

EIS investigation of CO₂/H₂S corrosion

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Abstract

This paper covers one of the building blocks required to complete a mechanistic CO₂/H₂S corrosion model: electrochemistry of carbon steel CO₂ corrosion in the presence of traces of H₂S (3-250 ppm in the gas phase). Electrochemical impedance spectroscopy and linear polarisation resistance were used to investigate the mechanism of CO₂/H₂S corrosion in a glass cell at room temperature, at atmospheric pressure, pH5, using a rotating cylinder electrode at 1000 rpm.

Very thin sulphide film was formed on the steel electrode in all experiments with H₂S. At low concentrations (<15 ppm) the sulphide films reduced the corrosion rate while at higher concentrations of H₂S (up to 250 ppm) the trend was reversed and a mild increase of the corrosion rate was seen.

Keywords: CO₂ corrosion, H₂S, electrochemical impedance spectroscopy, linear polarisation resistance.

Introduction

In the case of pure H₂S corrosion and CO₂/H₂S corrosion, a number of experimental studies can be found.¹⁻¹⁴ Most of these studies focused on the effect of H₂S on the formation of various forms of iron sulfide scales. Several research efforts^{7,10-14} have attempted to elucidate the mechanism of CO₂/H₂S corrosion, nevertheless, our understanding of the underlying processes is still lacking.

Progress has been made in providing a framework for equilibrium calculations which is helpful in determination of Fe / CO₂ / H₂S / H₂O system chemistry.¹⁵⁻¹⁷ There are no equivalent mechanistic models that cover kinetics of corrosion, transport and scaling phenomena in similar systems. A research project is currently under way with an aim to develop an integrated *mechanistic* model of CO₂ / H₂S corrosion that includes all the important processes occurring such as: the electrochemical and chemical reactions, the transport processes within the boundary layer and the protective film formation.

Several studies¹⁸⁻²¹ have demonstrated that the electrochemical behaviour of iron in the acidic solutions containing H₂S can be investigated by means of AC impedance measurement. This research project will follow similar methodology and will focus on a

systematic investigation on the influence of traces of H₂S on the mechanism of iron dissolution in CO₂/H₂S solution.

For many years, most studies about the cathodic and anodic polarization behavior of mild steel in CO₂ solutions (with and without H₂S) have been confined to traditional steady state techniques such as potentiodynamic sweep measurements. However, steady-state techniques are limited because they give information only on the rate-determining step. Moreover, during the measuring process, techniques such as potentiodynamic sweep polarize the electrode surface to such a great extent, in order to uncover corrosion mechanisms, that the validity of the results can be questioned particularly in the cases when protective films form. In a preliminary study, it was concluded that the steady-state potentiodynamic sweep technique was not a sufficiently sensitive tool for studying the mechanisms of CO₂/H₂S corrosion as it disturbed the system irreversibly during the measuring process.²²

Transient electrochemical technique such as Electrochemical Impedance Spectroscopy (EIS), are less intrusive because they can provide information about the processes without disturbing the reactions too much, by applying a small amplitude, sinusoidal perturbation to the electrochemical system. As the various elementary processes change at different rates, the system responses can be obtained from different frequencies in a single experiment. Therefore, EIS is a powerful diagnostic method for analyzing CO₂/H₂S corrosion mechanisms in complex cases that may involve multiple charge transfer steps, with adsorbed intermediates at the metal surface, mass transfer, chemical reactions, etc. No systematic studies about CO₂/H₂S corrosion have been made using the EIS technique. In this report the CO₂ corrosion reaction with and without traces of H₂S was investigated using the EIS technique at different H₂S concentrations in a low temperature, low pressure and low pH condition.

Experiments

In order to determine the mechanism of H₂S/CO₂ corrosion, experiments were conducted in a glass cell on API 5L X65 carbon steel at the following conditions: T=20°C, pH 5, P_{CO₂} =1 bar, gaseous H₂S concentration in CO₂ = 0, 3,15,100 and 250 ppm, ω= 1000 rpm. In these experiments the corrosion process was monitored with two different electrochemical measurement techniques: Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR). The experiments for each H₂S concentration were conducted at least twice to make sure the results were reproducible and reliable.

