MATERIALS PROBLEMS IN INCINERATION PLANTS

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ABSTRACT

Corrosion problems in present-day incinerators can range from insignificant to catastrophic, depending upon their design, the type of waste being incinerated, and the materials of construction. Because each incinerator is unique, the best means of finding the solution to an existing problem is to place test racks in the field and evaluate the results after an extended period of exposure. This paper covers the results obtained from such studies and how existing problems were solved. It is shown that laboratory tests can further aid in making materials recommendations, but care must be taken to establish that the laboratory environment evaluated is relevant to the actual application.

INTRODUCTION

Depending on incinerator design, nature of the fuel utilized, and type of waste incinerated, there is a wide variation in the extent of metallic corrosion encountered from one installation to another. Some plants have operated for years with very few maintenance problems, whereas others are under continual repair. The presence of sulfur and/or chlorine which can arise from either the fuel or waste is well-recognized as being potentially very harmful. The situation can be further aggravated if substances such as lead, sodium, potassium, etc. are also present.

A possible first approach to solving high-temperature materials corrosion problems that can arise in such systems is the use of laboratory testing to establish the relative performance capabilities of various possible alloy alternatives. In this paper, it is demonstrated that such an approach must be taken with care, as lack of information regarding the actual nature of the field environment can lead to laboratory testing results which are misleading. At the same time, an example is presented which shows how laboratory testing can be used to full advantage in solving materials problems in incineration plants.

The key consideration in approaching an issue of materials corrosion performance in incineration plants is that corrosion problems really can only be addressed meaningfully after a plant is constructed and operational. This allows for laboratory testing of materials to be guided by the results obtained from field test rack exposures, or by the results of an analysis of field failures. Of course, a detailed analysis of the actual composition and nature of the field environment could be ideally used to guide the reproduction of the field conditions in the laboratory; however, such information is rarely available in sufficient detail to be definitive.

CASE NO. 1

An incinerator incorporating a waste heat boiler was used to treat chemical wastes which included paint sludges. Its combustion chamber was divided into two sections: an incineration section and a boiler section. The wastes were incinerated in the upper incineration section, and No. 6 fuel oil was used for combustion in the lower boiler section with a boiler heat exchanger to produce steam for process applications. These two different combustion sections were separated by a partition which consisted of a refractory-lined steel plate with refractories being exposed to the combustion products in the incineration side. Combustions in both sections were maintained at a gas temperature of approximately 1900°F (1038°C). A 10-percent excess air was used for combustion in the boiler
section, and a much higher percentage of excess air was employed in the incineration section. The combustion products, which were not analyzed, are believed to consist of N₂, O₂, CO₂, H₂O, CO, solid particles (e.g., ash), and possibly small amounts of chlorine or chlorides for both sections. For the boiler section, the flue gas might also contain small amounts of SO₂ since No. 6 fuel oil containing 1- to 2-percent sulfur was used.

The boiler section was shut down approximately once a week in order to remove fuel ash deposits from boiler tube surfaces. As a result of this frequent shutdown on the boiler side, the refractory partition had suffered severe cracking due to thermal cycling. The metallic materials, in general, are much more resistant to cracking induced by thermal cycling. However, because of unknown, complex combustion products, particularly in the incineration side, a field test program was initiated in order to determine the viable alloy to replace refractories as a partition material.

Two test racks were assembled, each containing sample coupons (approximately 1 in. (2.54 cm) x 4 in. (10.16 cm)) of nine different alloys. The nominal chemical compositions of these alloys are listed in Table 1. One rack was placed in the boiler side, the other, in the incinerator side. The racks were exposed to the operating environments for two months and then subjected to metallurgical evaluation.

Figure 1 is a photograph of the rack exposed to the boiler-side environment subsequent to brushing off loose debris. The incinerator side was similar in appearance. Figures 2 and 3 show the appearance of each coupon after exposure. The coupons were cathodically descaled in a salt bath in order to remove corrosion scales formed on the specimens. Average metal losses were then calculated from the weight change before and after testing. The continuous internal penetration (CIP) was determined metallographically by examining a cross-sectional area of the descaled coupon.

