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# Use of Electrochemical Noise (EN) Technique to Study the Effect of sulfate and Chloride Ions on Passivation and Pitting Corrosion Behavior of 316 Stainless Steel

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**In the present paper, studies were conducted on AISI Type 316 stainless steel (SS) in deaerated solutions of sodium sulfate as well as sodium chloride to establish the effect of sulfate and chloride ions on the electrochemical corrosion behavior of the material. The experiments were conducted in deaerated solutions of 0.5 M sodium sulfate as well as 0.5 M sodium chloride using electrochemical noise (EN) technique at open circuit potential (OCP) to collect the correlated current and potential signals. Visual records of the current and potential, analysis of data to arrive at the statistical parameters, spectral density estimation using the maximum entropy method (MEM) showed that sulfate ions were incorporated in the passive film to strengthen the same. However, the adsorption of chloride ions resulted in pitting corrosion thereby adversely affecting noise resistance ($R_N$). Distinct current and potential signals were observed for metastable pitting, stable pitting and passive film build-up. Distinct changes in the values of the statistical parameters like $R_N$ and the spectral noise resistance at zero frequency ($R^\circ_{SN}$) revealed adsorption and incorporation of sulfate and chloride ions on the passive film/solution interface.**

**Keywords** 316SS, adsorption, chloride, electrochemical noise, passive film, sulfate

## 1. Introduction

In the past there have been a few studies wherein the role of sulfate ions was studied along with that of the chloride ions in establishing its effect on pitting corrosion of stainless steels (SS), particularly 304SS. It was reported that the growth of corrosion pits on 304SS in presence of sulfate ions caused the distribution of available pit sites to be shifted to a higher potential, implying that pit nucleation was inhibited and that sulfate showed inhibitory effect on the nucleation of pits (Ref 1). Pit propagation in both the metastable and stable states was also inhibited by the sulfate ions (Ref 1). The chloride pitting corrosion of 304SS was strongly influenced by the presence of sulfate ions. Addition of sulfate ions to 0.1 M NaCl increased pitting potential, $E_{pp}$, and above 1 M $Na_2SO_4$ concentration, the pitting was suppressed. The results revealed that the competitive adsorption between $Cl^-$ and $SO_4^{2-}$ on the surface led to inhibition of pitting attack (Ref 2). In their studies on pit growth studies in 304SS foils, Ernst and Newman (Ref 3) found that the addition of sulfate to NaCl solution was shown potentially to stabilize pit growth despite the increase in pitting potential. They reported that by adding 0.5 M $Na_2SO_4$ to 1 M NaCl solution, the pit growth rate was greatly reduced and a fragile cover was formed. Non-halide ions inhibited pit initiation but might make pitting more stable by encouraging growth under the surface (Ref 4) or other non-halide ions on pit initiation: This was also demonstrated for 904L steel via critical pitting temperature (CPT) measurements (Ref 5). In all these studies the influence of sulfate was studied in presence of chloride ions and not in isolation. Ameer et al. (Ref 6) studied the electrochemical behavior of Mo-containing SS in presence of $Na_2SO_4$ and NaCl solutions independently.

In the present paper, effects of sulfate ions and chloride ions on the electrochemical behavior of 316SS have been discussed. Electrochemical noise (EN), a fairly recent technique was used for this study. EN is referred to as the spontaneous current and potential fluctuations in the process of corrosion. Spontaneous EN can be a rich source of information from corrosion processes (Ref 7). EN technique measures the stochastic fluctuations of the corrosion potential and the corrosion current. EN can be measured in potentiostatically polarized conditions and in freely corroding system. The first technique is suitable for the study of corrosion processes (Ref 8), while the second technique is more appropriate for corrosion monitoring (Ref 9). Analysis of the spontaneous fluctuations of potential and current is used for understanding of different corrosion processes, such as general corrosion, pitting corrosion, crevice corrosion, stress corrosion cracking (SCC) as well as passive film build-up (Ref 10–15). In the present work, the EN current and potential signals from 316SS electrodes immersed in sulfate and chloride ions were analyzed to understand the influence of these ions on the passivation and/or pitting corrosion properties of the material under study.

