

Effect of sulphate on the pitting corrosion of AISI 310 and AISI 316 in synthetic mine water

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Abstract

Failure of equipment due to corrosion is a major problem in South African mining industry. Mild steel which was previously being used as constructional material are now being replaced with AISI 310 and AISI 316 stainless steels. However, the synergistic effect of chloride and sulphate ions on the pitting corrosion of both materials has not been extensively investigated in mine environments. Therefore, the pitting corrosion of AISI 310 and AISI 316 stainless steels have been assessed using potentiodynamic polarisation testing in synthetic mine waters containing different permutation levels of chloride and sulphate ions. The results show that increasing the sulphate content improves the pitting and general corrosion resistance of the alloys. However, at sulphate-to-chloride ratio of 1.0, the pitting potentials for both alloys are reduced due to precipitation of sulphate. The results were correlated with the beneficial action of the corresponding alloying elements.

Keywords: Corrosion, Stainless steels, Sulphate, Chloride, Synthetic mine water.

1. Introduction

Failure of equipment due to corrosion is a major problem in the South African mining industry. Corrosion of pipes, valves, and fittings account for one of the highest expenditures on equipment and spares [1]. Mild steel which was previously being used as constructional material for components in contact with South African mine waters are now being replaced by a more corrosion resistant material such as AISI 316 and AISI 310 stainless steels. South

African mine waters contain both chloride and sulphate derived from soluble salts (i.e. NaCl, Na_2SO_4 , MgSO_4 , and CaCl_2) which make up the bulk of the total solids in solution [2]. The deleterious effect of high levels of chloride ions on the resistance of stainless steels to localised corrosion is well known [3-8]. Sulphate ions have been shown to improve the localised corrosion behaviour of stainless steels including pitting, crevice and stress corrosion cracking in chloride containing environments [9-14]. However, little data in this area of study is available for AISI 316 and AISI 310. The effect of sulphate ions appears to be less understood in South African mine waters [2, 10, 15]. The synergistic effect of chloride and sulphate ions on the pitting corrosion of a more pitting resistant AISI 310 has not been investigated in mine environments. It has been found that sulphate could also act as a promoter of localized corrosion under certain environmental conditions in some stainless steels and nickel alloys [12, 13, 16, 17]. Therefore, the presence of sulphate ion could act as an inhibitor, or as an accelerator of localized corrosion, depending on several parameters including concentration ratio of sulphate and chloride ions in solution, environmental and metallurgical factors.

The present study was undertaken to determine and compare the effect of sulphate on the pitting corrosion of AISI 310 and AISI 316 stainless steels in mine water environment using polarisation techniques. The composition of the synthetic mine water used represent the most aggressive mine water in the gold mines in South Africa [18] and the ratio of sulphate to chloride was varied to elucidate the inhibition effect or otherwise of sulphate ions on the corrosion behaviour of selected materials.

2. Methodology

2.1 Materials

Commercial stainless steel grades AISI 310 and AISI 316 were supplied by Columbus Stainless (Pty) Ltd., South Africa in hot rolled and annealed condition. The chemical composition of the alloys is given in **Table 1**. All experiments were conducted in as-received state. Corrosion test specimens were cut from the bulk having dimension of 1.5 cm x 1 cm x 0.5 cm. The specimens for electrochemical testing were prepared by attaching an insulated copper wire using aluminium tape to one face of the specimen and cold mounted in an epoxy resin, except for measurement area of 1.5 cm^2 . The specimens were abraded to 1000 finishes with SiC grit papers and polished to $1 \mu\text{m}$ surface finished using alumina slurry. The

specimens were ultrasonically cleaned in ethanol before immersion in electrolyte for corrosion testing.

