

# Welcome

# 1<sup>ST</sup> NACE - JUBAIL INDUSTRIAL FORUM

## Water Treatment & Cathodic Protection

### **“Impact of Deposit on Operation of Package Boiler ”**

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# **INTRODUCTION**

- **Currently SABIC has about 100 package boilers : Few LP; about 90% MP; 8 % HP**
- **UB rather complex and expensive units fabricated in 7 countries with 13 companies**
- **Problem dramatically aggravated by fact that there is no idle boiler.**
- **Generally, investigation into UB failures is a complicated multidisciplinary process with involvement of water treatment, operation, metallurgy, high pressure welding, mechanical integrity, NDE, refractory, fuel quality, cleaning technologies, etc.**
- **Most of plants commissioned in early 80s have a service life ranging between 1 to 29 years and above.**
- **Before 1997 there are no records in MCS database of UB failures.**

# DEPOSIT

Generally, boiler feed water must be sufficiently free of deposit  
Actually, deposits result from feed water hardness contamination, and corrosion products moved from condensate and feed water system

## 4 sources:

water born minerals; used different water treatment chemicals; loose corrosion products moved from preboiler and boiler systems; different contaminants (oxides formed adherent tenacious layer at origination sites are not deposits)

## Common components boiler deposits :

phosphates, carbonates, silicates, hydroxides, sulfates, metal oxides, copper, alumina etc.

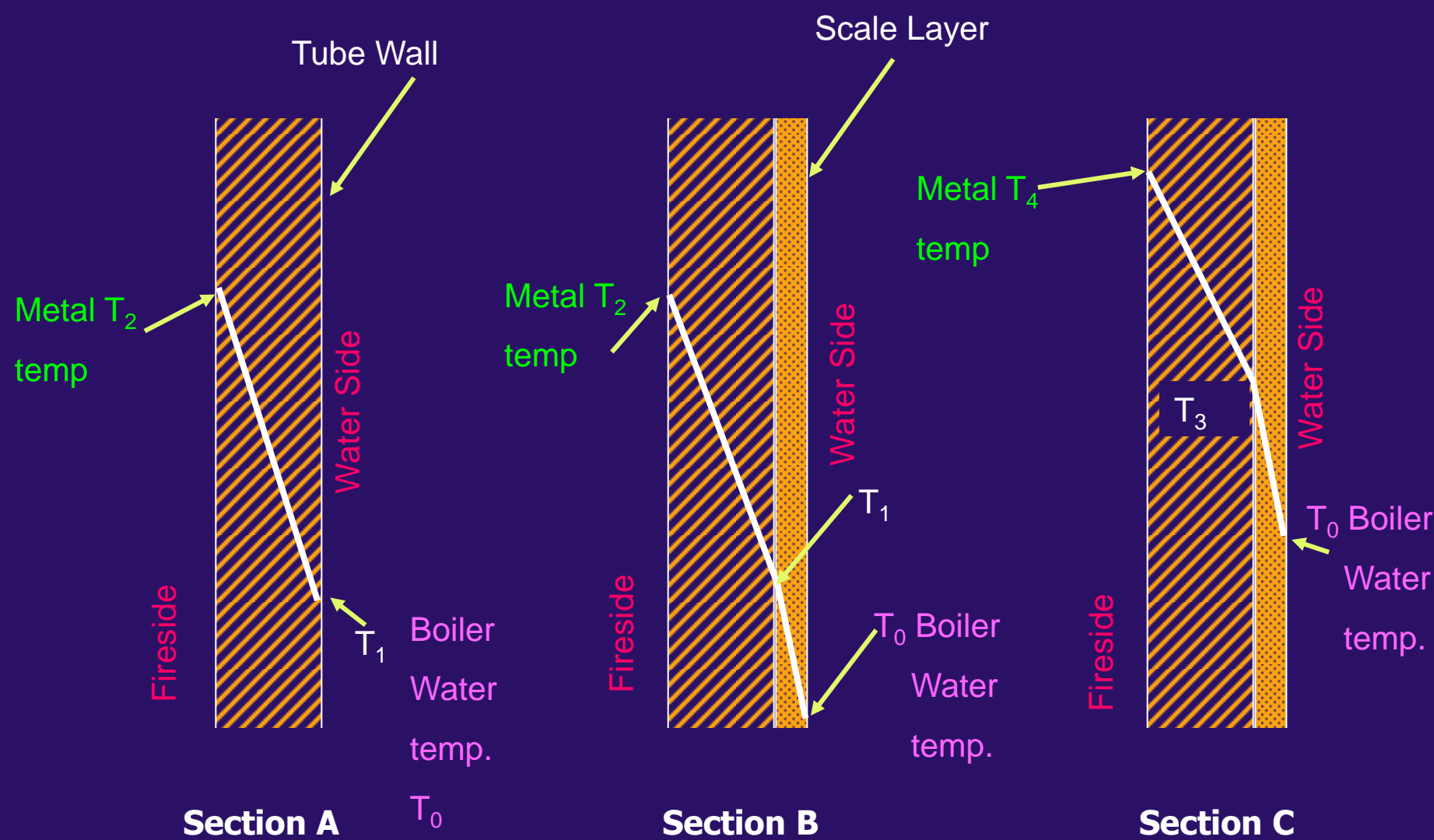
## Deposits act as insulators:

