

Application of the Polarised Potential-pH Diagrams to Investigate the Role of Sulfate and Dissolved Oxygen in the 3550-ppm NaCl Solution on the Corrosion Behaviour of AISI 316L Stainless Steel

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The cyclic polarisation technique was applied to determine the corrosion, primary-passivation, transpassive, and protection potential of AISI 316L stainless steels immersed in 3550-ppm NaCl solution containing sulfate in the content up to 3000 ppm. The solutions were kept constant at 27°C and saturated by laboratory air. The solution pH was varied from 3 to 11. Each type of potentials was plotted in function of pH and linked as lines to determine the different zones in the constructed potential-pH diagram. The predominant regimes of the immunity, general corrosion, perfect passivation, imperfect passivation, and pitting corrosion were determined based on those lines of potentials. Comparing to the potential-pH diagram of specimens immersed in the aerated and deaerated 3550-ppm NaCl solutions, the addition of 3000-ppm Na₂SO₄ to these solutions increased the overall, perfect and imperfect, passivation regime by shifting the transpassive-potential line to the noble direction. However, it also widened the imperfect passivation area. The addition of Na₂SO₄ did not significantly affect the corrosion potential. It was found that the dissolved oxygen tends to negatively shift the transpassive-potential and protection-potential lines at all studied pH. The considerable effect of dissolved oxygen on corrosion and primary-passivation potentials could not be observed.

Keywords : potential-pH diagram, AISI 316L stainless steel, and sodium sulfate

1. Introduction

The potential-pH diagram was first constructed by M. Pourbaix by using thermodynamic data based on the equilibrium of electrochemical system.¹⁾ In the aqueous corrosion aspect, it can be applied to determine the regime of immunity, passivation and corrosion of metals at different solution pH and reversible potentials.²⁾ However, there are some limitations of the construction of this thermodynamic potential-pH diagram, especially when the metal is alloy and the solution is dissolved by various ions. The construction of the potential-pH diagram by potentiokinetic polarisation method has then alternatively been proposed.³⁾ The potential-pH diagram of AISI 304 stainless steel was constructed.⁴⁾ This technique has recently been applied to

establish the potential-pH diagram of AISI 316L stainless steel in the simulated underground water by considering only the effect of chloride ion in solution.^{5),6)} However, the presence of various ions, such as the sulfate one, in natural water or water from factories were also reported. According to the field report,⁷⁾ sulfate ions are dissolved in the underground water in Bangkok and peripheral provinces with the content of 1 up to 300 milligrams per litre. In some areas in the world, the sulfate content can be up to 3000 milligram per litre.⁷⁾ The content of sulfate can be higher in the case of waste water from the factories. Not only the effect of dissolved ions, the dissolved gases in solution especially oxygen from air also play the role on the corrosion behaviour of the alloy contacted with solution. The objectives of this work are then to investigate the role of dissolved ions, particularly the sulfate one in chloride-containing aqueous solution, and dissolved oxy-

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gen on the corrosion behaviour of stainless steels. The cyclic polarisation method is primarily performed in order to obtain data to construct the potential-pH diagram. The effect of dissolved ions and gases on the corrosion behaviour will further be discussed based on the established potential-pH diagrams.

2. Experimental

A material used in this experiment was an AISI 316L stainless steel. The chemical composition is given in Table 1. Specimens were cut as disk with the area contacted to solution of 78 mm². They were polished by SiC paper from 180 to 1200 grid. Then, they were ultrasonically cleaned with distilled water and kept in air for 24 hours before the potentiodynamic measurement.

The solutions were prepared by the addition of 3550-ppm sodium chloride (NaCl), 3000-ppm sodium sulfate (Na₂SO₄), 3550-ppm NaCl mixed with 300-ppm Na₂SO₄, 3550-ppm NaCl mixed with 3000-ppm Na₂SO₄, to de-ionised water. Each solution was saturated by laboratory air and nitrogen to investigate the role of dissolved oxygen. The solution pH was varied as 3, 5, 7, 9, and 11, which was adjusted by hydrochloric acid and sodium hydroxide.

