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Corrosion in coal gasification environments at 550 °C

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Abstract. — Coal gasification combined cycle power plants promise lower emissions and higher efficiencies than conventional pulverized coal power plants. Process economics favor compact, high pressure, slagging gasifiers, usually of the entrained type, for most coals. The high raw gas temperature in such plants prevent the use of uncooled metals in contact with the gas. Direct metal/gas contact usually occurs in downstream syngas coolers. Water or steam cooled heat exchangers are used to extract heat from the syngas to produce steam at temperatures generally not exceeding 500 °C. Under the dynamic process conditions in the syngas cooler, the syngas composition does not shift to low temperature equilibrium, but the high temperature (1100-1300 °C) gas composition is quenched in. Laboratory corrosion studies on model alloys, with 20Cr and 35% Ni, were carried out at 550 °C using nonequilibrium gas compositions, representative of commercial oxygen blown entrained slagging gasifiers. Such processes can broadly be divided in two types: those in which little or no water or steam is added to the gasifier, and processes where 10-30% steam or water is added (dry coal basis). The former processes produce syngas with a very high CO content, and a very low CO₂ and H₂O content. The latter processes produce a syngas which usually contains 10-20% steam and have a somewhat lower CO content. In the water-free syngas nonprotective oxide/sulfide scales formed and significant corrosion rates were observed. Oxide/sulfide scales also formed in syngas containing 15% steam, but corrosion rates were generally low.

1. Background.

Coal gasification technology is close to commercial reality. Several large demonstration plants in the 100-200 MWe range are in operation or have successfully completed several years of operation. Development of coal gasification has gone through several stages. It was originally conceived as a means to produce clean gaseous and/or liquid fuels from coal. Later on it was thought that integrated coal gasification, combined cycle power plants, (IGCC's) would be able to produce electricity at a lower cost than conventional pulverized coal boiler-steam turbine plants, because of their higher efficiency. More recently environmental concerns have increased interest in IGCC technology, because such plants promise to produce electricity with much lower emissions and waste products than conventional boilers. The efficiency of IGCC plants using modern gas turbines is also considerably higher than that of pulverized coal-fired power stations. Therefore, IGCC plants will also produce considerably less CO₂ per unit of electricity produced.

The most favored processes operate at relatively high temperatures, generally above the melting point of coal ash as they produce the lowest volume and the most inert solid waste. The gasification reactors of such processes generally operate in the 1300-1600 °C range.
They are refractory lined, as the service life of metal alloys is too short at these temperatures to be practical. The sensible heat in the raw syngas must be recovered to increase the overall efficiency of the process. This is generally done by raising steam in both radiant and convective syngas coolers. In most systems the syngas coolers are only used as evaporators because most superheating can be accomplished in the waste heat boiler of the gas turbine. This limits the metal temperature to 325-450 °C. In some systems, it is desirable to superheat or reheat some of the steam in the syngas coolers. High steam temperatures and pressures are usually not economically justified. Thus, steam superheat temperatures range from 500-550 °C and corresponding metal temperatures are 550-600 °C. Thus, the temperature range of greatest economical interest for the study of high temperature corrosion in coal gasification environments is 300-600 °C. 550 °C was selected for corrosion studies reported here.

2. Gas compositions and equilibria.

Gas compositions in syngas coolers depend on the coal gasification process and the type of coal used. The oxygen partial pressure is mostly process related. Entrained slagging gasifiers, with a dry pulverized coal feed system produce a syngas with a very low steam content generally less than 1% and a high CO/CO₂ ratio. Gas composition 1 (Tab. I) is typical for such processes. Entrained slagging gasifiers using a coal-water slurry feed system, produce a syngas with a higher H₂O and CO₂ content, depending on the coal/water ratio of the feed material. Gas composition 2 is fairly typical of the syngas produced by such gasifiers. The H₂S content of the syngas depends mainly on the sulfur content of the coal being gasified. Low sulfur coals with about 1% S or less generally produce syngas with an H₂S content of 0.15-0.25%, while high sulfur coals containing 2-3% sulfur generally result in syngas with 0.6-1% H₂S.

Table I. — Syngas compositions, vol. %.

