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Crevice Corrosion of Chlorine Recuperator Tubes

Faisal S. Al-Otaibi

Section Head, Inspection – Sipchem

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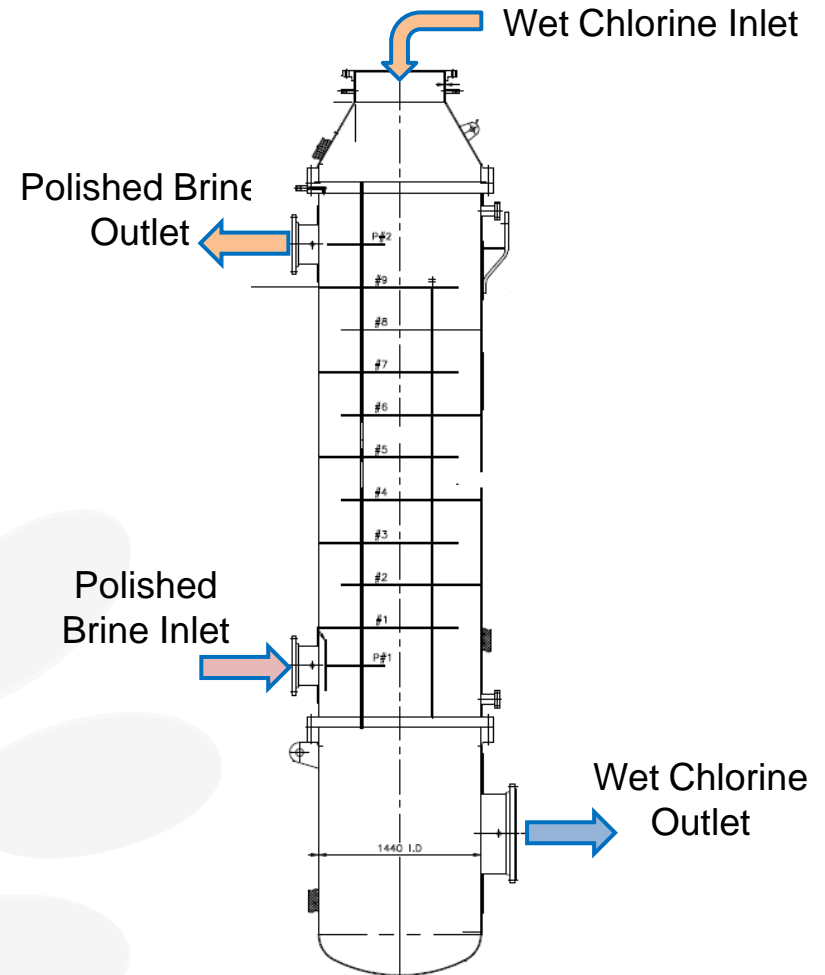
Introduction

A Titanium heat exchanger tubes (Gr. 12) had experienced severe corrosion after less than 6 years of service in Chlor Alkali plant. During plant turnaround maintenance the exchanger was opened for cleaning and inspection and severe deformation on the tubes (toward inner diameter) were noticed on 7 tubes at the tube to tubesheet area. The tubes were preserved for the purpose of analysis and investigation.



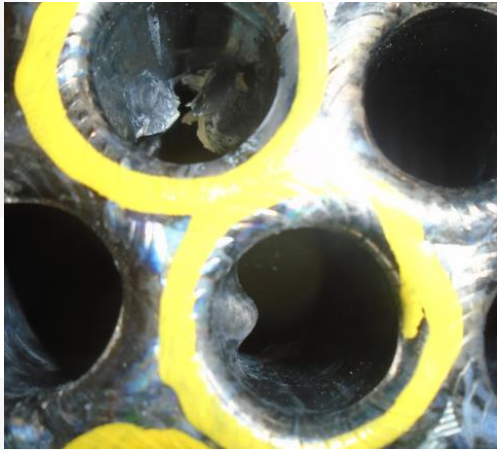
Process Description

After the separation of brine to NA & Cl using electrolysis, wet chlorine goes through drying process which include boiling it to a certain temperature to achieve separation from the moisture, the vapor of water is cooled through three exchangers, one is E12103 chlorine recuperator using polished brine, where wet chlorine (tube side) enters the exchanger at 87C and leaves it 60 C. And the polished brine (shell side) enters at 55 C and leaves at 63 C.



History

- The exchanger was commissioned in 2013.
- The first tube inspection attempted was on April 2019.
- During this period, there were two Turnaround maintenance opportunities, and the exchanger was opened for cleaning only.
- The bends were discovered with the first visual inspection and tube ECT.



Investigation and Lab Analysis

Visual Inspection

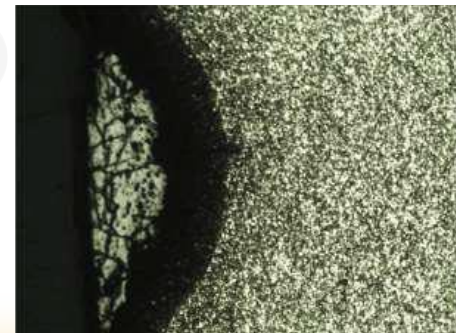
Severe deformation and white deposits on the tube to tubesheet portion.