Equipment

Experiments were conducted at atmospheric pressure in a glass cell at room temperature. Gas (with varied concentration of H₂S in CO₂) was continuously bubbled through the cell. A three-electrode set-up (Figure 1) was used in all electrochemical experiments. A rotating cylinder electrode with a speed control unit was used as the working electrode. A concentric platinum ring was used as a counter electrode. A saturated Ag/AgCl reference electrode was used and was externally connected to the cell

via a Luggin capillary and a porous wooden plug. The pH was followed with an electrode directly immersed into the electrolyte. Upon leaving the cell, H₂S was scrubbed by an absorbent. Electrochemical measurements were made with a potentiostat connected to a computer.

Material

API 5L X65 carbon steel was tested. The chemical composition of the steel is given in Table 1. The working electrode was machined from the parent material into a cylinder 12 mm in diameter and 14.3 mm long. The exposed area of the specimen was 5.4 cm².

Experimental Procedure

The glass cell was filled with 2 liters of electrolyte: de-ionized water + 3 mass% NaCl. Initially CO₂ gas was bubbled through the electrolyte (at least one hour prior to experiments) in order to saturate and deaerate the solution. Monitoring of pH was used to determine whether the solution is in equilibrium. Sodium bicarbonate (NaHCO₃) solution was deaerated before being added to adjust the solution to pH 5. In different experiments various H₂S /CO₂ gas mixtures were bubbled through the electrolyte (at least 1 hour) in order to saturate the solution. The H₂S concentration was maintained precisely by adjusting the flow rate ratio of CO₂ to H₂S with a gas rotameter. The gaseous concentration of H₂S was verified by colorimetric tubes before the any measurements was taken. The steel working electrode surface was polished with 220 and 600 grit silicon carbide paper, washed with alcohol, mounted on the specimen holders, and immersed into the electrolyte. The free corrosion potential was followed immediately after immersion. The Linear Polarization Resistance (LPR) technique was used to measure the polarization resistance R_p.

After 20 minutes of immersion at the free corrosion potential, EIS measurements were conducted by applying an oscillating potential $\pm 5\text{mV}$ around the free corrosion potential to the working electrode using the frequency range 0.001 Hz-5000 Hz. The experimental conditions are listed in Table 2

Results and discussion

Before any experiments were conducted in slightly sour environments, a number of baseline experimental results needed to be established in the absence of H₂S to serve as reference points in order to better understand the role of H₂S on the corrosion of carbon steel. Figure 2 demonstrates the effect of 3 ppm H₂S concentration on the characteristics of the impedance plots at the corrosion potential. In the H₂S-free saturated pure CO₂ solution at the corrosion potential, the characteristics of the impedance diagram did not change with immersion time and exhibited a depressed semi-circle indicating a double-layer capacitance, as well as an inductive loop at lowest frequencies. A depressed semi-circle is not uncommon for iron dissolution in acidic media and it was suggested in the literature that the heterogeneous surface roughness and the nonuniform distribution of

current density on the surface might be related to it.^{23,24} The Nyquist impedance diagram showed no mass transfer controlled impedance under these conditions; however, it was not a pure charge transfer controlled process either because the inductive loop at low frequencies indicated that the iron dissolution mechanism might occur in two steps involving an adsorbed intermediate. According to Keddam et al.,^{25,26} the inductive loop at the low frequency can be related to the relaxation time of the intermediate adsorbed species, e.g. $(\text{FeHCO}_3)^+_{\text{ad}}$. With the addition of 3 ppm gaseous H_2S , the impedance diagram at corrosion potential demonstrated a larger depressed semi-circle with similar characteristics, however, the polarization resistance (R_p) value that intercepted the real axis of the Nyquist plot was three times larger than that of the H_2S free solution. The change of the Nyquist impedance diagram in the presence of 3 ppm gaseous H_2S suggested that a very thin somewhat protective film of mackinawite might have formed at the electrode surface.²⁷ This thin layer of protective film was not observable to the naked eye, as the electrode surface was shiny throughout the experiment. The resulting corrosion rate measured by LPR (shown in Figure 3) of 0.25 mm/year was 3 times lower than measured in H_2S -free CO_2 solutions. The polarization resistance (R_p) values measured by the LPR technique agreed well with the EIS results for the R_p .

