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FULL LENGTH ARTICLE

Cyclic voltammetric studies of carbon steel corrosion in chloride-formation water solution and effect of some inorganic salts

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KEYWORDS

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Abstract The influence of sulfide, sulfate and bicarbonate anions on the pitting corrosion behavior of carbon steel in formation water containing chloride ions were analyzed by means of cyclic voltammetry technique and complemented by X-ray diffraction (XRD) investigation. The anodic response exhibits a well-defined anodic peak A, followed by a passive region. A pronounced increase in the anodic current density is observed in the passive region at pitting potential (E_{pit}). On the other hand, the cathodic sweep shows two cathodic peaks CI and CII. The data show that the presence of chloride ions causes pitting corrosion of carbon steel in formation water. It was found that both the pitting potential E_{pit} and the repassivation potential (E_{pro}) decreased with increase in Cl^- ions concentration. Data clearly show that the presence of Na_2S with 0.3 M of chloride ions has a strong accelerating effect on the active dissolution and pitting corrosion of carbon steel in formation water, while the presence of Na_2SO_4 and $NaHCO_3$ with chloride ions has an inhibiting effect on the active dissolution and pitting corrosion.

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1. Introduction

Carbon steel has been extensively used under different conditions in petroleum production, where many of the components of drilling gears, downhole tubular and production vessels are fabricated from low carbon steel. The pitting corrosion behavior of carbon steel in chloride solutions has been extensively studied by a number of authors [1–4]. Particular interest has been paid to the chloride ion on account of its presence as a high percentage of formation water and its role as an active pitting agent. It has been reported that a majority of metals suffer pitting only in solutions containing a chloride ion [5–7]. The electrochemical behavior of carbon steel in formation water containing the Cl^- ion is of particular significance to the corrosion problems encountered in drilling for the production of oil and gas [8–10]. Sweet wells can deliver formation water, which contains a variety of salts and bicarbonate ions

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in various concentrations. Most salts are active participants on the corrosion process, with the exception of carbonate, which forms an adherent scale on most metals and reduces corrosion. Therefore, the accurate determination of chloride, sulfate and sulfide portions of the total salt content in formation water is an important element in determining corrosivity. The objective of the present work was to study the role of chloride ion concentration on the pitting corrosion of carbon steel in formation water and to study also the pitting corrosion of carbon steel in a mixture of chloride ion with other salts like Na_2S, Na_2SO_4 and $NaHCO_3$ by using the cyclic voltammetry technique and complemented by X-ray diffraction (XRD) investigation.

2. The experimental details

The electrochemical measurements were performed on carbon steel specimen with the chemical composition (wt.%), 0.06 C; 0.06 Si; 0.7 Mn; 0.005 P; 0.001 S; 0.012 Ni; 0.015 Cr; 0.004 Mo; 0.002 V; 0.02 Cu and 99.12 Fe. The specimen was machined into cylindrical form electrode of 0.384 cm^2 cross-sectional area. The electrode was sealed with epoxy resin so that only the cross-section area was exposed to the electrolyte. Prior to each experiment, the surface pretreatment of working electrode was performed by mechanical polishing (using polishing machine model Poliment I, Buehler Polisher) of the electrode surface with successive grades of emery papers down to 1200 grit up to a mirror finish. The polished electrode was then degreased with acetone and washed with running double distilled water. A saturated calomel electrode (SCE) and a platinum foil were used as reference and auxiliary electrodes, respectively. All experiments were thermostated at 30 °C in aerated solution. The cyclic voltammograms curves were recorded using a potentioscan type (potentiostat/Galvanostat EG&G model 273) connected with a personal computer. The cyclic voltammogram curves were carried out by changing linearly the electrode potential from the stating potential (−2.0 V) with respect to (SCE) toward more positive direction with the required scan rate till the end of the experiment at −0.1 V and reverse back to starting potential at −2.0 V. The XRD analysis was carried out on powder, which had been previously scratched from the corrosion layer on the coupons and grounded in a mortar. The equipment used consisted in a 3720 X-ray diffractometer with a fine structure air insulated X-ray tube with a copper anode (Cu Ka1 5406 Å). Full X-ray diffraction patterns were recorded for the scan angles (°2Theta) from 4.01° to 69.99° to identify iron oxides. Using the ICDD-PDF database, individual crystalline phases were identified from their observed XRD patterns. The test solution used was formation water associated with crude oil from Egyptian western desert (pH 6.8). The analysis of the formation water has been carried out using an ionic chromatograph instrument and its chemical composition is given in Table 1. The solutions were prepared using analytical reagent grade chemicals and distilled water. The temperature of the test solution was maintained thermostatically with an accuracy of ±1 °C.

