

## Corrosion Concepts

In dieser Rubrik können Sie, die Leser, praxisorientierte Beiträge zur Diskussion stellen. Es werden Korrosionsprobleme, aber auch Lösungswege und praktische Erfahrungen veröffentlicht. Damit soll der Erfahrungsaustausch unter den Lesern dieses Periodikums zu einer ständigen Einrichtung werden. Vor allem die Praktiker und die „Senior Scientists“ sind aufgefordert, von ihrem reichhaltigen Wissen abzugeben. Wir bitten Sie um Ihre Mitarbeit in Form von Beiträgen und Leserbriefen.

In this forum readers will be able to present practical problems for discussion. It is envisaged that these contributions will include not only discussion of general problems and incidents of corrosion but that suggested remedies will also be presented and discussed. It is hoped that this exchange of knowledge and experience will become a permanent feature of this periodical. We are particularly anxious that both Senior Scientists and those with more practical experience will make use of this forum to exchange information, problems and potential remedies.

# An investigation on the effect of bleaching environment on pitting corrosion and transpassive dissolution of 316 stainless steel

M. H. Moayed\* and M. Golestanipour

Pitting corrosion and transpassive dissolution of 316 stainless steel in a solution containing five percent of commercial bleaching liquid was investigated by employing potentiodynamic polarization method and recording corrosion potential during immersion. Today commercial bleaching liquids are widely used as a cleaner additive. Therefore those house appliances made from stainless steels are in contact with aqueous solution containing bleaching liquid. This may cause severe localized corrosion and transpassive dissolution. In order to investigate the possibility of transpassive dissolution of stainless steel by bleaching liquid, potentiodynamic polarization and recording the variation of corrosion potential of specimens were carried out in 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution containing 5%wt. com-

mercial bleaching liquid. A 500 mV drop in transpassive potential and also instantaneously ennobled corrosion potential revealed the possibility of transpassive dissolution due to the oxidizing effect of the species such as free chlorine and its derivatives in bleaching liquid. Evaluation of the occurrence of localized corrosion at the presence of Cl<sup>-</sup> and bleaching liquid was investigated by similar electrochemical experiments in 0.2 M Na<sub>2</sub>SO<sub>4</sub> + 0.4 M NaCl containing 5%wt. bleaching solution. Initiation of stable pitting at potentials lower than the transpassive potential as well as a sharp increase of the corrosion potential in this environment demonstrates the possibility of pitting corrosion.

## 1 Introduction

The excellence of corrosion resistance of stainless steels is due to the passive layer that covers its surface. Stainless steel surfaces can show three different types of behavior in electrolyte: active dissolution, passivation and transpassive dissolution depending on the metal/electrolyte interface potential. In the active and transpassive states the state of corrosion is uniform while in the passive state the rate of corrosion is very slow and in the range of  $\mu\text{A}/\text{cm}^2$ . Pitting is a result of the

breakdown of the passive film at the presence of aggressive anions such as Cl<sup>-</sup>. Once the breakdown of passive film occurs, the anodic reaction takes place inside the pit cavity and the cathodic reaction at the passive metal surface. Pitting corrosion has been usually characterized by the pitting potential ( $E_{\text{pit}}$ ) and the potential at which propagating pits can be repassivated named protection potential ( $E_{\text{pp}}$ ) [1].

Pitting corrosion depends not only on the concentration of Cl<sup>-</sup> ions which decreases by an increasing of the Cl<sup>-</sup> concentration, but also on the concentration of nonaggressive anions, and more precisely on the ratio of aggressive to nonaggressive anions. It has been reported by *Pistorius* and *Berstein* [2] that SO<sub>4</sub><sup>2-</sup> and OH<sup>-</sup> anions are not aggressive to pitting corrosion. These anions cause the shift of pitting potential of stainless steel to more positive values. No pitting corrosion of stainless steels has been reported at the absence of aggressive anions such as Cl<sup>-</sup> and Br<sup>-</sup>.