significantly reduce heat transfer; rapid rise in tube metal temperature and may lead to tube-failure by overheating

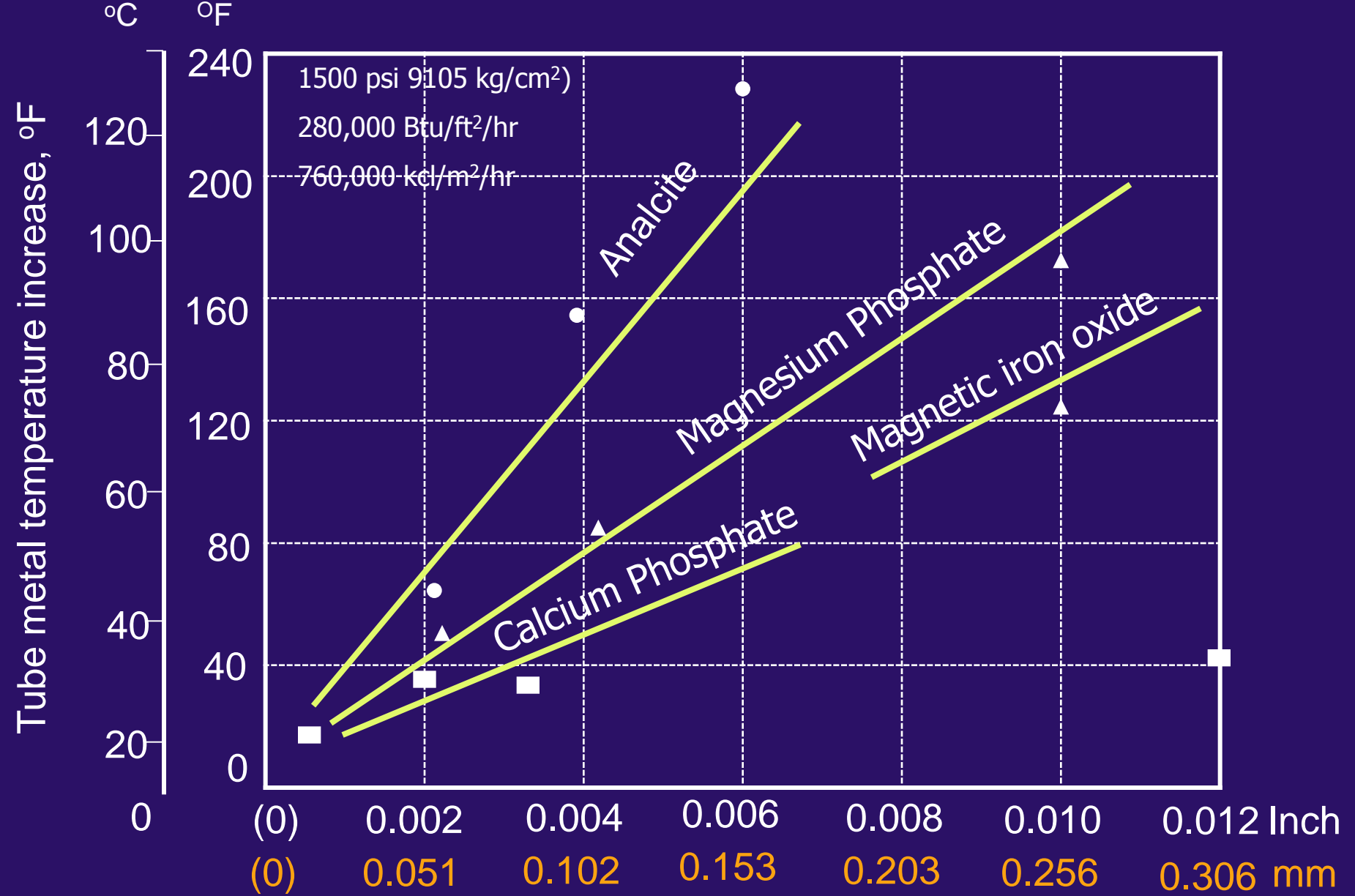
Large amount of thick deposits throughout boiler can reduce its efficiency