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## 2. Experimental

AISI type 316SS (chemical composition, wt.%: C = 0.055%, Cr = 18.00%, Ni = 11.86%, Mo = 2.30%, Mn = 1.7%, Si = 0.45%, P = 0.067%, S = 0.027%, Fe balance) in solution-annealed condition was used in the present study. The EN studies on this material were performed using two nominally identical electrodes of the same size ($0.05 \times 0.025 \times 0.003$ m) that were polished up to 600 grit, washed in soap water and degreased in acetone. The area of the electrodes immersed in the solution was about 0.0008 $m^2$. Potential and current noise measurements were performed by shorting together two identical working electrodes. The current flowing between the two working electrodes, as well as the potential between the working electrode and a reference electrode were monitored. Electrochemical current and potential studies were conducted in deaerated 0.5 M sodium chloride as well as deaerated 0.5 M sodium sulfate solution at open circuit potential (OCP) and noise signals were collected at the sampling frequency of 4 Hz. Saturated calomel electrode (SCE) was used as a reference electrode for the measurement of potential noise. After the EN experiments the specimens were observed under optical microscope for any corrosion attack.

The potentiostat, which can perform this experiment actively, holds the working electrode connection at the 'ground' potential by a small amplifier circuit. If one 'working' electrode is directly connected to ground and the other is connected to the working electrode cable, they are both held at the same potential and are, in effect, 'shorted' together. Any current, which flows between the two electrodes, is measured by the instruments of current measurement circuits thus creating a Zero Resistance Ammeter (ZRA). The potential is measured between the 'working' electrodes (since they are shorted together, both 'working' electrodes are at the same potential) and a reference electrode.

The linear trend component was estimated by least squares method and then eliminated by subtraction using commercial software. All the potential and current noise data collected in the time domain were transformed in the frequency domain through the MEM method, by a dedicated software. It has been reported that MEM computed with few coefficients produces a very smooth spectrum, preferable to that obtained by fast Fourier transform (FFT), even after averaging and that is why low values of M are commonly used in corrosion applications (Ref 16). Bertocci et al. (Ref 17) reported that MEM computed with an order of 10 gave better precision than FFT with one average and hence lower values of M were adequate. In the present work, power spectral density (PSD) data were obtained by computing MEM with an order of 15. In order to reduce the leakage of the low as well as the high frequencies in the calculated PSD values, Welch window was used for signal analysis.

## 3. Results and Discussion

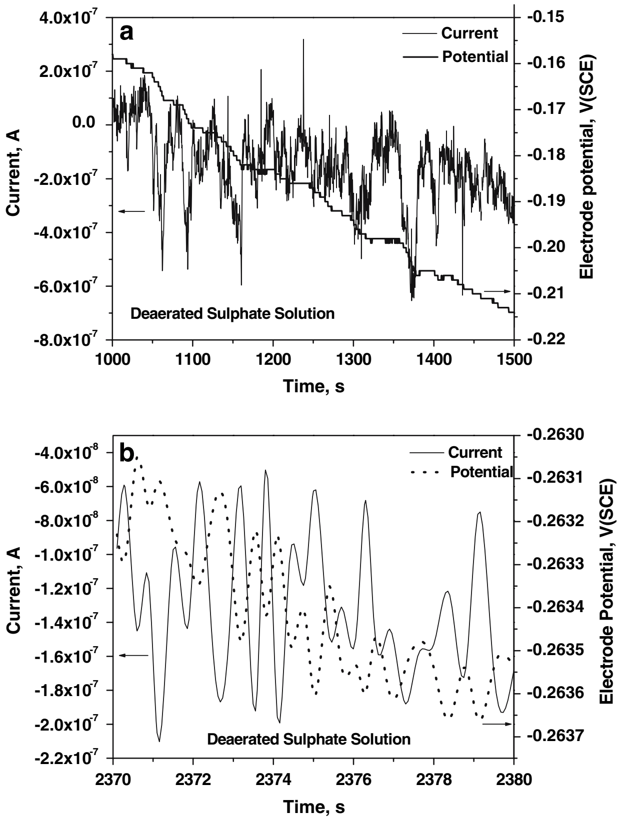

**Fig. 1** Current and potential records for 316SS in deaerated sodium sulfate solution at different time intervals (a, b)