Metal wastages (or metal losses) were found to be relatively small for all the alloys in either the incineration or boiler side. Internal corrosion attack upon alloys was found to be greater in the boiler side than in the incinerator side. This is illustrated in Figs. 4, 5, and 6.

Corrosion scales of selected alloys exposed in both the boiler and incinerator sides were analyzed by scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDX analysis). The results are shown in Table 2. The results are more or less indicative of what would be expected from an oxidizing environment for the boiler-side specimens with Cr₂O₃ and various spinels containing iron, chromium, and nickel in evidence. This was confirmed by x-ray diffraction analysis. No sulfidation was found. Small amounts of zinc were detected in the corrosion scales formed on the HASTELLOY® alloy X and HAYNES® alloy No. 188 coupons. The fuel oil used for combustion was probably the source of these impurities.

The high concentration of titanium found in the scale of CABOT® alloy No. R-41 is believed to be attributed to the titanium oxide formed on the alloy during exposure. (Alloy R-41 is the only alloy tested with a sufficient level of titanium to form titanium oxides.)

All the incinerator-side coupons exhibited very high levels of titanium and silicon along with lesser amounts of zinc and calcium. These impurities were presumably from the wastes being incinerated. No chlorine or chlorides were detected in the scales. This cannot rule out the possibility of the involvement of Cl₂ and/or HCl in the high-temperature corrosion, since metal chlorides (if formed) can escape from the corrosion products because of their high vapor pressures. SEM-EDX analyses performed on the through sections of these selected alloys confirmed that the internal phases seen in Fig. 4, 5, and 6 were oxides. No sulfides were detected.

Since, in service, one side of the partition sees the boiler environment, and the other, the incinerator environment, corrosion rates were calculated by averaging the results for each set of specimens. This is shown in Fig. 7 where the corrosion rates are presented on a mils-per-year (µm-per-year) basis by assuming linear kinetics. As can be seen, the CIP is much more of a factor than the metal wastage for each alloy. The results indicate that CABOT alloy No. R-41 was the best performer followed by Type 310 stainless steel, HAYNES alloy No. 556, and HASTELLOY alloy X. After taking several factors into consideration, including thermal stability and fabricability, HASTELLOY alloy X, and HAYNES alloy No. 556 were recommended as suitable candidates for this application.

Although the examination of the field test samples revealed that oxidation was the predominant mode of corrosion, the relative performance of the alloys in the field environments was found to be significantly different from the results of laboratory oxidation tests conducted in air. The results of laboratory oxidation tests conducted in air at 1800°F and 2000°F (982°C and 1093°C) for 1008 hours are given in Table 3. Comparing the ranking order of materials according to laboratory oxidation testing with that obtained from field exposures, it is clear that the laboratory data is not in agreement with the field performance observed.

While the relative performances of materials such as Type 310 stainless steel, HAYNES alloy No. 556 and HASTELLOY alloy X are reasonably well predicted, the capability of HAYNES alloy No. 188 is clearly overstated by the laboratory tests. Even more importantly, the best performing alloy in the actual service environment, CABOT alloys No. R-41, is the worst alloy in the two
### TABLE 1  NOMINAL COMPOSITION OF ALLOYS TESTED