\* M. H. Moayed, M. Golestanipour,  
Department of Materials and Metallurgical Engineering,  
School of Engineering, Ferdowsi University of Mashhad,  
Mashhad, P.O. Box 91775-1111 (Iran)

**Table 1.** Chemical analysis of investigated alloy (%wt.)

Stainless steel grade	Main alloying elements					
	Fe	C	Mn	Cr	Ni	Mo
316	Balance	0.035	1.25	16.75	10.25	2.1

Transpassivity of chromium is a well-known phenomenon, due to the oxidation of solid Cr(III) oxide to soluble Cr(VI). Every corrosion scientist is familiar with the rise in current that occurs at high potentials when stainless steel is polarized anodically. There have been few reports of practical corrosion problems connected with transpassivity, but such a problem is theoretically possible in the presence of oxidants such as hypochloride, chlorine dioxide and hydrogen peroxide [3–6].

Investigation on the corrosion behavior of stainless steels at the presence of bleaching environments has been concentrated on the effect of residual free chlorine in industrial plants (e.g. desalination systems, pulp and paper plants, power plant cooling water systems) due to chlorination treatment that were carried out by dosing with hypochloride compounds (e.g. NaOCl). There is a general agreement in the literature [7–9] that the presence of oxidizing species can ennoble the free corrosion potential of stainless steels and increase the risk of localized corrosion and transpassive dissolution. Neville and co-workers [7] reported the effect of residual chlorine on the depolarization of the cathodic reaction that promotes localized corrosion propagation. They also reported a very high crevice corrosion rate in chlorinated seawater in comparison to nonchlorinated seawater. High crevice propagation was attributed to the influence of oxidizing species that oxidized  $Fe^{2+}$  in the early stage of crevice corrosion to  $Fe^{3+}$  which promotes autocatalysis of crevice corrosion by increasing the severity of the crevice solution. The presence of the level of chlorine below 10 ppm on localized corrosion of 304 stainless steel was investigated by Bardal et al. [8]. They reported that the presence of the highly oxidizing species can shift the corrosion potential to positive values and increase the risk of localized corrosion initiation.

In this paper it is shown that the bleaching liquids that are widely used as a cleaner additive may cause severe corrosion of stainless steels. Since the main constituents of bleaching liquids are hypochloride, sodium hydroxide and free chlorine, it has the capability of causing transpassive dissolution in the absence of aggressive anions and pitting corrosion in the presence of aggressive anions of  $Cl^-$ .

## 2 Experimental procedure

The working electrode used was taken from 15 mm thick stainless steel sheet. The stainless steel grade used in this work was fully austenitic. Chemical composition of employed alloy is shown in Table 1.

In order to prepare the working electrode, a piece of  $1\text{ cm}^2$  of the alloy was cut from the bulk sample, then the electrical connection was made by soldering of 1 mm copper wire to one end of the specimen. The dried mounted specimen in acrylic resin was laboratory abraded with polishing paper to a finish corresponding to 320 grit.

Analytical grade of sodium sulphate and sodium chloride chemicals and distilled water were used for the electrolyte

**Table 2.** Chemical composition and pH of investigated electrolytes

Electrolyte composition	pH
0.2 M $Na_2SO_4$	7.2
0.2 M $Na_2SO_4$ + 5% bleaching liquid	11.7
0.2 M $Na_2SO_4$ + 0.4 M NaCl	7
0.2 M $Na_2SO_4$ + 0.4 M NaCl + 5% bleaching liquid	11.5

preparation in this work. A 0.2 M  $Na_2SO_4$  and 0.2 M  $Na_2SO_4$  + 0.4 M NaCl in the presence of 5%wt. concentration of commercial bleaching solution with main constituents of sodium hypochloride, sodium hydroxide and free chlorine were prepared. For each experiment a fresh test solution of 300 ml exposed to air and fresh abraded specimens were used. All the measurements were carried out at ambient temperature. Table 2 illustrates the composition and pH of the electrolytes that were used in this work.