3. Results and discussion

Fig. 1 represents the cyclic voltammograms curves of carbon steel in formation water in the presence of increasing amounts (0.1–0.3 M) of NaCl at a scan rate of 10 mV s^{-1} and at 30 °C between −2.0 and −0.1 V. The pH was ≈6.8 for all solutions and no pH adjustment was done. On the positive going scan, the current decreases continually and changes its sign at the corrosion potential E_{corr}. The active dissolution region involves one anodic peak A prior to the permanent passive region. This anodic peak is maybe due to the formation of ferrous hydroxide [11]. When the concentration of ferrous oxide at the anodic surface exceeds its solubility product, precipitation of solid oxide occurred on the electrode surface. When the surface is entirely covered with oxide passive film, the anodic current density falls to a low value ($j_{pass.}$), indicating the onset of passivation. When the anodic polarization of carbon steel reaches a certain critical potential, the pitting potential E_{pit}, the current rises suddenly (pitting current) without any sign of oxygen evolution indicating initiation and growth of pitting attack. When the potential is reversed, the pitting current exhibits a hysteresis loop and decreases rapidly reaching to the passivation current j_{pass} (measured during the increasing potential scan) at a certain repassivation potential E_{pro}, when all growing pits repassivate. The repassivation process could be achieved by the removal of accumulated Cl^- ions from the pits by diffusion [12]. On the other hand, the cathodic sweep shows two cathodic peaks CI and CII. The appearance of cathodic peak CI maybe due to reduction of corrosion product and the appearance of cathodic peak CII maybe due to the reduction of pitting corrosion products precipitate on the electrode surface. Further inspection of Fig. 1 gives us three marked potential regions: (i) $E \geqslant E_{pit}$ (pits initiate and propagate), (ii) $E \leqslant E_{pro}$ (no initiation and propagation of pits) and (iii) $E_{pit} < E < E_{pro}$ (no initiation and existing pits will propagate). The data of Fig. 1 clearly show that, anodic peak current density j_{PA} increases with increasing Cl^- ion concentration and shifts its potential (E_{PA}) to a more negative value, indicating the aggressiveness of Cl^- ion toward the corrosion process of carbon steel. This behavior could be attributed to the formation of the soluble complex between Fe^{2+} and Cl^- ion [12–14]. Such complexing processes lead to a further decrease in the free Fe^{2+} ion concentration at the electrode surface.

In the passive state, the Cl^- ions can be adsorbed on the bare metal surface in competition with OH^- ions. As a result of high polarizability of the Cl^- ions, the Cl^- ions may adsorb preferentially [15]. Moreover an increase in chloride ions concentration shifts the pitting potentials toward a more negative (active) direction corresponding to decrease the resistance to pitting. The dependence of the pitting potential on the concentration of chloride ions is given in Fig. 2 which shows E_{pit} vs.

Table 1 Chemical composition of the formation water.

Element	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	Br^-	SiO^{2-}
Concentration (ppm)	67,675	1272	7708	2449	1321.18	370	568	11.8

