HIGH TEMPERATURE CORROSION BEHAVIOUR OF MATERIALS FOR INCINERATION PLANTS

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ABSTRACT
The present research was undertaken to study the corrosion resistance of three types of candidate materials for superheater sections under simulated waste incineration conditions. A 9Cr1Mo steel, an AISI 310SS and the Ni-based alloy Sanicro 28, were tested on a laboratory scale and on a pilot scale. Different flue gas composition (up to 2500 mg/Nm$^3$ of HCl and 1500 mg/Nm$^3$ of fly ash) were selected. Laboratory tests were carried out on an appropriate furnace in static condition (very low flue gas velocity), up to 200 hrs. Metal and gas temperature were kept constant at 500°C. Pilot scale tests were carried out by using a 0.3x0.3m cross-section combustor, with flue gas velocity of 5m/s. Appropriate air-cooled probes designed to operate at metal temperature of 500°C were used, up to 200 hrs as test time. Qualitative correspondence was found between the two sets of experimental tests, but quantitative results were not comparable. Methallographic evaluations, metal loss measurements and weight loss analysis evidenced as best results were obtained with Sanicro28. Maximum corrosion attack observed on the tested materials was 240µm, 182µm and 107µm respectively for 9Cr1Mo, AISI310 and Sanicro 28 under the most aggressive conditions, but intergranular corrosion attack could not be neglected for AISI310. Main experimental results are reported and discussed.

INTRODUCTION
Environment friendly managing systems for waste incineration plants are nowadays one of the main items to deal with. Modern flue gas cleaning equipment can meet very strict emission requirements and if heat or power is generated from incineration, alternative fuels are saved and waste incineration becomes more attractive from an economical point of view. Household waste contains a number of different compounds which are very corrosive to the boiler tubes (evaporators and superheaters). Since materials performance is strictly related to steam and flue gas temperatures, additional information on corrosion performance of candidate metals alloys is needed for selecting materials to design new plants with higher operating temperature. The type and extent of corrosion depends markedly on metal temperature and the waste being burnt. When high amount of plastics are burnt (i.e. refuses containing PVC), chlorination seems to cause a major corrosion problem (Rahmel, 1989; Krause, 1989; Krause, 1996; Starr, 1997). Metal chlorides and oxychlorides are formed, which are generally non-protective and tend to evaporate because of their high vapour pressures (Ihara, 1982; Ihara, 1983; Haanappel, 1992). In addition attack by ashes, metal compounds and alkali salts, which condense on the boiler tubes, play an important role on corrosion attack. With these operating
condition a proper selection of materials to be used in high temperature sections represent a very important item to reduce corrosion failures. In this paper results obtained with laboratory tests and with pilot scale tests are reported and discussed.

MATERIALS AND METHODS
Materials selected for the experimental programme were a ferritic steel 9Cr1Mo (9Cr), an austenitic low carbon stainless steel AISI 310 (310) and the Ni-Cr alloy Sanicro 28 (S28). Two test methodologies were adopted: a) test in a laboratory furnace with selected flue gas composition and low gas velocity (cm/s); b) tests on a 0.3mx0.3m cross-section combustor, with flue gas velocity of 5m/s and selected flue gas composition.

In case b) an appropriate probe design was adopted in order to operate at a constant metal temperatures of about 500°C. Each probe was independently supplied with cooling air, air flow rate was measured on a rotameter and thermocouples were located at the interface between the probe body and first test specimen, to ensure the specified temperature were maintained during the test period. Selected flue gas temperature was 600°C. Each probe was designed to carry on 6 specimens and three probes were inserted directly into the combustor in well defined locations, where test conditions were fitted. In tab.1 and tab.2 testing parameters for case a) and b) are summarised.

**TABLE 1 Testing conditions for laboratory investigations**

<table>
<thead>
<tr>
<th>Test run</th>
<th>Flue gas composition in addition to 9%O₂, 11% CO₂, 9% H₂O, N₂ rem</th>
<th>Testing time (h)</th>
<th>Materials and number of specimens tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fly ash 1500 mg/Nm³ HCl 2500 mg/Nm³</td>
<td>100</td>
<td>9Cr 310 S28 n. 6 n. 6 n. 6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>9Cr 310 S28 n. 6 n. 6 n. 6</td>
</tr>
<tr>
<td>2</td>
<td>Fly ash 250 mg/Nm³ HCl 200 mg/Nm³ NaCl 250 mg/Nm³</td>
<td>See test 1</td>
<td>See test 1 See test 1 See test 1</td>
</tr>
<tr>
<td>3</td>
<td>Fly ash 250 mg/Nm³ HCl 20 mg/Nm³ NaCl 250 mg/Nm³</td>
<td>See test 1</td>
<td>See test 1 See test 1 See test 1</td>
</tr>
<tr>
<td>Other conditions</td>
<td>Flue gas temperature 500°C Materials (specimens) temperature 500°C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 2 Testing conditions on the 0.3x0.3 combustor**