Two electrochemical techniques including potentiodynamic polarization and corrosion potential measurement were used. In potentiodynamic polarization after cathodic polarization from 250 mV from the corrosion potential, the specimen was continuously polarized through the anodic region with a 1 mV/s sweeping rate. In order to find out whether breakdown current density from the passive state of potentiodynamic polarization test is due to transpassive dissolution or localized corrosion, the applied potential was backscanned from 300  $\mu A/cm^2$  anodic current density. The corrosion potential of the working electrode with respect to Ag/AgCl reference electrode was continuously recorded through a high input resistance electrometer. After each test the specimen was examined visually and microscopically for evidence of localized corrosion initiation and propagation.

## 3 Results and discussion

Localized corrosion of steels is suppressed in general by alloying with beneficial elements such as chromium and molybdenum. Although the addition of these elements to steel suppress active dissolution it exposes steel to localized corrosion in particular media (e.g. pitting and crevice corrosion in  $Cl^-$  containing solutions) and transpassive dissolution in highly oxidizing environments. Performing potentiodynamic polarization on stainless steel working electrodes in solutions without aggressive anions ( $Cl^-$  or  $Br^-$ ) at two different pH exhibits passivity leading to transpassivity. Fig. 1 illustrates this behavior. The working electrode in the anodic region shows passivity with a passive current density of less than  $10\ \mu A/cm^2$  and followed by transpassivity at a quiet high anodic potential of 1200 mV. Addition of 5% bleaching liquid to the solution of 0.2 M  $Na_2SO_4$  results in decreasing of the transpassive potential from 1200 to 750 mV. Considering and com-

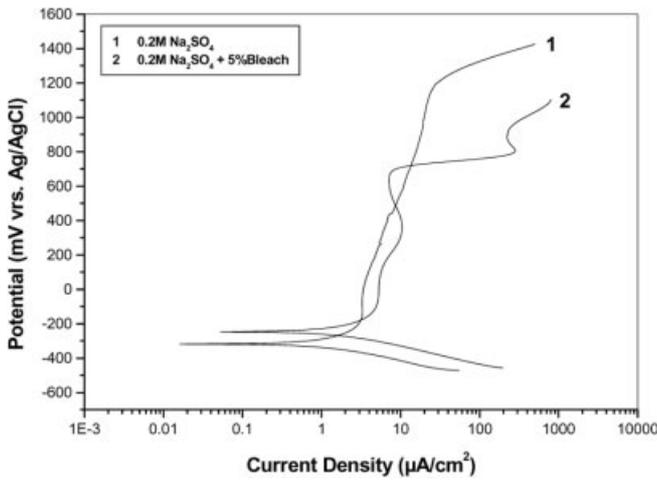


Fig. 1. Polarization curves for 316 stainless steel in 0.2 M Na<sub>2</sub>SO<sub>4</sub> with and without 5%wt bleaching liquid at ambient temperature with a potential scan rate of 1 mV/s

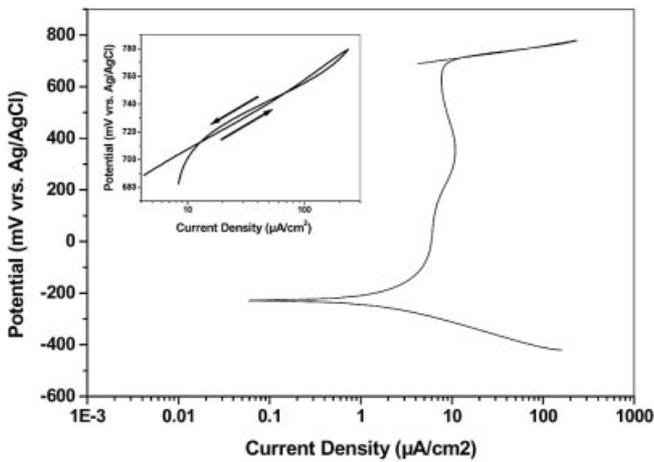
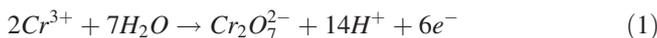


