STRESS CORROSION CRACKING AND INTERGRANULAR CORROSION OF A 316Ti STAINLESS STEEL PREHEATER TUBE

SUMMARY:

A cracked 316Ti stainless steel preheater tube was analyzed to determine the failure mechanism. A second non-cracked tube section from a different elevation was also analyzed to determine the condition of the tube material. The interior of the tube carries process gas that reportedly contains hydrogen, carbon dioxide and monoxide, water and water vapor, methane, nitrogen and traces of hydrogen sulfide. The tube exterior is heated with flue gas.

Results indicate that the tube failed due to ID initiated, transgranular, chloride stress corrosion cracking (SCC) near the tubesheet interface at the transition of a roll expansion. Circumferential cracking was localized at the roll transition indicating that residual tensile stress from the roll expansion process contributed to cracking. The expansion appeared to be oversized at the crack site. An extensive network of SCC cracking was observed that appeared to propagate primarily from the inner diameter (ID) surfaces. Some outer diameter (OD) initiation sites were also noted. Microstructural analysis of the cracked tube revealed that the SCC cracks that originated from the ID were rapidly corroded along the cracks once they formed. Heavy oxide deposits were also observed along the ID surface.

Elemental analyses of the opened crack surface, and outer and inner diameter surface deposits indicated the presence of sulfur and chlorine. The ID deposit reveals higher levels of sulfur and is attributed to traces of hydrogen sulfide in the
process gas. Both constituents contribute to SCC and corrosion of the crack surfaces in moist environments. The SCC and corrosive attack are aggravated by the presence of moisture at the inlet of the vertical tube where temperatures are lower.

The tube section trimmed from another elevation (above the insulated tubesheet region) did not exhibit cracking (i.e. SCC or otherwise). However, uniform intergranular corrosion was observed on the ID surface. The intergranular corrosion was attributed to a sensitized microstructure (chromium carbide precipitation along grain boundaries when held at 932-1562°F or 500 to 850°C) resulting from the high flue gas temperatures. The OD surface deposits were primarily chromium oxide, whereas, the ID deposits were mainly iron oxide. Some chlorine was detected in the OD and ID deposits.

A sensitized microstructure was not observed in the cracked tube section due to the location at the tubesheet where lower inlet temperatures and protection of the tube by the refractory insulation are found. Cutting out and re-using the preheater tube sections above the tubesheet (question posed by the client) would place the sensitized material into a more corrosive environment. Rapid and extensive cracking would be likely, due to the reduced corrosion resistance of the sensitized microstructure and the moist conditions at the tube inlet.

Chemical analysis indicated the preheater tubes were fabricated from a Type 316 austenitic stainless steel with a titanium addition, stabilized for elevated temperature service. Hardness values indicated the tube has a hardness of 77 – 79 HRB, consistent with annealed tubing after elevated temperature service.

Elimination of the over-expansion of the tubesheet roll would reduce the residual stress in the critical area and increase the life of the tubes. For longer service life, a more SCC resistant grade, not susceptible to sensitization and with high temperature corrosion resistance, should be used. Alloys that fit these requirements and for consideration for replacement material are: Alloy 556 (Haynes, UNS R30556), Alloy 333 (UNS N06333), Alloy 617 (UNS N06617), and Alloy 625 (UNS N06625). Inserting a sleeve manufactured from one of the above alloys and roll expanding into place in the inlet end would extend the life of the heat exchanger. However the cost may be considerable.

**ANALYSIS:**

A portion of failed stainless steel preheater tube containing a circumferential crack at the edge of the roll expansion joint of the inlet tubesheet was submitted for failure analysis as pictured in Figure 1. A piece of a second tube from a higher elevation was also analyzed to determine the condition of the material and investigate for possible early stages of cracking. The two tubes are analyzed in separate sections of this report.
The preheater tubes are inverted "U-shaped" where flue gas is used to preheat the process gas on the inside of the tube that consists of hydrogen (40.3%), carbon dioxide (17.1%) and monoxide (20.8%), water vapor (18.6%), methane (2.0%), nitrogen (1.2%) and traces of hydrogen sulfide (~10 – 30 ppm). Some liquid water along with some chemical contaminants from the water and gas is also present. The cracking occurred at the inlet side of the tubesheet that has ~3-in. of refractory lining on the OD (flue gas side). The temperature at the inlet is 176°F (80°C). The preheater tube / process gas near the outlet side is hotter and closer to the flue gas temperature of ~698°F (370°C). The comparison piece of tubing is from a higher elevation above the refractory lining of the preheater tube (i.e. a hotter portion of the preheater).

The cracked end of the tube was removed from the heat exchanger using an abrasive saw. After the cracked end of the tube was removed, the U-shaped preheater tube was re-inserted and the end welded to seal the tubesheet.