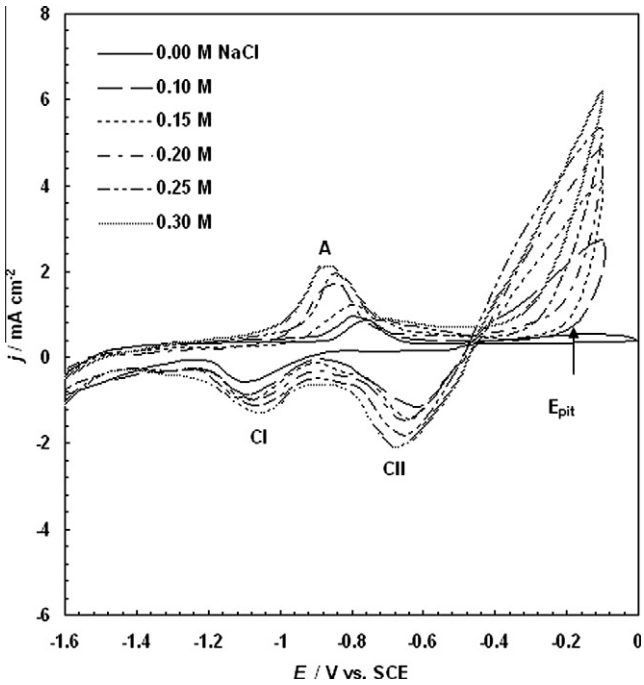

Fig. 1 Cyclic voltammograms for carbon steel at 30 °C with scan rate of 10 mV s^{-1} in formation water in the absence and presence of increasing addition of NaCl.

log[Cl^-] whereby a straight line obtained according to the following equation:

$$E_{pit} = a - b\log[Cl^-] \quad (1)$$

where a and b are constants depending on the metal composition, electrolyte composition, etc. From Eq. (1) it is possible to estimate the maximum chloride level above which pitting is expected to occur immediately in relevant environment. The maximum chloride level is determined as the intersection between the regression line and the value of E_{corr} [16]. The pitting corrosion could be related to the ability of the chloride ion to adsorb on the passive film and create an electrostatic field across the film/electrolyte interface [17]. When the field reaches a certain value, the adsorbed ion penetrates the oxide film especially at the flaws and defects in the oxide film [18]. When the penetrated chloride ion reaches the metal surface they promote local anodic dissolution resulting in a pit nucleus. Following this a pit growth takes place rapidly as a result of an increase in chloride ion concentration resulting from its migration, and increases the acidity inside the pits [18,19]. It is obvious to observe from Fig. 1 that an increase in Cl^- ion concentration increases the current density of the two cathodic peaks (j_{PCI}, j_{PCII}) and shifts E_{PCI} to more positive potential values (from −1.08 to −1.05) and shifts E_{PCII} to more negative potential values (from −0.61 to −0.67).

Fig. 3 shows cyclic voltammograms for carbon steel in formation water in the presence of 0.3 M of Cl^- ion at a scan rate of 10 mV s^{-1} with a progressively increasing potential limit in the anodic sweep. It is clear that no cathodic peak is observed if the anodic sweep has been reversed at a value more negative than that of peak A. Reversal of potential limit with in the potential ranges of peak A and pitting potential E_{pit} give rise to the reduction peak CI. Therefore it is likely that the cathodic peak CI corresponds to the reduction of iron oxide. When the potential limits reversed at potential more positive that E_{pit}, the pitting current density exhibits a hysteresis loop and decreases rapidly reaching zero at a certain repassivating potential. It is clear that the appearance of the second cathodic peak CII may be due to the reduction of pitting corrosion product.

The influence of potential scan rate (form 10 to 50 mV s^{-1}) on the cyclic voltammograms E/j profile of carbon steel in formation water in the presence of 0.3 M of Cl^- ion at 30 °C was examined; the results obtained are not included here. Results

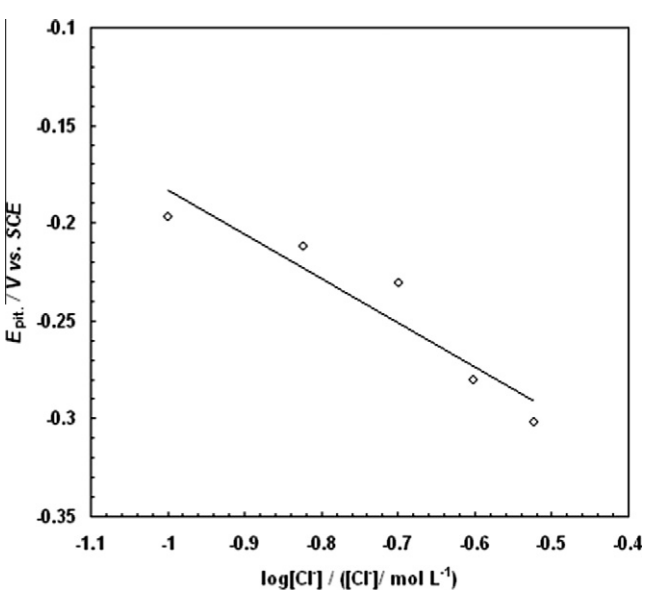

Figure 2 The dependence of the pitting potential on the concentration of chloride ion.