# Thermal conductivities ( $\text{W/m}^2 \cdot ^\circ\text{C}$ ) of metals, alloys and deposits

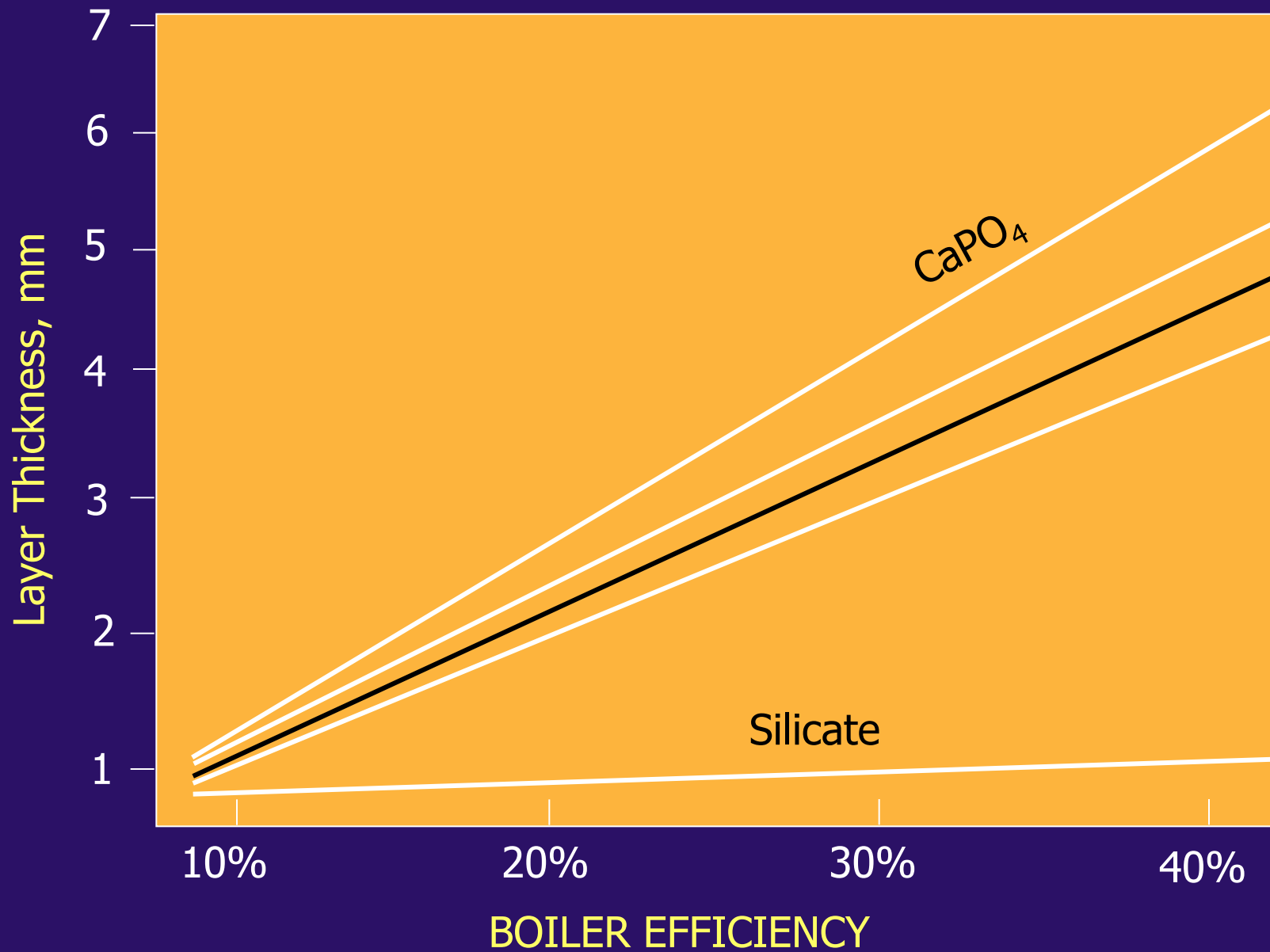
<b>304 SS</b>	<b>Fe-Cr-Ni</b>	<b>22 (500°C)</b>
<b>410 SS</b>	<b>Fe-Cr</b>	<b>28 (400°C)</b>
<b>Carbon steel</b>	<b>Fe</b>	<b>55*</b>
<b>Aluminum</b>	<b>Al</b>	<b>235*</b>
<b>Copper</b>	<b>Cu</b>	<b>420*</b>
<b>Calcium carbonate (Aragonite)</b>	<b>CaCO<sub>3</sub></b>	<b>0.14</b>
<b>Calcium phosphate</b>	<b>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub></b>	<b>0.55</b>
<b>Calcium sulfate (Anhydrite)</b>	<b>CaSO<sub>4</sub></b>	<b>0.21</b>
<b>Magnesium oxide</b>	<b>MgO</b>	<b>0.17</b>
<b>Magnesium phosphate</b>	<b>Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub></b>	<b>0.33</b>
<b>Serpentine</b>	<b>3MgO · 2SiO<sub>2</sub> · 2H<sub>2</sub>O</b>	<b>0.16</b>
<b>Aluminum oxide</b>	<b>Al<sub>2</sub>O<sub>3</sub></b>	<b>3.6</b>
<b>Quartz</b>	<b>SiO<sub>2</sub></b>	<b>0.24</b>
<b>Ferric oxide (Hematite)</b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>	<b>0.09</b>
<b>Magnetite</b>	<b>Fe<sub>3</sub>O<sub>4</sub></b>	<b>0.45</b>
<b>Acmite</b>	<b>Na<sub>2</sub>O · Fe<sub>2</sub>O<sub>3</sub> · 4SiO<sub>2</sub></b>	<b>0.01</b>
<b>Analcite</b>	<b>Na<sub>2</sub>O · Al<sub>2</sub>O<sub>3</sub> · 4SiO<sub>3</sub> 2H<sub>2</sub> O</b>	<b>0.10</b>
<b>Porous materials</b>		<b>0.01</b>