<table>
<thead>
<tr>
<th></th>
<th>Gas 1</th>
<th>Gas 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>32</td>
<td>30</td>
</tr>
<tr>
<td>H₂O</td>
<td>–</td>
<td>15</td>
</tr>
<tr>
<td>CO</td>
<td>64</td>
<td>45</td>
</tr>
<tr>
<td>CO₂</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>H₂S</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>HCl</td>
<td>400 ppm</td>
<td>400 ppm</td>
</tr>
</tbody>
</table>

It has generally been the practice to carry out corrosion tests in equilibrated gas compositions, to better control oxygen and sulfur partial pressures during exposure. However in gasifiers the hot syngas is cooled rapidly in its passage through the syngas coolers and the high temperature equilibrium composition established at 1000-1600 °C is essentially unchanged. The gas is generally also considerably hotter than the metal gas exchanger surface. Thus, nonequilibrium conditions are likely in syngas coolers. It is of interest to compare the oxygen and sulfur partial pressures of equilibrium and nonequilibrium gases, derived from the gas compositions given in table I. Oxygen and sulfur partial pressures of equilibrium gas
compositions were calculated by Norton [1] using an in-house computer program. Nonequilibrium partial pressures were calculated using a procedure suggested by Perkins [2]. For instance, the $p_{O_2}$ partial pressure is calculated as follows:

$$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$$  \hspace{1cm} (1)

$$K_p = \frac{p_{CO_2}}{p_{CO}(p_{O_2})^{1/2}}$$  \hspace{1cm} (2)

$$\log p_{O_2} = 2 \log \frac{p_{CO_2}}{p_{CO}} - 2 \log K_p$$  \hspace{1cm} (3)

where $K_p =$ equilibrium constant at temperature of interest (from Janaf tables)

$$\frac{p_{CO_2}}{p_{CO}} = \text{pressure ratio of high temperature syngas}$$

$p_{O_2} =$ pseudo equilibrium oxygen pressure for high temperature syngas at lower temperatures

For water containing syngas, the nonequilibrium $p_{O_2}$ can also be calculated using the $H_2/H_2O$ ratio. This gives a different value when the gas is not in equilibrium. A similar approach is used to calculate the nonequilibrium $p_{S_2}$, using the high temperature $H_2/H_2S$ ratio, but the low temperature $K_p$ for the reaction.

Fig. 1. — Oxygen partial pressure of dry syngas.
Fig. 2. — Oxygen partial pressure of wet syngas.

Fig. 1. — Oxygen partial pressure of dry syngas.
Fig. 2. — Oxygen partial pressure of wet syngas.
Oxygen partial pressures for gas composition 1 are shown in figure 1. It can be seen that the nonequilibrium partial pressure is significantly lower than the equilibrium pressure at temperatures below 700 °C. The equilibrium partial pressure also depends somewhat on total pressure while the nonequilibrium pressure is pressure independent. Oxygen partial pressures for gas composition 2 are shown in figure 2. The nonequilibrium $p_{O_2}$ is again considerably lower than the equilibrium $p_{O_2}$, especially when calculating the $p_{O_2}$ from the CO$_2$/CO ratio. A comparison of the nonequilibrium oxygen partial pressures in figures 1 and 2 shows a constant difference between the $p_{O_2}$ of the gases of about one order of magnitude.

Figure 3 shows the equilibrium and nonequilibrium sulfur partial pressures for syngas containing 0.2 and 0.8% H$_2$S. The $p_{S_2}$ was found to be largely independent of the oxygen partial pressures of the two gases. The nonequilibrium $p_{S_2}$ curves show a discontinuity between 400 and 500 °C, which is associated with the boiling point of sulfur at 440 °C. The equilibrium curves do not show this discontinuity. This may be an extrapolation error in the computer program, which was originally developed for use at elevated temperatures, and may not take into account the change of the sulfur at 440 °C.

![Sulfur partial pressure of syngas](image)

**Fig. 3.** Sulfur partial pressure of syngas.

### 3. Corrosion experiments.

EPRI and Lockheed have carried out corrosion studies in gasifier environments, mostly with gas compositions similar to composition 2 in table I, for several years [2, 3]. Corrosion tests are generally carried out in 200-500 h cycles, using nonequilibrium gases. Experimental details are given in the cited references. It is of interest to note that flow rates are kept high enough to prevent shifts in gas composition, generally 50-60 liter/h. Under these conditions corrosion losses of stainless steels containing 20-25%Cr are generally quite low as shown in table III for the 3 model alloys, whose composition is given in table II. Corrosion in the dry gas composition 1 was many times more rapid and quite erratic due to scale spallation in cyclic
tests. Therefore, isothermal tests of different length were used to study corrosion without excessive scale spallation. Results are also given in table III. The metal losses reported are obtained mostly from direct thickness measurements using an optical microscope. When the corrosion loss becomes very low, direct measurements become less accurate. Therefore, the thickness of the inward growing part of the scale was also measured and was used instead of metal loss when it was larger than the metal loss observed. The data presented in table III indicate not only that corrosion rates in gas 1 are considerably higher than in gas 2, but that the effect of the two alloying additions is also different in the two gas compositions, despite their relatively modest difference in $p_{O_2}$ and a similar $p_{S_2}$.