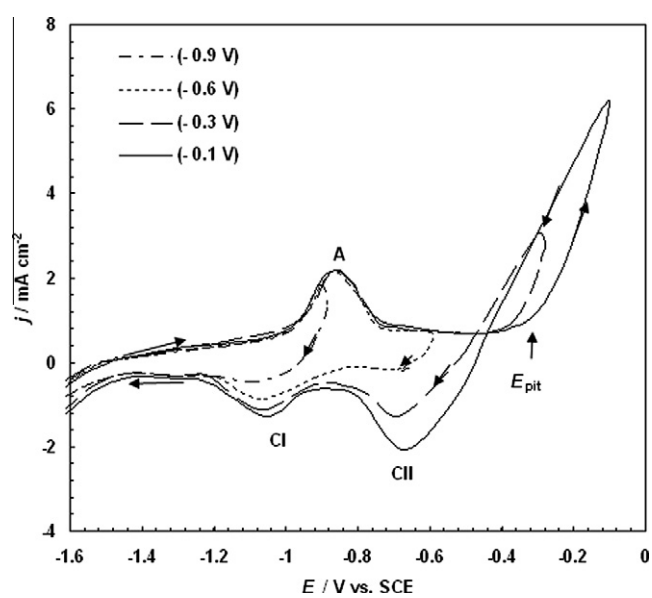

Figure 3 Cyclic voltammograms for carbon steel in formation water in the presence of 0.3 M of Cl^- ion at a scan rate of 10 mV s^{-1} with a progressively increasing potential limit in the anodic sweep.

indicated that the current density of peak A, j_{PA}, increases and its potential shifts toward more negative values with increasing scan rate. Fig. 4 illustrates the dependence of j_{PA} on (scan rate)$^{1/2}$. A linear relationship is obtained that does not pass through the origin. This result is evidence that the reactions occurring within the potential range of peak A, namely carbon steel dissolution and metal hydroxide formation, are partial controlled by diffusion. However, an increase in the scan rate reduces the tendency of carbon steel for pitting corrosion since an increase in scan rate shifts E_{pit} towards more positive values. This trend can be explained in terms of incubation time [20]. When scan rate is high, a pitting initiation can be observed only at more noble potentials, corresponding to a sufficiently short pit incubation time. The incubation time for initiation of passivity breakdown (i.e. for a first pit nucleation) is caused by the time required for chloride ions to break down the passive layer and reach the metal surface.

The effect of adding increasing amounts of Na_2S, Na_2SO_4 and $NaHCO_3$ on the corrosion of carbon steel in formation water containing 0.3 M Cl^- ion has been studied using cyclic voltammetry measurement at a scan rate of 10 mV s^{-1} and at 30 °C.

Fig. 5, as an example, shows the cyclic voltammograms curves for carbon steel in formation water containing 0.3 M Cl^- ion in the absence and presence of various concentrations of Na_2S; similar results were obtained for Na_2SO_4 and $NaHCO_3$. It is obvious that addition of increasing amounts (0.01–0.04 M) of Na_2S (The pH was ≈10.88 for all solutions and no pH adjustment was done) to the formation water containing chloride ions caused an increase in both the active and pitting corrosion of carbon steel. Fig. 5 shows that anodic peak current density j_{PA} increase and its potential E_{PA} shift to a more negative value with increasing Na_2S concentration. It is clear also that E_{pit} shift to negatives values with increasing in sulfide concentration (as shown in Fig. 6), indicating that an increase in pitting corrosion owing to the autocatalysis effect of SH^- [21]. The decrease in the pitting corrosion resistance of carbon steel in chloride–sulfide solution is confirmed by the decrease in the E_{pit} value compared with that obtained in a pure chloride solution. Generally, the presence of sulfide ions in the formation water containing chloride ions resulted in a marked increase in the corrosion rates due to the local acidification caused by iron sulfide formation. The localized replacement