Figure 1(a, b) shows the current and potential record for 316SS in deaerated sulfate solution during 1000-1500 s and 2370-2380 s time durations respectively. It was observed that the time to rise and fall for most of the current transients (Fig. 1b) was almost equal. The potential noise too showed the similar pattern (Fig. 1b); the changes in the potential noise transients could be observed only in the 4th decimal place. As against these features observed in sulfate solution, the current and potential records showed distinctly different patterns in deaerated chloride solution (Fig. 2a, b). Pitting attack was clearly observed as early as 1000-1500 s time duration. Current transients with characteristically a sharp and abrupt rise and a very slow fall marking the growth of a pit and its slow repassivation are observed in Fig. 2(a). There are many smaller peaks observed in the current noise pattern that were generated owing to the formation of metastable pits which could either grow into stable pits or repassivate again. It is generally accepted that the growth of a metastable pit is essentially the same as the early growth of a stable pit (Ref 18). However, the lifetime of a metastable pit is cut short by repassivation when the pit fails some critical test of its stability (Ref 19). A typical current noise pattern spanning over 10 s indicating the generation of a metastable pit is shown in Fig. 2(b).

The standard deviation of current ($\sigma_I$) as well as potential ($\sigma_V$), mean current, and mean potential were calculated over a period of 2500 s time interval for convenience. The $\sigma_I$ and $\sigma_V$ values indicate the current and potential amplitude and their trends reflect the progress of corrosion. Figure 3(a, b) show the plots of $\sigma_I$ and $\sigma_V$ values for 316SS in sulfate and chloride solutions respectively. The $\sigma_I$ value decrease sharply up to 7500 s in sulfate, the decrease thereafter was gradual; toward the end of the experiment the $\sigma_I$ value reached a very low value, which indicated the attainment of a good passive state (Fig. 3a). The change in $\sigma_I$ values was plotted for both solutions (Fig. 3c). The rise in the change in $\sigma_I$ values is much slower in sulfate solution than in chloride, indicating slower

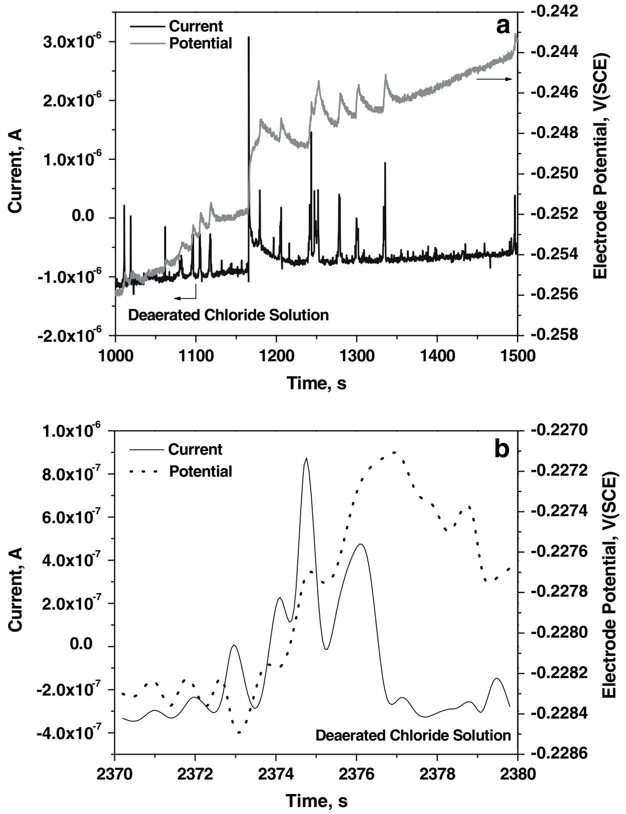

**Fig. 2** Current and potential records for 316SS in deaerated sodium chloride solution at different time intervals (a, b)