<table>
<thead>
<tr>
<th>Test run</th>
<th>Flue gas composition in addition to 9%O₂, 11% CO₂, 9% H₂O, N₂ rem</th>
<th>Testing time (h)</th>
<th>Order of specimens in the probes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fly ash 1500 mg/Nm³ HCl 2500 mg/Nm³</td>
<td>20 70 130 180 200</td>
<td>9Cr 310 S28 9Cr 310 S28 9Cr 310 S28 9Cr 310 S28</td>
</tr>
<tr>
<td>2</td>
<td>Fly ash 250 mg/Nm³ HCl 200 mg/Nm³ NaCl 250 mg/Nm³</td>
<td>See test 1</td>
<td>See test 1</td>
</tr>
<tr>
<td>3</td>
<td>Fly ash 250 mg/Nm³ HCl 20 mg/Nm³ NaCl 250 mg/Nm³</td>
<td>See test 1</td>
<td>See test 1</td>
</tr>
<tr>
<td>Other conditions</td>
<td>Flue gas temperature 600°C Materials (specimens) temperature 500°C</td>
<td>Flue gas velocity 5 m/s</td>
<td></td>
</tr>
</tbody>
</table>
Solid NaCl particles, with controlled size, was introduced into the flue gas since the flue gas cleaning system to be realised on a real plant was based upon an innovative process which requires a Na-based absorbent.

RESULTS AND DISCUSSION

Laboratory tests
Experimental results were evaluated in terms of metal loss on samples tested at 200h by means of SEM-EDS analyses, weight changes (according to ASTM G1) and microstructural investigations. Metal loss measurements were affected by wide scattering, so that they were considered not really significative. Weight loss data (Fig.1) allowed more consistent considerations: it existed a significative difference between values measured after test 1 and after tests 2/3; scattering for results of test 1 was higher; the best behaviour was obtained with S28, followed by AISI310 and 9Cr.

Test 1, with 2500 mg/Nm3 of HCl, was the most aggressive environmental condition. For AISI310 and S28 (materials with higher content of Cr and Ni), the difference among test 1 and tests 2/3 was very clear after 200h as exposure time: weight loss values reduced to about 40% and 20% of those obtained after test 1. This results were compatible with the existence of a threshold value for HCl of about 200 mg/Nm3 and indicated also that material damages for low HCl values were essentially controlled by under deposit corrosion for the presence of fly-ash and NaCl. Only for 9Cr, less resistant to corrosion attack, the difference among various tests was always significative, less damages were still obtained with lower HCl concentration in the flue gas.

![Fig. 1 Weight loss results after laboratory tests](image)

The previous analysis must also take into account results of microstructural characterisation. In particular data obtained for AISI 310 should be considered with great attention since intergranular corrosion was present (Fig. 2).

![Fig. 2 AISI 310 - Test 2 after 200 h (chemical etching HNO3- acetic acid HCl-glicerolo, 30 s)](image)
Pilot scale tests
Experimental tests were carried out on a fluidised bed combustor 0.3x0.3x2.1 m in size at CoalTechnology Dev. Division of British Coal (UK). Each specimen was weighted before each test and then measured at six different radial position before being assembled on the probe carrier. Prior to assembly and measurements samples were also cleaned with acetone to ensure that surfaces were free from dirt and grease. For each run and exposure time, average values of weight loss are reported in Fig. 3, 4 and 5.

Fig. 3. Test no.1 - Weight loss vs. exposure time for tested materials

Fig. 4. Test no.2 - Weight loss vs. exposure time for tested materials

Fig. 5. Test no.3 - Weight loss vs. exposure time for tested materials
As general consideration, test no.1 with highest concentration of HCl in the flue gases realised the most aggressive environmental condition. Starting from 70 h as exposure time a significative difference in weight loss was evidenced between test no. 1 and tests nos. 2/3. Taking into account the calculated standard deviations, the possible threshold value of about 200 mg/Nm3 for HCl concentration was confirmed. Metal loss results showed as maximum corrosion attack 240 µm, 182 µm and 107 µm respectively for 9Cr1Mo, AISI310 and Sanicro 28 under the most aggressive conditions after 200h. In any case intergranular corrosion could not be neglected for AISI310. A comparison between results obtained in laboratory tests and those related to pilot scale experiments evidenced that laboratory tests gave lower values of corrosion attack, in particular for test no. 1 when corrosion mechanisms were essentially dominated by the gas phase. Lower values were also obtained when spalling of corrosion products was observed on the pilot tests as for 9Cr in tests nos. 2 and 3. Methallographic analyses and SEM-EDS evaluations of the corrosion scale (morphology and composition) confirmed as main damaging mechanism was due to the formation of metals chlorides (mainly iron chlorides) for tests no.1, oxychlorides and under deposit attack for tests nos. 2 and 3. Results can be explained according to the cyclic oxidation model (Ihara, 1981; Hupa, 1989; Bramhoff, 1989; Gottjaelp, 1996) based upon chemical reactions (I), (II), (III), as also confirmed by X Ray diffraction analyses.

\[
\begin{align*}
\text{Fe} + \text{Cl}_2 &= \text{FeCl}_2 \quad (I) \\
\text{Fe} + 2\text{HCl} &= \text{FeCl}_2 + \text{H}_2 \quad (II) \\
4\text{FeCl}_2 + 3\text{O}_2 &= 2\text{Fe}_2\text{O}_3 + 4\text{Cl}_2 \quad (III)
\end{align*}
\]

Nevertheless, formation of FeCl₃ could not be excluded due to the higher vapour pressure of this compound with respect to FeCl₂.

