Chemicals (EDTA)

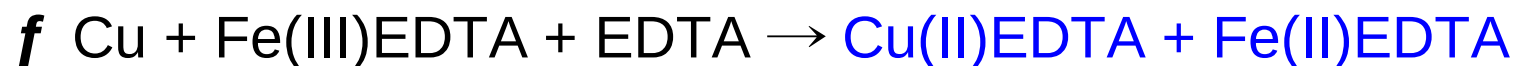
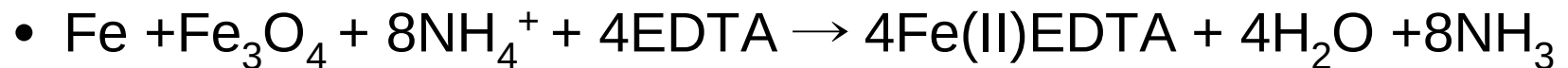


■ EDTA(ethylenediaminetetraacetic acid)

- Can be used in the wide pH range
- Its cost is high
- Small amounts of wastewater are produced
- ACR(Alkaline copper removal) method

: the single solvent cleaning

<Reaction formula>





Cleaning Chemicals (Alkali agents)



■ Alkali agents

1) Ammonia

To cleaning the scale contained large quantities of copper

2) Sodium hydroxide

To dissolve silica, vegetable oils and fats.

3) Sodium carbonate

It is used as alkaline boiling agent to remove oil material



Cleaning Chemicals (Cleaning aids)



■ Cleaning aids

- Make up for the disadvantages of the main chemical
- Strengthen and improve its advantages of the main chemical
- The selection of these aids is very important



Cleaning Chemicals (Cleaning aids)



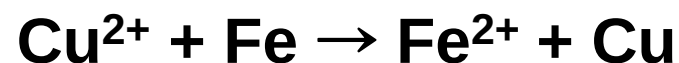
1) Acid inhibitor

To reduces the corrosion of the material

2) Reducing agents

To prevent the corrosion of the base metal
by oxidative ions

※ Oxidative ions : Fe^{3+} and Cu^{2+}





Cleaning Chemicals (Cleaning aids)



3) Copper dissolution accelerator

To improve the effect of copper removal

4) Silica dissolution accelerator

To accelerate removing silica during acid cleaning

5) Degreasing and wetting agents

To accelerate emulsification in acid and alkaline solutions



Cleaning Chemicals

(Neutralization and passivation agents)



■ Neutralization and passivation agents

The stabilization of the metal surface after the acid cleaning : form magnetite

1) Pretreating agents

- ① They can dissolve iron hydroxide, etc.
- ② They are practically not corrosive at low concentrations.
- ③ Metal ion sequestering ability is strong enough



Cleaning Chemicals

(Neutralization and passivation agents)



2) Neutralization agents

To neutralize to pH 9~10.

3) Passivation agents

To form a passive thin film on the metal surface

① Sodium phosphate

② Hydrazine

③ Nitrites



2. Commission Cleaning



Commission Cleaning



■ Introduction

- To remove **oil, grease, mill scale, rust, and any other debris**
- The condensate and feed-water systems :
mechanically cleaning → an **alkaline cleaning**
- The economizer and boiler :
an **alkaline boil-out** → an **acid cleaning**
- The superheater, steam piping and reheater :
steam blowing



Commission Cleaning



■ Preboiler Cycle cleaning (The basic operations)

- 1) Manual cleaning
- 2) Cross flushing
- 3) Preheating of circulation water (about 90°C)
- 4) Circulation of alkaline solution at about 90°C
(0.5 percent trisodium phosphate, Na_3PO_4)
- 5) Rinse to remove alkaline material.
- 6) Wet lay-up(demineralized water containing 100 ppm hydrazine)

※ Cleaning end point : When the oil concentration is not changed



Commission Cleaning



■ Chemical Cleaning of Boilers

● Alkaline boil-out : lubricants, oil, rust, sand, metal fragments and assorted debris

※ Experience has shown that an effective boil-out for a drum-type boiler can be attained by any of the following combinations :

- | | |
|--------------------------------------|-----------|
| 1) Sodium hydroxide | 2,000 ppm |
| Sodium carbonate or sodium phosphate | 2,000 ppm |
| 2) Sodium phosphate | 5,000 ppm |
| Caustic soda | 500 ppm |

