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Corrosion Resistance of Intermediate Chromium-alloy Steels in Mine Waters

P.V. SCHEERS, M.U. KINCER, T. RUMPF, and J.J. McEWAN

Mintek, Randburg, South Africa

The corrosion in mine waters of four low-chromium alloy steels was examined. Their general corrosion rate and susceptibility to localized corrosion were determined by electrochemical and immersion techniques. It appears that, for a significant improvement in corrosion resistance, the chromium content of the alloy must be at least 5 per cent, and the pH value of the solution 8 or 10 according to the concentration of chloride ions. Immersion tests in acidic or neutral mine water also showed that these alloys are prone to localized corrosion.

Introduction

It is well known that steels with a chromium content of 12 per cent or higher offer good corrosion resistance in various environments. However, the costs of these materials put them out of reach for several applications. Investigations of the corrosion performance of chromium-containing steels having a lower percentage of chromium than, for example, 3CR12 may yield a viable alternative with a better balance between cost and corrosion resistance.

In this investigation, electrochemical techniques, immersion tests in the laboratory, and field tests were used to evaluate the corrosion performances of four low-chromium steels in mine waters. The results were then compared with those obtained with mild steel and 3CR12.

Experimental Method

Four low-chromium steels, with chromium contents ranging from 2,3 to 9 wt per cent, were melted and heat-treated in a way that made them comparable with commercially available alloys, i.e. UNS designation K21590, K41541, K61595, and K90941. All the alloys were heated at 930°C for 1 hour.The alloys with a chromium content of 2,3 and 9 per cent were then air-cooled, while those with 5 and 7 per cent chromium were oil-quenched. These heat-treatments gave them a microstructure equivalent to that of the commercial alloys. Their compositions are given in Table I.

The electrochemical tests were performed in a synthetic mine water[1] based upon samples of machine water taken

TABLE I
CHEMICAL COMPOSITION OF THE LOW-CHROMIUM ALLOYS (wt %)

Element	Alloy 1	Alloy 2	Alloy 3	Alloy 4
Cr	2,35	5,04	6,91	8,9
Mo	1,01	0,58	0,75	1,04
Ni	<0,01	0,49	-	-
C	0,11	0,11	0,12	0,11
Si	0,46	0,42	0,78	0,3
Mn	0,47	0,46	0,46	0,45
P	0,015	0,014	0,014	0,015
S	0,015	0,015	0,013	0,014
Cu	0,011	0,007	0,01	0,009
Al	0,004	0,004	0,003	0,003
O	0,02	0,03	0,02	0,02
N	0,002	0,002	0,003	0,003
Fe	95,5	92,8	90,8	88,6

from the Orange Free State goldfield, where corrosion problems tend to be greater than those experienced on the Witswatersrand. However, in order to widen the range of the experimental conditions, the pH and chloride ion concentrations were adjusted to various values. The composition of the synthetic mine water is given in Table II.

TABLE II
COMPOSITION OF THE SYNTHETIC MINE WATER (mg/l)

pH	4 to 10
$NaCl$	165 to 2473
$CaSO_4.2H_2O$	1290
$MgSO_4.7H_2O$	608
NH_4NO_3	317
KNO_3	216
Na_2SO_4	142
KNO_2	60
$NaHCO_3$	42
$FeSO_4.7H_2O$	15
Kaolin	45

The test electrode was immersed in a glass vessel with two graphite rods, which acted as counter electrodes, and a Haber-Luggin capillary, which formed the junction with a saturated calomel reference electrode (SCE). All the potential values in this paper are quoted with respect to the SCE. The aerated solution was stirred with a magnetic stirrer, and no gas purging was performed during the experiment.

In order to avoid the formation of crevices, which can interfere with measurements of the pitting potential, a modified[2] electrode holder, based on the 'Avesta pitting cell'[3] was used in all the experiments.

