ORIGINAL PAPER

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The effect of H₂S concentration on the corrosion behavior of API 5L X-70 steel

Abstract This work presents electrochemical data measured during the corrosion of API 5L X-70 pipeline steel immersed in aqueous environments containing dissolved H₂S. Three different electrolyte were used: a 3 wt% NaCl solution containing 100, 650 and 2,550 ppm of H₂S respectively. The corrosion of steel is described by means of electrochemical impedance spectroscopy. The electrochemical data obtained from the steel monitoring are presented in terms of Nyquist plots. The influence of the total H₂S concentration as well as the effect of temperature on the corrosion of API 5L X-70 steel were also studied. In the presence of H₂S the R_{ct} values decrease as the H₂S concentration increases.

Keywords Hydrogen sulfide in chloride solutions · API 5L X-70 steel · Corrosion · Electrochemical impedance

Introduction

The electrochemical behavior of both iron and many grades of steel in H₂S solutions has been investigated through the years by many researchers [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12] by simulation of field conditions in the laboratory. Most of them propose as the first corrosion product formed on steel surface the ferrous sulfide phase known as mackinawite [13]; however, formation of other phases is also thermodynamically possible with changes in the pressure and/or the temperature of the test conditions. Shoesmith et al. [14] reported the formation of three iron monosulfide phases: mackinawite, troilite and ferrous sulfide, at 21 °C, in unstirred and saturated aqueous H₂S solutions. Param et al. [15] proposed that steel immersed in H₂S-containing solutions will corrode leading to the formation of a series of iron sulfide phases, with mackinawite as the first corrosion product. Other authors paid attention to the kinetics of mackinawite formation. Pound et al. [16] have investigated the anodic behavior of iron in H₂S solution.

Vedage et al. [17] described the corrosion of 4130 steel in a 3 wt% sodium chloride solution in H₂S in terms of two different processes: charge transfer at high frequencies and a diffusion processes at low frequencies. Ma et al. [10] have investigated the protective/nonprotective behavior of the FeS film formed on a steel surface by means of alternating current impedance and pointed out that H₂S may have an inhibiting effect on the corrosion.