**Figure 1: Temperature profile across clean tube and tube having a water-side deposit.**



**Figure 2: Effects of differing deposit composition and thickness on temperature increase**



**Figure 3: Influence of deposit thickness on boiler efficiency**



# INFLUENCE OF COPPER

**Generally, copper is undesirable element in BFW**

**Boiler failures caused solely by copper are rare. Can contribute to failure mechanisms**

**Influence: -**

- **weakening integrity of magnetite layer;**
- **decreases protective properties of magnetite layer;**
- **promotes adsorption of chlorides (easier activation of metal, shifting pitting potential to more negative value);**
- **accelerates localization of already initiated corrosion;**
- **galvanic corrosion in specific conditions (oxide free surface, DNB)**
- **copper oxide can "cement" porous iron oxide layer into a hard scale (poor thermal conductivity, localized overheating, failure);**
- **significantly effects on chemical cleaning procedure and solvent formulation. At high amounts separate Cu-removal stage required (layering, plating)**
- **induces liquid metal embrittlement (LME) at temperatures above 871°C (welding of Cu-plated tubes), rare case**

**Main sources: corrosion/erosion of Cu-Ni and Cu containing alloys of heat exchangers, coolers, valves, pumps, evaporators & etc.**

**Limit concentration Cu in BFW - less than 20-30 ppb for LP; 10-15 ppb for MP and less than 5 ppb for HP boilers**

**Limit concentration of SiO<sub>2</sub> - less than 15-25 ppm for LP; 2.5-5.0 ppm for MP and less than 0.5 ppm for HP boilers**

**THUS, BUILD-UP DEPOSITS CONSIDERED SERIOUS PROBLEM FOR PLANT**

**Worldwide experiences shows Chemical Cleaning – most effective way to extent service life of heavily fouled by waterside deposit package boiler**

# CHEMICAL CLEANING DECISION

Primary reasons for cleaning boilers to:

prevent tube failures &  
unscheduled s/d; increase boiler  
operating efficiency

**Chemical cleaning must be planned  
carefully several months ahead**

First step - deposit density determination – most commonly used primary parameter ( $\text{mg}/\text{cm}^2$ ). Practically varied from 20 to 300  $\text{mg}/\text{sm}^2$  Deposit thickness (mm), constituent, morphology and adhesion also important.

**Generally accepted values for boilers within 600-1300 psi (41-90 bar):**

**Less than 25-30 mg/cm<sup>2</sup> - no problems**

**25-75 " - consider cleaning within 15 months maximum**

**Above 60-100 " - immediate cleaning required**

**Deposit thickness limit - 0.4 mm maximum**

**At pressures 1700-2500 psi DWD limit - less than 15 mg/cm<sup>2</sup>**

**Second step** - solvent selection based upon deposit constitute, thickness and adhesion with metal and compatibility with MOC

Other influencing factors include: safety and environment concerns, time limitation, chemicals availabilities, specific recommendations boiler manufacturer and etc.