adsorption of sulfate ions and consequent dissolution rate of the passive film in the former medium compared to the latter. However, change in the $\sigma_I$ values reach saturation somewhat slowly in sulfate solution compared to the chloride solution. Thus, the dissolution rate of the passive film in the sulfate solution would be a little less than that in the chloride solution. The $\sigma_V$ values showed a much lower change over the entire time span (0.01 V(SCE)) in sulfate medium compared to the chloride solution (0.06 V(SCE)) (Fig. 3a, b).

The plots of the mean current values and the mean potential values are shown in Fig. 4(a, b). Mean current values initially decrease before increasing in sulfate solution compared to the mean current values in chloride solution, which rapidly increase before attaining a somewhat, steady state. The time when mean current dipped and rose gradually seemed to be have been utilized for the adsorption and incorporation of sulfate ions in the passive film thereby decreasing the dissolution of the film initially. However, mean current values increased sharply in chloride solution and reached almost a steady state. Mean potential values showed an initial rapid decrease in sulfate solution and a continuous rise in chloride solution. As the mean potential continuously increased in chloride ions and fell in the passive state, environment conducive for localized corrosion is created.

Noise resistance is defined as, $R_N = \sigma_V/\sigma_I$. Spectral noise plots ($R_{SN}(f)$) can also be obtained from the ratio of PSD plots according to:

$$R_{SN}(f) = |V_{FFT}(f)/I_{FFT}(f)| = |V_{PSD}(f)/I_{PSD}(f)|^{1/2}$$

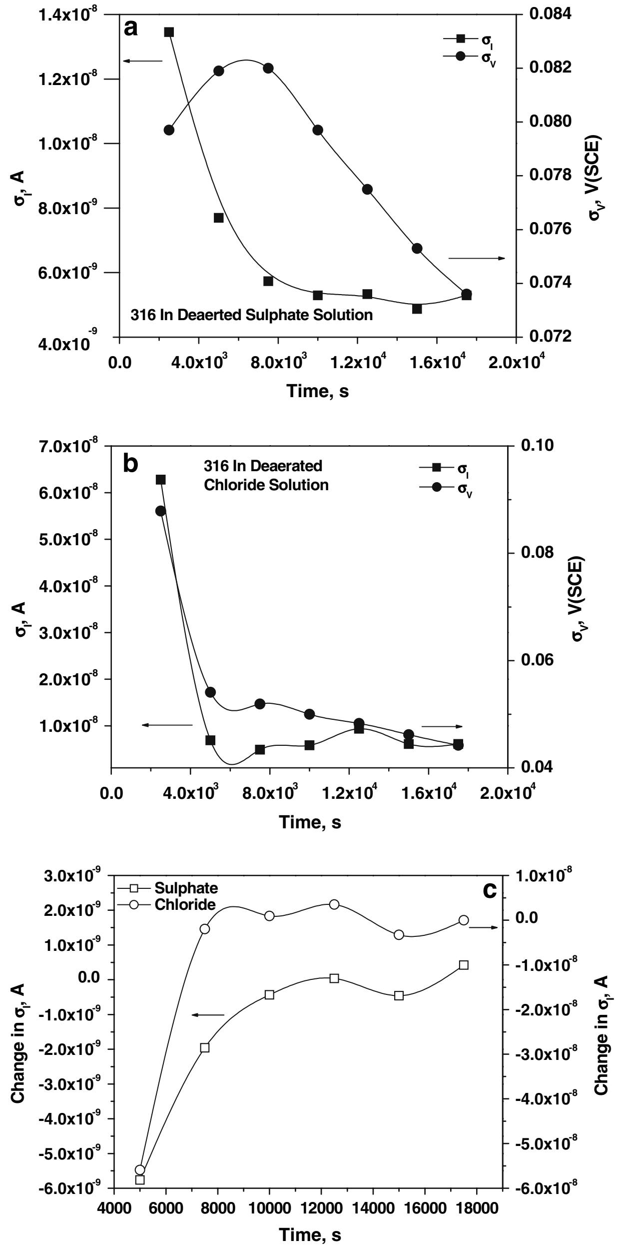

**Fig. 3** Standard deviation of current ($\sigma_I$) and potential ($\sigma_V$) for 316SS in deaerated sodium sulfate (a) and sodium chloride (b) solutions and change in $\sigma_I$ in both solutions (c)