No pitting corrosion was observed, but a combination of uniform wastage and erosion corrosion was revealed. The predominant attack was uniform wastage in which the attack was highest on the side facing the flue gas direction suffering direct impingement from the same gases. In order to have a possible estimation of corrosion attack for exposure times higher than 200h, experimental data were used for a regression fit, in the case of a supposed linear-parabolic kinetic (attack due to oxidation and metal chloride formation with evaporation, eqn. V) and parabolic kinetic (oxidation attack, eqn. IV). WL represents experimental weight loss values.

\[
\begin{align*}
\frac{d(WL)}{dt} &= K_p/WL + K_v \quad (IV) \\
\frac{d(WL)}{dt} &= K_{p^*}/WL \quad (V)
\end{align*}
\]

Results must be used with extreme caution since some hypothesis are needed for the extrapolation procedure, such as uniform wastage, constant operating conditions, no acceleration of corrosion attack due to spalling phenomena or molten compounds, no reduction of corrosion attack due to formation of protective scale. With these assumptions linear and parabolic coefficients calculated are summarised in tab. 3.

**TABLE 3 Constants to be used with linear-parabolic and parabolic kinetic models**

<table>
<thead>
<tr>
<th>Test run</th>
<th>Materials</th>
<th>Kp (mg/cm²)²h⁻¹</th>
<th>Kv (mg/cm²)h⁻¹</th>
<th>r (%)</th>
<th>Kp⁺ (mg/cm²)²h⁻¹</th>
<th>r (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9Cr</td>
<td>negligible</td>
<td>0.453925</td>
<td>99</td>
<td>31.17</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>AISI310</td>
<td>negligible</td>
<td>0.250600</td>
<td>85</td>
<td>9.26</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>S28</td>
<td>negligible</td>
<td>0.227212</td>
<td>89</td>
<td>7.08</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>9Cr</td>
<td>0.96637</td>
<td>0.227212</td>
<td>97</td>
<td>2.70</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>AISI310</td>
<td>0.0388</td>
<td>0.00399</td>
<td>93</td>
<td>0.084</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>S28</td>
<td>0.094</td>
<td>0</td>
<td>99</td>
<td>0.094</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>9Cr</td>
<td>4.15</td>
<td>0</td>
<td>90</td>
<td>4.15</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>AISI310</td>
<td>0.053</td>
<td>0</td>
<td>97</td>
<td>0.053</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>S28</td>
<td>0.115</td>
<td>0</td>
<td>92</td>
<td>0.115</td>
<td>92</td>
</tr>
</tbody>
</table>

With values reported in tab. 3 estimated corrosion attack for one year operation where prohibitive for all materials tested with 2500 mg/Nm3 HCl in flue gas (> 5 mm/y for linear-parabolic, 1.0-1.5 mm/y for
parabolic) and they reduced to 0.2-0.5 mm/y for 250 mg/Nm3 HCl in flue gas. Best behaviour was obtained with S28 (about 0.20 mm/y for test no. 2/3) A comparison of values obtained with the model and data related to exposure in real waste incineration plants, the Högdalen incinerator (Häggblom, 1994) gave satisfactory results for maximum exposure time of 1000h as well as for other literature data (Kim, 1990; Haanappel, 1992; Salmenoja, 1995; Klower, 1995; Gottjaelp, 1996; Starr, 1997).

CONCLUSIONS

Laboratory tests and pilot scale tests were carried out on three candidate materials for waste incinerator superheaters, 9Cr1Mo, AISI310 and Sanicro 28, for a total testing time of 200h and with particular concerns about chlorination. Qualitative correspondence was found between the two sets of experimental tests. Quantitative results were not comparable and pilot scale tests were more indicative of real materials behaviour. For high HCl content in flue gas iron chlorides formation and evaporation were the main damaging mechanisms. With HCl concentration values higher than about 200 mg/Nm3 and materials temperature of 500°C the kinetic of the corrosion attack was linear rather than parabolic. For this case, in addition to metal chlorides evaporation (iron, chromium, nickel chlorides), surface scale resulted also porous and non protective. High chromium content (without σ phase formation) and high nickel content in materials selected, significantly reduced the corrosion attack, since higher vapour pressure of iron chlorides and chromium tendency to form protective chromium oxides up to 500°C.

REFERENCES