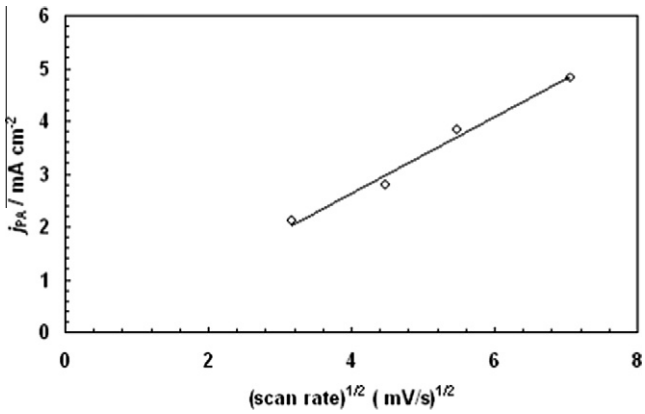

Figure 4 Relation between j_{PA} vs. (scan rate)$^{1/2}$ for carbon steel in formation water in the presence of 0.3 M of Cl^- ion at 30 °C.

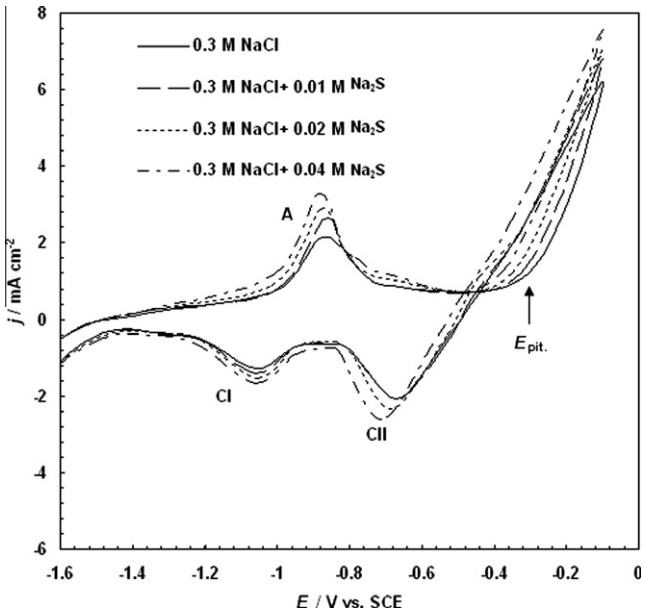

Figure 5 Cyclic voltammograms curves for carbon steel in formation water containing 0.3 M Cl^- ion at 30 °C with scan rate of 10 mV s^{-1} under influence of adding increasing concentrations of Na_2S.

of the protective Fe-oxide film by a non-protective iron sulfide film is responsible for increasing the pitting corrosion [21–23]. The surface of carbon steel in formation water containing chloride and sulfide ions was analyzed by X-ray diffraction at a potential more positive than E_{pit} (see Fig. 7, as an example). A higher concentration of sulfur was found in the pits, and the surface film was mainly composed of FeS, α-FeOOH and γ-Fe_2O_3 [24]. Wranglen [24] pointed out that the greater effect of FeS can be explained by (1) the higher solubility of FeS, (2) the higher electrical conductivity of FeS. He suggests that the corrosive effect of sulfide is due in part to this increase in S^- and HS^- activity in the solution as the sulfide dissolves. The reason why sulfide ions, S^- and HS^-, are activators which greatly accelerates localized corrosion is apparently related to their high electric polarization and consequent strong contact adsorption on metal surface.