The cyclic potentiodynamic experiment was carried out using potentioestat model 352/252. The scan rate was 0.1 mV/sec. Reference and counter electrodes were Ag/AgCl and platinum respectively. The cyclic polarisation curves illustrating the polarized potential as a function of current density were obtained. The corrosion potential (E_{corr}), primary passivation potential (E_{pp}), protection potential (E_{pr}), and transpassive potential (E_t) were further determined by methods previously described elsewhere.^{5,6} Each type of potentials was plotted in function of pH and linked as lines to determine the different zones in the constructed potential-pH diagram. The predominant regimes of immunity corresponds to the area under the corrosion-potential line. The regime of general corrosion is bounded by the corrosion-potential and primary-passivation-potential lines. The perfect passivation regime is bounded by the primary-passivation-potential and protection-potential lines. The imperfect passivation regime is bounded by the protection-potential and transpassive-potential lines. The transpassive regime, or pitting one in the case that chloride ion is contained in solution, corresponds to the area upper the transpassive-potential line.

Table 1. Chemical composition of type 316L specimens (wt. %)

C	Si	Mn	P	Ni	Cr	Mo	N
0.03%	0.002%	1.62%	0.023%	11.05%	17.44%	2.09%	0.032%

3. Results and discussion

3.1 Effect of chloride and sulfate

Fig. 1 presents the potential-pH diagram of specimen immersed in 3550-ppm NaCl solution. The transpassive-potential line of AISI 316L stainless steels immersed in aerated 3550-ppm NaCl solution obtained in the present work is lower than that of specimens immersed in aerated de-ionised water reported in literature.⁶ Furthermore, it was reported⁶ that the imperfect passivation area did not exist in the potential-pH diagram of specimens contacted to aerated de-ionised water. This area still did not exist when the slight content, 50 ppm, of NaCl was added to aerated de-ionised water. The imperfect passivation area was observed only at low solution pH when 500 ppm of NaCl was added to aerated de-ionised water. In the present work, NaCl was added to aerated de-ionised water up to 3550 ppm. It was found that the imperfect passivation area existed at all studied-low, neutral and high-solution pH. The decrease of transpassive potential with the decreased solution pH was also observed.

When the 3000-ppm Na₂SO₄ was added to aerated 3550-ppm NaCl solution, the predominant areas in the potential-pH diagram were transformed as shown in Fig. 2. It was primarily observed that the addition of 3000-ppm Na₂SO₄ to aerated 3550-ppm NaCl solution significantly leveled the transpassive-potential line up to the noble direction. The shift of primary-passivation-potential line could not be considerably observed. The addition of 3000-ppm Na₂SO₄ to 3550-ppm NaCl solution then gave rise to the widening of the overall, perfect and imperfect, passivation regime due to the noble shift of the transpassive-potential line. However, the addition of 3000-ppm Na₂SO₄ slightly shifted the protection-potential line to the negative direction at the solution pH of 3 to 9. Then the

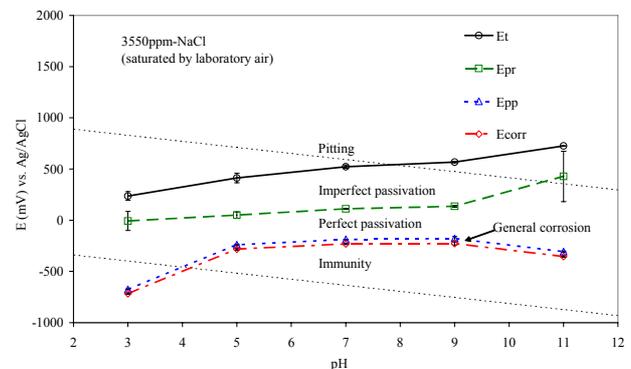


Fig. 1. Potential-pH diagram of AISI 316L stainless steel in 3550-ppm NaCl solution saturated by laboratory air