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Experimental

Apparatus

Electrochemical impedance spectroscopy was carried out with a Solartron 1280B potentiostat. Impedance spectra were measured in a frequency range from 0.001 to 20,000 Hz at an alternating current amplitude of 10 mV. Monitoring for 24 h was carried out for all the conditions studied. The three-electrode system was used in all experiments, the working electrode being a cylindrical X-70 steel bar with an exposure area of 0.8184 in.², a saturated calomel electrode as a reference and a rod of sintered graphite as a counter electrode. The chemical composition of the steel was 0.26% C, 1.65% Mn, 0.03% P and 0.03% S.
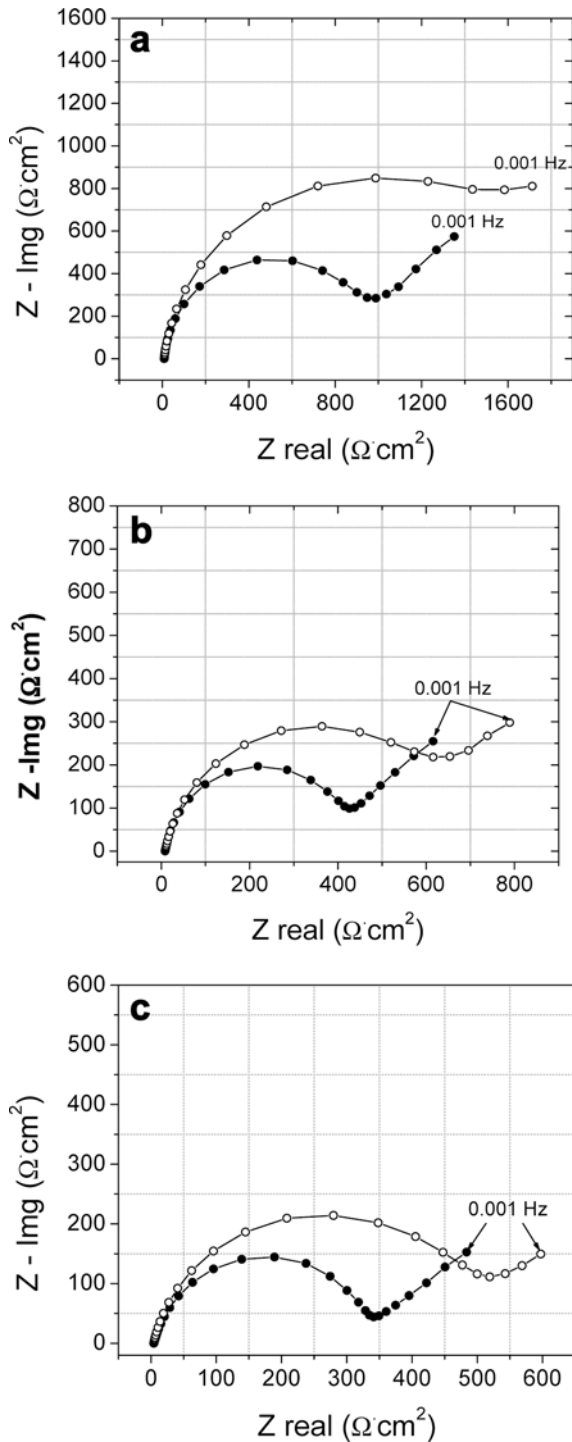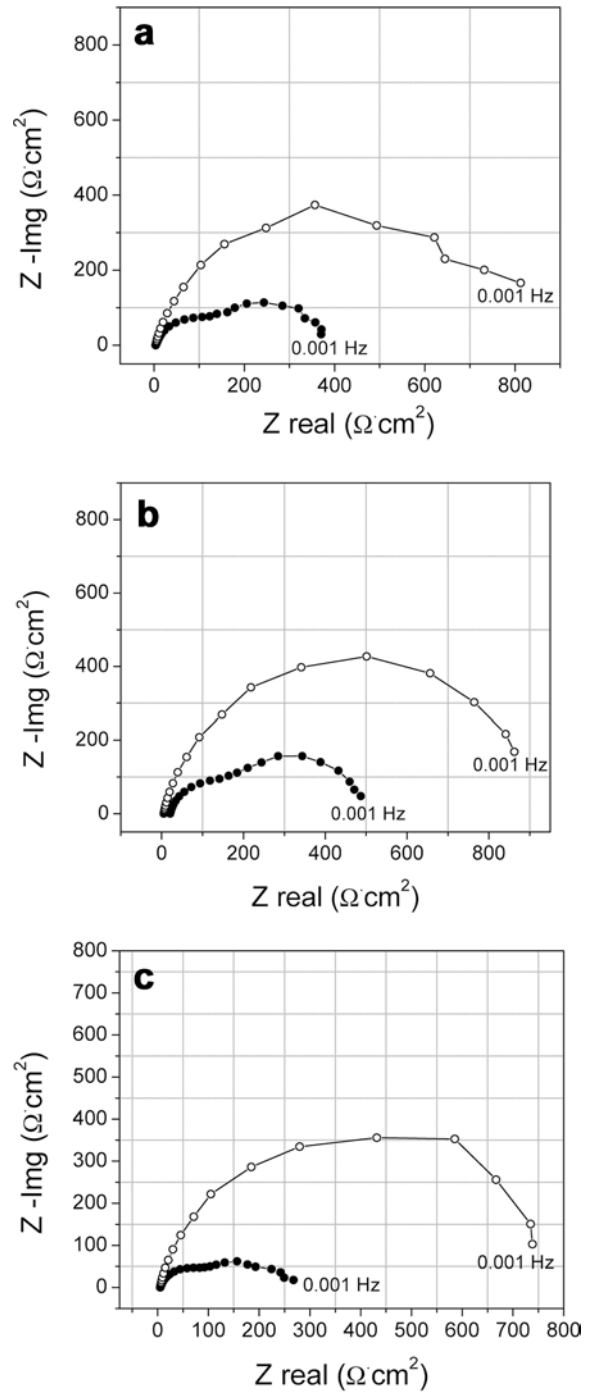
Electrolytes

Three different electrolytes were prepared to conduct the experimentation. Table 1 summarizes the different elec-

Table 1 Electrolyte solutions

Electrolyte	H$_2$S concentration (ppm)	pH
3 wt% NaCl solution	100	5.34
3 wt% NaCl solution	650	4.38
3 wt% NaCl solution	2,550	4.11

Fig. 1 Impedance spectra of X70 steel measured in a 3 wt% NaCl solution with 100 (**a**) 650 (**b**) and 2,550 ppm H$_2$S at 20 °C at 0 (*closed circles*) and 24 h of exposure (*open circles*)

Fig. 2 Impedance spectra of X70 steel measured in a 3 wt% NaCl solution with 100 (**a**) 650 (**b**) and 2,550 ppm H$_2$S at 60 °C at 0 (*closed circles*) and 24 h of exposure (*open circles*)

trolyte solutions studied in this work. All solutions were purged with N$_2$ for about 45 min to eliminate the dissolved oxygen; subsequently H$_2$S gas was bubbled through the solution until the saturation condition was reached. The H$_2$S concentration was determined by the iodometric titration method.