where $V_{FFT}(f)$ and $I_{FFT}(f)$ are the FFT of the potential, and current fluctuations, respectively and $V_{PSD}(f)$ and $I_{PSD}(f)$ are the corresponding PSD data (Ref 20). In order to obtain the best results with least scatter, potential, and current PSD spectra derived from the MEM analysis, with sufficiently high order, are used (Ref 16). The dc limit of the spectral noise resistance at zero frequency, $R^\circ_{SN}$, values were then calculated. Mathematically $R^\circ_{SN}$ is represented as,

$$R^\circ_{SN} = \lim_{f \to 0}\{R_{SN}\}$$

Since dc limit was not usually detected in the present experiments, $R^\circ_{SN}$ was calculated as the mean value of the 10 data points at the lowest frequencies (Ref 21). Figure 5(a, b)

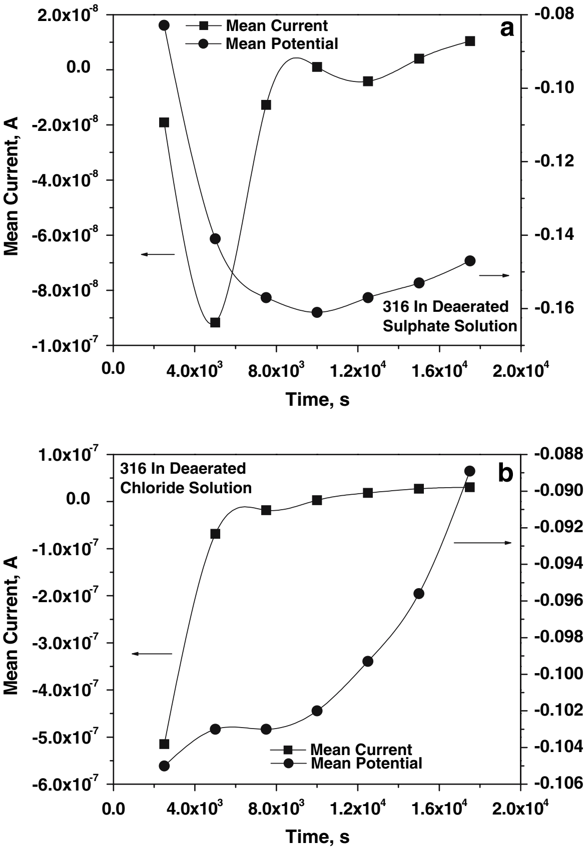

**Fig. 4** Mean current and potential for 316SS in deaerated sodium sulfate (a) and sodium chloride (b) solutions

shows the plots of $R_N$ and $R^\circ_{SN}$ values calculated at 2500 s interval for 316SS in sulfate and chloride solutions. It was observed that $R_N$ values in sulfate solution gradually increased up to about 10,000 s and reached almost a stage of saturation. The same pattern was found to have been repeated with $R^\circ_{SN}$ values too in this medium. However, the $R_N$ values in chloride medium increased initially, reached the peak at about 8000 s and thereafter decreased; the $R^\circ_{SN}$ values followed the same trend. The difference in trends of $R_N$ and $R^\circ_{SN}$ values in both media is attributed to the enhanced passivation in sulfate medium as against the pitting corrosion attack in chloride medium. The process of pitting corrosion begins with an induction period during which the $R_N$ and $R^\circ_{SN}$ continuously increased. Hoar and Jacob (Ref 22) showed that with austenitic SS there existed the induction period $\tau_i$, which varied with the chloride ion concentration $(1/\tau_i) > [Cl^-]^n$, where $n = 2.5$-$4.5$ and that the process leading to pitting appeared to involve a complex incorporating three to four chloride ions and also high-apparent activation energy, 60 kcal/mol and was in operation presumably due to a mechanical process of film rupture. Thus, it is concluded that there is an induction period