

# Failure Analysis of Ethanol Vaporizer Heat Exchanger Tubes

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**Abstract** A series of tube failures due to corrosion occurred in shell-and-tube heat exchangers that utilized high-temperature steam within horizontal tubes to distill ethanol within the shell. On the basis of the investigation, it was determined that the tubes were made of 316L stainless steel, and the ethanol (and tube corrosion product) had elevated sulfur content. The corrosion of the tubes was predominantly located in the areas of high sulfur concentration along the surfaces with the highest temperature where sulfuric surface deposits were allowed to form. Alternative tube materials which may offer improved corrosion resistance were recommended.

**Keywords** Heat exchanger · Corrosion · Materials selection

## Introduction

A series of heat exchanger tube failures occurred in several ethanol vaporizers. The ethanol vaporizers (shown in Fig. 1) were two-pass, shell-and-tube heat exchangers that utilized high-temperature steam within horizontal tubes to distill ethanol within the shell. The vaporizers had been in service for approximately 1 year, but were gradually removed from service when high levels of contamination were detected in the outlet steam condensate. When tubes were removed from the vaporizers, corrosion was found to

be concentrated closest to the tube sheet at the steam inlet, as shown in Fig. 2. Heavier concentrations of corrosion pits were also found along the tubes situated toward the top of the evaporator (in the vapor-filled region) and along the top half of the tubes located toward the bottom of the evaporator (in the liquid-filled region). The analysis presented in this article was based on the authors' investigation of the failed heat exchanger tubes.

## Metallurgical Evaluation

Sections of the corroded tubes were submitted for metallurgical analysis. All of the samples possessed notable pitting corrosion over both the OD and ID surfaces, though predominantly it was concentrated on the OD, as seen in Fig. 3. The vaporizer tubes were allegedly made from 316L stainless steel, an extra-low carbon version of 316 stainless steel, which offers greater resistance to general corrosion and increased strength at elevated temperatures. It might be noted that although Material Handbooks refer to 316 and 316L, the steel industry has adopted 316L as the available alloy. Given that ethanol is typically not corrosive to 316L stainless steel, one of the tube samples provided was sent to an independent laboratory for identification of material composition. Optical emission spectroscopy (OES) confirmed that the tube material was indeed 316L stainless steel, the results of which are reported in Table 1.

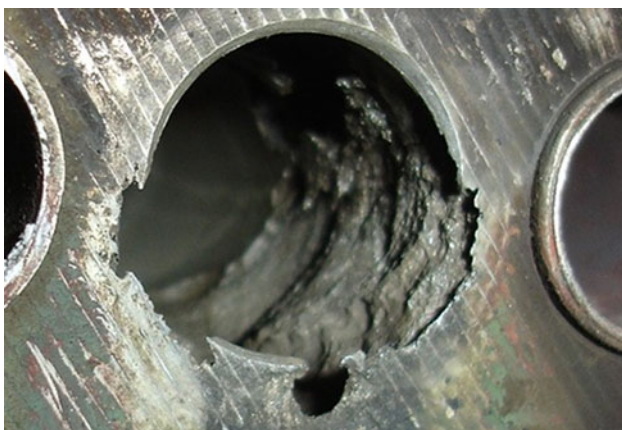
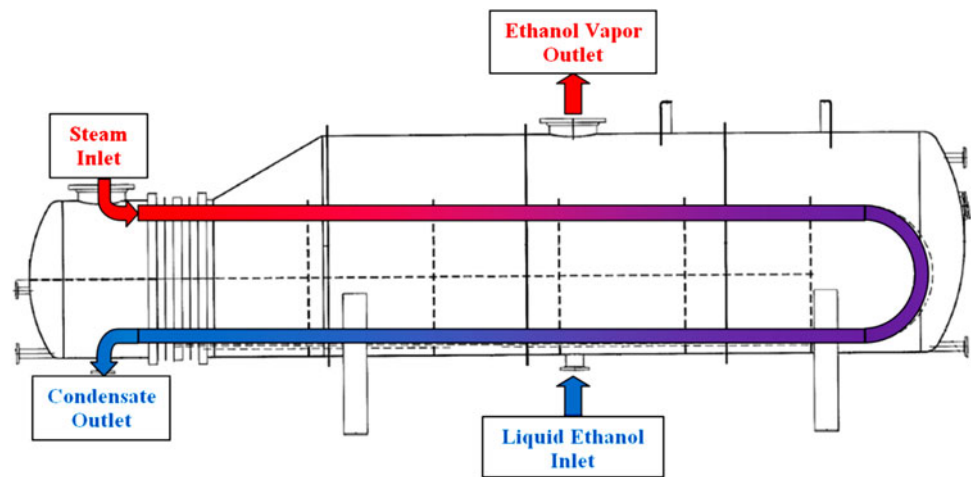
In order to identify the corrosion mechanism, tube samples were examined using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS/EDX), which provided semi-quantitative chemical compositions of the tube surfaces and media build-up. The areas on the tube OD surface where EDS was performed

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**Fig. 1** Drawing of two-pass shell-and-tube heat exchanger used to vaporize ethanol (annotated to show process flows)



**Fig. 2** Observed corrosion of the tube sheet at the steam inlet

can be seen in Fig. 4. Figure 4 was taken using backscatter electron image (BEI) detector, which displays objects based on their atomic weight, where lighter elements appear darker and heavier elements appear brighter.

