

This case study is an edited version of Case Study 2 in *Operational Tube Failures in Heat Recovery Steam Generators: Metallurgical and Water Chemistry Perspectives* by Kevin J. Shields (formerly with STPA) and Ewa M. Labuda (of STPA), *Boiler & HRSG Tube Failures and Inspections*, November 2001.

Tube Failures in High Pressure Evaporator from Phosphate Gouging (Acid Phosphate Corrosion)

This case study involves two dual pressure HRSG units located in the northeastern United States. In this case the High Pressure (HP) Evaporators were experiencing multiple tube failures in both HRSGs, making it difficult to meet contractual commitments to supply power. A representative failed tube sample was provided for metallurgical assessment. This was done to augment an ongoing review of plant water treatment and surveillance practices and to provide an additional opinion as to the responsible damage mechanism, underlying root causes, and appropriate corrective actions.

Metallurgical Evaluation

Other failed tube specimens from this HRSG had been examined by others laboratories. Therefore, the subject examination focused on identification of the under-deposit corrosion mechanism responsible for the damage experienced. This was accomplished by visual examination of the tube and assessment of the waterside deposit material.

Visual Examination

Figure 1 shows the inner diameter (ID) surface of the tube sample in the "as received" condition. The tube sample was split longitudinally into two halves arbitrarily labeled Side A and Side B. Side A exhibited a thick longitudinal band of deposit and corrosion products covering a severely gouged tube surface. In contrast, the ID surface of Side B was covered with a fairly even gray-black deposit. The thick accumulation on Side A exhibited orange material at its edge, possibly indicative of copper deposits. White material was observed in thin layers throughout the buildup; however, the bulk deposit was gray-black, indicative of magnetite (Figure 2).

A transverse cross section through the tube wall on Side A at a gouge site is shown in Figure 3. The gouge penetrated 100% of the wall thickness beneath the thick accumulation of deposited material and corrosion products. Smaller gouges (not shown) exhibited a "bath tub" shape.

Analysis of Deposits

The thick, ID deposits in and over the gouge in the surface of Side A of the tube sample were examined in the scanning electron microscope (SEM) utilizing energy dispersive x-ray spectroscopy (EDS). Initially, the sample was examined normal to the ID surface.

Table 1 summarizes the EDS analysis results. A thin layer of white material was targeted as site 01. This material appeared as oblong crystals (not shown). Site 02 attempted to target a single crystal. It was suspected this crystalline material was a manganese oxide. Sites 03 and 04 targeted another area of the deposit, normal to the ID surface. The EDS spectra from these sites are similar to published spectra of maracite (NaFePO_4), the presence of which is indicative of acid phosphate corrosion⁽¹⁾.

Sites 05 through 08 and 10 through 13 targeted the deposit-filled gouge cross section for EDS analysis. (Site 09 targeted the OD surface.) Sites 05 and 13 were at the top surface, where the deposit contained a high level of copper. The remaining sites concentrated on various locations in the bulk deposit within the gouge. Site 06 targeted the deposit at the bottom of the gouge and contained mostly iron. Sites 07 and 08 also targeted the bulk deposit and contained mostly iron. Sites 10 through 12 targeted what appeared to be another thin layer of white material within the gouged area. The EDS analysis of these sites detected high levels of sodium, aluminum and silicon.

Summary of Metallurgical Findings

The HP Evaporator tube specimen failed due to under-deposit corrosion. Thick, hard accumulations of corrosion products and deposited material filled deep, longitudinal gouges in the ID surface on one side of the tube specimen examined. The EDS analysis of the deposit material detected levels of sodium, possibly indicative of the caustic corrosion mechanism. However, sodium and phosphorus were detected at levels that more strongly suggest an acid phosphate corrosion mechanism. In addition, the presence of high levels of manganese detected at several sites indicated a possible contamination of the makeup water or the condensate. Furthermore, the presence of significant levels of copper suggests corrosion of any components with copper alloy materials.

Water Chemistry Considerations

The facility water chemistry review identified a number of deficient practices, several of which appeared to potentially have some bearing on the HP Evaporator tube failures. These include the following.

1. The evaporators were treated with sodium phosphates and control limits used corresponded to those often employed in conventional low pressure industrial boilers however, other mechanisms which involve concentration of corrosives within heavy, porous waterside deposits may also have been present at various times during the service life of the

equipment.