Table II. — Alloy composition (wt %).

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Nb</th>
<th>V</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy 1</td>
<td>bal</td>
<td>35</td>
<td>21</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>bal</td>
<td>37</td>
<td>20</td>
<td>3.7</td>
<td>-</td>
<td>1.0</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>bal</td>
<td>35</td>
<td>20</td>
<td>-</td>
<td>3.6</td>
<td>1.0</td>
<td>0.3</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Table III. — Metal loss at 550 °C (µm).

<table>
<thead>
<tr>
<th></th>
<th>150 h</th>
<th>Gas$^1$</th>
<th>Gas$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600 h</td>
<td>1350 h</td>
<td>600 h</td>
</tr>
<tr>
<td>Alloy 1</td>
<td>30</td>
<td>80</td>
<td>134</td>
</tr>
<tr>
<td>Alloy 2 (Nb)</td>
<td>40</td>
<td>114</td>
<td>155</td>
</tr>
<tr>
<td>Alloy 3 (V)</td>
<td>25</td>
<td>40</td>
<td>49</td>
</tr>
</tbody>
</table>

$^1$ isothermal exposure, cyclical exposure loses significantly higher.

$^2$ exposure in three 200 h cycles.

4. Microscopic examination and scale analysis.

Figure 4 shows optical photomicrographs of the alloys after isothermal exposure to gas 1 for 1350 h. Scale growth on all alloys exposed was rapid and resulted in a coarse grained inhomogeneous inner scale, with a coarsely crystalline outer scale. Extensive SEM/EDS and XRD analyses of the scales are in progress and will be reported elsewhere. In general, the scales have 3 major components:

1) Outer scale: consists mainly of Fe, Ni sulfides with minor amounts of chromium;

2) Light gray layer on top of inner scale. It consists mainly of Cr Fe (Ni) sulfides, i.e. a mixture of Cr$_2$S$_3$ and FeCr$_2$S$_4$ spinel. The latter was identified by XRD;
Fig. 4. — Photomicrographs of alloy after 1350 h exposure to dry syngas: a) alloy 1; b) alloy 2 (Nb); c) alloy 3 (V).

3) The dark inner scale consist generally of oxides and sulfides with sulfur rich and sulfur poor areas, sometimes with a high iron content. Probable mineral species present are FeCr$_2$O$_4$ and Cr$_2$O$_3$, and Fe (N, Mn) S, in oxide rich areas. FeCr$_2$O$_4$ was identified by
Fig. 5. — Photomicrographs of alloys after 600 h exposure to wet syngas: a) alloy 1; b) alloy 2 (Nb); c) alloy 3 (V).

XRD in some samples. \( \text{Cr}_2\text{S}_3 \) and \( \text{FeCr}_2\text{S}_4 \) were predominant in sulfur rich areas;

4) Nb and V are only present in the inner scale of alloys containing these elements.
Figure 5 shows optical photomicrographs of the alloys after exposure for 600 h to gas composition 2. The scales are much thinner, which is in agreement with the much lower metal loss observed. Generally a sulfur rich outer scale and an oxide rich inner scale is present. SEM/EDS analysis showed that the outer scale again consists mainly of iron sulfide, generally with less Ni present than after exposure to gas 1. The inner scale is more homogeneous than after exposure to gas 1. The inner scale consists mainly of Cr₂O₃, FeCr₂O₄, and Fe (Mn, Ni) S. V and Nb are again present in the inner scale only.