In order to investigate the effect H_2S concentration, another set of experiments was conducted by saturating the solution with a gas mixture containing 15 ppm of H_2S in CO_2 , while keeping all other conditions the same. The Nyquist plot shown in Figure 4 demonstrated that the corrosion mechanism has not changed much while the corrosion rate decreased further. Figure 3 illustrated that the steady-state corrosion rate (measured by LPR) in the presence of 15 ppm H_2S was around 0.07 mm/year, which was even lower than that obtained in a 3 ppm H_2S solution. In Figure 5, one can observe how in the 15 ppm H_2S experiment the depressed semi-circle increased in diameter over time, implying that the protective film took 6 hours to be established. The characteristics of the impedance diagram stopped changing after 6 hours of immersion indicating that the film had reached an equilibrium and the corrosion rate remained constant throughout the rest of the experiment. The effect of immersion time on the Nyquist plot and the time required for the corrosion process to stabilize were different for various H_2S concentrations, as shown in Figure 6 for 100 ppm and in Figure 7 for 250 ppm.

The shape of the steady-state Nyquist plots was virtually the same in all experiments with various H_2S concentrations (shown in Figure 8). The diameter of the semicircle increased with increasing H_2S concentration indicating that the corrosion rate was reduced due to the presence of H_2S traces. It is obvious that the retardation was a strong function of H_2S concentration clearly confirmed by steady-state LPR measurements (shown in Figure 9). However, in the presence of H_2S concentrations higher than 15 ppm, a mild increase of the corrosion rate was observed seen both by LPR and EIS.

It can be speculated that the formation of the sulfide surface films has played a double role. At the low concentrations the sulfides reduced the corrosion rate most likely by coverage of the steel surface, which prevented the underlying iron from dissolving. This is supported by the facts that the sulfide films detected in the experiments (by EDS) were too thin to be an effective diffusion barrier. The secondary effect, which became dominant at higher concentrations of H_2S , is related to an increase of the corrosion rate. It is most likely related to the conductive sulfide films being a catalyst for the cathodic

reaction. Simple calculations have indicated that the concentration of H₂S was too low to consider dissolved H₂S an important cathodic species.

Although only limited information was extracted from EIS measurements so far, this technique has the potential to provide a deeper insight into the processes underlying H₂S/CO₂ corrosion. Mechanistic modeling of measured EIS spectra shall be pursued in order to elucidate and quantify the mechanism of H₂S/CO₂ corrosion.

Conclusions

- Very thin sulfide film, possibly mackinawite, was formed rapidly on the steel electrode in all experiments with traces of H₂S.
- At low concentrations (<15 ppm H₂S) the sulfide films reduced the corrosion rate an order of magnitude compared to H₂S-free CO₂ corrosion.
- At higher concentrations of H₂S (up to 250 ppm H₂S) the trend was reversed and a mild increase of the corrosion rate was seen.

Acknowledgments

The authors would like to acknowledge the contribution of the consortium of companies whose continuous financial support and technical guidance led to this publication. They are BP, ConocoPhillips, ENI, Petrobras, Saudi Aramco, Shell, Total, Champion Technologies, Clariant, MI Technologies and Nalco. The authors are grateful to the Russ College of Engineering and Technology for providing a scholarship for K-L. Lee.

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Table 1. Chemical composition of the API 5L X65 carbon steel used for the working electrode (mass%)

C	Mn	Si	Nb	V	Fe	P	S	Cr	Cu	Ni	Mo	Al
0.150	1.34	0.24	0.03	0.055	balance	0.011	0.004	0.011	0.01	0.02	0.103	0.032

Table 2. Experimental conditions

Test solution	Water + 3 mass% NaCl
Test material	API 5L X65 Carbon steel
Temperature	20°C
Pressure	1 bar
pH	5
Fe ⁺⁺	<1 ppm
Velocity	1000 rpm
Gaseous H ₂ S concentration in CO ₂	0, 3, 15, 100, 250 ppm
LPR sweep rate	0.125 mV/s
LPR potential range	From -5 to +5 mV vs. E _{oc}
EIS DC current	0 mV vs. E _{corr}
EIS AC potential range	±5 mV
EIS frequency range	0.001 – 5000 Hz
EIS test duration	4 – 48 hours