2. Examination of waterside deposits indicated the existence of regions of enrichment of various elements to levels well above average concentrations reported present in the bulk deposit material. However, it was not possible to identify the events responsible for contaminant ingress since chemistry surveillance was limited to analysis of grab samples twice daily. A sample panel and analyzer package was included in the plant design but only the grab samples were operational during initial unit operations.
3. Analysis of water samples collected during site visits indicated significant levels of organic matter in the condensate makeup. Low levels of manganese were also present, probably as part of the organic matter in the treated makeup.
4. Samples collected from the system during the chemistry review reflected no significant contamination by inorganic species such as sodium, chloride, sulfate, silica, etc. However, levels of organics - including acetate and formate - appeared significant. Although these findings were attributed primarily to the organics present in the makeup, use of organic-based treatments may have some effect.
5. A sample of HP Evaporator steam was found to contain levels of impurities that may be indicative of a carryover problem.
6. Issues existed with respect to HRSG waterside cleanliness. Concerns existed that corrosion had been experienced during construction and only alkaline cleaning was performed prior to initial service. Operational chemical cleaning was recommended to remove waterside deposits and passivate tube metal surfaces.
7. Corrosion within the condensate and feedwater system and metals transport activity was poorly defined. Steps needed to improve included surveillance and control of condenser air inleakage, and of feedwater dissolved oxygen levels.
8. The practice of continuing to add treatment chemicals to the HP Evaporators during idle periods may have contributed to underdeposit corrosion by creating regions of high chemical concentration. Temperature increases associated with startup activity would have provided opportunity for concentration of treatment chemicals in adjacent waterside deposits, and underdeposit corrosion attack.
9. Examination of fiber optic inspection tapes and other assessment findings raise concern as to the condition of other components in contact with steam and water, both within the external to the HRSG.

- Development of a facility chemistry manual with action-oriented water chemistry response procedures was needed, as well as provision of formalized training of the operators to allow them to have defined roles in contributing to the future success of the chemistry program.

Another facility water chemistry review was conducted about three years later. Most of the prior deficiencies had been addressed. The evaporators utilized a modified version of EPRI phosphate treatment, employing a specially blended product from their chemical vendor. This approach maintained sodium to phosphate ratios in the range of about 2.8 to 3.0. Most of the on-line instrumentation was working, and a plant operator had been assigned responsibility for chemistry surveillance and control activities. Makeup treatment operations had been improved significantly. HRSG HP and LP Evaporators had been chemically cleaned and fiber optic examinations were performed during major outages to watch for signs of deposition and corrosion. Condenser air in-leakage rates and feedwater dissolved oxygen levels were being monitored and determined to be at very satisfactory levels. The practice of feeding chemicals when the HRSG was idle was discontinued and efforts were underway to develop suitable lay-up procedures. Operator chemistry training was also under consideration.

Conclusion

Tube failures in HRSG units require metallurgical evaluation to identify the responsible damage mechanism. Consideration of the water chemistry is often needed to identify the responsible root causes of damage and thereby establish an effective strategy of corrective actions applicable to the situation.

References

- Interim Cycle Chemistry Guidelines for Combined Cycle Heat Recovery Steam Generators (HRSGs)*. Palo Alto, CA: EPRI, November 1998. TR-110051.

Table 1: Deposit Analysis Results, Weight %

Site Numbers	01	02	03	04	05	06
Element, as						
Sodium, Na	7.39	5.13	15.51	16.74	15.49	4.70
Magnesium, Mg	2.39	2.10	2.04	2.56	2.89	2.33
Aluminum, Al	1.95	1.66	3.97	3.32	2.01	1.49
Silicon, Si	1.67	1.44	4.11	2.23	1.26	1.08
Phosphorus, P	5.22	6.11	15.05	16.23	0.99	0.46
Sulfur, S	1.89	0.12	0.11	1.05	1.08	0.27