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Fe</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Ti</th>
<th>Al</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>La</th>
<th>Cb</th>
<th>N</th>
<th>Zr</th>
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<tbody>
<tr>
<td>HAYNES STEELITE® alloy No. 68</td>
<td>3.0*</td>
<td>3.0*</td>
<td>Bal.</td>
<td>30</td>
<td>1.5*</td>
<td>4.5</td>
<td>—</td>
<td>—</td>
<td>2.0*</td>
<td>2.0*</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HASTELLOY alloy X</td>
<td>Bal.</td>
<td>19</td>
<td>1.5</td>
<td>22</td>
<td>9</td>
<td>0.6</td>
<td>—</td>
<td>—</td>
<td>1.0*</td>
<td>1.0*</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Type 310 Stainless Steel</td>
<td>19</td>
<td>Bal.</td>
<td>—</td>
<td>24</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>2</td>
<td>1.5</td>
<td>0.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CARAT alloy No. R-41</td>
<td>Bal.</td>
<td>5.0*</td>
<td>11</td>
<td>19</td>
<td>10</td>
<td>—</td>
<td>3.0</td>
<td>1.5</td>
<td>0.1*</td>
<td>0.5*</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MULTIFIT alloy</td>
<td>20</td>
<td>Bal.</td>
<td>20</td>
<td>21</td>
<td>3.0</td>
<td>2.5</td>
<td>—</td>
<td>—</td>
<td>1.5*</td>
<td>1.0*</td>
<td>0.1</td>
<td>—</td>
<td>1.0</td>
<td>0.15</td>
<td>—</td>
</tr>
<tr>
<td>HAYNES alloy No. 556</td>
<td>20</td>
<td>Bal.</td>
<td>20</td>
<td>22</td>
<td>3.0</td>
<td>3.0</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
<td>0.4</td>
<td>0.1</td>
<td>0.02</td>
<td>1.0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>HAYNES alloy No. 188</td>
<td>22</td>
<td>3.0*</td>
<td>Bal.</td>
<td>22</td>
<td>—</td>
<td>14</td>
<td>—</td>
<td>—</td>
<td>1.3*</td>
<td>0.4</td>
<td>0.1</td>
<td>0.04</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>HAYNES alloy No. 25</td>
<td>10</td>
<td>3.0*</td>
<td>Bal.</td>
<td>20</td>
<td>—</td>
<td>15</td>
<td>—</td>
<td>—</td>
<td>1.5</td>
<td>0.4*</td>
<td>0.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>CARAT alloy No. 800H</td>
<td>33</td>
<td>Bal.</td>
<td>2.0*</td>
<td>21</td>
<td>—</td>
<td>—</td>
<td>0.38</td>
<td>0.38</td>
<td>1.5*</td>
<td>1.0*</td>
<td>0.08</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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* Maximum
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Incinerator Side</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Boiler Side</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Cr</td>
<td>Ni</td>
<td>Si</td>
<td>Ti</td>
<td>Zn</td>
<td>Ca</td>
<td>K</td>
<td>Al</td>
</tr>
<tr>
<td>CABOT alloy No. 556</td>
<td>34</td>
<td>14</td>
<td>3</td>
<td>17</td>
<td>23</td>
<td>4</td>
<td>5</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>HASTELLOY alloy X</td>
<td>36</td>
<td>15</td>
<td>2</td>
<td>10</td>
<td>23</td>
<td>11</td>
<td>3</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>HAYNES alloy No. 188</td>
<td>31</td>
<td>9</td>
<td>--</td>
<td>17</td>
<td>34</td>
<td>7</td>
<td>2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>CABOT alloy No. R-41</td>
<td>24</td>
<td>3</td>
<td>--</td>
<td>15</td>
<td>55</td>
<td>1</td>
<td>--</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>32</td>
<td>12</td>
<td>4</td>
<td>--</td>
<td>--</td>
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<td>--</td>
</tr>
<tr>
<td>HASTELLOY alloy X</td>
<td>26</td>
<td>52</td>
<td>11</td>
<td>7</td>
<td>--</td>
<td>3</td>
<td>--</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>HAYNES alloy No. 188</td>
<td>3</td>
<td>72</td>
<td>8</td>
<td>--</td>
<td>--</td>
<td>2</td>
<td>--</td>
<td>--</td>
<td>3</td>
</tr>
<tr>
<td>CABOT alloy No. R-41</td>
<td>1</td>
<td>49</td>
<td>7</td>
<td>--</td>
<td>34</td>
<td>--</td>
<td>--</td>
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<td>1</td>
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### TABLE 3 COMPARATIVE OXIDATION DATA FOR LABORATORY EXPOSURES OF 1008 HR AT 1800°F (982°C) and 2000°F (1093°C)*