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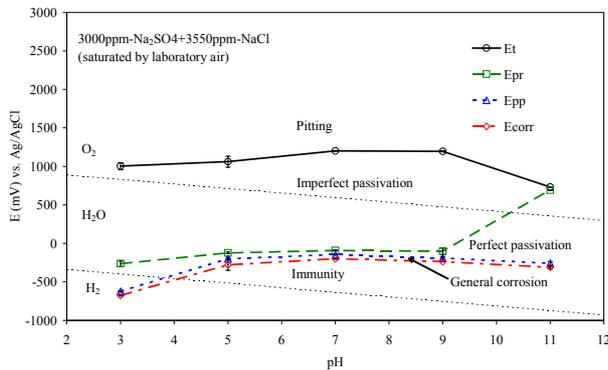


Fig. 2. Potential-pH diagram of AISI 316L stainless steel in 3550-ppm NaCl solution mixed with 3000-ppm Na₂SO₄ saturated by laboratory air

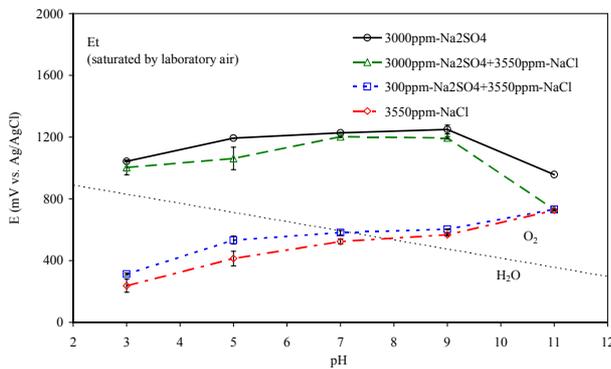


Fig. 3. Transpassive-potential line of AISI 316L stainless steel in chloride and sulfate solutions saturated by laboratory air.

significantly positive shift of the transpassive-potential line and the slightly negative shift of the protection-potential line due to the addition of 3000-ppm Na₂SO₄ to aerated 3550-ppm NaCl solution widened the imperfect passivation regime.

To investigate the role of sulfate in more detail, the polarisation curves of specimens immersed in 3550-ppm NaCl, 3550-ppm NaCl mixed with 300-ppm Na₂SO₄, 3550-ppm NaCl mixed with 3000-ppm Na₂SO₄, and 3000-ppm Na₂SO₄ solutions saturated by laboratory air were investigated at all studied pH. The transpassive potentials extracted from these curves are shown in Fig. 3.

It was found that the addition of 300-ppm Na₂SO₄ to aerated 3550-ppm NaCl solution slightly increased the transpassive potential. However, when Na₂SO₄ was added up to 3000 ppm, the transpassive-potential line significantly shifted to the positive direction as also observed in Figs. 1 and 2. Comparing the transpassive-potential line of specimens immersed in aerated 3000-ppm Na₂SO₄ solution and that of specimens immersed in such solution with the containing of 3550-ppm NaCl, it was found that

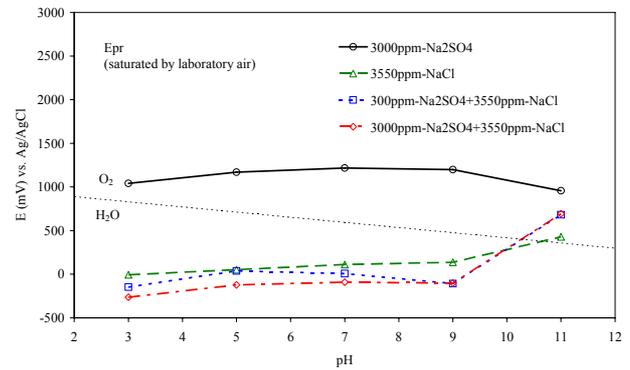


Fig. 4. Protection-potential line of AISI 316L stainless steel in chloride and sulfate solutions saturated by laboratory air.