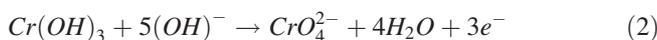
Fig. 2. Polarization curve accompanied with potential backscanning for 316 stainless steel in 0.2 M Na<sub>2</sub>SO<sub>4</sub> + 5%wt bleaching liquid at ambient temperature with a potential scan rate of 1 mV/s

paring the pH of two used electrolytes (Table 2) reveals pH dependence of the transpassive potential. It means that increasing the pH of the test solution from 7.3 to 11.7 has a pronounced effect on decreasing the transpassive potential.

It is generally accepted that passivity of stainless steels are due to formation of chromium hydroxide or chromium oxide in aqueous solution. The electrochemical transpassive reaction that is commonly presented for stainless steels consists formation of Cr<sup>6+</sup> from Cr<sup>3+</sup> as follow:



Clayton and co-workers [9] proposed the following reaction for tranpassive dissolution:



Reversible equilibrium potential of both reactions is pH dependent and decreases with increasing pH of the solution.

In order to prove whether the dissolution that occurs at 750 mV potential at the presence of bleaching liquid is due to transpassivity, the applied potential was backscanned (scanned in reverse direction) when the anodic current density reaches 300 µA/cm<sup>2</sup>. Fig. 2 illustrates backscanning of applied potential when transpassive dissolution occurs. Since tranpassive dissolution is a type of active dissolution and happens on all of the surface, the current density of forward and reverse state should be associated to a similar potential.

The possibility of transpassive corrosion of stainless steel immersed naturally in an electrolyte happens when its corrosion potential exceeds the transpassive potential; thus:

$$E_{corr} > E_{tr} \quad (3)$$

Where  $E_{corr}$  and  $E_{tr}$  are the corrosion and transpassive potential. Similar criteria can be written for possibility of localized corrosion such as pitting corrosion occurrence.

$$E_{corr} > E_{pit} \quad (4)$$

Where  $E_{pit}$  is the pitting potential initiation [1]. Fig. 3 illustrates schematically described criteria for transpassive and pitting corrosion occurrence.

The influence of addition of bleaching liquid into 0.2 M Na<sub>2</sub>SO<sub>4</sub> on corrosion potential of tested specimen is presented in Fig. 4. In agreement with several other studies [7, 8] it is

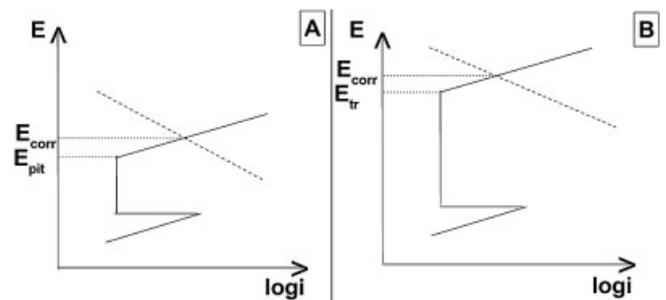


Fig. 3. Schematic illustration of E-log i diagram showing the criteria for pitting corrosion (A) and transpassive dissolution (B) occurrence. Solid and dashed lines are associated with anodic and cathodic current densities