Cracked Tube Analysis:

Visual examination of the cracked inlet end tube section was performed at low magnification using a stereomicroscope. The crack was oriented in a circumferential manner, approximately 300 degrees around the tube adjacent to the edge of the tubesheet as shown in Figure 2. The tube was slightly bent. Numerous crack branches were noted as presented in Figure 3. No crack was observed away from the tubesheet. The tube has a slight bulge and appears to have been expanded past the end of the tubesheet as revealed in Figure 4. Dimensional measurement across the tubesheet interface indicated the diameter inside the tubesheet was ~2.040-in. and outside was ~2.010-in. The diameter of the comparison tube was 2.015-in. The localized circumferential crack at the roll expansion transition suggests that residual tensile stress from the roll expansion process contributed to cracking.

The interior surface was covered with a thick oxide layer as revealed in Figure 5. Heavy score marks from pushing the tube out of the tubesheet during removal are noted. In these regions, the oxide had been removed and evidence of pitting was observed.

The failed tube section (Figure 5) was cut dry to open the crack surface and analyze the OD and ID oxide deposits. The oxides were analyzed using energy dispersive x-ray spectrographic (EDS) micro-analysis in general accordance to ASTM E1508-98. Figure 6 exhibits the bulk spectrum of the OD surface away from the crack region. The spectrum consisted primarily of oxygen (O), aluminum (Al), silicon (Si), calcium (Ca), and iron (Fe). Smaller sodium (Na), molybdenum (Mo), chlorine (Cl), potassium (K), titanium (Ti), chromium (Cr), manganese (Mn), and nickel (Ni) peaks were observed. A trace of sulfur (S) is likely present. [Note: molybdenum and sulfur peaks both overlap making analysis of the two difficult.] The iron, titanium, chromium, nickel, molybdenum,
manganese, and silicon are alloying elements from the 316Ti stainless steel tube. In some localized regions, the chlorine levels were higher as illustrated in Figure 7. Chlorine can contribute to SCC in austenitic stainless steels.

The ID deposits (Figure 8) consisted primarily of oxygen, calcium, and iron. Smaller aluminum, silicon, sulfur / molybdenum, chlorine, chromium, manganese, and nickel peaks were observed. The deposit consists of corrosion (i.e. iron oxide) and water deposits. The underside of the ID deposit was observed to have a higher concentration of sulfur.

EDS analysis was also performed on the opened crack surface (Figure 9) and was found to exhibit similar deposits to the ID surface, except the sulfur and chlorine levels were higher.

The crack surface was cleaned and prepared for analysis at high magnification using a scanning electron microscope (SEM). A low magnification SEM view of a typical region of the opened crack surface is shown in Figure 10. The crack surface appears to be transgranular in nature. The surface is heavily oxidized/corroded as revealed at high magnification in Figure 11. The original fracture surface is obscured by corrosive attack.

Two cross-sections, one transverse and a second one longitudinal, were taken through the crack tip. The cross-sections were prepared for metallographic examination to determine the crack morphology and to investigate for any anomalies in the microstructure. Sample preparation was in accordance with ASTM E3-01. Etching techniques per ASTM E407-99 revealed the microstructure that was evaluated in accordance with ASTM E883-02.

An overview of the transverse cross-section is revealed in Figure 12. Numerous heavily oxidized corrosion penetrations with multiple branching features are visible along the ID surface. An extensive network of stress corrosion cracking penetrating to the OD surface is also observed. Multiple crack branching, a characteristic of SCC, is noted all along the tube. A heavy oxide layer along the ID surface is also noted. Figure 13 details the extensive SCC network and the oxidized ID corrosion penetrations at increased magnification. Fine SCC cracks are observed at the tips of the heavily oxidized corrosion penetrations with branch-like features (Figure 14). This indicates corrosion along the SCC cracks as they propagate.

Etching reveals the SCC cracking is transgranular in nature in Figures 15 and 16. [Note: Chloride ion SCC in stainless steel is transgranular, occurs at somewhat elevated temperatures (typically above 150o F), and occurs under a tensile stress.] Figure 17 reveals a second oxidized corrosion penetration with branch-like features. The penetration appears to be an oxidized SCC crack. The oxidation of the crack tip is demonstrated in Figure 18. Figure 19 shows the etched microstructure is an annealed equiaxed austenitic microstructure. Fine
orange angular titanium carbides are noted. No evidence of sensitization (carbide precipitation along the grain boundaries) or any other material deficiencies is noted. Most of the cracking initiates from the ID.

The cross-section through the crack tip revealed a much more extensive SCC network with cracking originating from both the ID and OD surfaces in Figure 20. Much of the cracking appears to originate at shallow pits.