Table 1 Chemical composition of ASIS 310 and AISI 316 (wt%)

Material	C	N	Ni	Cr	S	P	Mn	Si	Mo	Fe
310	0.075	0.005	20.1	24.4	0.023	0.045	1.91	1.60	-	Bal
316	0.070	0.10	13.0	18.1	0.015	0.045	2.00	0.75	2.5	Bal

Synthetic mine water was used as electrolyte for the corrosion testing. The electrolytes were prepared from analytical grade NaCl, Na₂SO₄, MgSO₄ and CaCl₂ and deionised water. The electrolyte was prepared so as to approximate the chloride and sulphate contents found in a variety of actual mine waters in South Africa. The chemical composition of the minewater is given in **Table 2**. With chloride concentration fixed, sulphate concentration was varied from 500, 980, 1500 and 2000 ppm to obtain sulphate-to-chloride ratio of 0.33, 0.65, 1.0 and 1.33, respectively using Na₂SO₄. This was to investigate the effect of sulphate-to-chloride ratio on pitting behaviour of selected steels. The pH values of the solutions were adjusted to a constant value of 8.0 by the addition of appropriate amounts of sodium hydroxide and monitored using pH meter (827 pH lab). This pH value was selected because it lies close to that observed in the majority of mine waters in South African [10].

Table 2 Synthetic mine water concentration at pH = 8

Ions	SO ₄ ²⁻	Ca ²⁺	Cl ⁻	Mg ²⁺	Na ⁺
Concentration (ppm)	500	375	1500	40	943

2.2 Electrochemical corrosion testing

Electrochemical techniques were used to obtain information on the corrosion behaviour of AISI 310 and AISI 316 stainless steels in the electrolyte. The corrosion experiments were carried out using Princeton Applied Research Potentiostat (VersaSTAT 4) with versaSTUDIO electrochemical software (version 2.1). All the experiments were carried out using a three-electrode corrosion cell set-up with saturated Ag/AgCl as reference and platinum as counter electrode. All tests were conducted at room temperature (25 ± 2 °C).

Potentiodynamic polarization measurements were carried out using a scan rate of 0.167 mV/s at a potential initiated at -100 mV to +1500 mV versus open circuit potential (OCP). Before starting the polarization scan, the specimens were cathodically polarized at -1000 mV for 5 minutes followed by stabilization for about 1 hr. Linear polarisation resistance (R_p) method was used to calculate the corrosion rates of the alloys. Scans for linear polarisation were measured at the scan rate of 0.167 mV/s between -20 mV to +20 mV relative to the E_{corr} . Corrosion rates were calculated from values derived from polarisation resistance measurements. In all cases, triplicate experiments were carried out to ensure reproducibility. Corroded surfaces were observed using ultra high resolution scanning electron microscope (FE-SEM JSM 7600F).

3. Results and discussion

Fig. 1 shows the potentiodynamic polarization curves of the samples studied in synthetic mine water at varying sulphate concentration. Pseudo-passivity features were observed at 0.65 and 1.0 sulphate-to-chloride ratios for both AISI 310 and AISI 316 stainless steels. The passive region was narrow as expected in alkaline environments [19, 20]. The E_{corr} shifted to more positive values as the sulphate-to-chloride ratio increased in the electrolyte. The pitting potential (E_{pit}), defined as the potential at which the current density shows a strong increase, increased with increasing sulphate-to-chloride ratio for both AISI 310 and AISI 316 stainless steels except at sulphate-to-chloride ratio of 1.0 (**Fig. 2**). The onset of pitting was characterised by a sharp increase in current density which was more pronounced at lower sulphate-to-chloride ratio (i.e. 0.33). At corresponding potentials, the current densities were significantly higher in the electrolyte containing lower sulphate in the electrolyte.