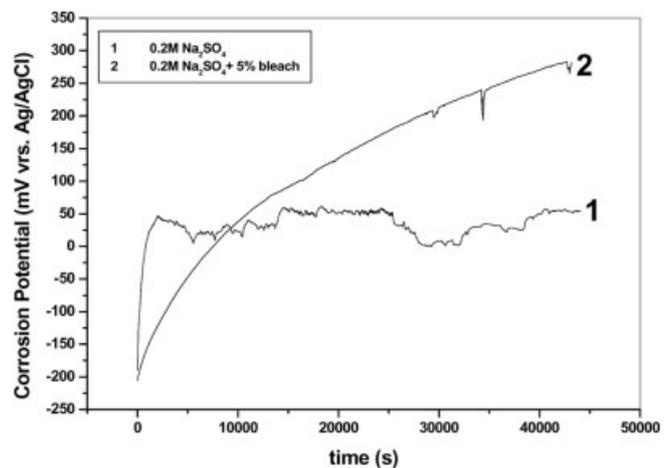


Fig. 4. Corrosion potential time dependence of test specimen in 0.2 M Na<sub>2</sub>SO<sub>4</sub> with and without 5%wt. bleaching liquid at ambient temperature

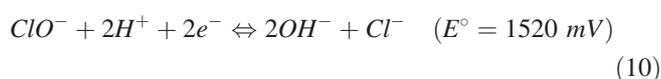
evident that the presence of hypochloride in bleaching liquid instantaneously and smoothly ennobles the corrosion potential during  $\sim 12$  hr immersion from  $-225$  to  $300$  mV. Considering the corrosion potential behavior in solutions without bleaching liquid reveals an increasing from  $-200$  mV to  $50$  mV for the first hour of immersion and then remaining constant on  $50$  mV for the last 12 hr of immersion. Chlorine when dissolved in aqueous solution hydrolyses to hypochlorous acid (HOCl) and hydrochloric acid:



Hypochlorous acid and sodium hypochloride are an active species and their dissociation produce  $\text{ClO}^-$ :



According to Ives et al. [10] the probable cathodic reactions in electrolytes containing chlorine ( $\text{Cl}_2$ ) and its derivatives ( $\text{ClO}^-$  and HOCl) are their reduction reaction that are denoted below with their standard equilibrium electrode potential values with respect to Ag/AgCl reference electrode. The rates of each reaction will depend on the pH of the electrolyte and hence the relative concentration of each species [10].



Since the corrosion potential ( $E_{\text{corr}}$ ) of specimens in test solutions containing bleaching liquid is more negative than all above equilibrium potentials, occurrence of the cathodic reaction of any of these electrochemical reactions is thermodynamically possible. This leads to gradual shifting of the corrosion potential towards noble values. If the corrosion potential exceeds the transpassive potential then active dissolution of the passive film begins by proposed electrochemical reactions for transpassive dissolution.

The presence of oxidizing species such as  $\text{Cl}_2$ , HOCl and  $\text{ClO}^-$  from bleaching liquid in the electrolyte on stainless steel corrosion significantly changes when aggressive anion such as  $\text{Cl}^-$  or  $\text{Br}^-$  exists in the electrolyte. In order to elucidate the facilitating occurrence of pitting corrosion in an electrolyte containing bleaching liquid, several potentiodynamic polarizations were carried out in  $0.2 \text{ M Na}_2\text{SO}_4 + 0.4 \text{ M NaCl}$  solution.

Fig. 5 shows three potentiodynamic polarization curves with a reproducible character in  $0.2 \text{ M Na}_2\text{SO}_4 + 0.4 \text{ M NaCl}$  solution. In order to find out whether the breakdown current density is associated with localized corrosion, the applied potential was backscanned from  $300 \mu\text{A}/\text{cm}^2$  and continued until the current density intercepts the passive current density at the protection potential. Pitting corrosion has happened at a potential of  $\sim 600$  mV. Comparing Fig. 2 and Fig. 5 proves that the presence of aggressive anions of  $\text{Cl}^-$  in solutions of  $0.2 \text{ M Na}_2\text{SO}_4$  initiates pitting corrosion at potentials well below  $E_{\text{tr}}$  instead of transpassive corrosion.