Chemical analysis was performed on the cracked tube base material using an optical emission spectrometer in accordance with ASTM E1086-94 (00). Results are presented in Table 1. The tube was fabricated from a Type 316Ti austenitic stainless steel. The titanium addition is to aid in prevention of intergranular carbides, however the titanium content is just above the minimum allowed. No other unusual conditions were noted.

Microhardness testing (per ASTM E384-99e1 guidelines and converted to Rockwell B values from Knoop 500-gram load using ASTM E140-02) was performed on the cracked tube cross-section. The average hardness value was 77 HRB and is typical for the annealed condition with elevated service temperature.

Comparison Tube Analysis:

The comparison tube (see Figure 1) had been removed by carbon arc cutting and one end was then cut using an abrasive blade. No evidence of a tubesheet was observed since the tube was from an upper hotter portion of the vertical U-shaped preheater tube. The exterior surface did not appear as oxidized as the cracked tube. The interior surface was covered with a thick oxide layer primarily on one side.

The tube section was cut dry and the OD and ID oxide deposits were subjected to EDS analyses as previously outlined. Figure 21 exhibits the bulk spectrum of the OD surface revealing primarily the chromium-rich oxidation products of the stainless tube (i.e. Si, Mo, Cr, Mn, Fe, and Ni). Traces of aluminum, sulfur, chlorine, potassium and calcium were also noted. The ID deposits (Figure 22) were similar except that they are primarily iron-rich oxidation products with water deposits. The chlorine level is also higher.

Two cross-sections, transverse and longitudinal, were prepared for metallographic examination for evidence of cracking and to investigate for any anomalies in the microstructure. Sample preparation was as previously outlined.

An unetched optical microscopic image reveals intergranular corrosion of the tube ID as presented in Figure 23. The oxide deposit is very thick. The intergranular attack is detailed at increased magnification in Figure 24. Etching reveals the microstructure is sensitized (carbide precipitation along grain
Figure 25 and 26. Figure 27 reveals the corrosion penetrations are not as deep along the OD surface. A sensitized, equiaxed annealed austenitic microstructure is observed. The sensitized microstructure is more prone to intergranular corrosive attack. No evidence of SCC cracking was observed, most likely due to the hotter service temperatures and the absence of significant moisture.

Chemical analysis was performed on the comparison tube base material as previously outlined and results are presented in Table 1. The tube was fabricated from a Type 316Ti austenitic stainless steel, same as the cracked tube.

Microhardness testing was performed through the comparison tube cross-section as previously outlined and the average hardness value was 79 HRB. The hardness is typical for the annealed condition with elevated service temperature and similar to the cracked tube.

**CONCLUSIONS:**

The 316Ti stainless steel tube cracked by transgranular stress corrosion cracking due to the presence of sulfur and chlorine in a moist environment at elevated temperatures. The cracked tube section exhibited an equiaxed microstructure without any evidence of sensitization or other material deficiencies. The sensitization was not observed along the tubesheet due to the lower inlet temperatures and protection of the tube by the refractory insulation. Chlorine was detected on the opened crack surface.

No cracking (i.e. SCC or otherwise) was observed in the comparison tube from a higher elevation due to higher operating temperature and reduced moisture content. However, uniform intergranular corrosion on the ID surface was observed. The intergranular corrosion was attributed to a sensitized microstructure resulting from operation at the normal flue gas temperatures. The OD surface deposits were primarily chromium oxide, whereas, the ID deposits were primarily iron oxide. Some chlorine was detected on both the ID and OD surfaces.

Elimination of the over-expansion of the tubesheet roll would reduce the residual stress in the critical area and increase the life of the tubes. For longer service life, a more SCC resistant grade, not susceptible to sensitization and with high temperature corrosion resistance, should be used.

**CHEMICAL ANALYSIS**

<table>
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<tr>
<th>Table 1</th>
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<td>Chemical Analysis of the Cracked and Comparison Preheater Tube Sections</td>
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<tr>
<td>Element</td>
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<tr>
<td>Carbon</td>
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<td>Manganese</td>
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<td>Molybdenum</td>
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<td>Titanium</td>
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The preheater tube was fabricated from Type 316Ti austenitic stainless steel or equivalent material. The carbon content is just above the minimum requirement.