**Most frequently and widely used solvents:**

- Inhibited hydrochloric acid (HCl);
- Citric acid (organic acid,  $C_6H_8O_7 \cdot H_2O$ );
- Ethylenediaminetetra-acetic acid (EDTA), chelant solution.

# **CASE STUDIES SABIC PACKAGE BOILERS AND CHEMICAL CLEANING IMPLEMENTATION**

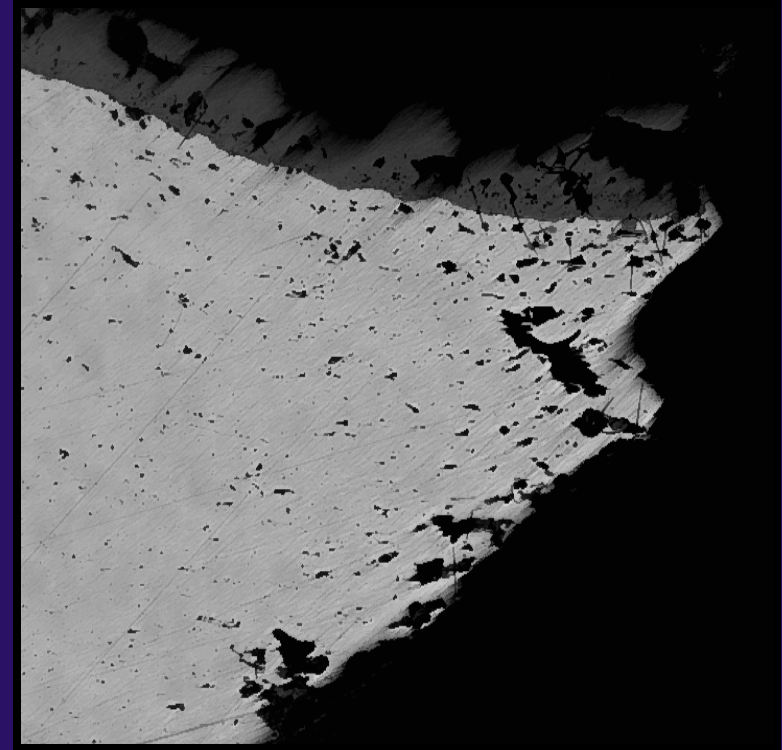
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## **CASE I: FAILURE ANALYSIS OF PACKAGE BOILER FIRST SCREEN TUBE & ACID CLEANING**

- **Mitsui Engineering And Shipbuilding Co. LTD Made, D-Type Package Boiler, Capacity 70T/h**
- **Carbon steel tubes (SA-192) were 76.2 mm (3.0 in.) In OD with wall thickness of 3.5 mm (0.14 in.)**
- **Operating temperature 310°C at pressure - 44 barg**
- **Previously – from commissioning up-to 1997 ammonia+hydrazine and polymer containing program**
- **Then coordinated orthophosphate BFW treatment program was used.**
- **Boiler tubes were not chemically cleaned previously.**
- **Time to failure – 15 years.**