A PARC 273 corrosion-measurement system was used in the electrochemical experiments. The test specimens were polished on 1200-grit emery paper, degreased with acetone, and left in the solution for half an hour. A potentiodynamic scan was then started from minus 200 mV versus the corrosion potential at a scanning speed of 0,2 mV/s. If an active to passive transition was observed, the scan was pursued until a current density of 5 mA/cm^2 was reached. Its direction was then reversed (cyclic polarization). If no active to passive transition was observed, the scan was stopped when enough data had been recorded for the evaluation of cathodic and anodic Tafel slopes. The corrosion current was calculated from the polarization resistance value using the Stern–Geary[4] equation and Tafel slopes determined by the PARC M342 corrosion software. All the experiments were performed at room temperature.

In addition to the electrochemical experiments, some immersion tests were performed at room temperature over a period of three months in the same synthetic mine water. These were intended to show the effect of longer exposure periods and the type of corrosion taking place.

Commercial samples of the same composition were inserted in the water circuits of two different mines for periods ranging from three to four months. One of the mines was situated on the West Rand, and the other on the Orange Free State goldfield.

The corrosion rate of the samples, both those used for immersion tests in the laboratory and those inserted in the mines' water circuits, were calculated from their weight loss, and the extent of localized attack was determined by microscopical techniques.

Experimental Results

Electrochemical Experiments

Anions of high total molar polarization, such as chloride ions, have a strong tendency, after being absorbed onto metal surfaces, to promote electron-exchange reactions, and are thus particularly active in corrosion reactions[5]. Sulphate ions can also increase corrosion, and it has been shown that small concentrations of sulphate ions in distilled water increase corrosion more than similar concentrations of chloride ions[6].

On the other hand, sulphate and nitrate ions are often regarded as inhibitors of localized corrosion, and in this case it is the ratio of chloride to sulphate and nitrate ions that becomes the important factor[7,8]. For this reason, two different concentrations of chloride ions (100 and 1500 p.p.m.) were added to the synthetic mine water to give ratios of chloride to sulphate and nitrate ions of 0,2 and 3,0 respectively.

The results show that, except for a pH value of 8, the ratio of chloride to sulphate and nitrate ions has a negligible influence on the general corrosion rate of the various alloys tested. At pH values below 8, although there was generally a slight decrease in corrosion rate with increasing chromium content of the alloy, the corrosion rates of the low-chromium alloys were very close to that of mild steel and much higher than the corrosion rate of 3CR12. On the other hand, at a pH value of 10, a sharp drop in corrosion rate was observed for a chromium content of 5 per cent or higher, and the corrosion rates approached that of 3CR12. A typical example of both cases is presented in Figures 1 and 2.

However the situation was different at a pH value of 8 (Figure 3). In that case, the corrosion rates of the alloys with a chromium content equal to or higher than 5 per cent decreased sharply when the concentration of chloride ions was only 100 p.p.m., while this did not happen for a chloride ion concentration of 1500 p.p.m.

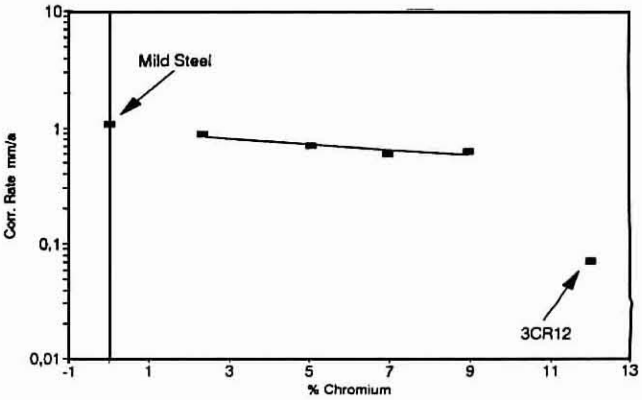

FIGURE 1. Corrosion rate as a function of chromium content, pH 6, 100 p.p.m. of Cl^-

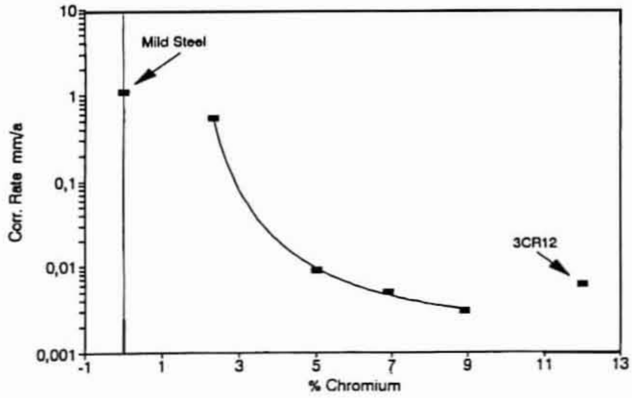

FIGURE 2. Corrosion rate as a function of chromium content, pH 10, 1500 p.p.m. of Cl^-