before stable pitting takes place. In their model of pit propagation, Dawson and Ferreira (Ref 23), proposed that the pitting process was essentially crack/heal and that the film rupture events being the result of mechanical effects due to chloride adsorption on the film and the electrostrictive mechanism. They further proposed that the pit-propagation process was a competitive mechanism between passivating species $[MOOH]_{ads}$, $[MOMOH]_{ads}$ and non-passivating species $(MOH)_{ads}$, $(MOMCl)_{ads}$, $(MOMOHCl)_{ads}$. The relationship between the $R_N$ and the polarization resistance ($R_p$) was studied by many workers (Ref 24, 25). It was established that they were equivalent, ($R_N \approx R_p$) (Ref 26) and later confirmed in some laboratories (Ref 27, 28). It has been reported that usually Mo content in austenitic SS appeared to be beneficial in neutral sulfate solution as it inhibited their corrosion due to an increase in the polarization resistance of the cathodic reaction; however, chloride medium is found to be detrimental owing to a decrease in the cathodic polarization (Ref 29). Ameer et al. (6) observed a much higher value for the resistance of the oxide film for 17-14-4LN austenitic SS in neural sulfate medium as compared to the chloride medium of equal concentration, during their electrochemical impedance spectroscopic studies (EIS). They attributed this behavior to be the stabilisation of the formed oxide or passive film due to the possible incorporation of $SO_4^{2-}$ anions in the oxide film during its growth to a much higher extent than in chloride medium. It is reported that the incorporation of the anions in the oxide films greatly reduced their porosity, which led to an increase in the electrode impedance value (Ref 30). It has also been observed that $Cl^-$ ions participate in enhancing the formation of soluble oxochloro complexes encompassing Mo, which initiate pit nucleation at the active inclusion sites leading to an increase in the corrosion rate or lower the value of the electrode

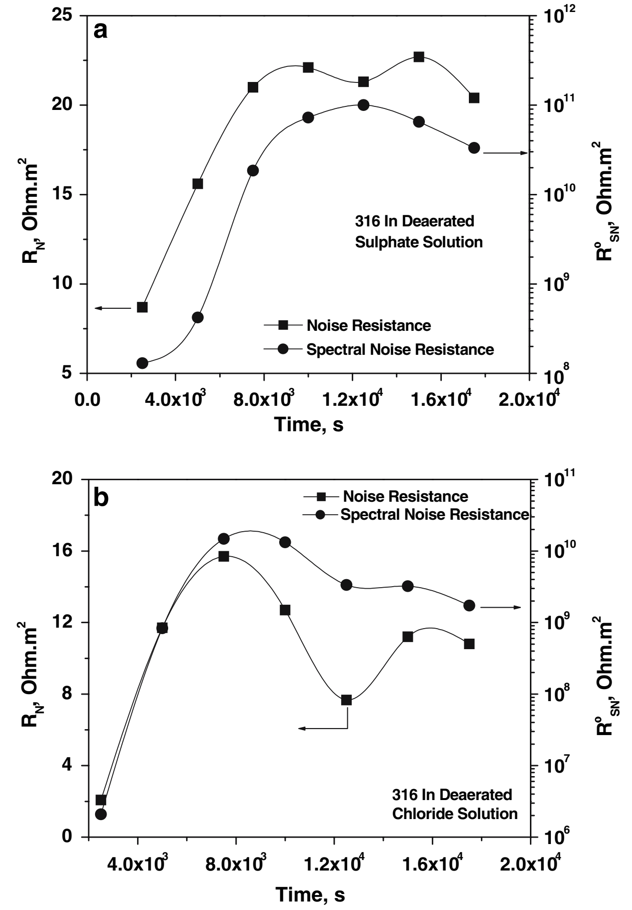

**Fig. 5** Noise Resistance ($R_N$) and spectral noise resistance ( $R^\circ_{SN}$) at $f_{min}$ for 316SS in deaerated sodium sulfate (a) and sodium chloride (b) solutions