**Figure 4**

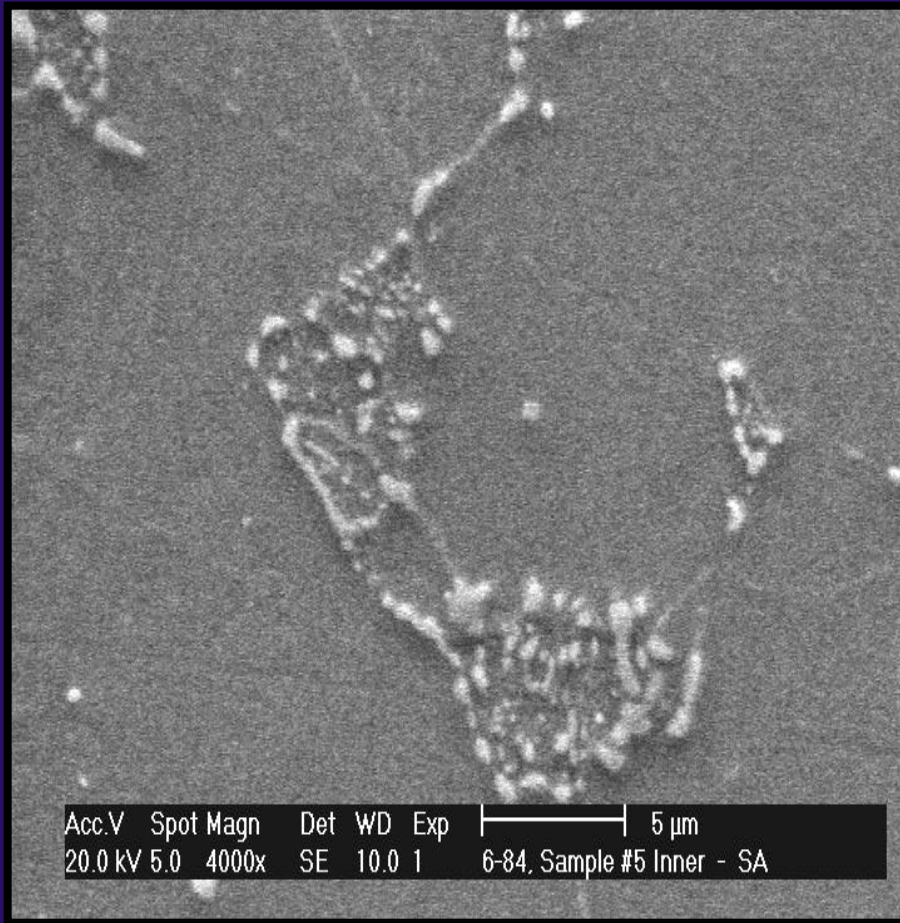


**Figure 5**

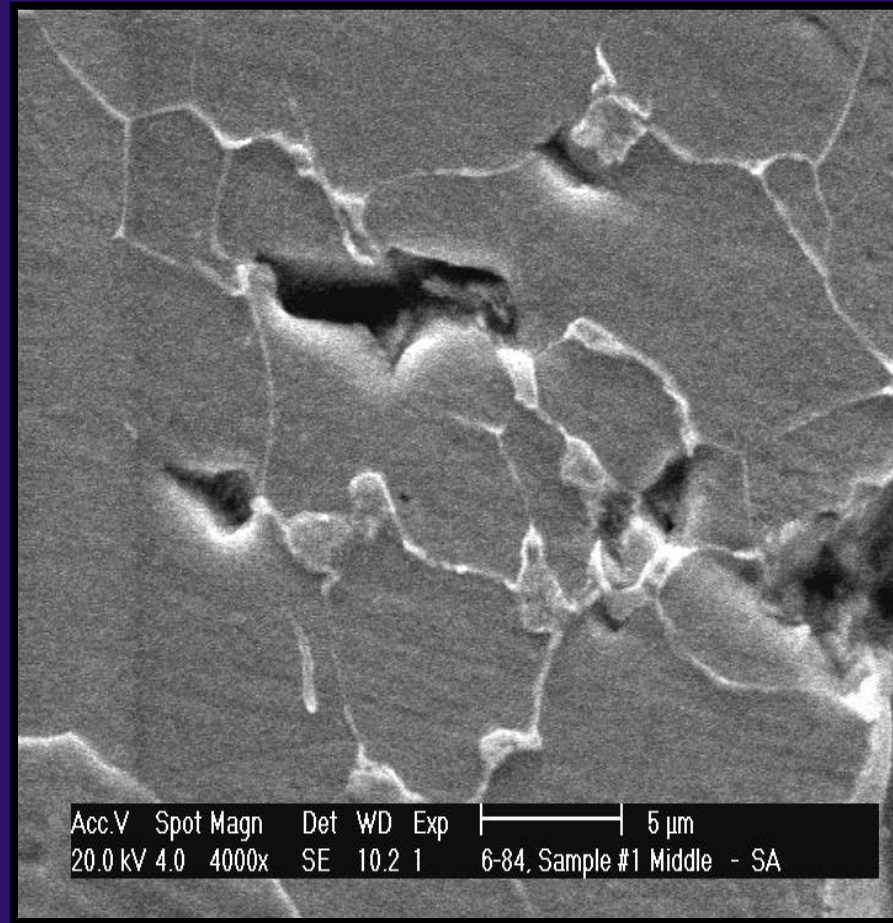
**FIGURE 4.** Close up photographs of the sample with clearly visible multiple abrupt bulges. Note the presence of spalled layer of the deposit inside the longitudinally split tube.