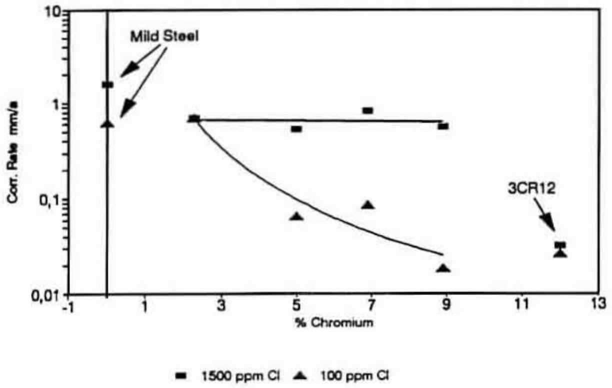

FIGURE 3. Corrosion rate as a function of chromium content, pH 8

TABLE III

CRITICAL CURRENT DENSITY OR CURRENT DENSITY IN THE PASSIVE STATE (100 p.p.m. OF Cl^-), $\mu A.cm^{-2}$.

Cr	pH				
%	4	6	7	8	10
2,3	Active	Active	Active	Active	Active
5,0	Active	Active	Active	4,7	3,5
6,9	Active	Active	Active	3,5	3,6
8,9	337	156	158	5,3	4,5
12,0	5,4	4,3	5,6	3,6	3,1

▨ Active to passive transition

■ Spontaneously passive

TABLE IV

CRITICAL CURRENT DENSITY OR CURRENT DENSITY IN THE PASSIVE STATE (1500 p.p.m. OF Cl^-), $\mu A.cm^{-2}$.

Cr	Ph				
%	4	6	7	8	10
2,3	Active	Active	Active	Active	Active
5,0	Active	Active	Active	Active	4,9
6,9	Active	Active	Active	Active	3,6
8,9	500	322	171	400	3,8
12,0	9,5	6,2	5,0	5,9	5,8

▨ Active to passive transition

■ Spontaneously passive

The potentiodynamic scans indicated that, depending on the pH value and the chromium content, some of the alloys showed an active to passive transition, or passivated spontaneously. The values of the critical passivation current or current in the passive state are given for the two concentrations of chloride ions in Tables III and IV. It is apparent from these tables, and from the results mentioned earlier, that the intermediate chromium alloys have a much lower corrosion rate than mild steel when the conditions are such that they become spontaneously passive, or have a critical passivation current density close to the value observed for 3CR12.

Although metals that become passive have a very low corrosion rate, they can still be subjected to pitting, which is an incidious form of corrosion since it frequently results in the perforation of a metal. The onset of pitting takes place at a critical potential, called the pitting potential, E_{pit}, which is characterized by a sudden increase in current density in the anodic polarization curve. Pourbaix and his collaborators[9,10] introduced the concept of a protection potential against pitting. The value of the protection potential is obtained when the direction of potential scanning is reversed from some arbitrary current density value after E_{pit}. The curve is then not retraced (electrochemical hysteresis), and the potential at which it intersects the forward-going segment is called the protection potential, E_{prot}. Although there is some controversy[11] concerning the real significance of the protection potential, it is usually admitted that existing pits or defects on a metal surface will propagate above the protection potential, but that pits will initiate only above the pitting potential.

Whether pitting will occur depends on the difference between E_{pit} and E_{corr}, the free corroding potential. If E_{corr} is close to E_{pit}, any small change in the oxidizing power of the solution can produce pitting by reducing the separation between E_{corr} and E_{pit}[12]. On the other hand, if some defects are present on the metal surface, it is the difference between E_{corr} and E_{prot} that should be taken into consideration. A separation of 300 mV is sometimes regarded as a minimum criterion for the avoidance of pitting.