● Acid cleaning : scales and deposits, mill scale and corrosion products

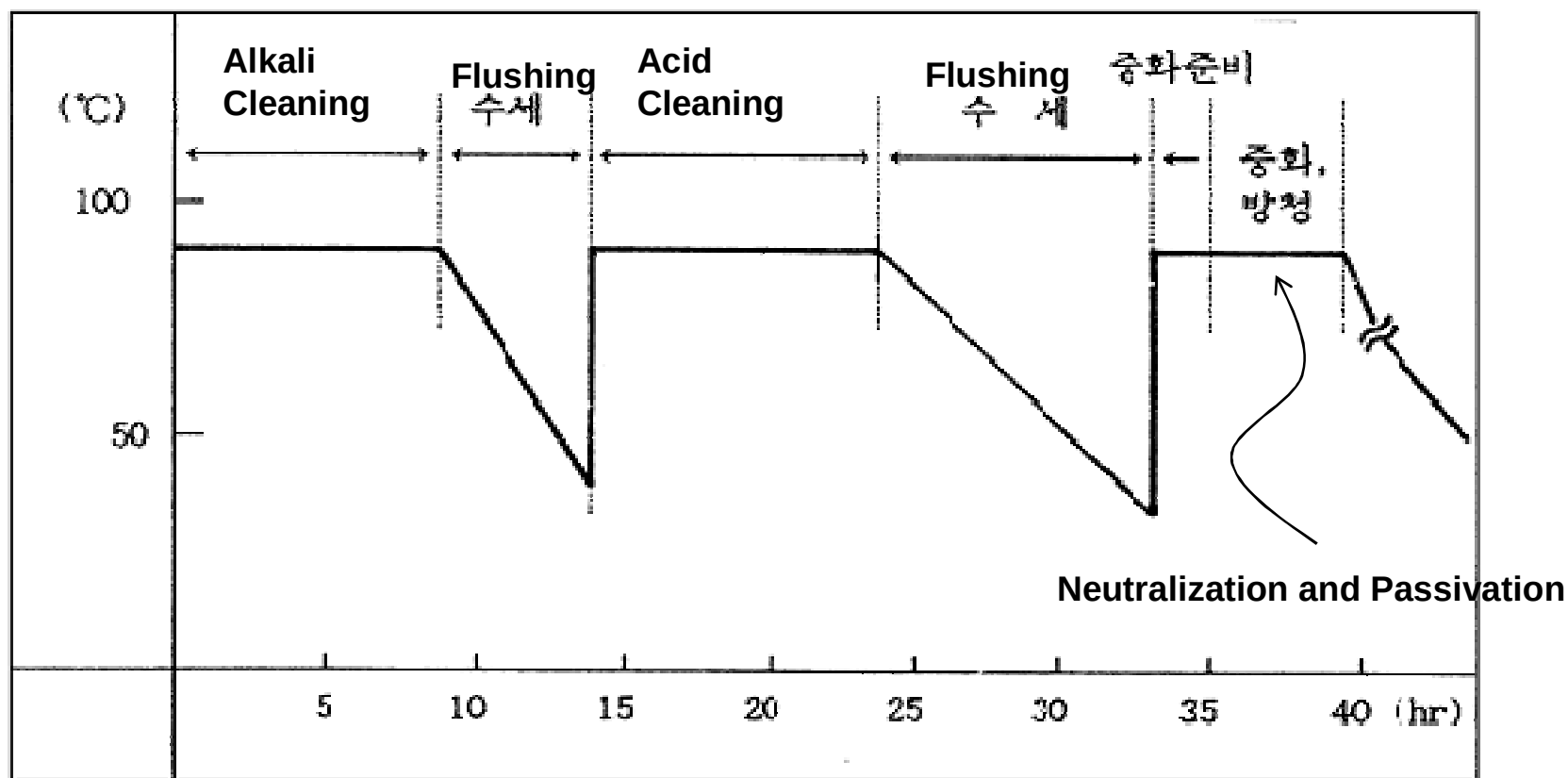


Chemicals for Boilers

Process	Chemicals	Conc. (%)	Criterion of Treatment
Acid Cleaning	Citric Acid	3.0	6~8 hrs Circulation at $80\pm 5^{\circ}\text{C}$, until Conc. of T-Fe are settled by 3 times
	Inhibitor	0.3	
	Degradable Agent	3.0	
	Activators	1.0	
	Surfactant	1.0	
	Ammonium Bifluoride	0.3	
Preliminary to Neutralization	Citric Acid	0.1	Circulation at $80\pm 5^{\circ}\text{C}$
Neutralization	Ammonia Water	0.1	pH 9~10
Passivation	Hydrazine	0.1	2~3 hrs Circulation at $80\pm 5^{\circ}\text{C}$



Commission Cleaning



Commission Cleaning Process

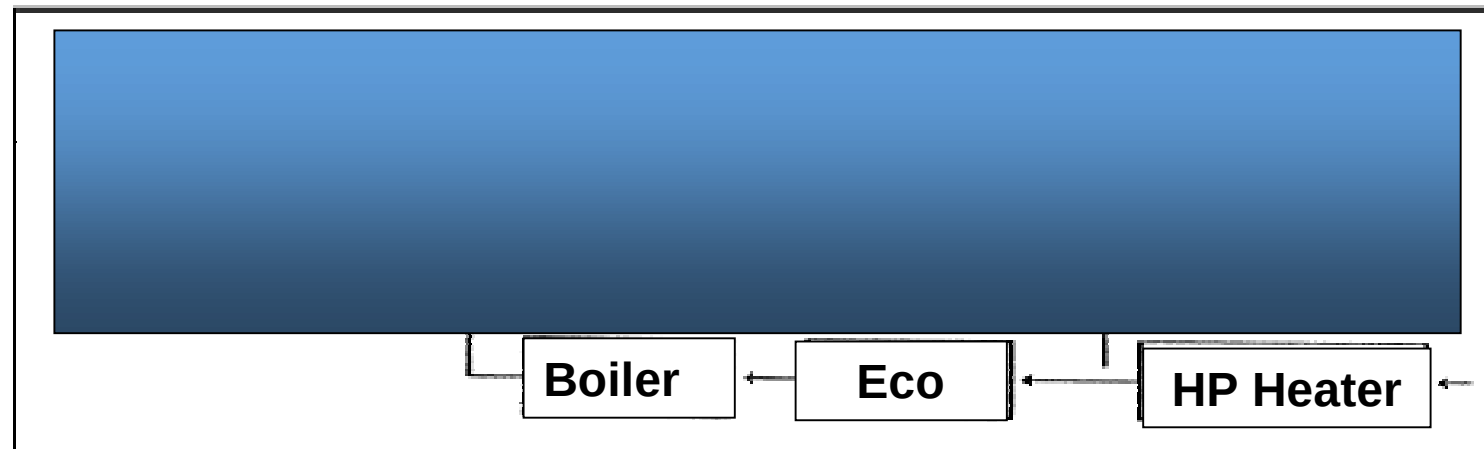


Commission Cleaning



■ Alkaline boil-out procedure

- 1) The boil out procedure is similar to the alkaline cleaning procedure of preboiler system.
- 2) After washing ending, test piece and tube install



Test Piece and Tube Attachment location



Commission Cleaning



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Commission Cleaning



■ Acid Cleaning procedure

- 1) Blend concentrated inhibited acid and hot water
- 2) Prevent the spillage of the solvent to superheater
- 3) Soak or circulate(4 to 6 hours)
- 4) Sample and check periodically the degree of reaction in the boiler.
- 5) Drained by pressurizing with nitrogen
- 6) Rinse (pH is between 5 and 6) with water containing N_2H_4 200 ppm solution
- 7) Neutralize and passivation of the metal with water containing N_2H_4 500 ppm solution



Commission Cleaning

■ Acid Cleaning procedure(1)