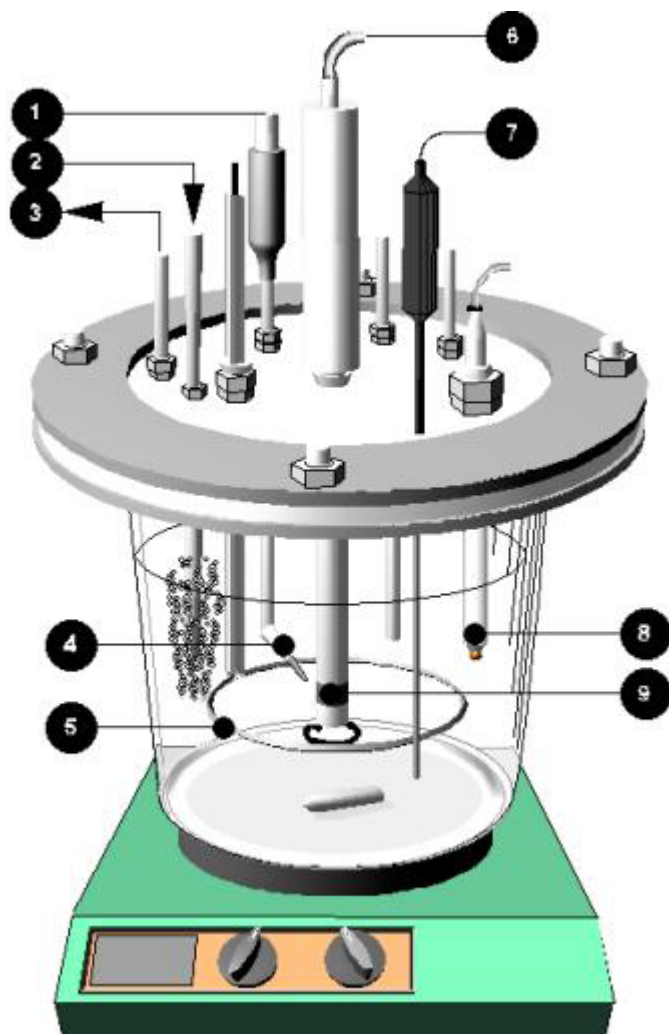


Figure 1. Schematic of the experimental test cell: 1-reference electrode, 2-gas in, 3-gas out, 4-Luggin capillary, 5-platinum counter electrode, 6-rotating cylinder, 7-temperature probe, 8-pH electrode, 9-working electrode

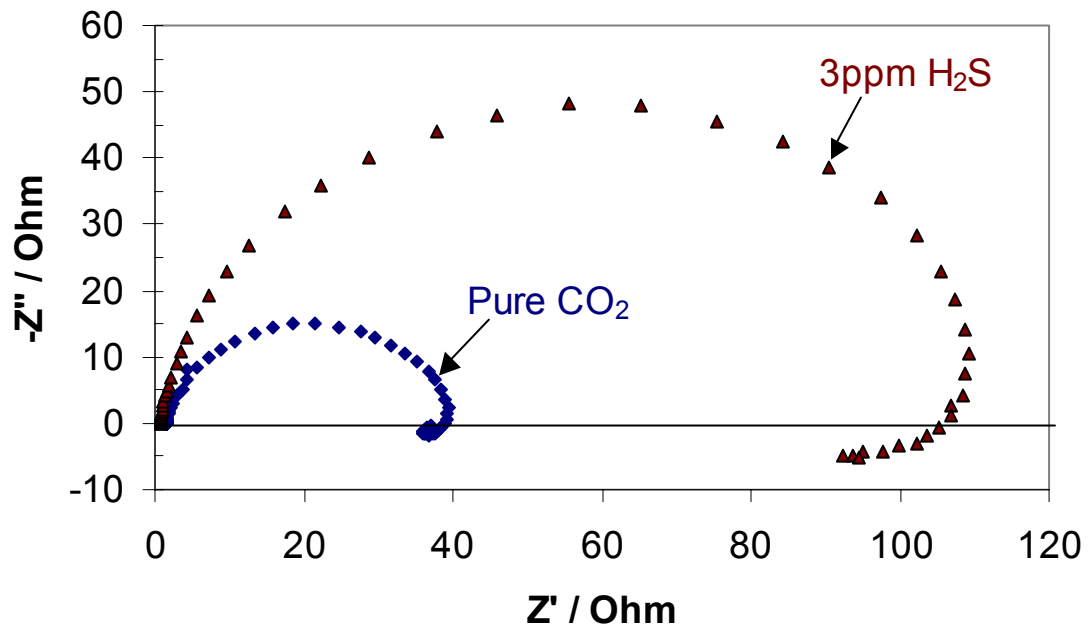


Figure 2. Effect of 3 ppm H₂S in CO₂ (gas phase) on the Nyquist impedance diagram for corrosion of carbon steel X65 in pH 5 solution of water + 3% NaCl, p = 1 bar, t = 20⁰C, ω = 1000 rpm at corrosion potential (vs. Ag/AgCl).