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Metal Wastage</th>
<th>Continuous Penetration</th>
<th>Total Oxide Penetration</th>
<th>Extrapolated Oxidation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mils/side (µm/side)</td>
<td>mils/side (µm/side)</td>
<td>mils/side (µm/side)</td>
<td>mils/year (µm/year)</td>
</tr>
<tr>
<td>HAYNES alloy No. 188</td>
<td>0.18 (4.6)</td>
<td>0.40 (10.2)</td>
<td>0.58 (14.7)</td>
<td>5 (127)</td>
</tr>
<tr>
<td>HAYNES alloy No. 556</td>
<td>0.39 (9.9)</td>
<td>0.66 (16.8)</td>
<td>1.05 (26.7)</td>
<td>9 (229)</td>
</tr>
<tr>
<td>HASTELLOY alloy X</td>
<td>0.37 (9.4)</td>
<td>0.70 (17.8)</td>
<td>1.07 (27.2)</td>
<td>9 (229)</td>
</tr>
<tr>
<td>Type 310 Stainless Steel</td>
<td>0.35 (8.9)</td>
<td>0.78 (19.8)</td>
<td>1.13 (28.7)</td>
<td>10 (254)</td>
</tr>
<tr>
<td>MULTIMET Alloy</td>
<td>0.41 (10.4)</td>
<td>0.90 (22.9)</td>
<td>1.31 (33.3)</td>
<td>11 (279)</td>
</tr>
<tr>
<td>CABOT alloy No. 800H</td>
<td>0.94 (23.9)</td>
<td>0.85 (21.6)</td>
<td>1.79 (45.5)</td>
<td>16 (406)</td>
</tr>
<tr>
<td>CABOT alloy No. R-41</td>
<td>0.65 (16.5)</td>
<td>1.26 (32.0)</td>
<td>1.91 (48.5)</td>
<td>17 (432)</td>
</tr>
</tbody>
</table>

|                           |               |                       |                         |                            |
|                           | 2000°F (1093°C) |                 |                         |                            |
| Type 310 Stainless        | 0.97 (24.6)   | 0.33 (8.4)          | 1.30 (33.0)            | 11 (279)                   |
| HAYNES alloy No. 188      | 0.43 (10.9)   | 0.90 (22.9)         | 1.33 (33.8)            | 12 (305)                   |
| HAYNES alloy No. 556      | 0.97 (24.6)   | 1.60 (40.6)         | 2.57 (65.3)            | 22 (559)                   |
| HASTELLOY alloy X         | 1.47 (37.3)   | 1.34 (34.0)         | 2.81 (71.4)            | 24 (610)                   |
| CABOT alloy No. 800H      | 5.39 (136.9)  | 2.00 (50.8)         | 7.39 (187.7)           | 64 (1626)                  |
| CABOT alloy No. R-41      | 3.38 (85.9)   | 4.30 (109.2)        | 7.68 (195.1)           | 67 (1702)                  |
| MULTIMET Alloy            | 8.86 (225.0)  | 2.73 (69.3)         | 11.59 (294.4)          | 101 (2565)                 |

*Samples Cycled to Room Temperature Once a Week. Tests Conducted in Flowing Air.
FIG. 1 AS-RECEIVED BOILER-SIDE TEST RACK AFTER TWO-MONTH EXPOSURE TO FLUE GASES
FIG. 2 BOILER-SIDE TEST COUPONS
FIG. 3 INCINERATOR-SIDE TEST COUPONS
FIG. 4 PHOTOMICROGRAPHS OF CABOT ALLOY NO. R-41 COUPONS: 250X
(A) INCINERATOR SIDE; (B) BOILER SIDE
FIG. 5 PHOTOMICROGRAPHS OF HASTELLOY ALLOY X COUPONS: 250X; (A) INCINERATOR SIDE; (B) BOILER SIDE
FIG. 6 PHOTOMICROGRAPHS OF HAYNES ALLOY NO. 25 COUPONS; 250X;
(A) INCINERATOR SIDE; (B) BOILER SIDE
FIG. 7 COMPOSITE CORROSION RATES OF ALLOYS TESTED
(BOILER-SIDE RATE + INCINERATOR-SIDE RATE)/2
FIG. 8 PHOTOGRAPH OF AS-RECEIVED PLATE

FIG. 9 PHOTOMICROGRAPH OF AN AREA WITHIN SECTION A, FIG. 8: 200X

FIG. 10 PHOTOMICROGRAPH OF SECTION B, FIG. 8, AT THE SURFACE, 100X
FIG. 11 RESULTS OF SULFIDATION TESTS CONDUCTED AT 871°C (1600°F) FOR 215 HR (*AVERAGE OF MORE THAN ONE TEST)
combined laboratory test rankings! It is evident from these considerations that simple laboratory oxidation testing would not have been suitable for establishing a reliable ranking of the expected performance capabilities of the various materials. This is likely due to the more complex nature of the service environment, including the possible influence of contaminating species such as zinc and potassium found on some of the test materials.