On the other hand, the addition of increasing amounts (0.02–0.1 M) of Na_2SO_4 (The pH was ≈6.8 for all solutions and no pH adjustment was done) to the formation water containing chloride ion causes a decrease in the anodic current density j_{PA} and shifts the E_{PA} to more positive direction. Moreover an increase in Na_2SO_4 concentration shifts the pitting potentials toward a more positive direction corresponding to increase the resistance to pitting (as shown in Fig. 6). The data reveal that the presence of sulfate with chloride has an inhibiting effect on the general corrosion and pitting corrosion of carbon steel in formation water. This behavior could be attributed to the fact that, at sufficiently high concentrations of SO_4^{2-} ion, practically low adsorption of Cl^- occurs [25]. Compared to the aggressivity of chloride ion levels, sulfate ions are generally considered to be less aggressive [26]. Thus in presence of SO_4^{2-} ion if the competitive adsorption mechanism is applicable; it will take longer for the Cl^- to achieve critical concentration required for pit formation [27]. This would result in a shift of E_{pit}

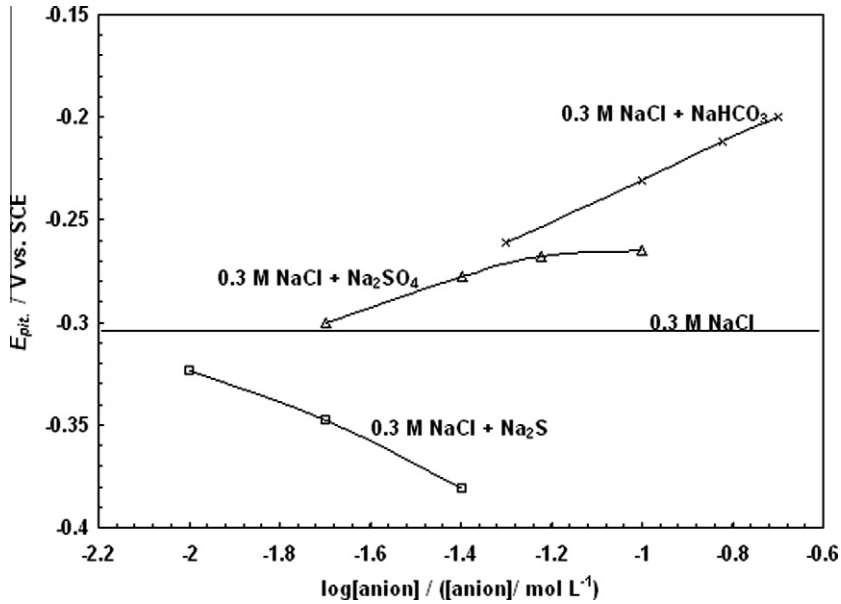

Figure 6 The dependence of the pitting potential of carbon steel on the concentration of Na_2S, Na_2SO_4 and $NaHCO_3$ in formation water containing 0.3 M Cl^- ion.

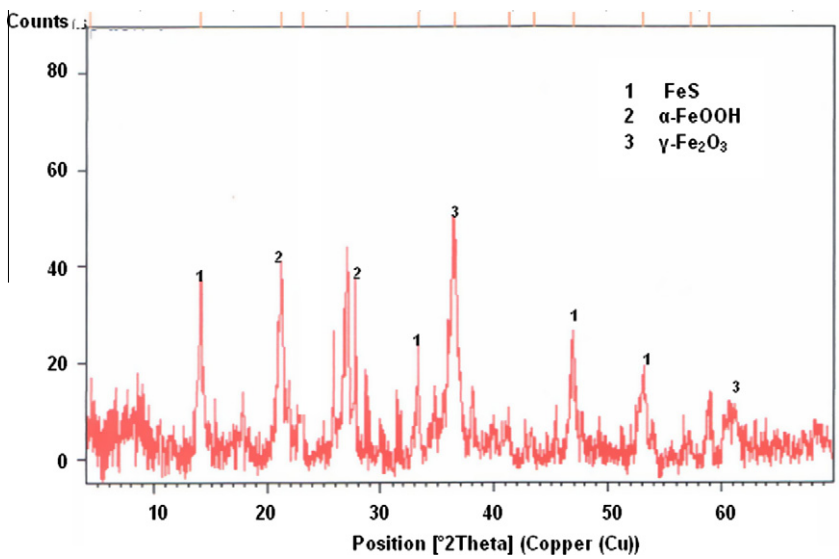

Figure 7 XRD spectra recorded for carbon steel in formation water containing 0.3 M Cl^- ion in the presence of 0.01 M Na_2S.

to move noble potentials. X-ray diffraction of the oxidation products formed on the carbon steel surface polarized potentiodynamically in formation water containing 0.3 M Cl^- and 0.1 M Na_2SO_4 solution at a scan rate of 10 mV s^{-1} was performed at specific polarization potential ($E_{PA} < E < E_{pit}$). The data obtained confirmed the existence of $Fe_4(OH)_8Cl_{(s)}$ (chloride green rust) and $Fe_6(OH)_{12}SO_{4(s)}$ (sulfate green rust) on the surface of metal.