As already mentioned, the ratio of chloride to sulphate and nitrate ions is an important factor in pitting corrosion, and no pitting or breakdown potential was observed for the low-chromium alloys that passivated in the synthetic mine water with a $Cl^-/(SO_4+NO_3)$ ratio of 0,2. However, pitting potentials were observed for a ratio of 3,0.

The values of E_{pit} minus E_{corr} and E_{prot} minus E_{corr} are given in Tables V and VI respectively. It follows from the values in Table V that the separation between E_{pit} and E_{corr} was fairly large, and no pitting would be expected in these conditions if the metallic surface were free of defects or existing pits. However, the values of E_{prot} minus E_{corr} given in Table VI were around or below 300 mV, and this suggests that, if any defects are present on the metallic surface, the propagation of pits must not necessarily be

TABLE V
SEPARATION BETWEEN PITTING POTENTIAL AND CORROSION POTENTIAL (1500 p.p.m. OF Cl^-), mV

Cr	Ph				
%	4	6	7	8	10
2,3	Active	Active	Active	Active	Active
5,0	Active	Active	Active	Active	372
6,9	Active	Active	Active	Active	436
8,9	688	692	672	660	500
12,0	768	852	741	773	532

▨ Active to passive transition

■ Spontaneously passive

TABLE VI
SEPARATION BETWEEN PROTECTION POTENTIAL AND CORROSION POTENTIAL (1500 p.p.m. OF Cl^-), mV

Cr	Ph				
%	4	6	7	8	10
2,3	Active	Active	Active	Active	Active
5,0	Active	Active	Active	Active	265
6,9	Active	Active	Active	Active	221
8,9	249	221	220	237	305
12,0	281	309	329	329	369

▨ Active to passive transition

■ Spontaneously passive

excluded. This is especially true in 'real life' conditions, where some debris or fouling can induce underdeposit corrosion.

Laboratory Immersion Tests

Samples of the same composition as those used in the electrochemical experiments were immersed in stirred synthetic mine water with a pH value of 7 for a period of three months. The results obtained with the different $Cl^-/(SO_4+NO_3)$ ratios were fairly similar, and only one set of results (ratio of 3,0) is presented in Figure 4, where the corrosion rates are compared with those obtained by the accelerated electrochemical technique.

It can be seen from Figure 4 that the corrosion rates of the alloys immersed for three months are constantly lower than the corrosion rates measured electrochemically. This is not unexpected, since the corrosion rate of mild steel in that kind of environment is known to be fairly high initially, but to decrease to a constant value after about 100 hours[1]. The initial high rate reflects the corrosion rate of the 'bare' surface before the formation of corrosion products that slow down the corrosion reaction. The same behaviour can be expected from the other alloys, on which a layer of corrosion product or passive layer will be formed after a certain period of time. As the electrochemical experiments were conducted after the specimens had been immersed in the solution for only half an hour, it is not surprising that the corrosion rates measured electrochemically were higher.

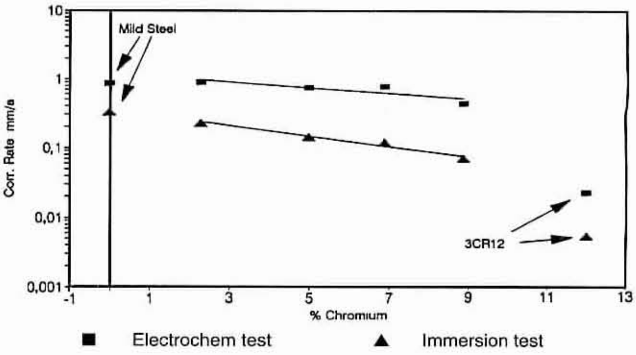

FIGURE 4. Corrosion rate as a function of chromium content, pH 7, 1500 p.p.m. of Cl^-

However, it was observed in these immersion tests that the intermediate chromium alloys suffered localized attack, while this was not observed for mild steel or 3CR12. The pit density was usually fairly high, about 10^5 pits/m^2, but pitting occurred only over parts of the total sample area.

The pit depths are given in Table VII, which shows that the pit depth increases with increasing chromium content of the alloy. This could be due to the fact that, with increasing chromium content, the alloy has a higher tendency to passivate and the attack then becomes more localized. In other words, the ratio of cathodic to anodic areas becomes larger and this, in turn, will increase the pit growth rate.