Chlorine, Cl	0.07	0.03	0.00	0.18	0.20	0.00
Potassium, K	0.00	0.00	0.00	0.07	0.07	0.00
Calcium, Ca	0.02	0.00	0.07	0.11	0.00	0.00
Titanium, Ti	0.00	0.00	0.09	0.08	0.02	0.00
Vanadium, V	0.00	0.00	0.14	0.06	0.03	0.00
Chromium, Cr	0.08	0.03	0.17	0.11	0.11	0.00
Manganese, Mn	11.33	12.04	6.84	2.80	1.45	0.74
Iron, Fe	58.15	69.47	51.59	51.74	33.32	88.77
Nickel, Ni	0.00	0.09	0.00	0.00	0.06	0.00
Copper, Cu	9.83	1.77	0.33	2.71	40.59	0.00
Zinc, Zn	0.00	0.00	0.00	0.00	0.44	0.00

Element, as	Site Numbers	07	08	09	10	11	12	13
Sodium, Na		4.40	8.62	4.48	12.34	21.30	18.37	13.90
Magnesium, Mg		1.90	3.38	3.18	3.11	2.33	1.94	3.08
Aluminum, Al		1.59	2.40	2.24	5.45	13.28	13.59	2.02
Silicon, Si		0.88	1.75	2.53	4.26	11.97	24.75	1.31
Phosphorus, P		0.26	2.05	0.94	1.40	2.70	5.49	1.36
Sulfur, S		0.24	0.84	7.13	0.53	1.03	0.78	1.27
Chlorine, Cl		0.00	0.21	0.19	0.21	0.28	0.25	0.20
Potassium, K		0.00	0.04	0.16	0.03	0.09	0.05	0.04
Calcium, Ca		0.00	0.00	4.47	0.00	0.03	0.00	0.06
Titanium, Ti		0.00	0.00	0.04	0.00	0.00	0.00	0.00
Vanadium, V		0.04	0.00	0.06	0.00	0.00	0.00	0.05
Chromium, Cr		0.36	0.04	1.29	0.03	0.02	0.10	0.12
Manganese, Mn		0.82	2.10	0.25	0.68	0.38	0.27	2.75
Iron, Fe		88.05	70.37	72.31	71.95	46.61	33.99	36.17
Nickel, Ni		0.00	0.00	0.58	0.00	0.00	0.00	0.16
Copper, Cu		0.00	8.20	0.13	0.00	0.00	0.43	37.14
Zinc, Zn		1.47	0.00	0.00	0.00	0.00	0.00	0.37

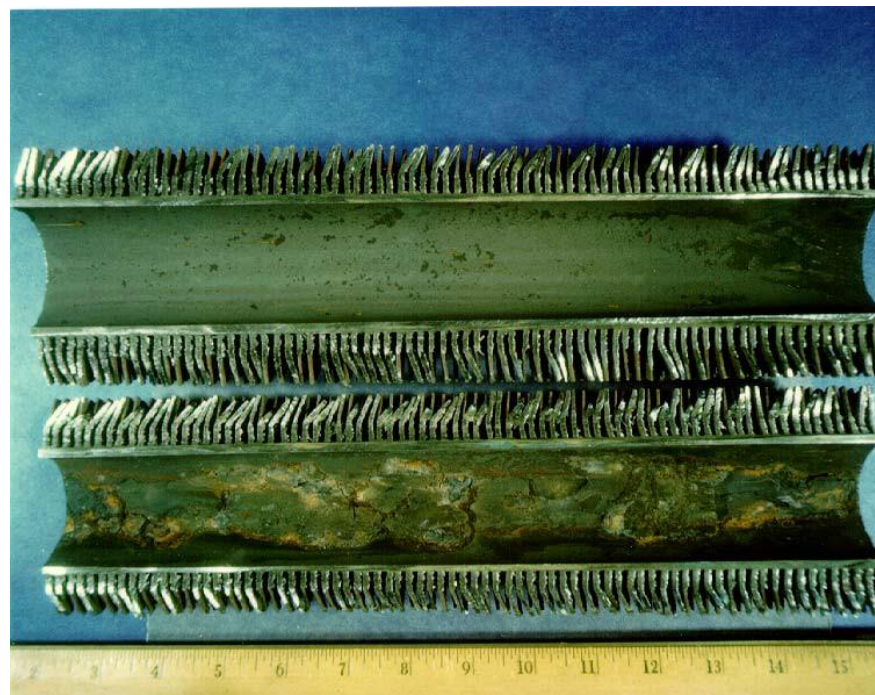


Figure 1

Failed HP Evaporator Tube



Figure 2

Close-up of Failure Location



Figure 3

Cross-Sectional View of Corrosion Site