Two of the EDS areas seen in Fig. 4 were of note: Probe 3 (top right box) examined an area of corrosion product, while Probe 5 (bottom box) examined an area free of any notable corrosion product. When comparing the results between these two areas, the corroded area (Probe 3) contained notably greater concentrations of sulfur, carbon, and oxygen than the non-corroded region of base metal (Probe 5). Carbon and oxygen are elements, and typical examples of iron-corrosion product; however, the high sulfur concentrations within the corrosion product indicated that sulfur concentration was associated with the deterioration of the vaporizer tubes.

### Corrosion Mechanism

Conversations with the facility at which the vaporizers were installed revealed the presence of sulfur and sulfuric



**Fig. 3** Pitting concentrated on the OD of a tube sample

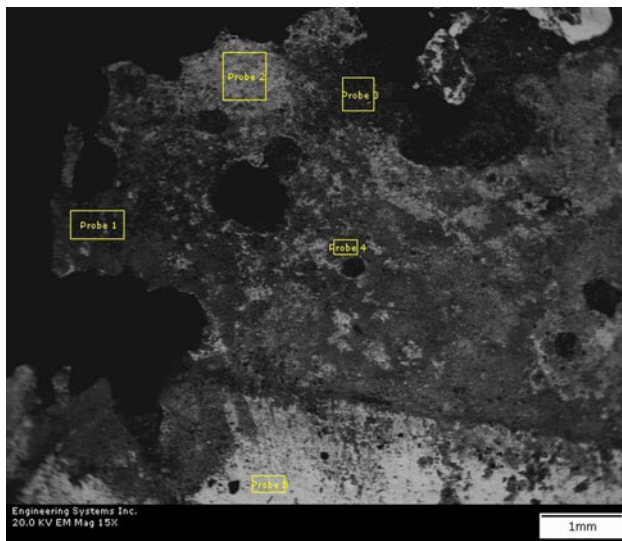
acid ( $\text{H}_2\text{SO}_4$ ) within the upstream ethanol process, resulting in the presence of sulfides within the ethanol being introduced into the vaporizers. The sulfides therefore precipitated out of the ethanol during the vaporization/distillation process.

While stainless steels offer varying degrees of corrosion resistance to  $\text{H}_2\text{SO}_4$ , elevated temperatures and the presence of small crevices are known to decrease corrosion resistance. These facts were well illustrated by the severe corrosion concentrated at the crevices located at the steam inlet tube sheets, where temperatures were the highest. The tubes that are situated in the vapor-filled region above the level of liquid ethanol within the vaporizer allowed sulfuric surface deposits to form along their surfaces. The fluid flow within the liquid-filled region of the vaporizer helped in preventing formation of sulfuric surface deposits; however, the boiling (nucleation) and vapor flow around the tubes were apparently such that localized deposits formed along the upper surfaces of the tubes.

Though the corrosion along the tube OD surfaces and within crevices due to sulfur precipitating-out during ethanol vaporization appeared to be the cause of failure, the

**Table 1** Results of OES performed on tube material

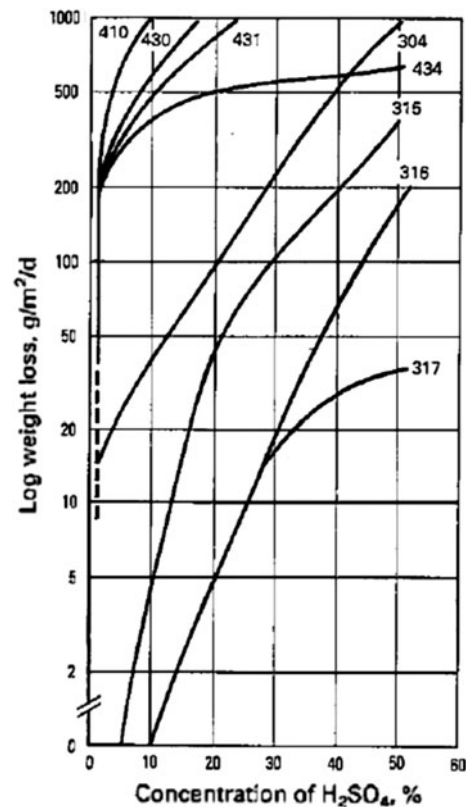
Element	Concentration, %
Carbon	0.015
Manganese	1.32
Phosphorus	0.028
Sulfur	<0.005
Silicon	0.43
Nickel	10.22
Chromium	16.34
Molybdenum	2.03
Copper	0.36
Nitrogen	0.04