Microstructural examination

Microstructural examination was conducted on various location, and specifically the impacted area.

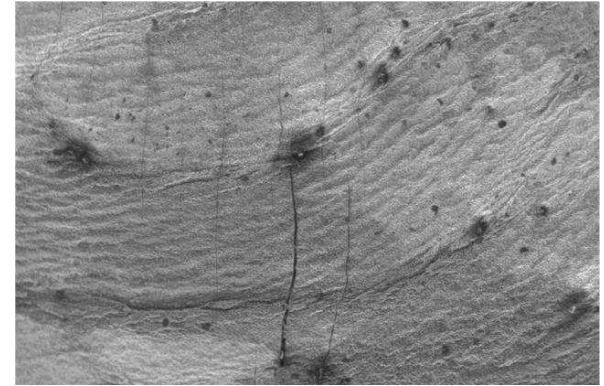
On the outer edge, pitting was observed along with pitting filled with deposits.



Investigation and Lab Analysis

Scanning Electron Microscopy (SEM)

SEM was conducted at fracture surface to showed cracks and metal wastage at different locations.



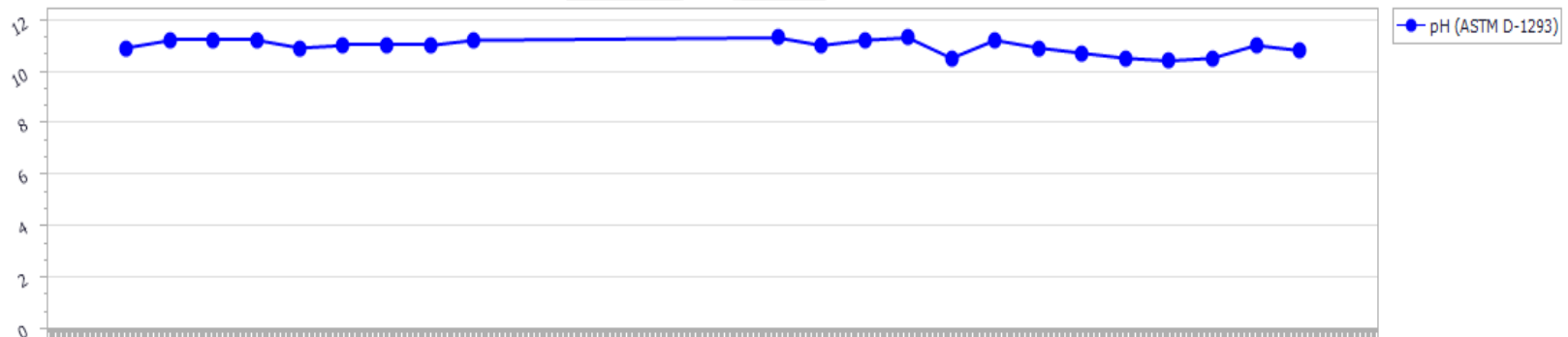
Energy Dispersive Spectroscopy (EDS)

EDS analysis highlights moisture contamination along with sulfur and chloride.

Element	Weight
Oxygen	42.89
Aluminum	3.96
Silicon	2.73
Sulfur	1.51
Clacium	30.14
Titanium	1.37
Iron	8.04
Zinc	5.51
Magnesium	1.97
Chlorine	1.87

Investigation and Lab Analysis

For titanium Gr.12 to corrode in crevice area, the solution within the crevice must become and remain significantly acid (~1). As per lab analysis, the pH of the polished brine (the inlet process to shell side) have usually remained in the range of 10-11 pH.



Sample of pH value during 2018

Discussion and Conclusion

- The metallurgical condition of the tube in terms of MOC, microstructure and hardness values appear to be sound.
- The brine sample analysis was conducted for the period of two years prior to the findings and the pH value was maintained at around 11.
- The corrosion damage noticed on outer surface of the damaged tube is in the form of pitting along with thinning.
- The damage is limited to the tube portion within the tubesheet.
- The EDS analysis indicates presence of oxygen and water based contamination along with chloride.
- After consultation with the licensor, it has been confirmed that in other Chlor Alkali plants, similar findings were observed.

Discussion and Conclusion

- The leak was not detected by operation because the wet chlorine on tube side is already containing brine, therefore no process abnormality observed.
- In the bulk solution in the shell of the exchanger, the tested sample have shown a normal pH value, however in the crevices the value can be different.
- Within the crevice, brine (NaCl) can be depleted into chlorine, creating strongly concentrated acid environment (around 1~pH).
- The temperate of the tubes can reach up to 90C (design temperature is 95C) at certain times of the year which can contribute to corrosion process.
- The corrosion product formed within the crevices was strong enough to bend the tubes.

Mitigation

- Titanium alloyed with palladium (Gr. 7 & 11) has been proven by other end users to be excellent in crevice corrosion resistance in brine services.
- Passivation by palladium oxides has been proven to be effective and have lower cost. However, in exposed to abrasive regions (such as tube-to-tubesheet region) the passivation layer might get disconnected. Therefore, this option was not recommended.
- After discussion with subject matter experts in reliability and process, and consultation with the licensor, we have decided to proceed with upgrading tubes material with Palladium alloyed Titanium tubes.

Thank You

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