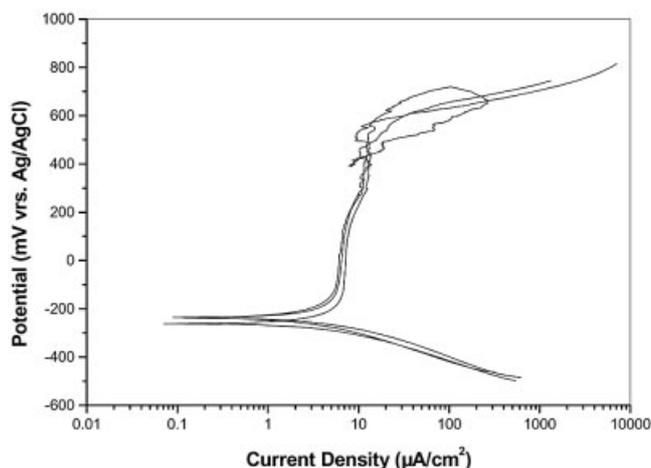


Fig. 5. Three polarization curves including one with backscanning of applied potential on 316 stainless steel in  $0.2 \text{ M Na}_2\text{SO}_4 + 0.4 \text{ M NaCl} + 5\% \text{wt}$  bleaching liquid at ambient temperature with a potential scan rate of  $1 \text{ mV/s}$

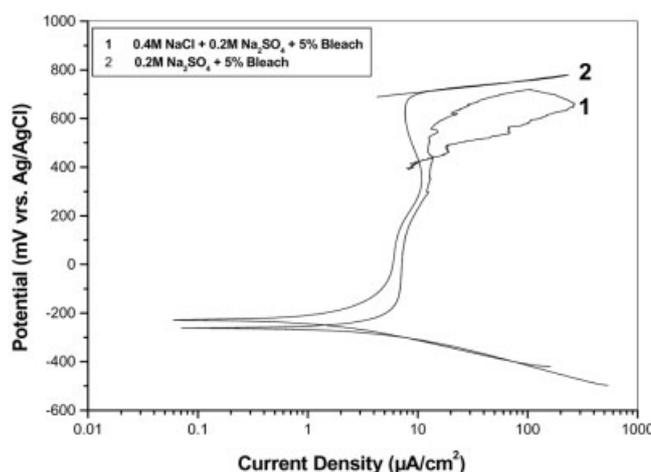


Fig. 6. Two polarization curves with backscanning of applied potential on 316 stainless steel in  $0.2 \text{ M Na}_2\text{SO}_4 + 5\% \text{wt}$  bleaching liquid with and without  $0.4 \text{ M NaCl}$  at ambient temperature with a potential scan rate of  $1 \text{ mV/s}$

Since the presence of sulphate and hydroxyl ions, as inhibitive anions for pitting corrosion of stainless steels [2], in test solutions result in shifting the pitting potential towards noble values, it was necessary to run some experiments with backscanning applied potential during the propagation step of pitting corrosion. It is generally accepted that if the breakdown potential in forward scan is coincided with the protection potential the state of corrosion is active dissolution, like transpassive corrosion. But if the potential at which the reverse current intercepts the passive current density is lower than the breakdown potential then localized corrosion occurred [1]. Fig. 6 illustrates the difference of active dissolution due to transpassive dissolution and localized corrosion due to pitting corrosion. Investigation of the specimen surface by optical microscope proved pitting corrosion occurrence (Fig. 7).

Measurements of the working electrode corrosion potential in solution of  $0.2 \text{ M Na}_2\text{SO}_4 + 0.4 \text{ M NaCl} + 5\% \text{wt}$  bleaching liquid were also recorded. The aim of these experiments was to determine the presence of both bleaching liquid and chloride ions on the variation of corrosion potential during