**FIGURE 5.** Presence of voids at and near the perforated edge (top of bulge, x400)





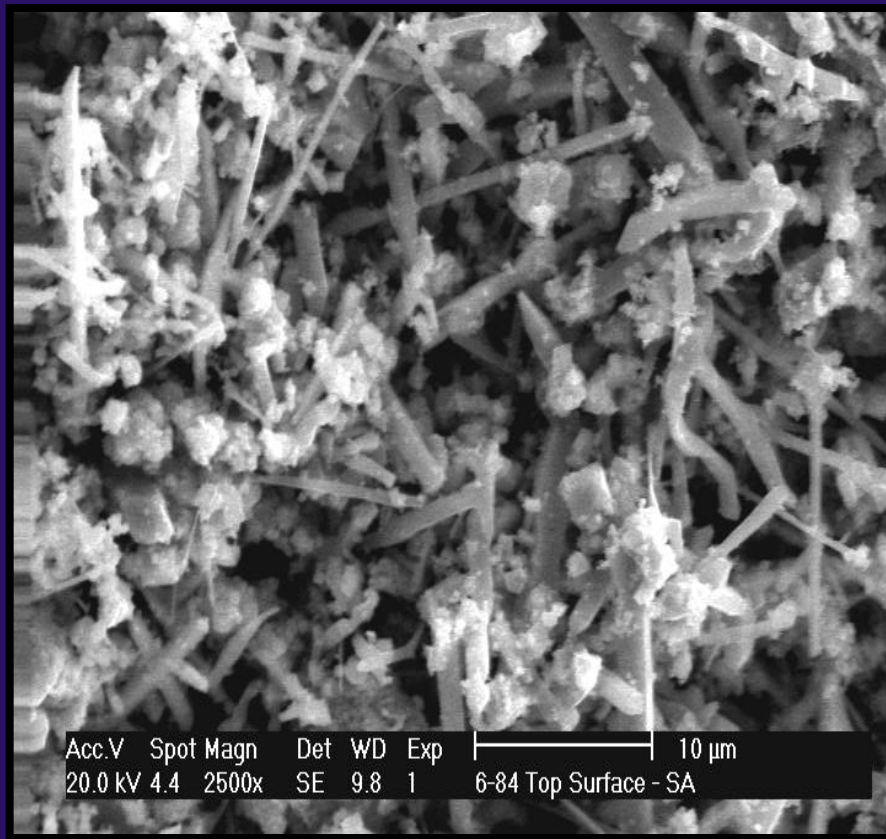
**Figure 6 a**



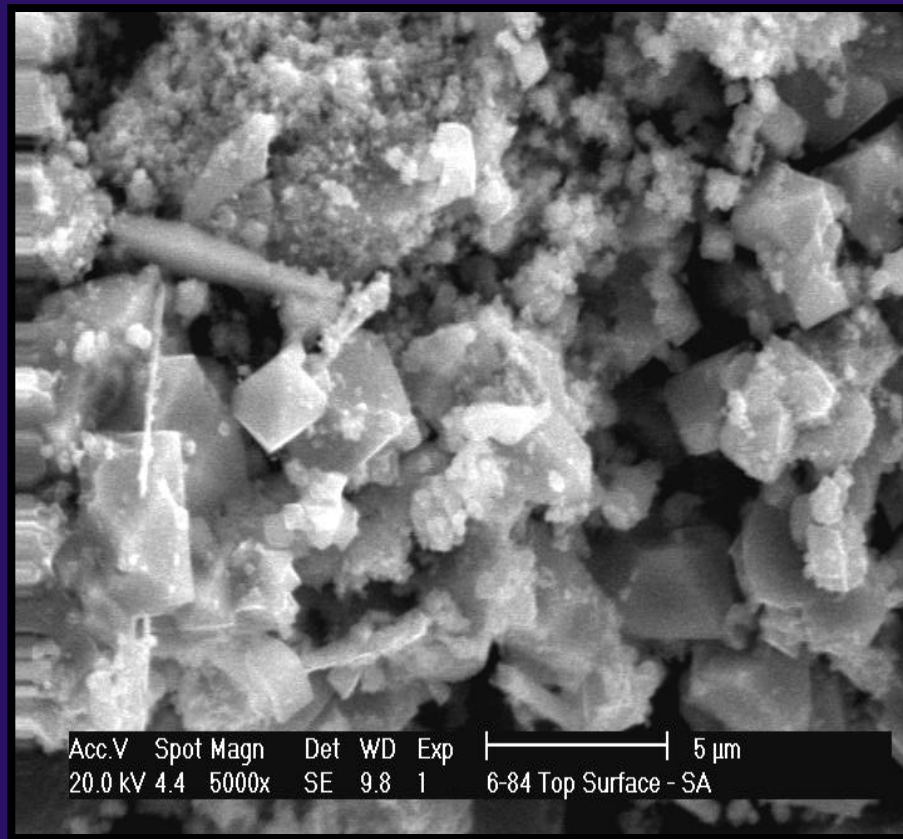
**Figure 6 b**

**FIGURE 6. SEM micrographs showing spheroidized morphology in pearlite colonies and the presence of voids (4000X)**





**Figure 7 a**



**Figure 7 b**

**FIGURE 7. SEM micrographs of the flakes showing the presence of fine particles, fibers and short rods (a, 2500X) along with the typical crystalline particles (b, 5000X).**