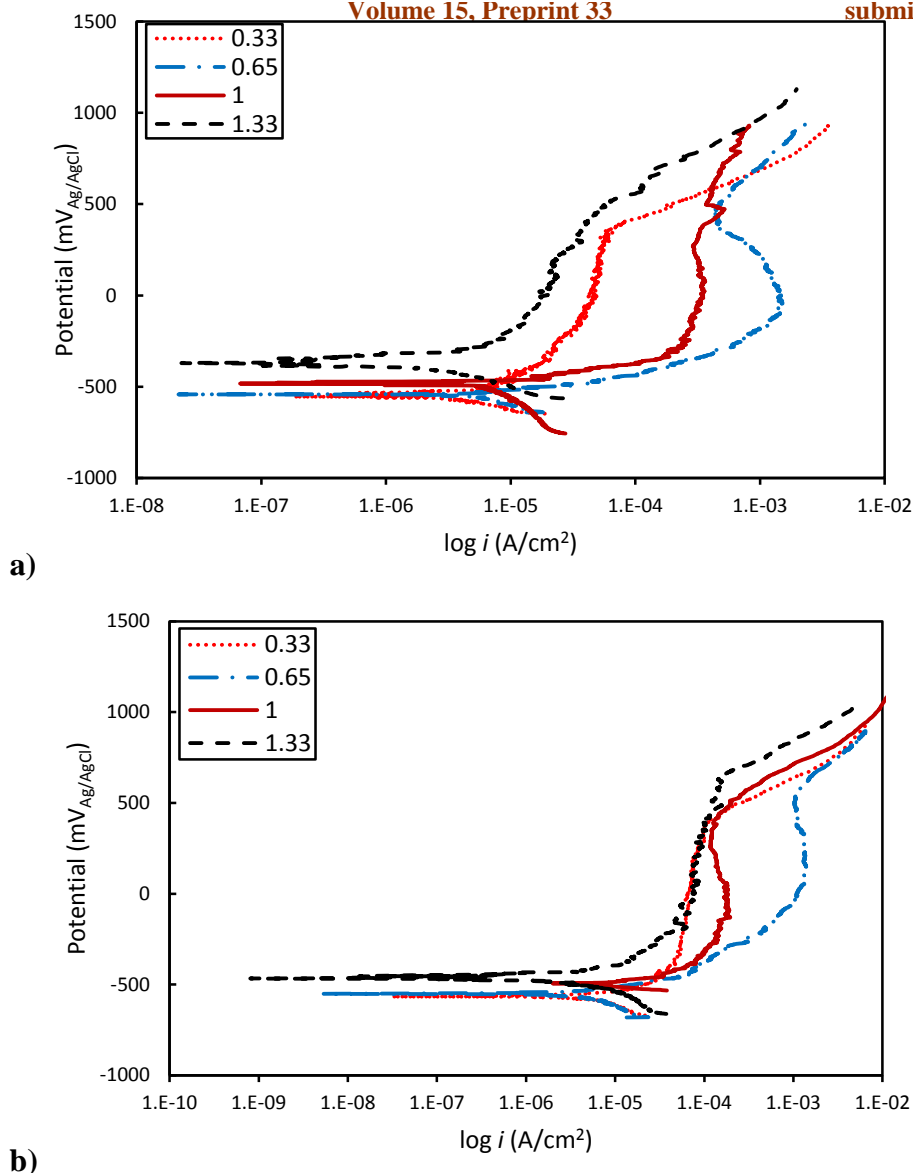


Fig. 1 Effect of sulphate-to-chloride ratio on the potentiodynamic polarisation curves of (a) AISI 310 and (b) AISI 316 in synthetic mine water at pH=8