**Fig. 4** BEI image of tube OD surface EDS analysis, with base metal appearing brighter and corrosion product appearing darker

possible contribution of microbiologic corrosion to the vaporizer tube failures was also investigated. Sulfate reducing bacteria (SRBs) reduce sulfate to sulfide in the absence of oxygen, which can cause corrosion in metals. Samples of corroded tubes were tested for the presence of SRBs using the Sani-Check SRB Test Kit, made by Biosan Laboratories, Inc. The corroded tube surfaces were swabbed using the applicator, placed back within the tube and monitored for a period of three weeks. The product website describes the test process by stating:

When sulfide is liberated, it reacts with iron in the tubed culture medium to form iron sulfide, a black precipitate. The degree to which the medium blackens, along with the length of time it takes to change color, allows for an estimated count of sulfate reducers to be made. [1]

Some darkening of the medium was observed; however, there was no significant change in the medium after 1

**Fig. 5** Figure 17 in the selected section of the referenced ASM Metals Handbook

week, which indicated no overwhelming evidence of SRB's presence on the corroded tube surfaces. Though there may have been a small amount of SRBs present, any significant contribution to the overall failure of the vaporizer tubes was determined to be unlikely.

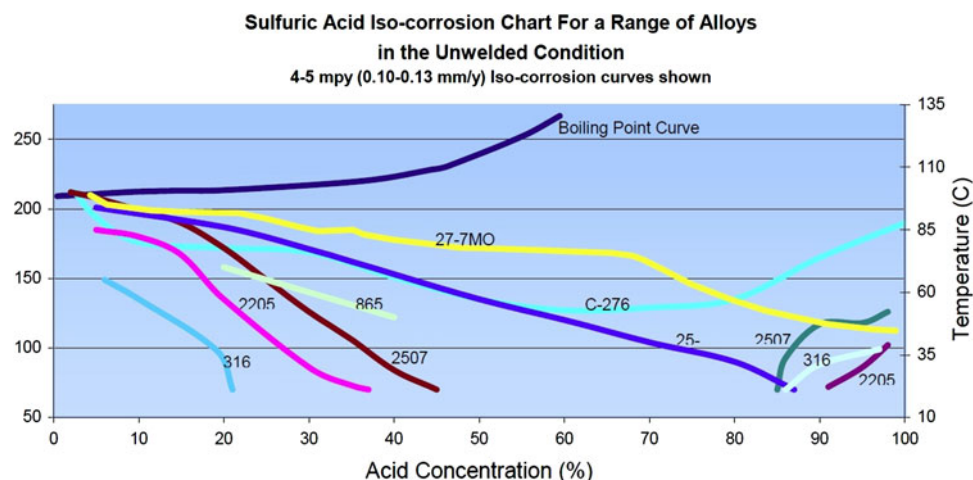
## Literature Review

A literature review found several publications that addressed alloy corrosion resistance to sulfuric acid at various concentrations and temperatures. Page 876 of the ASM Metals Handbook states:

In sulfuric acid, stainless steels can approach the borderline between activity and passivity. Conventional ferritic grades, such as type 430, have limited use in H<sub>2</sub>SO<sub>4</sub>, but the newer ferritic grades containing higher chromium and molybdenum (for example, 28% Cr and 4% Mo) with additions of at least 0.25% Ni have shown good resistance in boiling 10% H<sub>2</sub>SO<sub>4</sub> (Ref. 45), but corrode rapidly when acid concentration is increased.

The conventional austenitic grades exhibit good resistance in very dilute or highly concentrated

**Fig. 6** Figure 1 in the selected section of the referenced NACE paper



$\text{H}_2\text{SO}_4$  at slightly elevated temperatures. Acid of intermediate concentration is more aggressive, and conventional grades have very limited use. The resistance of several stainless steels in up to about 50%  $\text{H}_2\text{SO}_4$  is shown in Fig. 17 (see Fig. 5). Aeration or the addition of oxidizing species can significantly reduce the attack of stainless steels in  $\text{H}_2\text{SO}_4$ . This occurs because the more oxidizing environment is better able to maintain the chromium-rich passive oxide film.