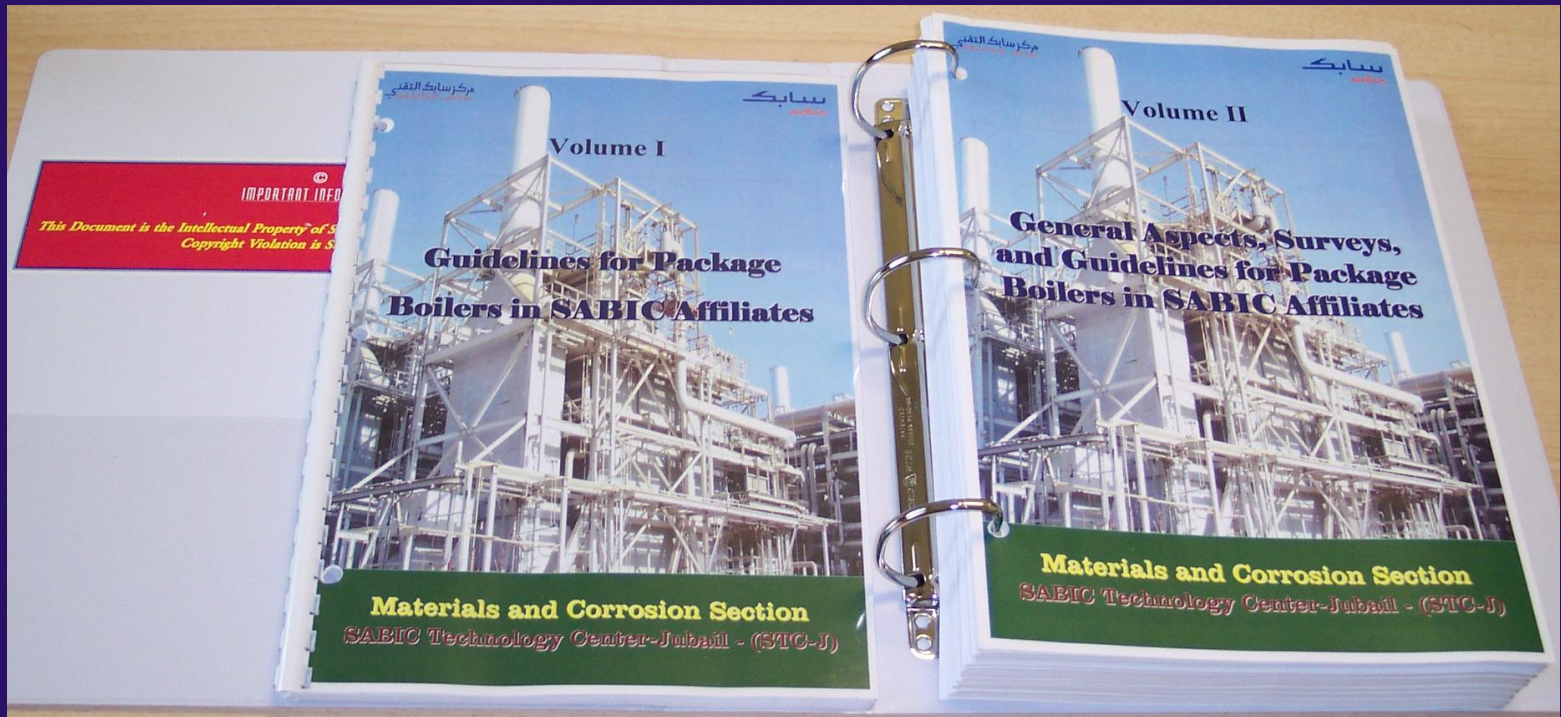
## CONCLUSIONS

- Screen tube failed due to creep rupture as result of local overheating caused by presence of excessive dense deposit layer inside tubes.
- Calculated density of internal deposit was more than 200 mg/cm<sup>2</sup> at average thickness of 1.2 to 1.5 mm.
- Determined cleanliness of tubes is considered as “very dirty”.

## RECOMMENDATION

- Acidic chemical cleaning was recommended and had been implemented.

**Since then, the boiler operates normally more than 9 years.**



Package Boilers ([http://ss-jhq-web-1.sabiccop.sabic.com/STC\\_J/Boilers/index.aspx](http://ss-jhq-web-1.sabiccop.sabic.com/STC_J/Boilers/index.aspx))

# Deliverables

- Mechanism and location of Corrosion damages in boiler Components
- Summary of Failures of Utility Boilers Components in SABIC Affiliates
- Guidelines on BWT
- Guidelines on condition and Remaining Life Assessment of UTB components
- Guidelines on UTB Chemical Cleaning.

Thank You