5. Discussion.

Until now most researchers have used equilibrium gas compositions in corrosion experiments. The curves shown in figures 1-3 indicate that the difference in oxygen and sulfur partial pressure between equilibrated and nonequilibrated gas compositions is rather small above 700 °C. However at syngas cooler operating temperatures of 300-600 °C, the difference is quite significant. In figure 6 equilibrium and nonequilibrium composition of the dry and wet gas have been plotted on the Cr-O-S phase equilibrium diagram for 500 °C. If the distance from the Cr₂S₃ - Cr₂O₃ phase boundary is taken as a measure of the sulfidizing potential of the gas, there will probably not be much difference in sulfidizing potential between equilibrium and nonequilibrium dry gases. In the wet gas the sulfidizing potential of the nonequilibrium gas may be significantly higher if its \( p_{O_2} \) is mainly determined by the \( CO_2/CO \) ratio. Experiments carried out by Perkins indicate that corrosion rates in nonequilibrium gases are significantly higher than in corresponding equilibrium gases [2]. The carbon activity of the calculated equilibrium gas composition increases rapidly with decreasing temperature and becomes much higher than unity, especially for the dry gas. This indicates that carbon would be deposited if equilibrium was obtained either in syngas coolers or corrosion experiments. This has not been observed in syngas coolers or in our experiments where a relatively high gas velocity (about 60 l/h) is maintained. It is concluded that nonequilibrium gases can be used in low temperature corrosion experiments and are preferred because they simulate actual service conditions more closely.

The corrosion experiments indicate significant differences in corrosion rate after exposure to the dry and wet gases. Since a protective Cr₂O₃ rich scale is not formed in either gas, the difference cannot be ascribed to a “kinetic boundary” as defined by Perkins [4] and Natesan [5]. It is not clear at this point whether the large difference in corrosion kinetics observed is due to the difference in \( p_{O_2} \) of the gases used or whether the presence of \( H_2O \) has an effect. Limited data reported by Stroosnyder indicate that the presence of steam may reduce the corrosion rate [6]. Experiments with nonequilibrium gases in which the \( p_{O_2} \) is kept constant but the steam content is varied, must be carried out to clarify the role of water vapor. These experiments will be carried out in the near future.

The effect of alloying additions on the corrosion rate observed is also not straightforward as previously thought. Niobium was shown to increase corrosion resistance at high temperature experiments by Baxter and Natesan [7]. This also appears to be the case in the wet gas at 550 °C where a thin seemingly protective inner scale is formed, although the scale composition is not much different from that of the Nb free alloy, except for the presence of about 10% Nb oxide. In the dry gas, the Nb addition to the alloy is definitely detrimental, despite the fact that the scale is more homogeneous than that of the base alloy and generally higher in Cr₂O₃. Vanadium additions were previously shown to result in dense low sulfur Cr₂O₃ scales under somewhat more oxidizing conditions and in field trials [8]. In this study the vanadium additions do not result in compact low sulfur scales in the wet gas. Surprisingly
the corrosion rate is significantly reduced in the more sulfidizing dry gas, despite the formation of an inhomogeneous iron rich scale. The only conclusion we can draw at this point is that the effect of alloying additions is critically dependent on the gas composition.

Although the model alloys tested here are not intended for commercial application, it is worthwhile to speculate if similar commercial alloys are suitable for commercial use. In the wet gas, corrosion rates are quite low. Even when a linear extrapolation is used, they are only 0.1-0.2 mm/year. This should be commercially acceptable, especially since it is likely that growth kinetics under steady state operations will be closer to parabolic, thus yielding an even lower corrosion rate. Linearly extrapolated corrosion rates in the dry gas are clearly unacceptable. However, the corrosion tests results in table IV indicate roughly parabolic kinetics. Calculations from the limited data indicate the following $K_p$'s and corrosion rates:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$K_p$ ($\mu$m$^2$/h)</th>
<th>$C$ (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>0.32</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>2.7</td>
<td>0.15</td>
</tr>
</tbody>
</table>

In-plant corrosion rates will probably be somewhat higher, due to thermal cycling and scale spallation at intervals less than one year. Even so the alloys may survive in dry gas environments for several years, if a corrosion allowance of about 3 mm is applied. However, the use
of alloys with lower corrosion rates is clearly desirable and necessary to obtain service lives in the 20 year range.

6. Conclusions.

1) Nonequilibrium gas composition formed at elevated temperatures are preferred to study mixed oxidant corrosion at 300-600 °C. Data from coal gasifiers and laboratory experience indicates that no major shifts towards an equilibrium gas composition occur in this temperature range.

2) Protective scales consisting mainly of chromium oxide do not form in gasifier environments typical of the present generation of coal gasifiers on the alloys investigated. However in the temperature range studied, mixed oxide/sulfide scales may have growth rates which are slow enough for commercial application; especially in environments containing steam.

3) Corrosion rates in the water-free gas are significantly higher than in the gas containing 15% steam. It is not clear whether this difference is due to the relative small difference in oxygen partial pressure, about 1 order of magnitude, or due to the presence of H₂O by itself.

References