The corrosion wear behaviour of selected stainless steels in potash brine

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Abstract

Tests were conducted at 25 and 85 °C to evaluate the corrosion wear resistance of selected stainless steels in potash brine using a reciprocating motion wear apparatus. Four materials were tested: Ferralium 255 (UNS S32550), AL6XN (UNS N08367), 254SMO (UNS S31254) and AISI 1018 (UNS G10180) for comparative purposes. The evaluation methods employed included weight loss analysis, optical microscopy and scanning electron microscopy (SEM). The results show that Ferralium 255 has superior corrosion wear resistance in potash brine environment compared to AISI 1018 plain-carbon steel and the other stainless steels tested. Wear surface analysis using SEM shows evidence of brittle fracture damage, which is attributed to the presence of Cl−.

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1. Introduction

The damage of materials due to conjoint action of corrosion and mechanical wear plays an important role in potash processing where vessels, pumps and transport systems used are in contact with coarse particle potash slurries [1]. Corrosion wear is the degradation of materials in which both corrosion and wear mechanisms are encountered and often interact. Passive metals are prone to corrosion wear damage because the mechanical wear action may remove the corroded layer or protective passive film exposing fresh metal surface to a corrosive environment. A rapid corrosion of the surface takes place before it repassivates. The kinetics and mechanisms of repassivation of metals have been studied by several authors [2–12]. Many investigators have studied corrosion wear damage using different experimental methods [11–29]. The general conclusion of these investigations is that the total metal removal rate during corrosion wear is greater than the sum of the corrosion rate and the wear rate measured in separate experiments. In many instances, corrosion is accelerated by wear while in others wear may be accelerated or decelerated by corrosion [22].

Stainless steels show good to excellent corrosion resistance in many industrial environments. However, in chlorine-containing environments such as potash brines encountered in potash production, many stainless steels are severely degraded by localized corrosion (e.g. pitting and crevice corrosion). A few corrosion studies on the performance of stainless steels in potash brine environments have been carried out at the University of Saskatchewan [30–34]. Shirazi [31] conducted a number of electrochemical tests to determine the pitting resistance of some stainless steels (e.g. AISI 304L, 304LN, 316L, 316LN, 904L and UNSS31254 (254SMO)) in stagnant potash brine at 22 and 90 °C by measuring their breakdown or pitting potential (Pp) and repassivation potential (Pr). The results showed that 254SMO steel has the highest pitting resistance among the alloys tested. The alloys were ranked in a descending order of their pitting potentials as follows: 254SMO > AISI 904L > AISI 316LN > AISI 316L > AISI 304LN > AISI 304L.

Blackmore [32] also conducted a wide range of exposure and electrochemical tests in potash brines to determine the corrosion resistance of AISI 430 and 446 ferritic stainless steels and the results showed that they have inferior localized corrosion resistance compared to austenitic and duplex stainless steels such as 254SMO, AISI 904L and S31803 (SAF 2205). Also, the resistance of AISI 430 and 446 to corrosion...
and wear in potash brine environment was investigated and it was shown that the AISI 446 alloy has superior pitting resistance to AISI 430[31,32]. The resistance of stainless steels to localized corrosion is quantified in terms of the localized corrosion resistance index (LCRI), which is also known as the pitting resistance equivalent (PRE). The formula suggested by Nadezhdin and Wensley[35] for determining the LCRI is given as

\[
\text{LCRI} = \% \text{Cr} + 3.3\% \text{Mo} + 16\% \text{N} - 0.33\% \text{Ni} \quad (1)
\]

The results of electrochemical tests conducted in 10 wt.% potash slurry show that there is a linear relationship between the pitting potential and the LCRI of several alloys[30].

Other workers have studied the corrosion wear behaviour of stainless steels in other chloride-containing solutions such as NaCl and acidified NaCl. Abd-El-Kader and El-Raghy[24] studied the conjoint effects of mechanical and electrochemical processes during the sliding wear of annealed 18Cr–10Ni stainless steel under potentiostatic control in NaCl solution. They concluded that the total wear rate is an additive product of the mechanical and corrosive wear. They also found that corrosive wear is due mainly to surface oxide film formation and proposed that it proceeds by successive stages of build-up and removal of the passive film. Graham et al.[2] observed that the growth rate of a passive film formed on selected stainless steels depends on the electrode potential and the chloride ion concentration in the electrolyte. This seems to contradict the results obtained by Landolt et al.[36] who concluded, on the basis of XPS analysis, that the apparent thickness of a passive film formed on a Fe–24Cr stainless steel is not significantly affected by the presence of chloride ions in the electrolyte. Hong and Pyun[25] studied the influence of chloride ion levels on the corrosion wear rate of 304L stainless steel in 1N H₂SO₄. The corrosion wear rate was found to increase linearly with increasing chloride concentration. Wu[26] studied the corrosion wear of AISI 304 stainless steel in various NaCl solutions under various loading conditions and concluded that chloride ions enhanced corrosion wear damage. In a different study, Shizhuo et al.[29] examined the influence of chloride ions on the corrosive wear of AISI 304 and duplex stainless steels in acidic solutions and reported that when the Cl⁻ content in H₂SO₄ solution was increased from 500 to 2000 or 4000 mg/l, the corrosion rate increased between 39 and 52%, while the corrosion wear rate increased between 104 and 178%. The general conclusion from these studies is that chloride ions adversely affect the corrosion wear resistance of stainless steels, irrespective of their source, but the extent to which they affect different stainless steels differs and needs to be investigated.