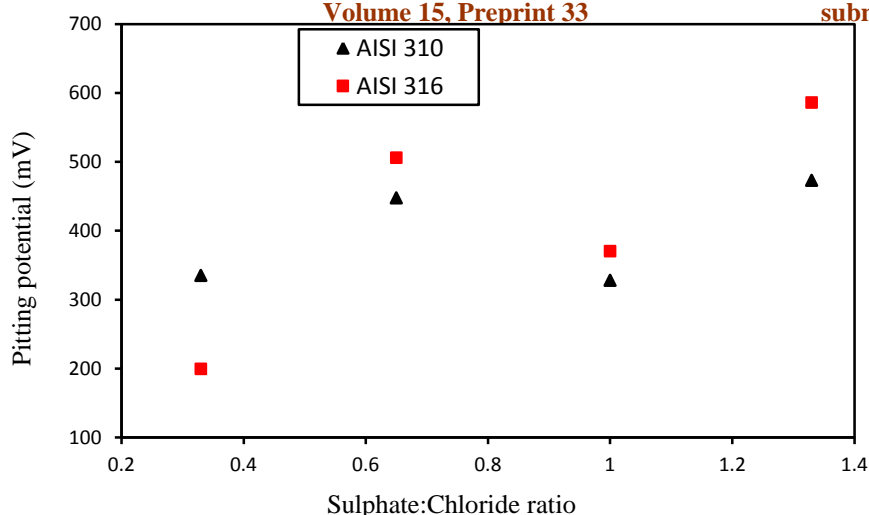
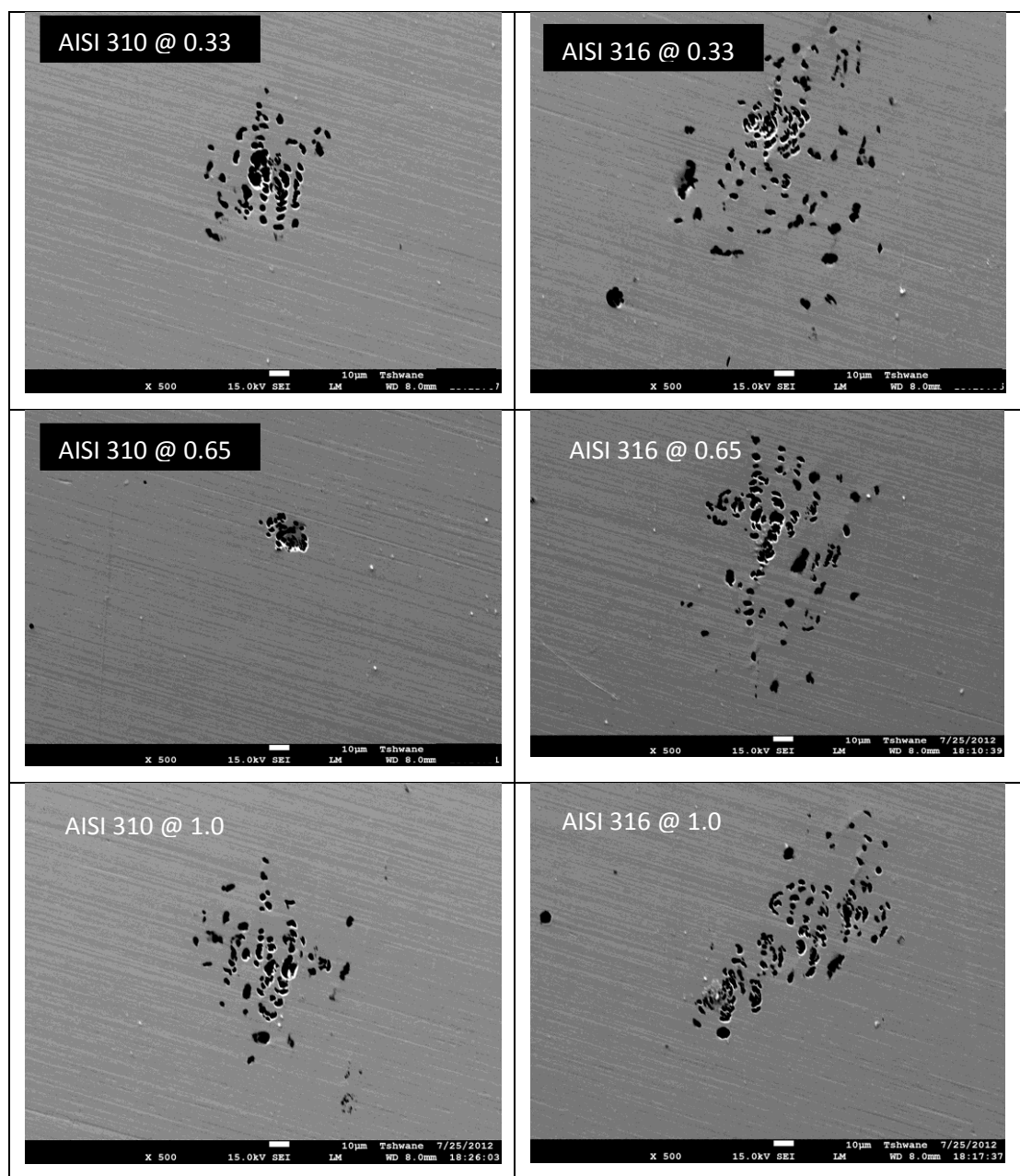