Process	Use chemicals		Cleaning condition	Analysis item	Criterion
	chemicals	Concentration			
BLR flushing and Hydraulic test	N_2H_4	50 ppm	Hydraulic : BLR Header Pressure	turbidity, N_2H_4	turbidity : satisfactory
Super heater and HP heater water filling	N_2H_4	100 ppm	Super heater and HP heater full water	Cl ⁻ , N_2H_4 , pH	Cl ⁻ : 0.1 ppm under N_2H_4 : 100 ppm over
alkaline cleaning	Na_2CO_3 Na_3PO_4 Surfactant	0.1% 0.2% 0.05%	90±5℃ Until the oil oncentration is fixed, circulation	pH, temp	oil, turbidity fixation
Water flushing	N_2H_4	100 ppm	Until below pH 9, flushing	pH ,temp N_2H_4	pH 9 under

<Establishment boiler chemical cleaning process>



Commission Cleaning



■ Acid Cleaning procedure(2)

Acid cleaning	HAA Formic Acid Inhibitor Ammonium Bifluoride Thiourea Sorbic Acid	2.0% 1.0% 0.3% 0.15% 0.1% 0.15%	90±5℃ Fe ²⁺ is fixed, circulation	pH, Fe ²⁺ , Fe ³⁺ , temp	Fe ²⁺ fixation
Water flushing	N ₂ H ₄	200 ppm	Until over pH 5, flushing	pH, T-Fe, N ₂ H ₄ , temp	pH 5 over
Neutralization preparation	Citric Acid	0.1%	90±5℃ 1 Cycle circulation		
Neutralization	Ammonia Water	750 ppm	90±5℃ 1 Cycle circulation	pH, temp	pH 9 ~ 10
Passivation	N ₂ H ₄	500 ppm	90±5℃ 2 ~ 3 Cycle circulation	N ₂ H ₄ , pH	N ₂ H ₄ 50 ppm

<Establishment boiler chemical cleaning process>



3. Acid Cleaning



Acid Cleaning



- Initial acid cleaning and future acid cleaning
- Mill and Operational Scale
 - Mill Scale : during fabrication or erection
 - Operational Scale : corrosion products, and iron and copper oxides



Chemical cleaning

▼ Primary reasons for chemical cleaning

§ To prevent tube failures

- Internal deposits produce excessive temperatures in the metal and then creep appear

§ To improve unit availability

- A small quantity of deposit can cause a caustic corrosion and hydrogen damage, which can produce tube failures at temperature well below the creep limit

☞ **Deposits** originating both from fabrication and during operation must be considered **potential problems**



Mill and operational scale



▼ Mill scale

- § Whenever carbon or low-alloy steels are subjected to high temperatures in the presence of air, oxidation occurs
- § The oxide produced is known as mill scale
- § Mill scale on boiler tubing is normally very thin and initially uniform
- § its brittleness upon cooling can produce flaking
- § Non-uniform surface is undesirable from the standpoint of corrosion susceptibility
- § Can be readily eroded from the steam-generating surfaces and subsequently be redeposited in critical areas
- Ä Pre-operational acid cleaning removes the mill scale and serves to remove atmospheric rust



Mill and operational scale



▼ Operational scale

- § Related to the quality of feed - water supplied to the boiler
- § The principal deposits in utility boilers
 - Corrosion products
 - Oxides of iron and copper



Chemical cleaning Procedures



- ▼ The procedure should include
 - § The system layout with proper identification of all equipment to be used
 - § A step-by-step description of the functions to be performed
 - § Precautions to be taken against possible inadvertent contamination of equipment not included in the cleaning system



Classify responsibilities



- V** The cleaning vendor
 - § Supply all of the chemicals and equipment
 - § Deliver the solvent to the boiler
 - § Operate the equipment and supervise
 - § Perform the necessary chemical analyses
 - § Determine when the cleaning has been completed



Classify responsibilities



V Plant operator

- § Operate all permanent plant equipment
- § Determine temperatures
- § Supplies the necessary water and steam
- § Sets up the solvent-delivery and waste-disposal systems
- § Assure that the solvent is not inadvertently introduced to any other part of the steam plant



Classify responsibilities



▼ The boiler manufacturer

- § Provide a boiler that can be cleaned safely and effectively
- § Establish a standard cleaning procedure
- § Inform of any unusual use of boiler components
- § Be ready to review any cleaning procedures that involve unusual steps or solvents



Selection of Cleaning Solvents

- 1. Materials of construction**
- 2. Deposit compositions**
- 3. Geometries**
- 4. Methods of disposal**



Selection of Cleaning Solvents

- ▼ Hydrochloric acid

- § Largely used

- § Advantage : low cost, availability, versatility

- § Remove most of the various deposit

- ▼ Organic acids, organic alkaline solvents

- § Particularly useful in situations where specific circumstances prohibit the use of hydrochloric acid

- § Ammonium citrate, glycolic, ammonium EDTA, sodium EDTA



Selection of Cleaning Solvents



▼ Criteria

§ Materials of construction

- Cleaning solvent must be compatible with the tube material
- HCl cannot be compatible with SS

§ Deposit composition

- Iron oxide, copper, zinc, nickel, aluminium, silica
- Large amounts of silica – Ammonium bifluoride
- Large amounts of copper – Ammonium bromate



Selection of Cleaning Solvents



▼ Criteria

§ Geometries

- Organic solvents are effective under dynamic conditions
- Complex circuits require special attention to assure removal of all air pockets and positive flow in all circuits

§ Methods of disposal

- Incinerating, to wastewater treatment system
- Adapt environmental regulations



Effective of velocity on scale removal of various solvent



Solvents and cleaning conditions	Velocity					
	Static	0.03 fps	0.1 fps	1 fps	2 fps	3 fps
Hydrochloric acid(5%) 6 hrs, 160-170°F	C	C	C	C	C	C
Phosphoric acid(3%) 6 hrs, 212°F	C	...	C	C	C	...
Ammonium citrate(5%) 6 hrs, 200-220°F	U	U	U	C	C	C
Formic Hydroxyacetic acid(3%), 6 hrs, 160-170°F	...	U	U	C	C	C
Ammonium EDTA(3%) 6 hrs, 275-300°F	...	U	U	C	C	C
Note ; U = Scale not removed(estimated 20-100% of scale remaining) C = Scale completely removed(estimated 95-100% of scale removed) All samples 5-10 mils scale						