As part of a materials selection project carried out for the Potash Corporation of Saskatchewan (PCS), the world’s leading producer of potash commonly used as fertilizer, the corrosion wear behaviour at 25 °C (pH 8.05) and 85 °C (pH 6.5)
in potash brine of AISI 1018 (UNS G10180), Ferralium 255 (UNS S32550), AL6XN (UNS N08367) and 254SMO (UNS S31254) was investigated using a reciprocating motion wear apparatus. No electrochemical polarization was employed in order to simulate as close as possible the actual conditions in potash mills owned by the PCS in Saskatchewan. The results are discussed in terms of weight loss and wear surface analysis conducted using optical microscopy and scanning electron microscopy (SEM).

2. Experimental

2.1. Apparatus

The corrosion wear apparatus used in this study is shown in Fig. 1(a) and (b). It consists of the following main parts: weights, test chamber, push rod, microswitch, pneumatic piston, solenoid valve, heater and counter. The test chamber holds four specimens, each measuring 38 mm × 38 mm × 6 mm. The applied weight on each weight pan was 890 g resulting in a 40 N load, which is applied to each specimen by means of a carbon steel ball fixed in a copper collar. The initial hardness of the steel ball was 920 VHN. Each specimen holder, which is connected to a stainless steel rod, was reciprocated back and forth in a horizontal motion by means of a pneumatic piston arrangement. The microswitch reverses the direction of airflow in the pneumatic piston and hence the motion of the specimen holder. A frequency of 105 cycles per minute was maintained throughout the experiment. Tests were conducted in saturated potash brine maintained at either 25 °C or 85 ± 1 °C by means of a heating system comprising two thermocouples, a heater, a circulating pump and a temperature controller (not shown in Fig. 1). The average pH values of the potash brine measured at the two temperatures were 8.05 and 6.5, respectively.

2.2. Materials

The composition limits of the major alloying elements and mechanical properties of all materials used in the present study are shown in Tables 1 and 2, respectively. The potash ore used was supplied by the Cory Mill owned by the Potash Corporation of Saskatchewan (PCS). Table 3 shows the chemical and mineralogical characterization of typical potash ore from Saskatchewan [37] while Table 4 shows the

<table>
<thead>
<tr>
<th>Material</th>
<th>C (wt.%)</th>
<th>Cr (wt.%)</th>
<th>Ni (wt.%)</th>
<th>Mo (wt.%)</th>
<th>Cu (wt.%)</th>
<th>Mn (wt.%)</th>
<th>S (wt.%)</th>
<th>P (wt.%)</th>
<th>Fe (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferralium 255</td>
<td>0.04</td>
<td>24.0–27.0</td>
<td>4.5–6.5</td>
<td>2.9–3.9</td>
<td>1.5–2.5</td>
<td>0.10–0.25</td>
<td>Balance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL6XN</td>
<td>0.05</td>
<td>20.0–22.0</td>
<td>23.5–25.0</td>
<td>6.0–7.0</td>
<td>0.75</td>
<td>0.18–0.25</td>
<td>Balance</td>
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<td></td>
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<tr>
<td>254SMO</td>
<td>0.02</td>
<td>19.5–20.5</td>
<td>17.5–18.5</td>
<td>6–6.5</td>
<td>0.5–1.0</td>
<td>0.18–0.22</td>
<td>Balance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AISI 1018</td>
<td>0.15–0.20</td>
<td>0.6–0.9</td>
<td>≤0.04</td>
<td>≤0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength (MPa)</th>
<th>Yield strength (MPa)</th>
<th>%Elongation</th>
<th>Hardness (VHN)</th>
</tr>
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<tr>
<td>Ferralium 255</td>
<td>910</td>
<td>758</td>
<td>22.0</td>
<td>468</td>
</tr>
<tr>
<td>AL6XN</td>
<td>772</td>
<td>389</td>
<td>51.0</td>
<td>468</td>
</tr>
<tr>
<td>254SMO</td>
<td>702</td>
<td>374</td>
<td>51.2</td>
<td>451</td>
</tr>
<tr>
<td>AISI 1018</td>
<td>475</td>
<td>275</td>
<td>38</td>
<td>218</td>
</tr>
</tbody>
</table>