Improved resistance to  $\text{H}_2\text{SO}_4$  has been obtained by using austenitic grades containing high levels of nickel and copper, such as 20Cb-3 stainless steel. In addition to reducing general corrosion, the increased nickel provides resistance to SCC. Because of its resistance to these forms of corrosion, 20Cb-3 stainless steel has been used for valve springs in  $\text{H}_2\text{SO}_4$  service. [2]

It can be seen in Fig. 5 that compared with other selected stainless steels, 316 offers greater corrosion resistance over a range of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) concentrations; however, 316 is still corroded in sulfuric acid, and Fig. 5 only displays results for tests conducted at 20 °C (70 °F). Conversations with the facility where the vaporizers were installed indicated that liquid ethanol enters the vaporizers at approximately 191 °F (88 °C) and exits as a vapor at 256 °F (124 °C).

Crum and Shoemaker evaluated the corrosion resistance of a range of both welded and non-welded alloys. When summarizing corrosion resistance tests in sulfuric acid, they found:

The curves in Figure 1 (see Fig. 6) represent a wide range of corrosion resistance. The stainless steels have two ranges of corrosion resistance. One range is at lower concentrations of sulfuric acid and another range at very high concentrations. The duplex

stainless steels are generally more resistant than the austenitic 316 stainless steel. Alloy 865 is somewhat superior the alloy 2507, while the standard 6% Mo alloy 25-6HN provides a marked improvement in corrosion resistance over the stainless steels at concentrations up to about 85%. However, the 27-7MO alloy displays much improved corrosion resistance, even better than the more expensive alloy C-276, at all concentrations up to 80%. Only alloy C-276 is resistant to higher temperature sulfuric acid at concentrations greater than 80%.

One compositional factor, which correlates with the relative corrosion resistance of the various alloys, is combined chromium and molybdenum and possibly nickel content. Another element known to increase corrosion resistance in sulfuric acid is copper content. The higher copper content of alloy 27-7MO makes a significant contribution to corrosion resistance, even though the copper addition is relatively small. [3]

It can be seen in Fig. 6 that 316 stainless steel only offers some degree of corrosion resistance in sulfuric acid concentrations below approximately 20% and above 85% for temperatures well below those present in the ethanol vaporizers. Though the exact concentrations of sulfuric acid formed within the vaporizers were unknown, the ethanol vaporizer operating temperatures were such that the corrosion resistance offered by the 316L stainless steel was reduced.

Through additional discussions with the user of the vaporizers, several important factors came to light. Specifically, the design of the vaporizer did not incorporate a clean-out ability, such that any biological or other debris collected during operation of the vaporizer could be removed. In addition, no schedule to wash down the external surfaces of the tubes had been provided for.

Upon semidestructive disassembly of the vaporizer, an appreciable amount of sulfur-containing sludge was found



in the bottom of the vaporizer. Therefore, over time, the concentration of the sulfur became increasingly concentrated. Although it was true that the sulfur content within the ethanol was very low (proprietary as to exact amount(s)), it was not appreciated that the concentration would precipitate out and consequently collect in the bottom of the vaporizer.

This would account for the sulfur-containing deposits on the tubes near the bottom of the tubes. The deposits found at the liquid line would be due to the separation of the biological precipitates from the ethanol at the liquid/vapor interface.

There were apparently multiple corrosion mechanisms occurring within the vaporizer. The formation of  $\text{H}_2\text{SO}_4$  was occurring due to the higher temperatures and presence of water vapor. This was evidenced by the substantial wall attack seen at the tube sheet. In addition, the tightly adhering biological material found at the bottom of the vaporizer and at the liquid interface would lead to oxygen depletion cells. If the presence of free oxygen is not available, then the stainless steel cannot maintain the necessary passivation layer and will suffer pitting corrosion at accelerated rates.

## Conclusions

A series of tube failures due to corrosion occurred in two-pass, shell-and-tube heat exchangers that utilized high-temperature steam within horizontal tubes to vaporize liquid ethanol within the shell. The heaviest corrosion observed was at the tube sheet near the steam inlet, and

tubes toward the top of the vapor region of the vaporizer as well as along the tops of the tubes within the liquid region of the vaporizer. It was determined that the tubes were made of 316L stainless steel, and the ethanol (and tube corrosion product) had elevated sulfur contents present. A body of literature that discussed the corrosion of various alloys (including 316L) as a function of service temperature and sulfuric acid concentration has been found. It was concluded that the corrosion of the tubes will concentrate along the surfaces with the highest temperature (at the steam inlet tube sheet and in the vapor region of the vaporizer) and along the tops of the tubes in the liquid region where localized nucleation and vapor flow around the tubes allowed localized corrosion to occur. Alternative tube materials which may offer improved corrosion resistance were recommended. In addition, when biological materials are refined, it appears to be necessary to have ample clean-out capabilities, as well as wash-out capabilities, to ensure that by-product built-up conditions are readily dealt with.

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