Determining the Need for Chemical Cleaning



▼ Tube samples

- § should be taken at yearly intervals from the high-heat-flux areas of the boiler(for example, several feet above the windbox) or other areas that have been prone to deposition
- § Should be given to a chemical cleaning vendor to allow determination of the best solvent and cleaning procedure
- § After the cleaning, tube samples need to be verified



Relationship of analyzed deposit quantity to unit cleanliness



Boiler type	Internal deposit quantity limits*		
	Clean surfaces, mg/cm ²	Moderately dirty surface, mg/cm ²	Very dirty surface, mg/cm ²
Supercritical units	less than 15	15 ~ 25	more than 25
Subcritical units (1800 psig and higher)	less than 15	15 ~ 40	more than 40

* All values are as measured on the furnace side of tube samples and include soft and hard deposits
 Note : For all practical purposes, 1 mg/cm² = ~ 1 g/ft

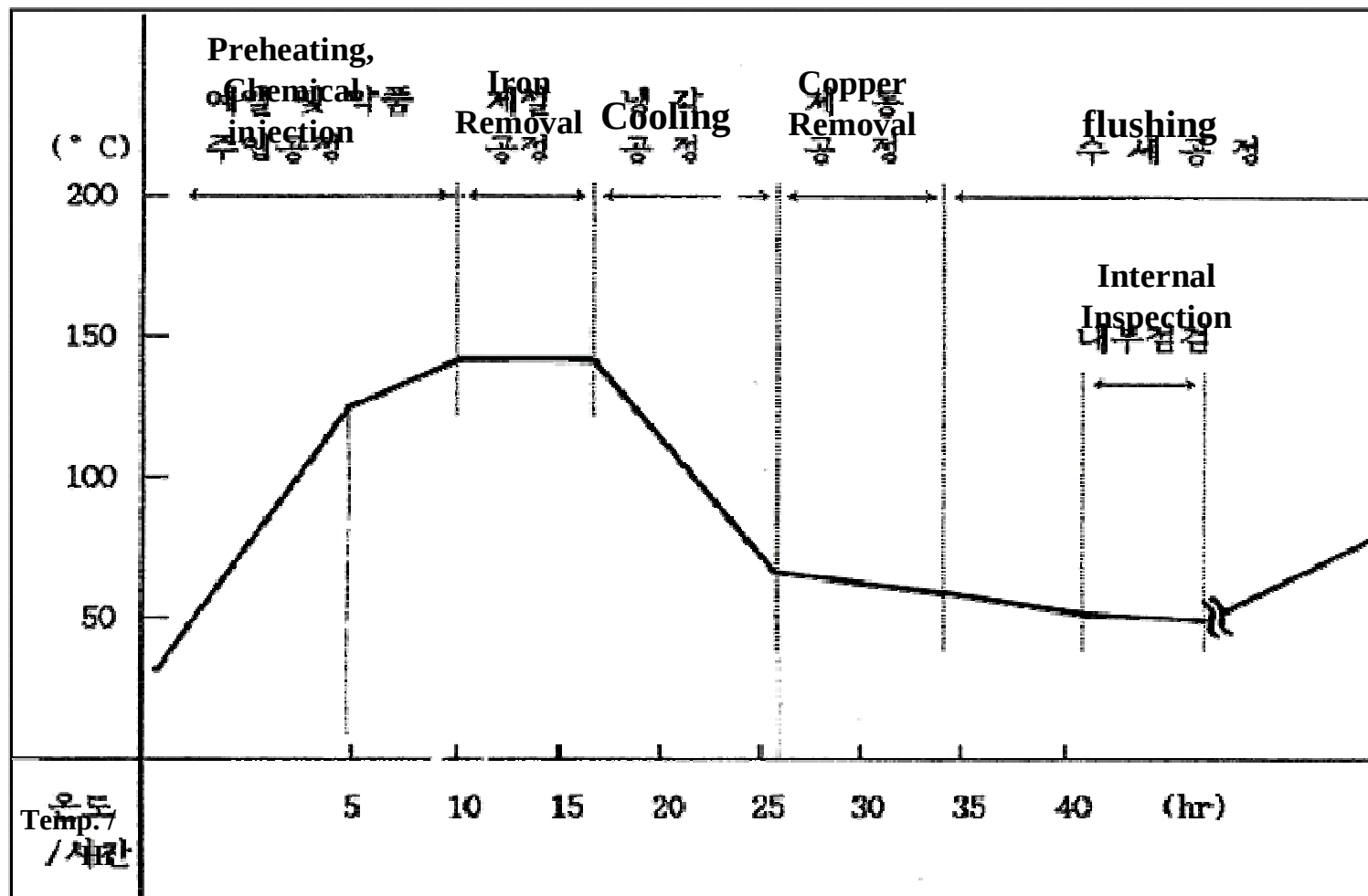


Chemical Cleaning Criterion for Operational Boiler

Pressure (kg/cm ²)	Drum Type		Once-through Type	
	~ 140	140 ~ 180	180	Super-Critical
Quantity of Deposit (mg/cm ²)	50 ~ 70	40 ~ 50	30 ~ 40	20 ~ 30



High Temp. EDTA Cleaning Process (ACR : Alkaline Copper Removal)