All conditions were evaluated at 20 and 60 °C and at atmospheric pressure of Mexico City.
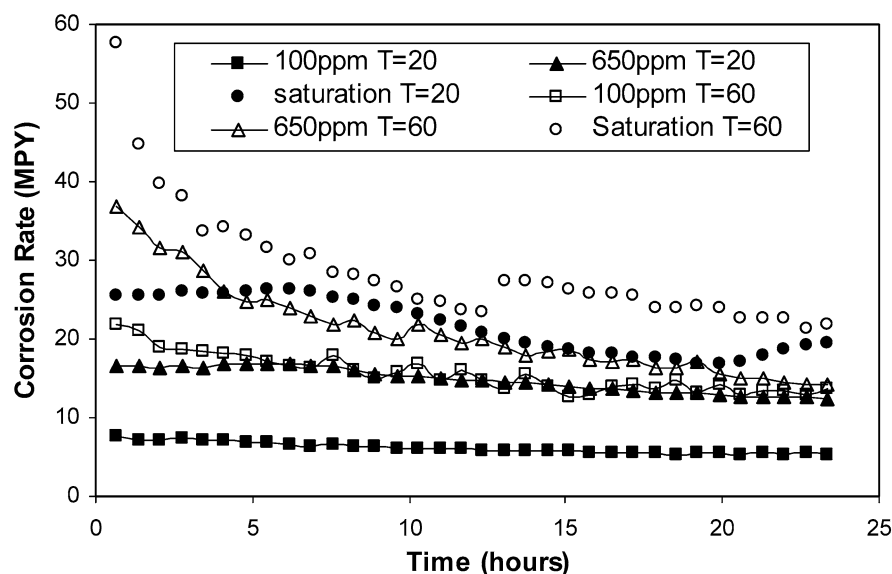
Results and discussion

Figures 1 and 2 show the corrosion behavior of steel in terms of Nyquist diagrams. When H_2S is present, the Nyquist plot is formed at high frequencies by a semi-circle characteristic of a charge-transfer process and at low frequencies by a Warburg resistance characteristic of a diffusion process with a slope of approximately 45°. After 24-h exposure this response is practically the same; however, the diffusion process it is not well defined because of the frequency range used.

According to Vedage et al. [17] this process may be attributed to iron dissolution at high frequencies, and at low frequencies diffusion may occur through the iron sulfide film formed because of the unstirred system conditions. There is a trend for the R_{ct} values to increase with time because of film formation on the steel surface. This film, as mentioned previously, is an iron sulfide known as mackinawite as reported by several authors [6, 8, 13, 14, 15, 16, 18, 19, 20, 21, 22]. The charge transfer resistance values in the 100 ppm H_2S solution become smaller, about 20 times lower than those for the sodium chloride solution [23].

At 60 °C the impedance spectrum shows two time constants at the beginning of the monitoring process, then these two time constants become one (representing only one process), characteristic of the charge transfer process. The temperature effect is the same for the three conditions as can be seen in Fig. 2, which shows at 24 h of monitoring the diameter of the semicircle with practically the same value. From Fig. 2, it is also possible to note that apparently the temperature effect (that promotes the transfer of species from the bulk to the electrode surface) becomes more important than the concentration of H_2S. This is confirmed by the corrosion values corresponding to each condition (Fig. 3).

It is clear from Fig. 2 that both temperature and H_2S concentration have a strong influence on the general corrosion process of X70 steel. For the solution with a concentration of 100 ppm H_2S, the lowest corrosion rate values were calculated at 20 °C but at a higher temperature (60 °C) the corrosion values are very close to those measured for 650 ppm H_2S at 20 °C. Very similar behavior occurs when the H_2S concentration increases from 100 to 650 ppm. These corrosion values are closer to those for the saturation condition, which means that an increment in temperature when H_2S is present will accelerate the corrosion process to very high levels as shown in Fig. 3.