CASE NO. 2

This case is an example of how performing an analysis of an actual part that failed in an incineration facility led to a sufficient understanding of the field environment to allow laboratory test data to be used with confidence. A large baffle plate fabricated from HASTELLOY alloy X had failed in service in an incinerator burning waste oil. The service temperature was not known. A photograph of the as-received plate is shown in Fig. 8, after samples had been cut from Locations A and B.

A detailed structural analysis of the failed plate at the aforementioned locations was performed using optical metallography and scanning electron microscopy. Field testing of possible alternate alloys in this application was not possible. It was highly important, therefore, that as much detail as possible be obtained from the examination of the failed part to develop a reasonable understanding of the nature of the service environment.

Figure 9 is a photomicrograph of a region within Area A on the baffle. The nature of the carbide morphology is clearly indicative of incipient melting having taken place. The blocky particles observed were identified by SEM-Energy Dispersive X-ray analysis to be chromium- and manganese-rich sulfides. Figure 10 is a photomicrograph of an area at and near the surface of Area B on the baffle. Although the microstructure appears normal, when subjected to SEM/EDX analysis, the scale was found to contain some form of nickel sulfide as well as chromium oxide.

Based upon these observations, it was clear that the major characteristic of the service environment related to the cause of failure was overheating combined with sulfidation/oxidation. Laboratory sulfidation-resistance tests were conducted at 1600°F (871°C) for 215 hr in a gas mixture consisting of 5 percent H2-5 percent CO-1 percent CO2-0.15 percent H2S-0.1 percent H2O-Balance Ar (by volume percent). Results are presented in Fig. 11.

Cobalt-base alloys (e.g., HAYNES alloys No. 25, No. 150, and No. 188) were most resistant to sulfidation attack. Next to this group of alloys were the Fe-Ni-Cr-Co alloys (e.g., HAYNES alloys No. 556 and MULTIMET® alloy) and some nickel-base alloys with aluminum and titanium (e.g., CABOT alloy No. 263). High-nickel alloys (e.g., HASTELLOY alloy X, CABOT alloy No. 600, and INCONEL® alloy 601) and Fe-Ni-Cr alloys (e.g., 310SS and CABOT alloy No. 800H) suffered severe sulfidation attack.

Considering these results, and the results of tests similar to those presented in Table 3, HAYNES alloy No. 188 was recommended as an alternate material of construction in view of its excellent combined resistance to both sulfidation and oxidation, its ready fabricability, and the small degree of added over-temperature capability afforded to cobalt-base alloys over lower melting point nickel-base alloys.

SUMMARY AND CONCLUSIONS

Two cases involving high-temperature corrosion of internal components of combustion chambers encountered in the waste incineration industry have been discussed. The first case involved an incinerator unit used for burning wastes, such as paint sludges, and a waste heat boiler using No. 6 fuel oil for combustion. The alloys that might perform adequately in both types of combustion environments are HAYNES alloy No. 556 and HASTELLOY alloy X. The results were obtained by placing test racks containing various candidate alloys in the operating plants. High-temperature oxidation with possible synergistic effects of corrosive contaminants, such as zinc, potassium, etc., was found to be the predominant mode of attack upon the alloys. As a result, laboratory oxidation tests conducted in air were not useful in predicting alloy performance in the actual plant environments.

The second case involved an incinerator used for burning waste oils. In this case, a failed sample obtained from the operating plant was analyzed. Sulfidation/oxidation was found to be the predominant mode of corrosion attack. Laboratory tests in sulfidizing environments were found to be useful in selecting an alternate material for the application. Consequently, HAYNES alloy No. 188 with its excellent combined resistance to both sulfidation and oxidation was recommended.

Key Words: Aluminium • Boiler • Corrosion • High-Temperature • Incinerator • Refractory • Waste Heat