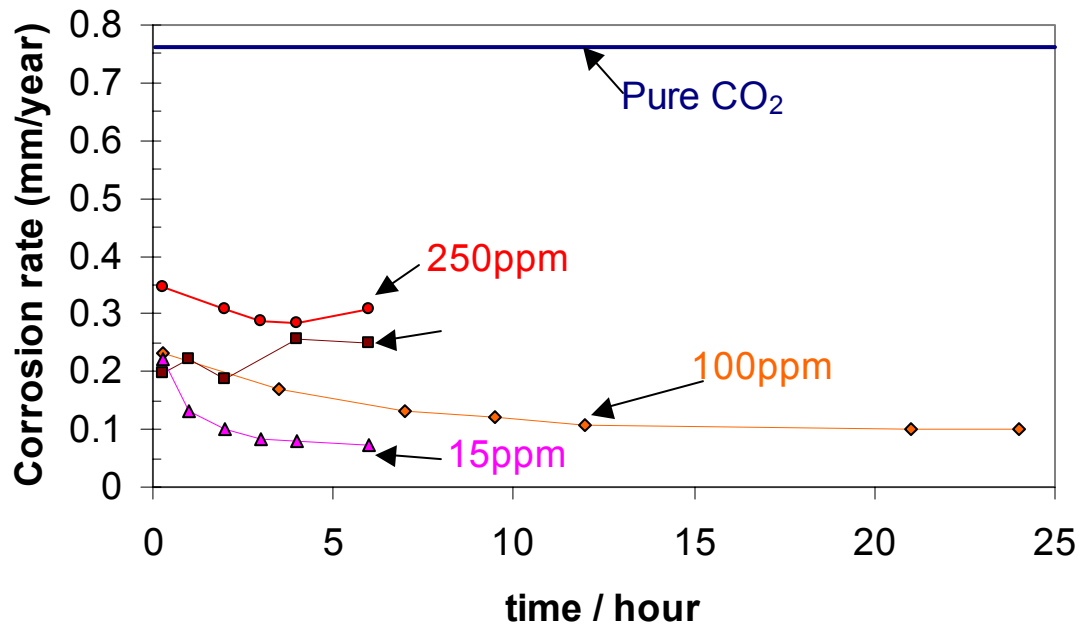


Figure 3. Effect of H₂S gaseous concentration on the corrosion rate (measured by LPR) of carbon steel X65 in pH 5 solution, water + 3% NaCl, p = 1 bar, t = 20⁰C, ω = 1000 rpm with respect to immersion time.

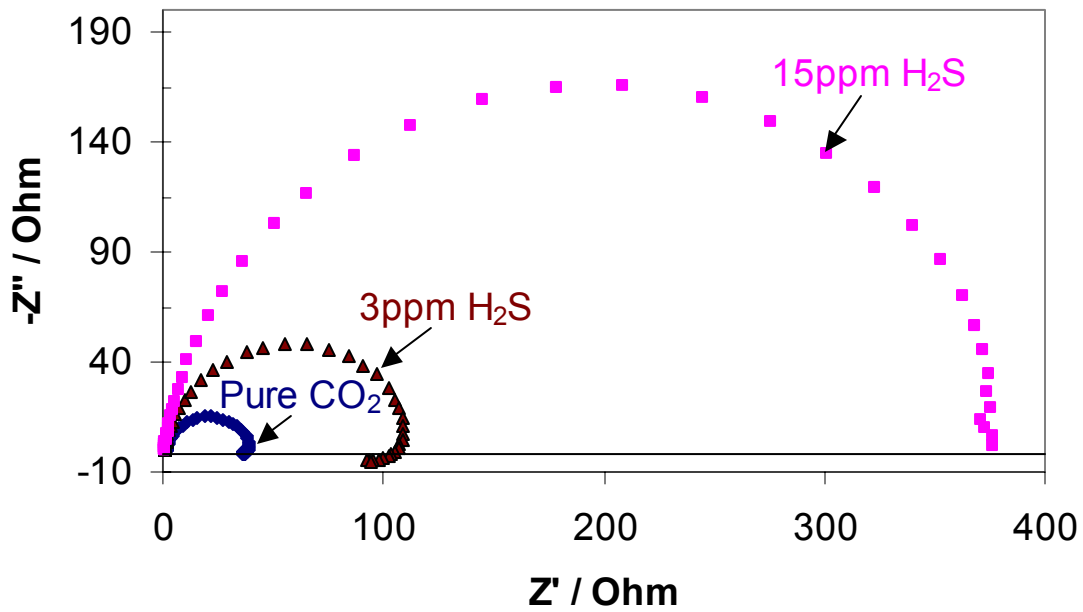


Figure 4. Effect of 15 ppm H₂S in CO₂ (gas phase) on the Nyquist impedance diagram for corrosion of carbon steel X65 in pH 5 solution of water + 3% NaCl, p = 1 bar, t = 20⁰C, ω = 1000rpm at corrosion potential.

