MATERIAL REQUIREMENTS FOR HEAT EXCHANGERS
IN GAS CONDENSING BOILERS

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Abstract
A corroded heat exchanger failing after only a few years of service has been investigated. Critical species causing corrosion were identified. These are sulfuric acid generated by oxidation of SO\textsubscript{2} to SO\textsubscript{3} and dissolution in water and nitric acid by dissolution of NO\textsubscript{2} in water. Corrosion products hydrolyse during service to a significant extent. By a calculation of burning of a extra light natural gas the origin and amount of aggressive reagents in the offgas is described. By condensation a sharp increase of concentration of aggressive reagents happens which is quantitatively described for sulfuric acid. In certain areas sulfuric acid condenses with a concentration of over 50%. There are only small amounts of this highly concentrated acid. Therefore only smaller corrosion rates of about 0.1 mm/a for aluminum occur. Condensates with lower concentrations however yield to a corrosion rate of aluminum up to 0.6 mm/a in practice because of their larger quantity and additional nitric acid condensation. Common stainless steels are recommended as heat exchanger material when taking corrosion resistance and price into consideration.

1. Introduction
After a service time of only a few years the heat exchanger of a gas condensing boiler showed significant corrosion and leakage in the lower (cooler) zone [1]. Heat exchanger consists of several aluminum alloys that are AlSi7Mg (body), AlMg0.5 (fins) and Al99.5 (sheet plates). In the upper zone corrosion rates of near 0.1 mm/a were obtained, in the lower zone after 5 years a 3 mm sheet showed leakages at a corrosion rate of 0.6 mm/a.

Figure 1 contains two views of the corroded heat exchanger. After slitting the body various corrosion products were found at heat exchanger tubes (Figure 2) and the tray and its fins (Figure 3), the latter part containing a hole. Table 1 summarizes chemical composition of corrosion products. During service in the upper zone mainly sulfates have been formed. In the lower zones mainly hydroxides with certain amounts of nitrates as well as some sulfates were main corrosion products.

Origin of SO\textsubscript{2} in the offgas can be calculated by a mass balance of burning reactions. Of special interest is a quantitative description of concentration effect of aggressive species during condensation. The last question that is evaluated is: "Which materials should be used for the boiler?"
Figure 1: Corroded heat exchanger. a) front view, b) top view

Figure 2: Corroded heat exchanger tube

Figure 3: Corroded tray with fins
### Table 1: Chemical composition of corrosion products

<table>
<thead>
<tr>
<th>species</th>
<th>eluate</th>
<th>[mg/g]</th>
<th>SO₄</th>
<th>Cl</th>
<th>NO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>fins, hot side</td>
<td>218</td>
<td>218</td>
<td>1.2</td>
<td>2.2</td>
<td>Al₂(SO₄)₃, Al(OH)₃</td>
</tr>
<tr>
<td>fins, cold side</td>
<td>0.8</td>
<td>0.8</td>
<td>0.9</td>
<td>57.8</td>
<td>Al(OH)₃, Al(NO₃)₃</td>
</tr>
<tr>
<td>crust in tray</td>
<td>4.4</td>
<td>4.4</td>
<td>1.3</td>
<td>81.4</td>
<td>Al(OH)₃, Al(NO₃)₃</td>
</tr>
</tbody>
</table>

2. Concentration of Corrosive Species in Gas Condensing Boilers

Sulfuric acid is the most detrimental chemical in such a heat exchanger with respect to corrosion. There are mainly two sources of sulfur: The gas and the burning air. The SO₂ and consequently the SO₃ content of the offgas can be calculated by the following assumptions/considerations.

Natural gas consists mainly of methane and reacts during burning according to equation 1:

$$CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$$ (1)

When using air with a humidity of 2 % (20.6 % O₂, 2 % H₂O, 77.4 % N₂, molar ratio O₂:H₂O:N₂ = 1:0.1:3.76) this reaction can be extended to equation 2:

$$CH_4 + 2 O_2 + 0.2 H_2O + 7.52 N_2 \rightarrow CO_2 + 2 H_2O + 0.2 H_2O + 7.52 N_2$$ (2)

This yields to an offgas composition with 9.3 % CO₂, 20.5 % H₂O, and 70.1 % N₂. Partial pressure of water is 0.205. 9.72 Moles of air react with 1 mole of natural gas to 10.72 Moles of offgas.

Below a mass balance for sulfur is made based on a sulfur content in the natural gas of 2 mg/m₃³ (average gas composition from austrian pipe system) and in the air of 4.5 mg/m₃³ (air analysis from Leoben, Austria, October 17th 2001 [3]). Equation 2 can be transferred into equation 3 (sulfur mass balance):

$$S_{natural \ gas} + 9.72 S_{air} = 10.72 S_{offgas}$$ (3)

Sulfur content in the offgas can be calculated from equation 3 as $(2 + 9.72\cdot4.5)/10.72 = 4.3 \text{ mg/m}^3 = 0.13 \text{ mole/m}^3 = 3\cdot10^{-3} \text{ l/m}^3 = 3\cdot10^{-6} \text{ bar SO}_2 \equiv 3 \text{ vpm SO}_2$. Assuming that 2 % of the SO₂ are further oxidized to SO₃, this yields to a concentration of SO₃ in the offgas of approximately 0.06 vpm.

This amount seems to be rather low, however by condensation of first liquid a significant concentration effect happens as shown in Figure 4. Only fractions of vpm of SO₃ yield to significant concentrations of sulfuric acid in the condensation zone. The mentioned 0.06 ppm
of SO$_3$ result in the hottest condensation zone in a 70 % sulfuric acid (black arrows in Figure 4). Only very few materials are resistant under such high concentrations of sulfuric acid at 60 to 100 °C. None of these resistant materials could be called technically widely used with a reasonable price when compared to most stainless steels.