Fig. 2 Effect of sulphate-to-chloride ratio on the pitting potential of AISI 310 and AISI 316 in synthetic mine water at pH=8.

Two hypotheses have been used to explain the deleterious effect of high chloride concentration on the pitting corrosion of stainless steels; (a) the chloride ions enter the passive film and thereby enhance the conduction of metal cations through the film, or (b) the adsorption of chloride ions around metal cations leading to enhanced dissolution over non- or aquo-complexed cations. It is also proposed that sulphate inhibits pitting corrosion because it absorbs on the metal surface preventing ingress of chlorides [9-14, 21]. When considering the inhibitive effect of sulphate, consideration must also be given to the precipitation of sulphates which can substantially change the ionic ratio between sulphates and chlorides. It has been reported that there is a critical concentration of sulphate-to-chloride ratio above which precipitation of sulphate compounds could occur [22], hence reducing the beneficial effect of sulphate additions on pitting corrosion. The results obtained from the potentiodynamic polarization curves reveals distinct beneficial effects of sulphate additions on the passivity and pitting potentials of both AISI 310 and AISI 316 alloys in mine water environment. However, at sulphate-to-chloride ratio of 1.0, the pitting potentials for both alloys are reduced, increasing their pitting susceptibility. Pohjanne et al. [23] has developed solubility limits for Na_2SO_4 in NaCl by estimation of ionic products of pure saturated salt solution. It was observed that at sulphate-to-chloride ratio of 1.0, there is potential precipitation of sulphate. In the current work, the beneficial effect of sulphates on pitting corrosion of both alloys was reduced at sulphate-to-chloride ratio of 1.0, possibly due to the precipitation of sulphate. Additionally, pitting potentials for AISI 316 were higher in all sulphate-to-chloride

ratios except 0.33 (**Fig. 2**). This is due to the combined effect of chromium and molybdenum additions to the steel [24-30]. Stainless steels alloyed with chromium and molybdenum increases pitting corrosion resistance either in concentrated chloride solutions or in diluted ones [25]. **Fig. 3** shows the SEM images after potentiodynamic polarisation in the different sulphate concentrations.