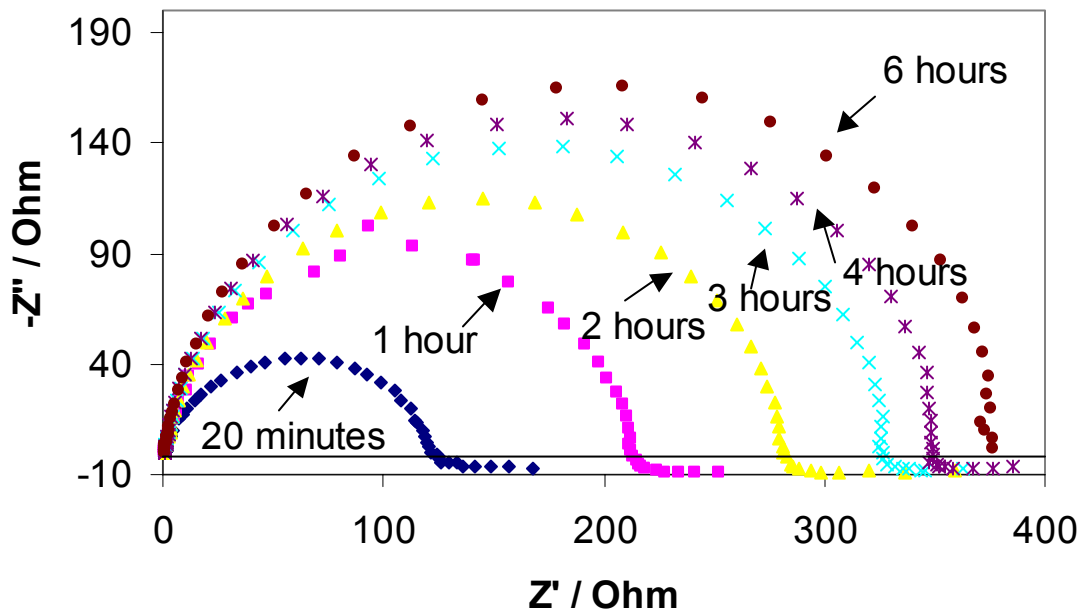


Figure 5. Effect of immersion time on Nyquist impedance diagram for corrosion of carbon steel X65 in pH 5 saturated CO₂ solution with 15 ppm H₂S (gas phase), water + 3% NaCl, p = 1 bar, t = 20⁰C, ω = 1000 rpm at corrosion potential.