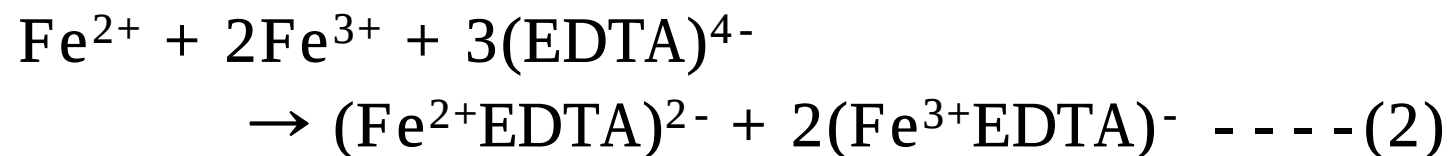
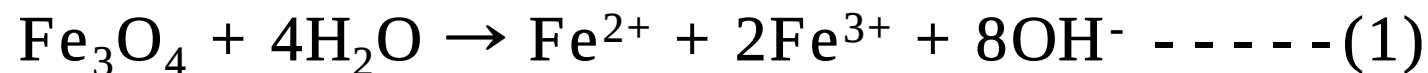
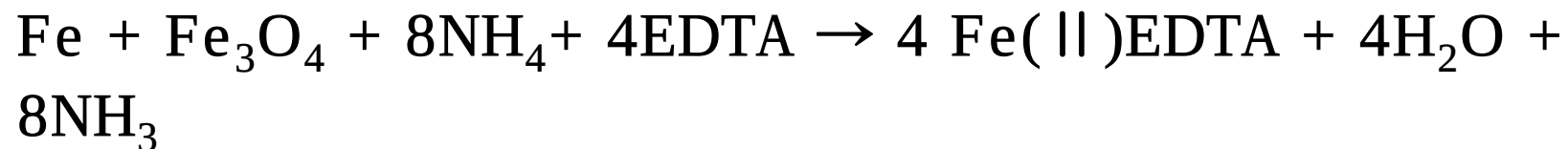


High Temp. EDTA Cleaning Process (ACR : Alkaline Copper Removal)



q Reaction Mechanism of EDTA with Scale in the Iron Scale Removal

● Iron Scale (Iron Oxide)



○ Condition of Chelate : Reducing Condition is preferable

∵ Fe^{2+} makes more stable complex with EDTA than Fe^{3+}

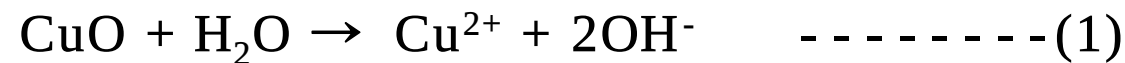


High Temp. EDTA Cleaning Process (ACR : Alkaline Copper Removal)

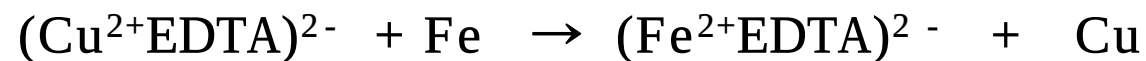


■ Change of Copper in the Iron Scale Removal Process

- Cu is not removed in the Iron scale removal process : Due to the reducing condition
- Reaction of Copper Oxide

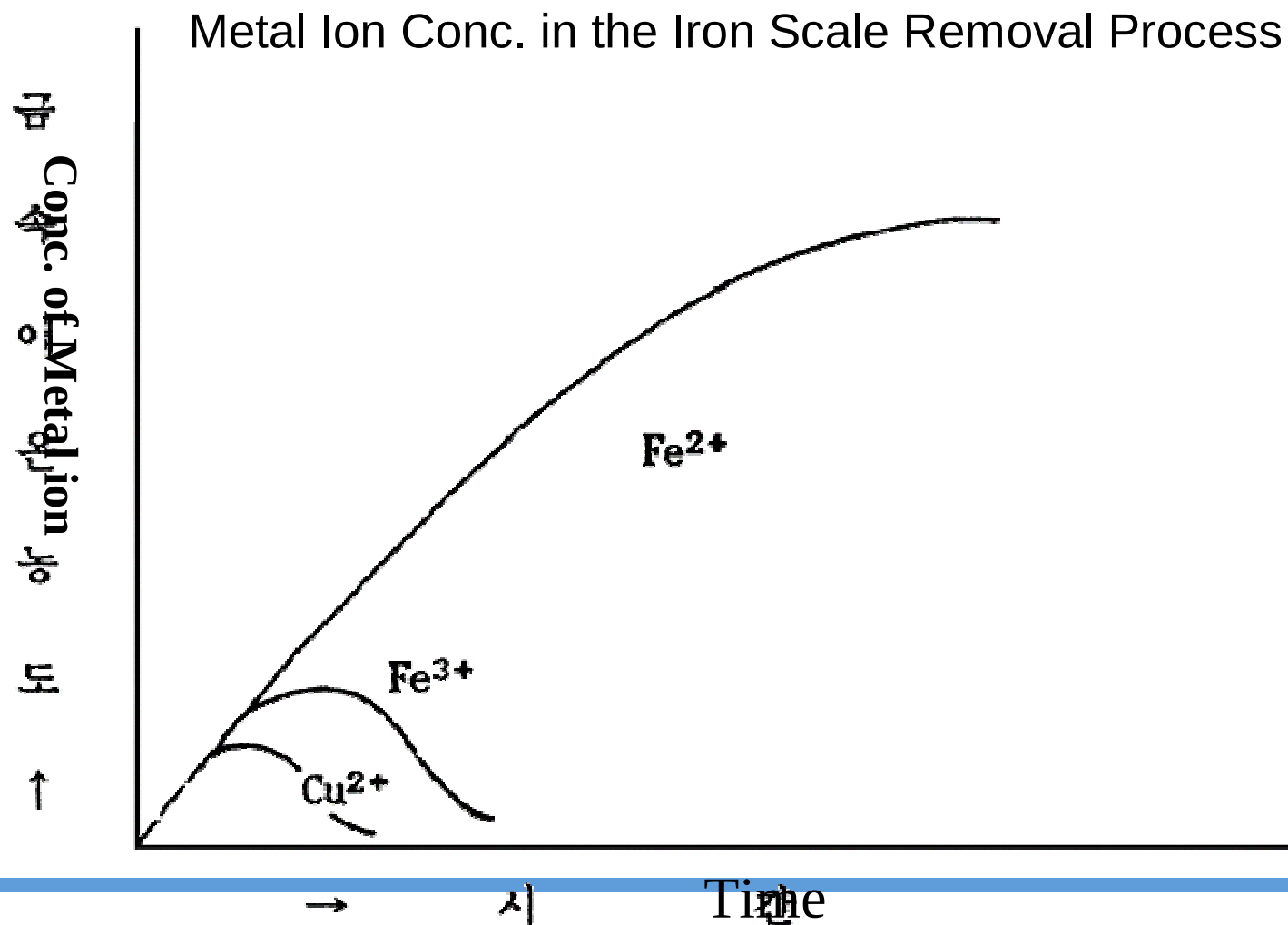


- But, $(\text{Cu}^{2+}\text{EDTA})^{2-}$ makes reaction with base metal(when, conc. of $\text{Fe}^{2+} > 90\%$), and makes deposition on the tube surface