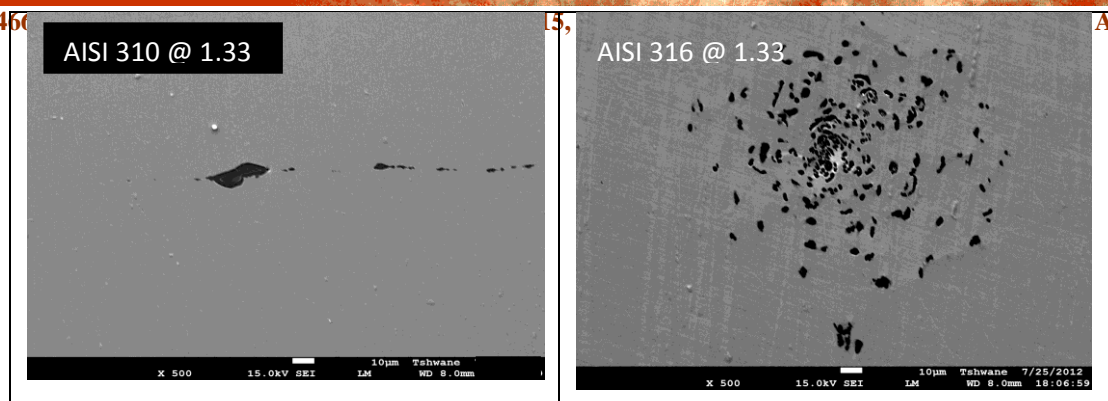


Fig. 3 SEM images of (a) AISI 310 and (b) AISI 316 in synthetic mine water at pH=8 after polarisation showing the extent of pitting corrosion in different sulphate:chloride ratios.

The corrosion current density (i_{corr}) for both materials also decreased with increasing sulphate-to-chloride ratio except for 1.0. As described earlier, this is due to the precipitation of sulphate. Thus sulphate addition mitigates the detrimental effects of chloride ions on the general corrosion rate (determined by linear polarisation resistance method) of AISI 310 and AISI 316 stainless steels (**Fig. 4**). It is also observed that the corrosion current densities were slightly higher for AISI 310 than AISI 316 at lower sulphate-to-chloride ratios (i.e. 0.33 and 0.65). This is due to the combined effect of chromium and molybdenum additions to AISI 316 which improves the pitting corrosion resistance at higher chloride concentrations [30].

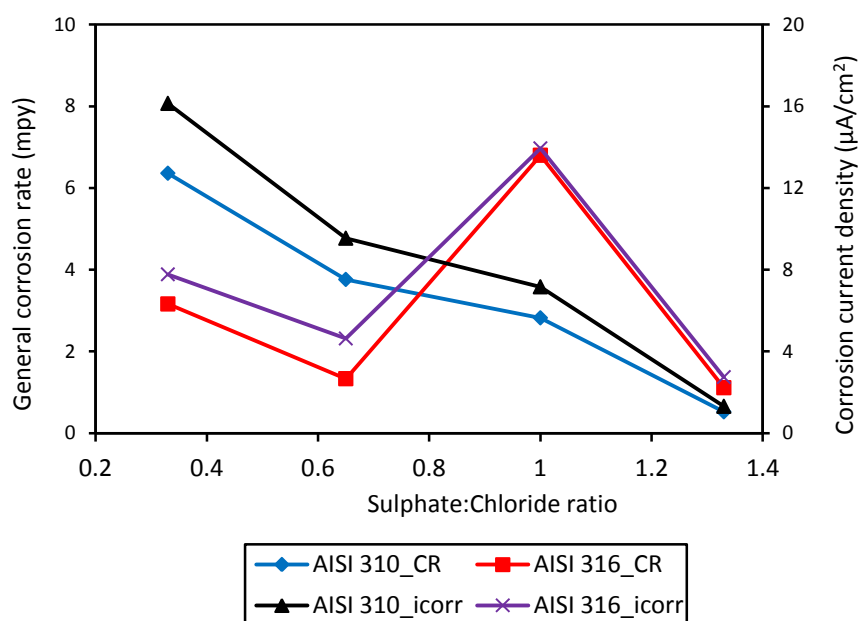


Fig. 4 Effect of sulphate-to-chloride ratio on the general corrosion rates of AISI 310 and AISI 316 in synthetic mine water at pH=8.

The effect of sulphate on pitting corrosion of AISI 310 and AISI 316 has been investigated in synthetic mine water using potentiodynamic polarisation method. The sulphate addition mitigates the detrimental effects of chloride ions on both the general corrosion rate and pitting potentials of AISI 310 and AISI 316 stainless steels. It is observed that the E_{corr} shifted to more positive values as the sulphate-to-chloride ratio increased in the electrolyte. The E_{pit} increased with increasing sulphate-to-chloride ratio for both materials except at sulphate-to-chloride ratio of 1.0. This is due to the precipitation of sulphate. The pitting potentials of AISI 316 were higher than AISI 310 in investigated electrolytes due to the combined inhibitive action of chromium and molybdenum in AISI 316.

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