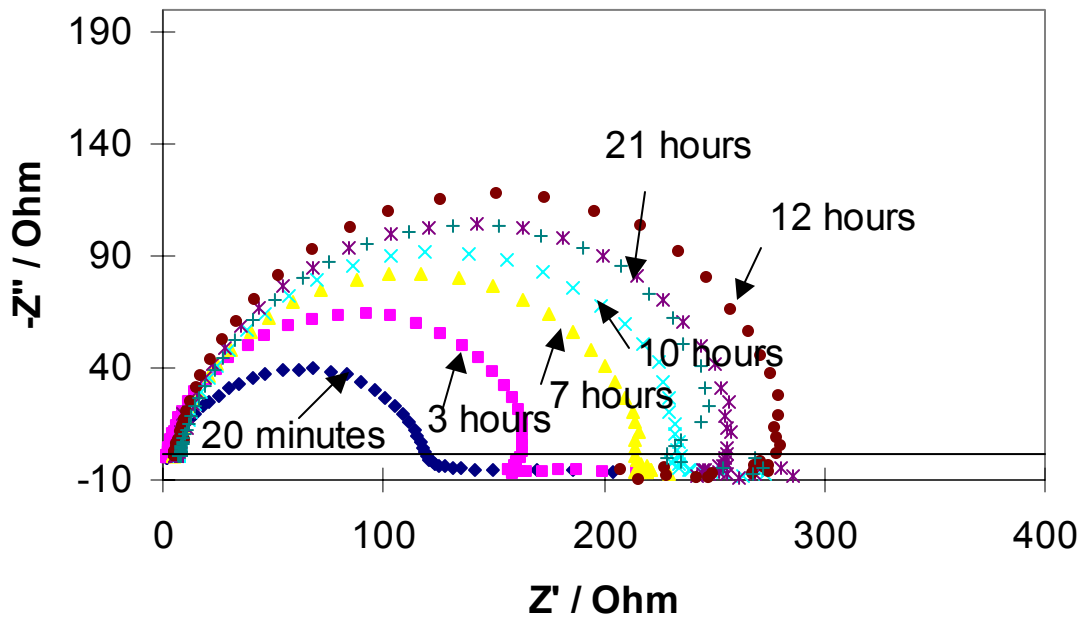


Figure 6. Effect of immersion time on Nyquist impedance diagram for corrosion of carbon steel X65 in pH 5 saturated CO₂ solution with 100 ppm H₂S (gas phase), water + 3% NaCl, p = 1 bar, t = 20⁰C, ω = 1000 rpm at corrosion potential.

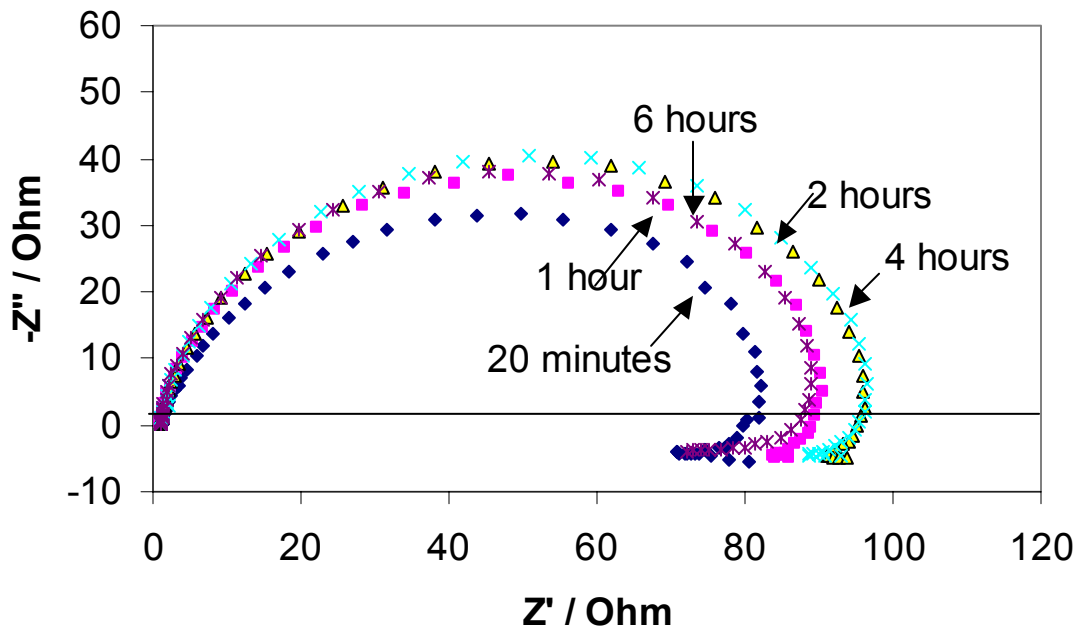


Figure 7. Effect of immersion time on Nyquist impedance diagram for corrosion of carbon steel X65 in pH 5 saturated CO₂ solution with 250 ppm H₂S (gas phase), water + 3% NaCl, p = 1 bar, t = 20⁰C, ω = 1000 rpm at corrosion potential.