High Temp. EDTA Cleaning Process (ACR : Alkaline Copper Removal)





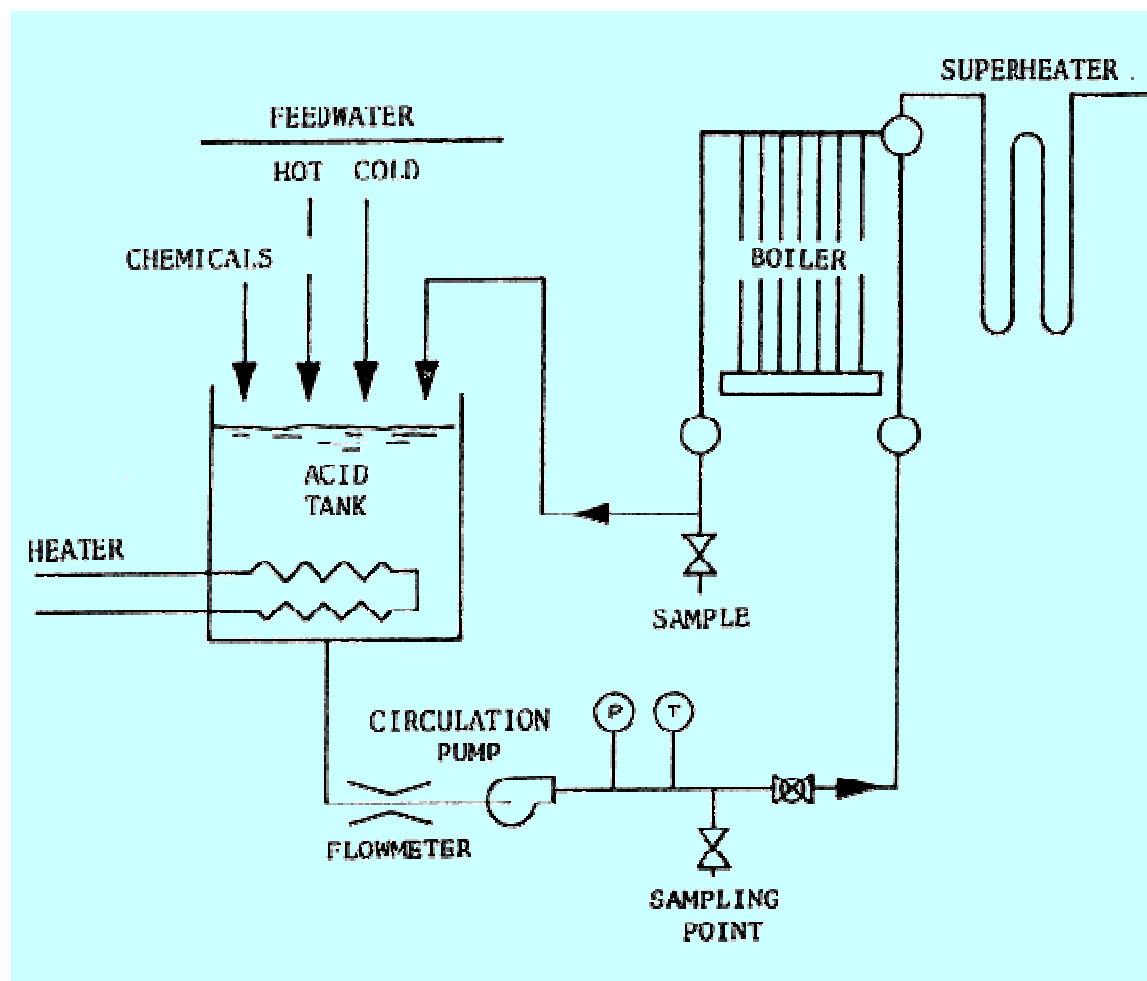
Acid cleaning



- ✓ Blend concentrated inhibited acid and hot water
- ✓ Prevent the spillage of the solvent to superheater
- ✓ Soak or circulate (4 to 6 hours)
- ✓ Sample and check periodically the degree of reaction in the boiler
- ✓ Drained by pressurizing with nitrogen
- ✓ Rinse (pH is between 5 and 6)
- ✓ Fill with water containing soda ash, 1.0 percent solution
- ✓ Neutralize and passivate of the metal with water containing N_2H_4 500 ppm solution



Acid cleaning schematic





Acid cleaning

- V** Procedures to prevent superheater contamination
 1. Examine to identify all possible areas
 2. Control and monitoring of drum level
 3. Fill or “back-flush” the superheater with demineralized or of condensate quality
 4. Consider the possibility of contamination before starting the pre-boiler cleaning operation.
 5. Suspicion of contamination warrants a careful assessment of water quality



Post-acid-cleaning Activities



- ▼ Flush and inspect the drums, the internals to the gage glass, and headers
- ▼ Remove the acid cleaning connections and temporary piping
- ▼ Flush and blow out the chemical feed and continuous blow down piping



Chemical Cleaning



chemicals injection equipment



Heat exchanger



Chemical Cleaning



S/H, HP HTR filling equipment



Temporary Circulation Pump



Chemical Cleaning



Test Piece (The circulating pump rear)