It is obvious from data also that the effect of adding of increasing amounts (0.05–0.2 M) of $NaHCO_3$ (The pH was ≈8.9 for all solutions and no pH adjustment was done) to the formation water contain chloride ion decreases the anodic dissolution of carbon steel and shifts its potential E_{PA} to more noble direction. Further inspection of Fig. 6 reveals that the pitting potential E_{pit} moves to a more positive direction with increasing bicarbonate ion concentration, indicating the protective effect of $NaHCO_3$ towards the pitting corrosion processes of carbon steel. This maybe resulted from reduced solubility of the corrosion product in the presence of bicarbonate ion, which stimulated the formation of protecting corrosion film [28,29]. The results are explained in terms of the more favorable formation of an iron hydroxy-carbonate complex (called green rust carbonate) than the formation of the corresponding green rust chloride complex [30]. The data obtained form X-ray diffraction analysis (as shown in Fig. 8) confirmed the existence of $Fe_2(OH)_2CO_3$ on the surface of metal.

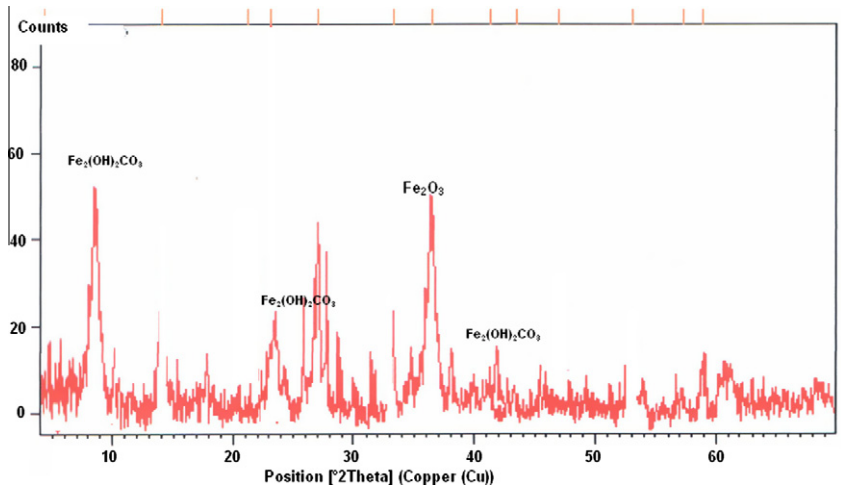

Figure 8 XRD spectra recorded for carbon steel in formation water containing 0.3 M Cl^- ion in the presence of 0.2 M of $NaHCO_3$.

4. Summary

We can conclude from the above

1. The anodic response of cyclic voltammogram for carbon steel in formation water in the presence of chloride ions exhibits a well-defined one anodic peak, followed by passive region. While, the cathodic response shows two cathodic peaks.
2. Chloride ions have a strong deleterious effect on the passivity of carbon steel in formation water.
3. The active anodic dissolution of carbon steel in formation water in the presence of chloride ions increases with increasing chloride ions concentration and scan rate.
4. The presence of Na_2S with 0.3 M of chloride ions has a strong accelerating effect on the active dissolution and pitting corrosion of carbon steel in formation water. The accelerating effect of sulfide ion on pitting corrosion is recognized by the shift of the pitting potentials E_{pit} to negatives values.
5. The presence of Na_2SO_4 and $NaHCO_3$ with chloride has an inhibiting effect on the active dissolution and pitting corrosion of carbon steel in formation water. The inhibiting effect of sulfate and bicarbonate ions on pitting corrosion is recognized by the shift of the pitting potentials E_{pit} to more positive values.

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