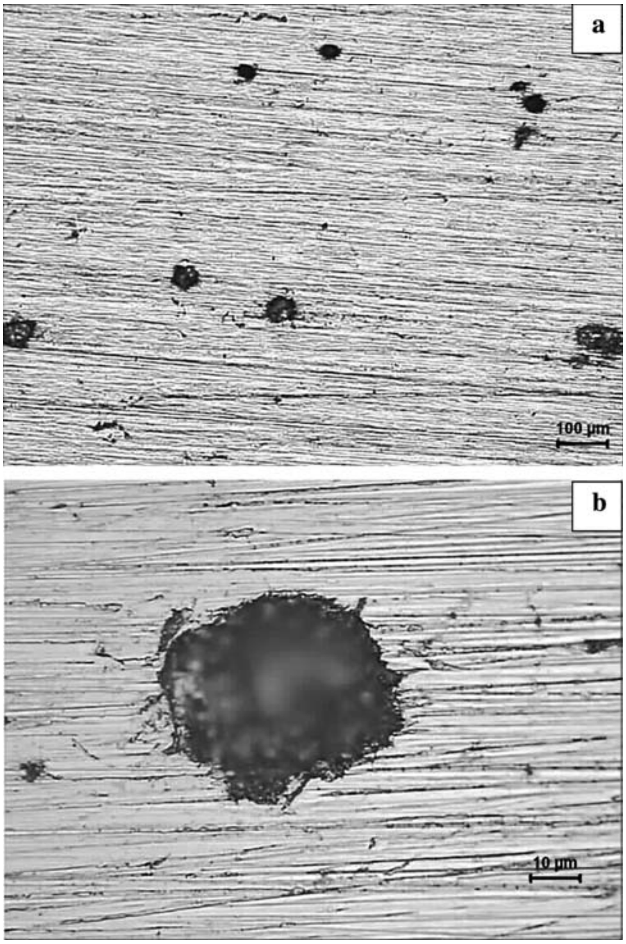

**Fig. 6** Photomicrograph showing many pits (a) and enlarged view of a pit (b) on the surface of 316SS specimen after the EN experiment in sodium chloride medium

impedance (Ref 6). The increase and saturation of $R_N$ as well as $R_{SN}^{\circ}$ values in sulfate medium was attributed to the incorporation of sulfate ions in the passive film whereas, the fall in the $R_N$ as well as $R_{SN}^{\circ}$ values after initial rise in chloride medium was attributed to the pitting corrosion attack. The specimens were observed under optical microscope after the EN experiments were completed. A number of pits were observed on the specimen immersed in chloride solution (Fig. 6a, b) whereas the specimen immersed in sulfate medium did not show any corrosion attack.

The current PSD plots in sulfate and chloride media are shown in Fig. 7(a, b), which show frequency independent region as well as the 1/*f* region as two distinct characteristics of these plots. The value of the current PSD at $f_{\min}$ is used to indicate the tendency to general corrosion. The MEM allows computation of the spectra below $f_{\min}$; however, it is imperative not to calculate PSD below $f_{\min}$ to generate misleading information (Ref 17). Thus the PSD values calculated at $f_{\min} = 4.94 \times 10^{-4}$ Hz were used to plot Fig. 7(c). The plot of the PSD values at $f_{\min}$ as a function of time is shown in Fig. 7(c). It is reported that the power level of the signal in the frequency independent region is related to the corrosion rate (Ref 31, 32). It was observed that the corrosion rate was high in chloride medium compared to the sulfate from the beginning of the experiment. The fall in the corrosion rate in sulfate medium was gradual as compared the rapid fall in the corrosion rate observed in chloride medium. However, the corrosion rate in chloride medium started to increase slowly after 7500 s, which was attributed to the pitting corrosion attack.