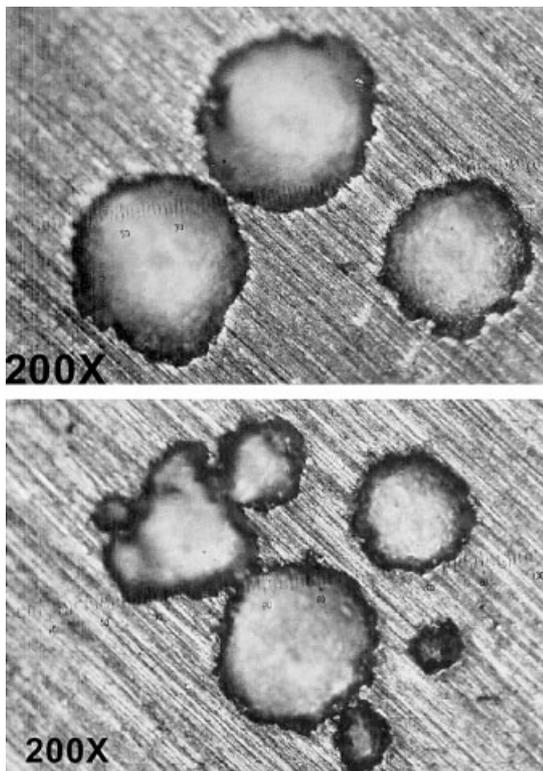


Fig. 7. Severe pitting corrosion on specimen polarized potentiodynamically beyond the pitting potential in 0.2 M Na<sub>2</sub>SO<sub>4</sub> + 0.4 M NaCl + 5%wt bleaching liquid solution at ambient temperature with a potential scan rate of 1 mV/s

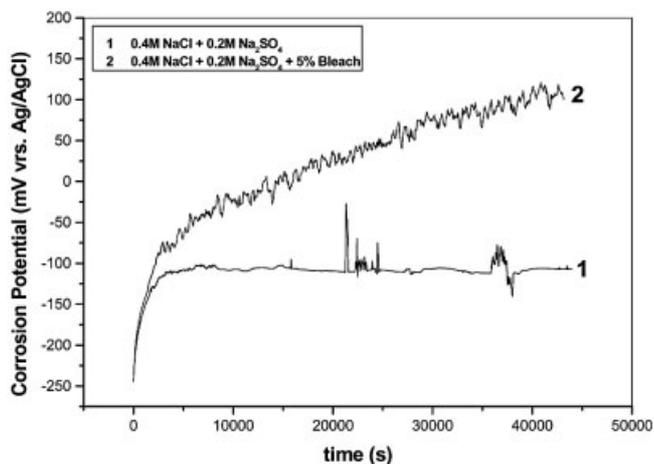


Fig. 8. Corrosion potential time dependence of test specimen in 0.2 M Na<sub>2</sub>SO<sub>4</sub> + 0.4 M NaCl with and without 5%wt. bleaching liquid solution at ambient temperature

immersion in test solutions. A comparison of these records is illustrated in Fig. 8. The corrosion potential of the specimen in solution without bleaching liquid has increased sharply from  $-100$  to  $-115$  mV during the early period of immersion and then remained constant without any significant change for the rest of the experiment. Any fluctuation of the corrosion potential reveals the occurrence of metastable pitting. A very different trend was observed in the corrosion potential of the specimen immersed in the same solution but with bleaching liquid. Corrosion potential varies instantaneously with significant fluctuations in the noble direction. As the corrosion potential increases the occurrence of metastable pits rise. For similar period of immersion in both solutions the difference of corrosion potential recorded at the end of experiment is about 250 mV. This predicts the possibility of reaching the corrosion potential to pitting potential which has been already measured by potentiodynamic polarization tests in the same test solution. When  $E_{corr} > E_{pit}$  then stable pitting happens and the trend of corrosion potential variation is changed towards negative direction.

#### 4 Conclusion

1. Addition of 5%wt bleaching liquid into 0.2 M Na<sub>2</sub>SO<sub>4</sub> solution caused a 500 mV decrease in transpassive potential. Presence of oxidizing species in bleaching liquid introduces several cathodic reactions with noble reversible equilibrium potentials that result in gradual increasing corrosion potential and then risk of transpassive corrosion occurrence.
2. In solution containing aggressive anions of Cl<sup>-</sup>, addition of bleaching liquid promotes the occurrence of pitting corrosion due to establishing the condition of  $E_{corr} > E_{pit}$

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