Chemical Cleaning



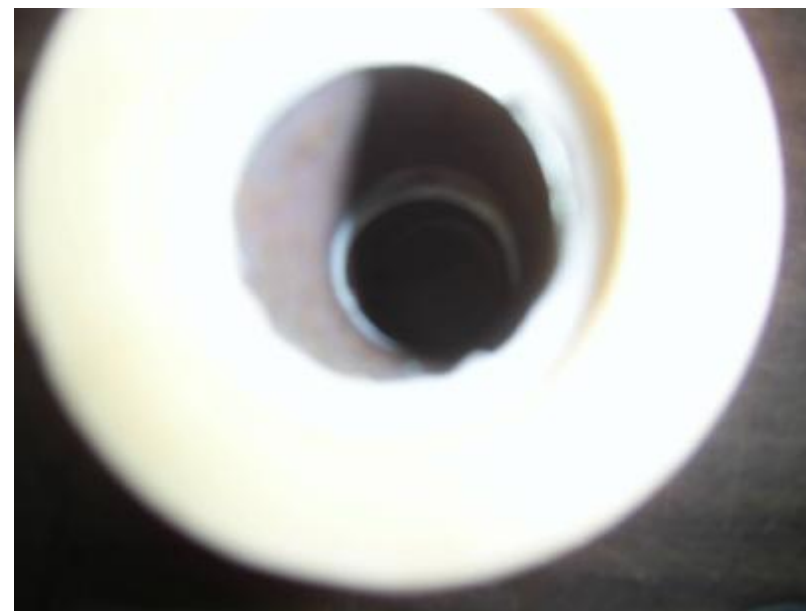
Test Tube(The circulating pump front)



Chemical Cleaning



Test Piece



Test Tube



Chemical Cleaning



Before Cleaning



After Cleaning



Chemical Cleaning



Before Passivation



After Passivation



4. Steam Blowing



Steam Line Blowing

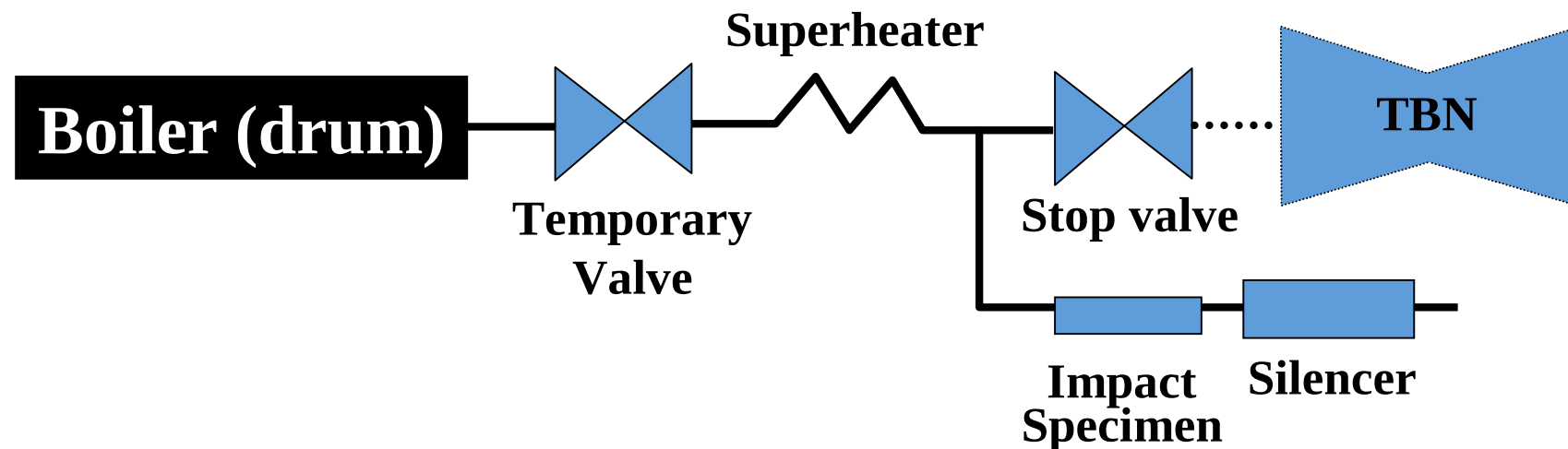


■ The purpose of the steam blowing

- To remove any foreign material (after erection)
- To prevent the considerable damage of the turbine