the addition of 3550-ppm NaCl in aerated 3000-ppm Na₂SO₄ solution only slightly shifted the transpassive-potential line to the less noble direction. Fig. 4 presents the protection-potential line of specimens immersed in chloride and sulfate solutions. The addition of 300 and 3000 ppm Na₂SO₄ to aerated 3550-ppm NaCl solution slightly decrease the protection potential at solution pH of 3 to 9. Comparing to aerated 3000-ppm Na₂SO₄ solution, the addition of 3550-ppm NaCl to such solution significantly decreased the protection potentials at all studied pH, contradictorily to the case of the transpassive potential in Fig. 3. It is then concluded that sulfate in aerated solution plays the strong role to withstand the effect of chloride ions by maintaining the pitting potential, but it cannot withstand the role chloride ions to promote the imperfect passivation regime caused by the lowering of the protection potential.

The corrosion-potential lines of specimens immersed in chloride and sulfate solutions are further drawn in Fig. 5. It was found that the addition of Na₂SO₄ to aerated 3550-ppm NaCl solution did not significantly affect the

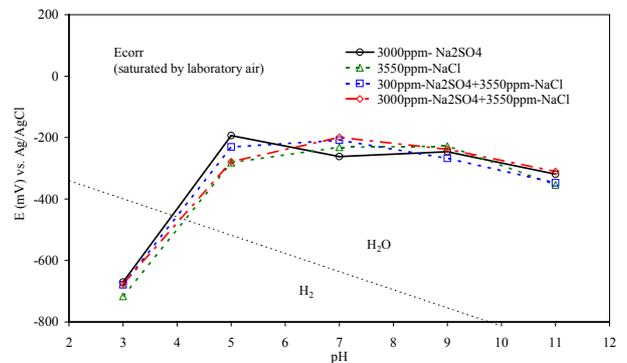


Fig. 5. Corrosion-potential line of AISI 316L stainless steel in chloride and sulfate solutions saturated by laboratory air.

corrosion-potential line. This indicates the similar rate of general corrosion of specimen immersed in these solutions.

3.2 Effect of dissolved oxygen

To investigate the role of dissolved oxygen, nitrogen gas was bubbled into solution instead of laboratory air. The potential-pH diagrams of specimens in 3550-ppm NaCl solutions without and with 3000-ppm Na₂SO₄ saturated by nitrogen were superposed on those saturated by laboratory air as in Figs. 6 and 7. It was observed that the dissolved oxygen decreased the transpassive and protection potentials of specimens immersed in 3550-ppm NaCl solutions without and with 3000-ppm Na₂SO₄, obviously at the solution pH of 3 to 9. The effect of dissolved oxygen on corrosion and primary passivation potentials could not be considerably observed.

As a matter of discussion, the shift of potential lines in different solutions can be from the role of sulfate and also the dissolved oxygen. In the case that the role of dissolved oxygen was eliminated by the saturation of nitrogen in solution, it was still found that the transpassive potentials of specimens immersed in 3550-ppm NaCl solution containing 3000-ppm Na₂SO₄ is higher than that immersed in 3550-ppm NaCl solution. This insists the role of sulfate to promote the positive shift of the transpassive potentials. However, when the role of dissolved oxygen was eliminated, it was found that the presence of sulfate in 3550-ppm NaCl solution did not considerably affect the protection potential at the solution pH of 3 to 9 as declared in Fig. 8. It can then be discussed that the decrease of protection potential due to the addition of Na₂SO₄ in aerated 3550-ppm NaCl solutions (Fig. 4) is not purely due to the effect of sulfate. This potential decrease may be due to the different solubilities of oxygen in each solution or by the synergistic effect of sulfate and dissolved oxygen in solution.