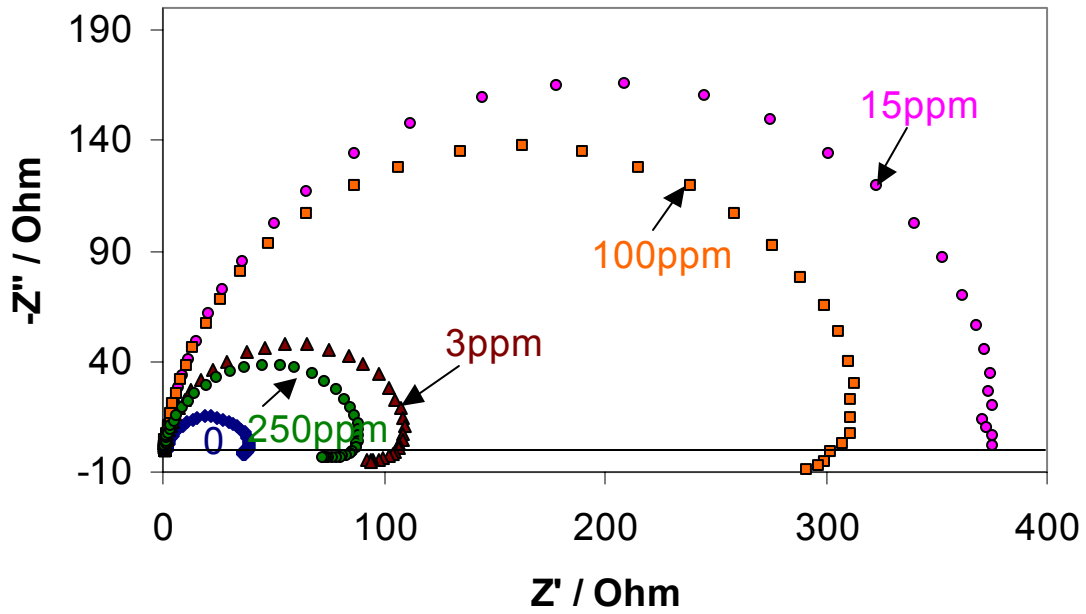


Figure 8. Effect of gaseous H_2S concentration on the Nyquist impedance diagram for corrosion of carbon steel X65 in pH 5 saturated CO_2 solution of water + 3% NaCl, $p = 1$ bar, $t = 20^{\circ}C$, $\omega = 1000$ rpm at corrosion potential.

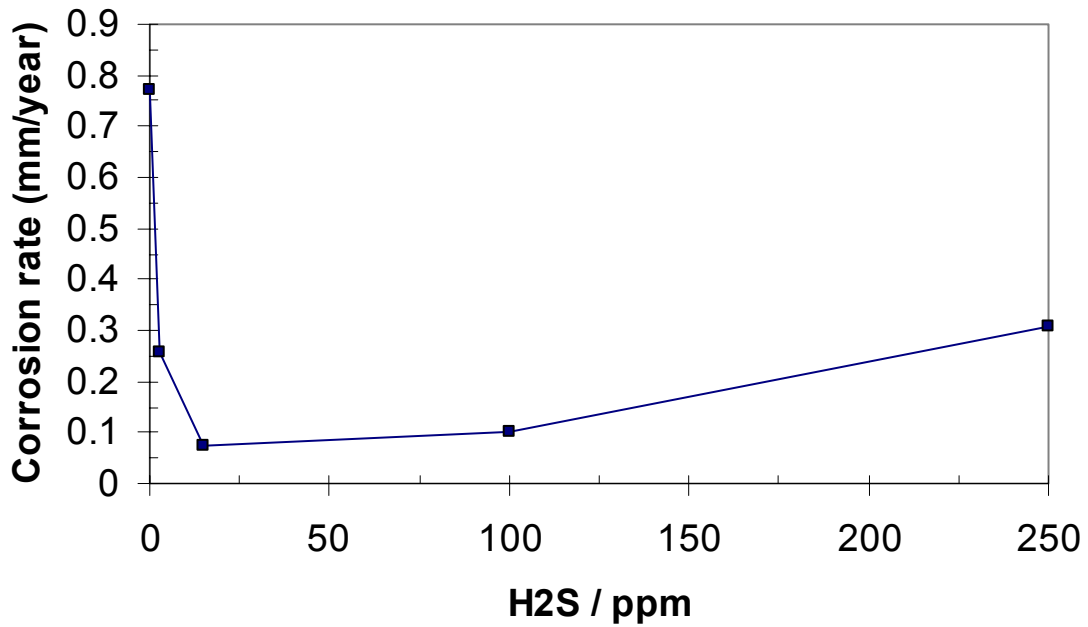


Figure 9. Effect of gaseous H_2S concentration on the steady-state corrosion rate (measured by LPR) of carbon steel X65 in pH 5 saturated CO_2 solution, water + 3% NaCl, $p = 1$ bar, $t = 20^{\circ}C$, $\omega = 1000$ rpm.