■ Lay-out of the steam blowing

- 1st step

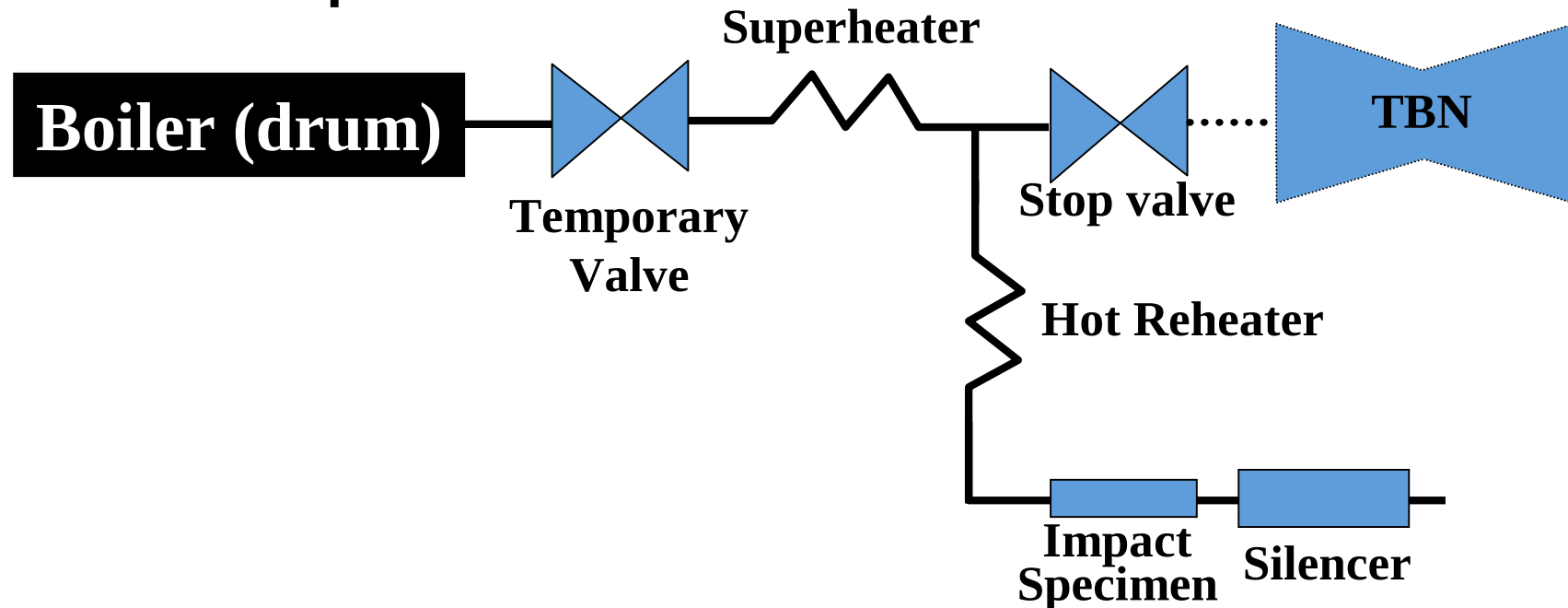




Steam Line Blowing

■ Lay-out of the steam blowing

● 2nd step

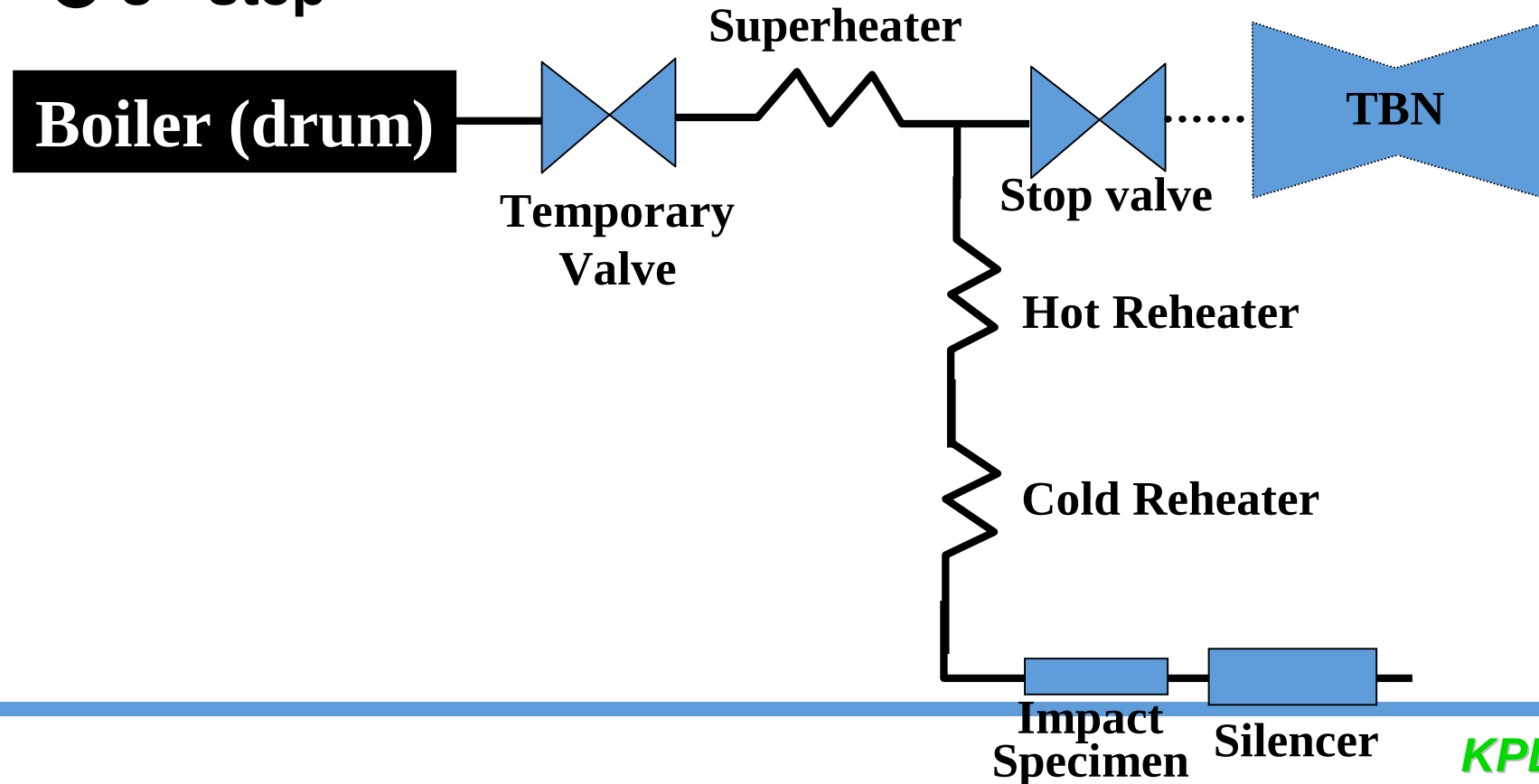




Steam Line Blowing

■ Lay-out of the steam blowing

● 3rd step



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Steam Line Blowing



■ Responsibility

- The responsibility for determining the effectiveness of the steam-line blowing operation rests with the turbine manufacturer's representative
- Unit operation : Operate in accordance with recommended procedures, with all control systems and protective interlocks functioning.
- The design, fabrication and installation of any temporary piping system : Requires careful attention by qualified engineers



Steam Line Blowing



■ Procedure

- 1) Three phases : main steam, hot reheater and cold reheater
- 2) The blowing flow : equal to normal operation flow
- 3) The blowing start-pressure : 600~800 psig (40~54 kg/cm²)
- 4) Blow in sections, each section being immediately :
To prevent foreign material from being transported from one section and deposited in the next
- 5) Start unit in the normal manner, following the cold start-up procedures
- 6) Pressure up
- 7) Fully open the temporary valve or main-steam valve
- 8) When the drum pressure drops to about 200 psig, close the blowoff valve
- 9) Repeat the cycle of blowing and stopping
- 10) Inspect the impact specimen

THANK YOU

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