The equivalent circuits used in the fitting of the electrochemical behavior of X-70 steel in a sodium chloride solution with H_2S, at 20 and 60 °C, are shown in Fig. 4. The circuit to fitting the mixed control process at 20 °C (Fig. 1) is formed by the solution resistance, R_S,

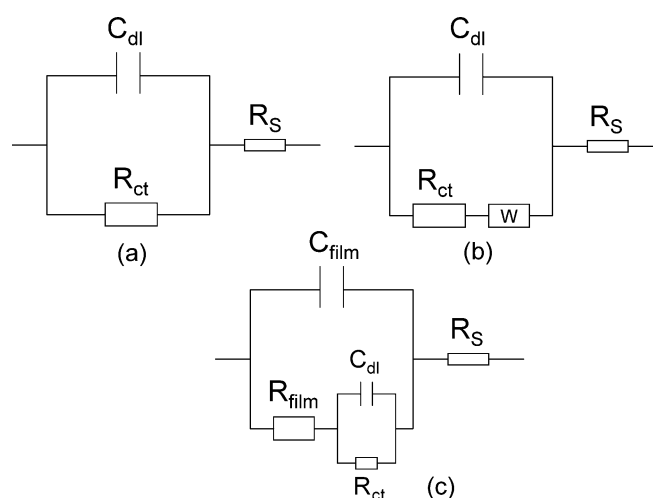**Fig. 4** Equivalent circuits proposed for the fitting of experimental data. R_{film} resistance of the film, C_{film} capacitance of the film

Fig. 3 Corrosion rate values for three H_2S conditions studied at 20 and 60 °C

Table 2 Charge transfer resistance variation as a function of H_2S concentration

| H_2S concentration (ppm)	R_{ct} (Ω cm^2)	
	0 h	24 h
0	24,667	11,471
100	1,315	2,059
650	465.4	864.8
2,550	298.7	462.1

the double-layer capacitance, C_{dl}, the charge transfer resistance, R_{ct} and a Warburg element, W (Fig. 4 b). At 60 °C, two different equivalent circuits were used to simulate experimental data. At the beginning of the monitoring the behavior of the system is described by two time constants: at high frequencies R_{ct} and at low frequencies the FeS film resistance R_{film} with their associated capacitances and R_S. After the first 2 h of exposure, the system at 60 °C seems to be described only by one time constant; therefore, it can be fitted to a Randless circuit. A constant phase element (CPE) was used to obtain better fitting of the experimental results. Even though the physical meaning for the CPE is not well defined, it has been used to simulate impedance data as proposed by Brug et al. [24].

There is an important shift in R_{ct} values due to H_2S addition to the NaCl solution. For the solution with 100 ppm H_2S the R_{ct} value changes from 1,315 to 2,059 Ω cm^2 (from the beginning to the end of monitoring), in the 650 ppm H_2S solution the R_{ct} value goes from 465.4 to 864.8 Ω cm^2 and, finally, the lowest charge transfer resistance values are those corresponding to the saturated solution and go from 298.7 to 462.1 Ω cm^2. Table 2 summarizes the charge transfer resistance variation as a function of H_2S concentration at two different exposure times.
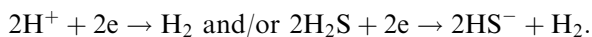
Conclusions

There are two processes involved in the corrosion of API 5L X-70 steel in H_2S media: at high frequencies a charge transfer process (the iron dissolution) and at very low frequencies a diffusion processes (the H^+ or H_2S species), according to the following reactions:

Anodic:

$$Fe \rightarrow Fe^{2+} + 2e.$$

Cathodic:

$$2H^+ + 2e \rightarrow H_2 \text{ and/or } 2H_2S + 2e \rightarrow 2HS^- + H_2.$$
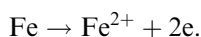
There is a clear dependence on the corrosion behavior of steel with H_2S concentration with changes in the polarization resistance of the system, as was demonstrated by the corrosion data.

For all conditions analyzed in this study there is no evidence of any protection against corrosion from the FeS film formed on the steel surface. Although the values of the corrosion data decrease with the exposure time because of the film formation, they are too high to be considered as protective.

The temperature effect becomes important in promoting the transfer of electrochemical species from the bulk to the steel surface and the FeS formation.

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