Figure 4: Phase diagram H$_2$O – H$_2$SO$_4$ with consideration of SO$_3$ content in the gas phase at $p_{H2O} + p_{SO3} = 76$ Torr [4]

Corrosion of a metal in sulfuric acid takes place according to reaction 4. After this corrosion products tend to hydrolyze (equation 5), which yields to a closed loop for the sulfuric acid.

$$\text{Me} + \text{H}_2\text{SO}_4 \rightarrow \text{MeSO}_4 + \text{H}_2 \hspace{1cm} (4)$$

$$\text{MeSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Me(OH)}_2 + \text{H}_2\text{SO}_4 \hspace{1cm} (5)$$

In the upper condensation zone however the amount of condensed highly concentrated acid is very small. Furthermore there are only very limited quantities of water, which is necessary for hydrolysis. As a consequence lower corrosion rates are expected as corrosion diagrams predict. In practice a rate of 0.1 mm/a was found for aluminum alloys.

In the lower condensation zone large quantities of sulfuric acid still up to a concentration of 10 % can occur (dotted arrows in Figure 4). Consequently there is a large amount of water for hydrolysis of corrosion products. Furthermore there are also significant amounts of nitric acid present. Reactions in the lower condensation zone are firstly the attack of sulfuric acid (equations 4 and 5) and secondly the attack by nitric acid (equations 6 and 7 representing the corrosion reaction and hydrolysis):

$$\text{Me} + 2\text{HNO}_3 \rightarrow \text{Me(NO}_3)_2 + \text{H}_2 \hspace{1cm} (6)$$
Me(NO$_3$)$_2$ + 2 H$_2$O → Me(OH)$_2$ + 2 HNO$_3$ \hspace{1cm} (7)

There are loops for consumption and formation of sulfuric and nitric acid. In practice for aluminum corrosion rates of 0.6 mm/a were obtained.

### 3. Materials Selection

The above conditions of the two condensation zones can be drawn in corrosion diagrams for different materials. There the corrosion rate is expressed usually in mm/a and is drawn as function of concentration and temperature. Consequently the lines in such diagrams express conditions under which same corrosion rates occur. For the investigated case history the windows of operation valid for the upper (60-100 °C, 60-70 % H$_2$SO$_4$) and for the lower (30-60 °C, 3 - 10 % H$_2$SO$_4$) condensation zone as well are shown in Figure 5 [5]. There is a high rate of corrosion of several mm/a in the upper zone. The reasons for lower corrosion rates in practice have been discussed already.

In the lower condensation zone there are large amounts of diluted acid that reach corrosion rates between 0.1 and 2.0 mm/a. This is in accordance to the obtained lifetime of several years and a corrosion rate of approximately 0.6 mm/a in reality.

![Corrosion diagram of aluminum in sulfuric acid](image)

**Figure 5:** Corrosion diagram of aluminum in sulfuric acid [5]

Figures 6 to 9 show corrosion diagrams of several important construction materials that are known as corrosion resistant in sulfuric acid. These are two stainless steels AISI 304 (CrNi 18-8) and 316 (CrNiMo 18-10-2), a nickel-base alloy (Hastelloy C: NiCrMoWFe 15-16-4-6) and titanium. The diagrams for sulfuric acid and not for nitric acid have had to be chosen since especially in case of stainless steels nitric acid yields to passivation.
Figure 6: Corrosion diagram of stainless steel 304 in sulfuric acid [5]

Figure 7: Corrosion diagram of stainless steel 316 in sulfuric acid [5]

Figure 8: Corrosion diagram of Hastelloy C in sulfuric acid [5]

Figure 9: Corrosion diagram of Titanium in sulfuric acid [5]

In Figures 6 to 9 conditions of upper corrosion zone are not drawn due to lack of relevance as explained above. Only the conditions in the lower condensation zone are shown. It can be
seen clearly that stainless steels have a similar or significantly better corrosion resistance than aluminum in sulfuric acid. Additionally one has to consider that nitric acid, which is also present passivates stainless steel in contradiction to aluminum. So there is a further improvement which cannot be seen in Figures 6 and 7 when comparing them with Figure 5. The higher alloyed steel has the better corrosion resistance.

Hastelloy C is completely immune to corrosive attack under such conditions however has the highest price. Titanium is a often mentioned a highly corrosion resistant material. Under the present conditions however it does not show a better performance than common stainless steels. Therefore and because of its high price it cannot compete with stainless steel in heat exchangers of oil condensing boilers.

Finally one argument has to be considered: Only a small portion of boilers even when made of aluminum failes during service, which at the first glance could be interpreted as a contradiction to the results presented above. However one should not forget that in reality many condensing boilers are not operated below dew point but instead at higher offgas temperatures above dewpoint. As a consequence no condensation happens and therefore instead of electrochemical corrosion only chemical corrosion can occur. This yields at given temperatures to corrosion rates significantly lower by several orders of magnitude.

4. Conclusion

After investigating a case study and taking some theoretical aspects into consideration the following conclusions can be drawn from the present study:

- Sulfuric acid and nitric acid are most corrosive reagents in oil condensing boilers.
- Even low amounts of both reagents in the offgas yield to high concentrations in the condensate and to highly aggressive environments.
- Aluminum is an improper material for the present application at temperatures below dew point.
- When considering corrosion resistance and price conventional stainless steels seem to be the most proper class of materials for heat exchangers in oil condensing boilers. Nitric acid yields to passivation of stainless steels.

As long as working temperature of the boiler is above the dew point of the offgas also aluminum can be used without large problems.

Literature