**IMAGES:**

**Figure 1:** Overview of the cracked and comparison as-received preheater tubes. The arrow points to the circumferential crack near the tubesheet interface. (Photo No. PA5221)

**Figure 2:** Rotated view of the cracked preheater tube showing the branched circumferential crack. (Photo No. PA5225)
Figure 3: Close-up view of the crack tip showing an extensive crack network. The OD was covered with a refractory insulation at this location. (Photo No. PA5229)

Figure 4: Overview of the cracked preheater tube along a straight edge on one side showing the roll expansion extended well beyond the tubesheet. (Photo No. PA5231)

Figure 5: Close-up of the heavy ID deposits at the roll expansion transition. The circumferential crack is noted by arrows. (Photo No. PA5230)

Figure 6: EDS analysis of the OD deposit on the cracked tube. Note the sulfur and molybdenum peaks overlap making positive identification of each at low levels difficult. (2SPT0428)

Figure 7: EDS analysis of the OD

Figure 8: EDS analysis of the ID
deposit showing higher chlorine levels in localized areas. Note the sulfur and molybdenum peaks overlap making positive identification of each at low levels difficult. (2SPT0429)

deposit on the cracked tube. Note the sulfur and molybdenum peaks overlap making positive identification of each at low levels difficult. (2SPT0427)

Figure 9: EDS analysis of the opened crack surface. Note the sulfur and molybdenum peaks overlap making positive identification of each at low levels difficult. Significant chlorine is detected. (2SPT0432)

Figure 10: Low magnification SEM image of the tube fracture surface showing a heavily oxidized surface. The fracture appears transgranular. (SEM Photo 2S2154, Mag: 35X)

Figure 11: High magnification SEM image of the tube fracture surface showing a heavily oxidized and corroded surface. (SEM Photo 2S2159, Mag: 1,000X)

Figure 12: Optical microscopic overview of the transverse tube cross-section showing heavily oxidized corrosion penetrations with branch-like features (arrows) and an extensive network of SCC cracking extending to the OD surface. A heavy ID oxide layer is just visible along the ID. (Photo C4241, Mag: 15X, unetched)
Figure 13: Optical microscopic composite view of the heavily oxidized corrosion penetrations with branch-like features and an extensive network of SCC cracking extending to the OD surface. (Photos 2MA0276 & 2MA0277, Mag: 50X, unetched)

Figure 14: High magnification optical microscopic view of the heavily oxidized corrosion penetrations with branch-like features. Fine SCC cracks are extending out of the corrosion penetrations. (Photo 2MA0279, Mag: 500X, unetched)

Figure 15: Same as Figure 14 except etched to reveal the microstructure. An equiaxed austenitic microstructure is revealed without sensitization. (Photo 2MA0288, Mag: 500X, Oxalic acid etch)

Figure 16: High magnification optical microscopic view of a crack tip showing transgranular progression of the multi-branched crack, characteristic of chloride SCC. An equiaxed austenitic microstructure is revealed without sensitization. Some orange titanium carbides are observed. (Photo 2MA0289, Mag: 500X, Oxalic acid etch)
Figure 17: Optical microscopic view of another heavily oxidized ID corrosion penetration with branch-like features at the edge of the opened crack. (Photo 2MA0280, Mag: 50X, unetched)

Figure 18: High magnification optical microscopic view of the tip of a heavily oxidized corrosion penetration with branch-like features. Fine SCC cracks are extending out of the corrosion penetrations. (Photo 2MA0282, Mag: 100X, unetched)

Figure 19: Same as Figure 18 except etched to reveal the microstructure. An equiaxed austenitic microstructure is revealed without sensitization. Some orange titanium carbides are observed. (Photo 2MA0285, Mag: 500X, Oxalic acid etch)

Figure 20: Optical microscopic overview of the longitudinal tube cross-section through the circumferential crack tip exhibits an extensive network of SCC cracks extending from pitted areas. A heavy ID oxide layer is just visible along the ID. (Photo C4240, Mag: 15X, unetched)
Figure 21: EDS analysis of the OD deposit on the comparison tube. Note the sulfur and molybdenum peaks overlap making positive identification of each at low levels difficult. (2SPT0430)

Figure 22: EDS analysis of the ID deposit on the comparison tube. Note the sulfur and molybdenum peaks overlap making positive identification of each at low levels difficult. Significant chlorine is detected. (2SPT0431)

Figure 23: Optical microscopic view of the comparison tube cross-section along the ID surface reveals intergranular corrosive attack. A thick oxidized layer is also noted. No SCC cracking is observed. (Photo 2MA0269, Mag: 100X, unetched)

Figure 24: High magnification optical microscopic view of the intergranular corrosive attack along the ID of the comparison tube. (Photo 2MA0270, Mag: 500X, unetched)
Figure 25: Optical microscopic view of the ID surface of the etched comparison tube reveals a sensitized microstructure. (Photo 2MA0274, Mag: 100X, Oxalic acid etch)

Figure 26: Same as Figure 25 except at high magnification detailing the sensitization condition (fine carbides outlining grain boundaries). An equiaxed austenitic microstructure with some orange titanium carbides is observed. (Photo 2MA0275, Mag: 500X, Oxalic acid etch)

Figure 27: High magnification optical microscopic view of the OD surface of the etched comparison tube showing a sensitized microstructure. An equiaxed austenitic microstructure with some orange titanium carbides is observed. (Photo 2MA0273, Mag: 500X, Oxalic acid etch)