TABLE VII
PIT DEPTHS MEASURED IN THE LABORATORY IMMERSION TESTS (pH 7, 1500 p.p.m. of Cl^-).

Cr	Pit depth, mm	
%	Av.	Max.
2,3	0,08	0,23
5,0	0,13	0,32
6,9	0,21	0,75
8,9	0,25	1,00

Field Results

Owing to the lack of available places in the test circuits, only one mass-loss coupon of each of the alloys could be inserted in the mine-water circuits, and the corrosion rates given in Figure 5 were calculated from the mass losses over a period ranging from three to four months.

The corrosion rates obtained with commercial alloys inserted in the water circuit of two different mines are represented graphically as a function of their chromium content in Figure 5. This figure shows clearly that, with the exception of 3CR12, there was a large difference in corrosion rate between the two water circuits.

However, the water quality was substantially different in the two mines, one of the major differences being the pH value, which remained neutral (between 7 and 8) in mine B, but was usually around 5 in mine A. Other factors, such as the ratio of chloride to sulphate and nitrate, the conductivity, and the Langelier index made the water of mine A more aggressive. These factors explain the observed differences in corrosion rate, but it is surprising that the corrosion rate of the intermediate chromium alloys that were inserted in the water circuit of mine A increased

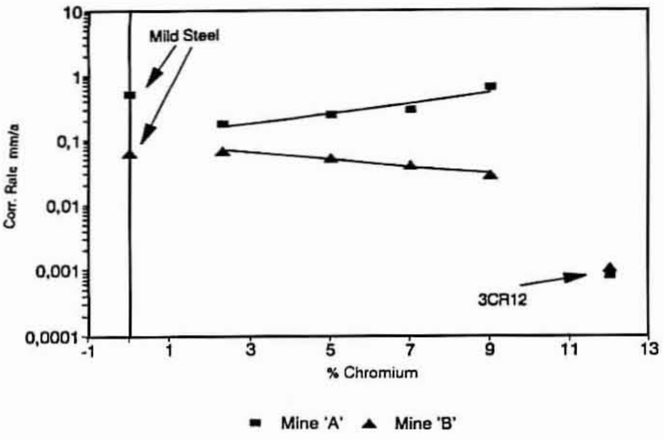

FIGURE 5. Corrosion rate as a function of chromium content – field tests

with increasing chromium content. An inspection of the samples showed that this increase was due to localized corrosion, which was fairly severe on the alloys containing 7 and 9 per cent chromium.

Localized corrosion was also observed on the samples that had been inserted in the water circuit of mine B, although to a lesser extent.

Discussion

These results emphasize the influence of three important factors on the corrosion behaviour of chromium-containing steels, i.e. the chromium content, the chloride ion concentration in an aqueous environment, and the pH value. The molybdenum content of the alloys was different and, although molybdenum increases the resistance to pitting, the concentration of molybdenum did not seem to have any influence on the general corrosion rate or localized corrosion of the alloys tested. However, the effect of molybdenum was difficult to assess owing to the greater variations in the chromium content of the alloys.

The passivation of a metal or alloy depends on its nature and on the nature of the solution; hence, the critical composition (e.g. the chromium content) will depend on the environment to which the alloy is exposed. The passive state of a material is characterized by a certain electrode potential (the primary passivation potential, E_{pp}) and a certain anodic current density (the critical passivation current density, i_{crit}) above which the dissolution rate changes from a relatively high to a relatively low value. The electrode potential associated with the onset of passivity and the maximum current density needed to reach the passive state from the active state are a function of the metal composition, the chemical composition of the environment, and the temperature.

It is apparent that the transition from the active to the passive state must be associated with a fundamental change in the nature of the metal surface, and it is now the generally accepted view that passivity is due to the formation of a very thin solid film of metal corrosion product, usually of oxide , on the metal surface[13].

In the case of Fe–Cr alloys, the composition of the film will be related to the chromium content and the nature of the environment.