Fig. 2. Total material loss vs. exposure time in saturated potash brine: (a) 25 °C and (b) 85 °C.
Table 3
Chemical and mineralogical characterization of typical potash ore in Saskatchewan [37]

<table>
<thead>
<tr>
<th>Chemical analysis</th>
<th>wt.%</th>
<th>Mineralogical analysis</th>
<th>wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>37.72</td>
<td>Sylvinite</td>
<td>96–99</td>
</tr>
<tr>
<td>NaCl</td>
<td>59.18</td>
<td>Langbeinite</td>
<td>Nil</td>
</tr>
<tr>
<td>MgO</td>
<td>0.58</td>
<td>Kainite</td>
<td>0–trace</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.10</td>
<td>Carnallite</td>
<td>1.06–1.50</td>
</tr>
<tr>
<td>Combined H₂O</td>
<td>1.61</td>
<td>Polyhalite</td>
<td>0–trace</td>
</tr>
<tr>
<td>Free H₂O</td>
<td>0.30</td>
<td>Others</td>
<td>Trace–0.10</td>
</tr>
<tr>
<td>Water insoluble</td>
<td>0.50</td>
<td>Water insoluble</td>
<td>0.70–1.00</td>
</tr>
</tbody>
</table>

Table 4
Chemical composition of saturated potash brine derived from the Cory mine [31]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl⁻</td>
</tr>
<tr>
<td>22</td>
<td>21.88</td>
</tr>
<tr>
<td>90</td>
<td>23.45</td>
</tr>
</tbody>
</table>

2.3. Procedure

The specimens were thoroughly cleaned to remove any contaminants, dried prior to and after each test, and weighed to the nearest 0.0001 g. The wear surface was analysed by measuring the surface area, the wear depth, and examining the surface morphology in an optical microscope and/or SEM. The specimens were removed from the test chamber six times during each test for weight loss measurements and surface analysis. The exposure times between stopovers were 48, 120, 168, 240, 288, and 360 h, which corresponded to about 300,000, 750,000, 1,050,000, 1,800,000, and 2,250,000 cycles, respectively.

Fig. 3. Variation of wear scar area with exposure time in saturated potash brine: (a) 25°C and (b) 85°C.

Fig. 4. Variation of wear depth with exposure time in saturated potash brine: (a) 25°C and (b) 85°C.
3. Results and discussion

Fig. 2 (a) and (b) shows the results of the weight loss measurements obtained for samples exposed to potash brine at 25 and 85 °C, respectively. It can be seen that Ferralium 255 outperformed the reference material (AISI 1018), AL6XN and 254SMO. This is quite surprising since AL6XN and 254SMO contain more molybdenum (≈6.0–7.0 wt.% Mo) than Ferralium 255 (2.9–3.9 wt.% Mo). Brookes et al. [3] have reported that molybdenum accelerates repassivation on freshly generated metal surface and improves the stability of passive films formed on stainless steels, especially to attack by Cl−. Similar conclusions were reported by Landolt et al. [36] for passive films formed on Fe–24Cr–11Mo stainless steel. Yaniv et al. [4] also suggested that molybdenum improves the quality of the bonding at the metal–film interface by creating a barrier-type oxide. However, Cieslak and Duquette [38] attributed increased film protectiveness to increased chromium.
enrichment of the film and decreased film thickness resulting from increased chromium content. A close examination of the data in the figures shows that there is a rather high rate of corrosive wear in the first 50 h of testing, after which time the rate of material loss is decreased. This was observed for all the four materials tested. The observed accelerated initial weight loss is thought to be caused by the existence of high contact stress between the specimen and the ball bearing at the beginning of each test. As the contact area between the ball and the specimen increased with time due to wear of the ball, the contact stress decreased and the overall corrosion wear rate decreased. It is readily discernable from Fig. 2(b) that temperature has a profound effect on the corrosion wear behaviour of the tested materials. The overall weight loss increased significantly with increase in temperature. This suggests that the corrosion wear mechanisms at 25 and 85°C may be different.