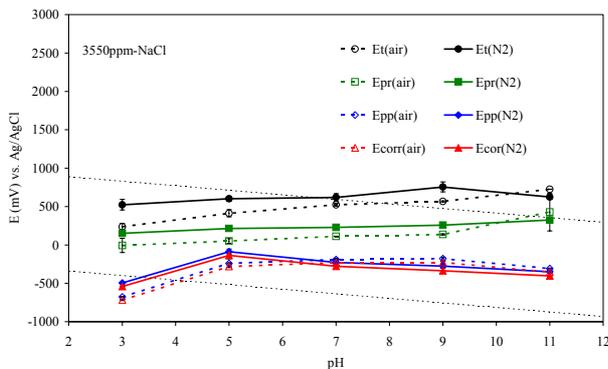


Fig. 6. Potential-pH diagram of AISI 316L stainless steel in 3550-ppm NaCl solution saturated by laboratory air and nitrogen.

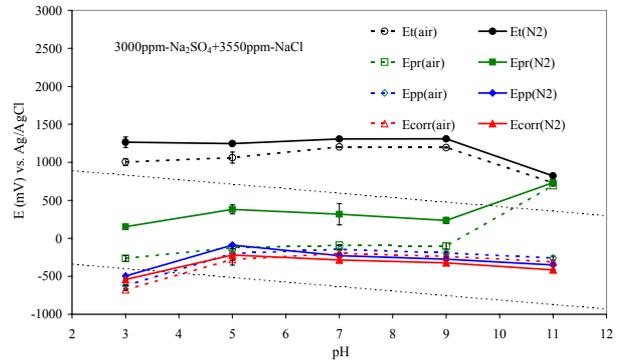


Fig. 7. Potential-pH diagram of AISI 316L stainless steel in 3550-ppm NaCl solution mixed with 3000-ppm Na₂SO₄ saturated by laboratory air and nitrogen.

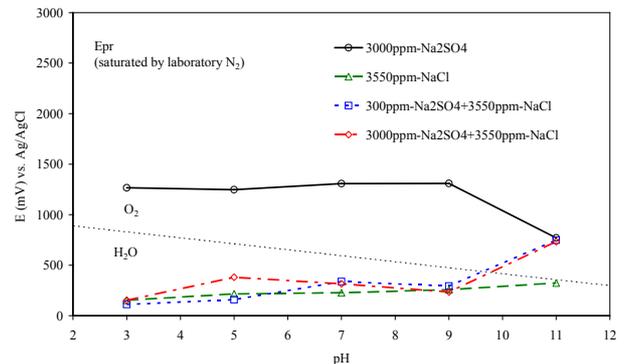


Fig. 8. Protection-potential line of AISI 316L stainless steel in chloride and sulfate solutions saturated by nitrogen.

4. Conclusions

The cyclic polarisation technique was applied to determine the corrosion, primary-passivation, transpassive, and protection potential of AISI 316L stainless steels immersed in 3550-ppm NaCl solution containing sulfate in the content up to 3000 ppm. The solution pH was varied from 3 to 11 and saturated by laboratory air and nitrogen. Each type of potentials was plotted in function of pH and linked as lines to determine the different predominant zones in the constructed potential-pH diagram. The following conclusions can be drawn.

(1) The addition of sulfate up to 3000 ppm to aerated and deaerated 3550-ppm NaCl solutions significantly increased the transpassive potential at all studied solution pH of 3-11. This gave rise to the widening of the overall passivation regime in the potential-pH diagram.

(2) The protection potential slightly decreased with the addition of Na₂SO₄ up to 3000 ppm to aerated 3550-ppm

NaCl solution. However, this addition did not shift the protection potential when solution was deaerated at solution pH of 3 to 9. In both aerated and deaerated conditions, the imperfect passivation regime was widened significantly by the positive shift of the transpassive-potential line previously summarised.

(3) The addition of 3000 ppm of sulfate to aerated and deaerated 3550-ppm NaCl solution did not affect the corrosion potential at all studied pH. This indicates the similar rate of uniform corrosion independent from the content of sulfate in solution.

(4) The dissolved oxygen decreased the transpassive and protection potentials, whereas it does not affect the corrosion and primary passivation potentials.

(5) In aerated and deaerated 3550-ppm NaCl solution, sulfate behaves as the inhibitor by shifting the transpassive potential to the noble direction. However, it also helps increase the imperfect passivation regime, and does not change the rate of uniform corrosion.

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