According to Grimley[14], two critical chromium contents must be considered when Fe–Cr alloys are exposed to oxygen gas. Below the first, only FeO is formed, between the first and the second only the spinel $FeCr_2O_4$, and above the second only Cr_2O_3. A Cr_2O_3 layer is certainly protective, while a spinel layer will be protective if the diffusion coefficient of Fe^{2+} (or Fe^{3+}) is lower than in the oxide of iron.

Asami *et al.*[15] examined the mechanism of passivation in Fe–Cr alloys and the causes of the difference in corrosion resistance between low-chromium alloys and stainless steels through the quantitative determination of the compositions of the surfaces on a series of Fe–Cr alloys polarized in 1N H_2SO_4. They observed that the passive film formed on the Fe–Cr alloys containing 12,5 per cent chromium or more consisted mainly of hydrated chromium oxi-hydroxide, $CrO_x(OH)_{3-2x}{\cdot}nH_2O$, where x and n change with the alloy composition and the passivation potential. On the other hand, the passive films on the pure iron and low-chromium alloys were composed mainly of $FeO_x(OH)_y{\cdot}nH_2O$.

McBee and Kruger[16] anodically polarized Fe–Cr foils of a range of chromium contents in 1N H_2SO_4 for film growth, and found that the foils of 5 per cent chromium alloy formed passive films somewhat similar to those formed on pure iron. As the chromium content increased, however, the films formed, although protective in nature, were not the same as the passive films formed on pure iron, and recent work using soft X-ray spectroscopy provides evidence that the changes in the films above 12 per cent chromium are due to an enrichment of these films in Cr^{3+}.

Apart from the chromium content, the chemical composition of the environment will also have an effect on the structure and composition of the protective films formed on Fe–Cr alloys.

Metal oxides are thermodynamically unstable in acid solutions so that oxides formed during passivation at low pH values must be regarded as a metastable form of oxide that is stable at higher pH values[13].

The effect of chloride ions is also well known. Surface compounds containing chloride ions (oxi-chlorides instead of pure oxides) are probably formed, which, owing to lattice defects and a higher solubility, lead to a local breakdown of the oxide film[17].

But the pH value and the chloride ion concentration do not only influence the nature of the passive film; they also affect the critical passivation current density needed to achieve passivation. Passivity is normally the result of a corrosion reaction involving both a cathodic and an anodic reaction and, for a metal to passivate spontaneously, two conditions must be satisfied: (a) the redox potential of the solution must be more positive than the primary passivation potential, and (b) the rate of the cathodic reaction must be greater than the critical passivation current.

The critical passivation current density depends on the chromium content of the alloy[18] but also on the composition of the electrolyte in contact with the metal, the amount and nature of the anions present, and the pH of the solution. Sato *et al.*[19], for instance, showed that the critical passivation current density of iron decreases strongly with increasing pH of the solution.

The effect of the pH value on the critical passivation current density of the 9 per cent chromium alloy appears clearly from Tables III and IV, while the effect of the chloride ion concentration is obvious only at pH 8.

The above considerations account for the results obtained in the environment considered here (synthetic mine water of various pH values and chloride ion contents). Although the low-chromium alloys generally had a slightly lower corrosion rate than mild steel, it was only at a pH value of 10 that the alloys with a chromium content of 5 per cent or higher became spontaneously passive and had a corrosion rate equivalent to that of 3CR12. However, when the chloride concentration was fairly low (100 p.p.m.), a substantial drop in corrosion rate was observed at pH 8 when the chromium content was equal to or higher than 5 per cent.

The electrochemical results also suggest that no pitting should be expected if the metallic surface is exempt from defects or existing pits, but that the propagation of existing pits is not excluded if defects are present on the metallic surface, or if debris or fouling can induce underdeposit corrosion. In fact, it was observed in all the long-term experiments that the intermediate chromium alloys suffered localized corrosion, and the general appearance of the samples seems to indicate that the localized attack was probably induced by the formation of local cells on certain parts of the total area.

Conclusions

The various results described in this paper indicate that intermediate-chromium alloys show a significant decrease in corrosion rate only at high pH values (8 or 10 according to the concentration of chloride ions).

In acidic or neutral mine waters, their corrosion rate is close to that of mild steel and, although a certain decrease in corrosion rate is usually noticed with increasing chromium content, various forms of localized corrosion are observed on all the intermediate-chromium alloys.

Acknowledgment

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