To quantify the corrosion wear resistance of the tested materials in a more meaningful way, the wear surfaces were further evaluated in terms of wear scar areas and wear scar depths. Fig. 3(a) and (b) shows the variation in wear surface area with exposure time for the test materials at 25 and 85°C, respectively, whereas Fig. 4(a) and (b) represents the wear depth data. The wear depth data are based on the average of seven depth measurements. Again, the wear surface area and depth results follow similar trend as those obtained for weight loss measurements at the same test temperatures. There is an initial high wear rate in the first 50 h which changes to a more gradual steady-state wear as exposure time increased. Ferralium 255 outperformed both AL6XN and 254SMO in terms of wear scar depth and wear scar surface area at 25 and 85°C. This is consistent with the weight loss data in Fig. 2(a) and (b). However, the wear scar area and wear scar depth results obtained for AISI 1018 plain-carbon steel at the two temperatures seem to contradict the weight loss data. For example, AISI 1018 is shown in Fig. 3 to have better performance than Ferralium 255 stainless alloy. However, an examination of Fig. 2(a) and (b) shows that the latter greatly outperfomed the former at both temperatures, which is a reflection of the actual volume of material removed during corrosive wear. The apparent contradiction is therefore attributable to the difficulty in accurately measuring the actual wear scar areas and depths due to occasional slipping of the wearing ball on Ferralium 255. Interestingly, Figs. 2–4 and Table 2 seem to indicate that the corrosive wear resistance of the tested stainless steels depend on Cr content, mechanical properties and hardness rather than on hardness alone. It is therefore difficult to single out the greatest contributory factor based on the results presented. Nevertheless, the high tensile and yield strengths of Ferralium 255 appear to offer great resistance against abrasive wear (two-body and three-body), especially at the early stages of the corrosive wear process when sand and other hard particles entrained in the brine solution create conductive conditions for this form of mechanical wear.

The increase in corrosion damage at 85°C is believed to be due to Cl−-induced brittle fracture of the protective passivating film [27,28]. It has also been reported that the increase in corrosion wear rate in the presence of Cl− is due to a change in the structure, growth rate or current efficiency for the formation of the passivating oxide film [25,38,39]. Ambrose and Knug [8] have reported that incorporation of Cl− in the passive film lattice accelerates breakdown of passivated steel. It seems also that the stability of the protective oxide film is affected less by the presence of Cl− in potash brine at 25°C. According to the adsorbed ion displacement model proposed by Kolotyrkin [40] and Leckie and Uhlig [41], the passive film is weakened when Cl− displaces the oxygen forming the passive film. The solubility of oxygen in an aqueous solution decreases with increasing temperature. There is more oxygen in the potash brine solution at 25°C than at 85°C. From Table 4 [31], it seems that the overall concentration of Cl− increases with temperature. As such, there are more chloride ions available to displace oxygen at 85°C. The oxygen atoms driven out of the brine solution at the temperature increased were replaced by the more strongly adsorbing Cl−, thereby further weakening the passive film. Hence, although new passive films are formed during corrosive wear at 85°C, these new films are more prone to breakdown since they contain more Cl− than those formed at 25°C. As such, the increased weight loss at 85°C can be attributed to passive film formation as suggested by Abd-El-Kader and El-Raghy [24].

Fig. 5(a)-(h) shows the SEM micrographs of worn surfaces of AISI 1018 steel and the stainless steels tested under the two temperature regimes. In all cases, the wear surfaces show wear marks in the sliding direction, which are characteristic scratches produced by abrasive wear. The abrasive wear was caused by hard particles caught between sliding surfaces (the steel ball and the specimen) during testing. The hard-wearing particles could be fractured corrosion products, sand or other hard particles carried over from the raw potash used in this study. Also, the worn surfaces of AISI 1018, 254SMO and AL6XN show discernable features of adhesive wear, which could be due to severe plastic deformation of the metal or to compacted wear particles. Adhesive wear, which is expected in a metal-to-metal configuration used in this study, leads to tearing out of relatively large particles of metals from the rubbing surfaces thereby leading to a significant material loss. The wear surface seems to degenerate with increasing temperature, especially for AISI 1018, 254SMO and AL6XN alloys. For example, in the case of 254SMO, there is an appreciable increase in scoring and the size of wear pits at 85°C. Shear fracture of protective oxide films occurs more easily at 85°C than at 25°C during testing. This would add more wearing particles to the potash brine. In alloy AL6XN tested at 85°C, lateral cracking occurred near the trailing edge of the sliding steel ball (see Fig. 6). The crack spread with time. This type of cracking phenomenon did not occur at 25°C under same testing conditions. It is not very clear what caused this type of cracking but it is probably a consequence of Cl−-induced corrosion fatigue cracking.
4. Conclusions

1. Ferralium 255 has superior corrosion wear resistance in potash brine environment than AL6XN and 254SMO stainless steels.
2. Corrosion wear resistance of stainless steels in potash brine is temperature-dependent. Material loss is higher at elevated temperatures than at 25 °C.
3. Chloride-induced shear fracture of protective films appears to be responsible for increased corrosion damage at elevated temperatures in potash brine.

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References