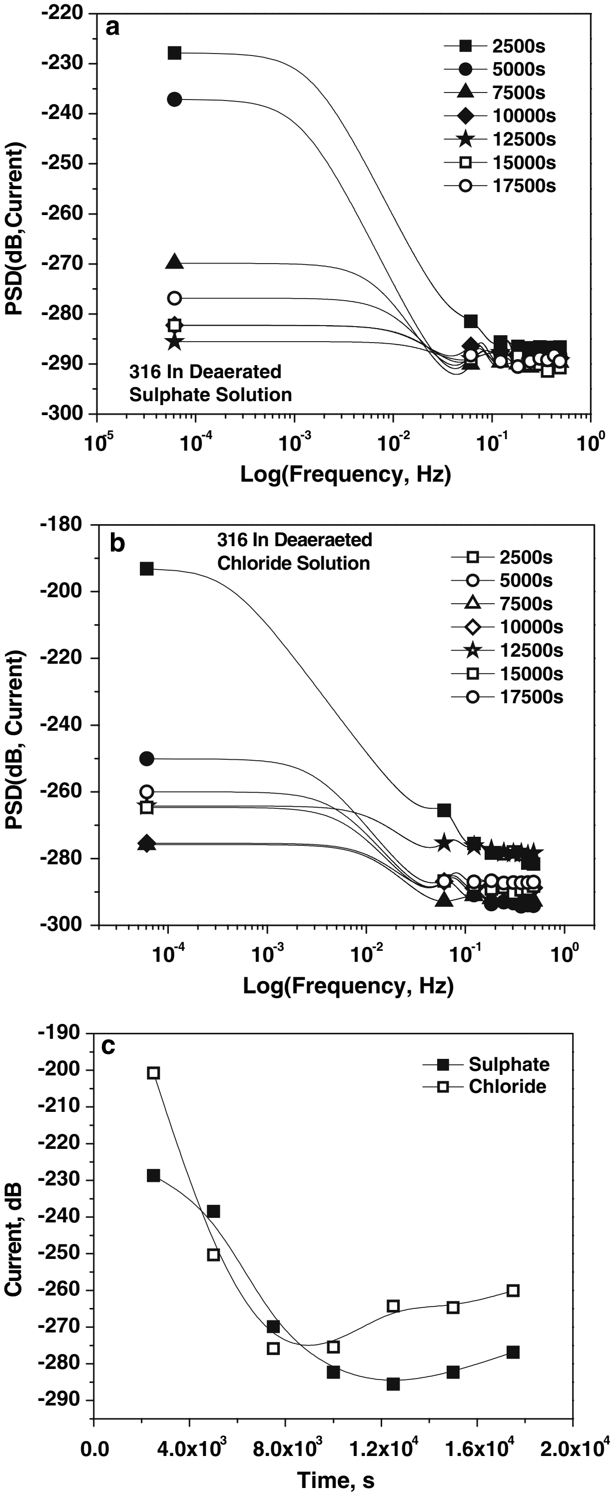

**Fig. 7** The current PSD plots for 316SS in sodium sulfate (a), sodium chloride (b) solutions and the current PSD value at the lowest frequency in both the media (c)

## 4. Conclusions

Based on the results of EN studies on 316SS in sulfate and chloride media, following conclusion were drawn:

1. Usually sulfate ions are incorporated heavily in the passive film as compared to the chloride ions; the incorporated sulfate ions strengthen the passive film whereas the adsorbed chloride ions destroy the passive film leading to stable pit formation. These processes are reflected in the changes in the EN parameters.
2. The statistical parameters as well as the $R_N$ and $R^{\circ}_{SN}$ values threw light on the mechanism of adsorption and incorporation of sulfate and chloride ions on the passive-film/solution interface.
3. Metastable pitting does take place during the induction period required to establish the stable pitting for a given concentration of chloride ions.

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