

Effect of the Acid Environment on the Electrochemical Behaviour of 1045 Steel Reinforced Cement

Ana Cecilia Vieira da Nóbrega^{1,a}, Luís Augusto Sousa Marques Rocha^{2,3,b}, Edith Ariza Avila^{2,c}, Antonio Eduardo Martinelli^{4,d}, Dulce Maria de Araújo Melo^{5,e} and Maria das Vitórias Vieira Almeida de Sá^{6,f}

¹Civil Engineering Department, Technology Center, Federal University of Pernambuco, Campus Agreste, 55002-970, Caruaru/PE, Brazil

²Centre for Mechanical and Materials Technologies, University of Minho, Campus de Azurém, 4800-058, Guimarães, Portugal

³Mechanical Engineering Department, University of Minho, Campus de Azurém, 4800-058, Guimarães, Portugal

⁴Material Engineering Department, Federal University of Rio Grande do Norte, 59072-970, Natal/RN, Brazil

⁵Chemistry Department, Federal University of Rio Grande do Norte, 59072-970, Natal/RN, Brazil, 59072-970, Natal/RN, Brazil

⁶Civil Engineering Department, Federal University of Rio Grande do Norte, 59072-970, Natal/RN, Brazil 59072-970, Natal/RN, Brazil

^aacvn@supercabo.com.br, ^blrocha@dem.uminho.pt, ^cedith@dem.uminho.pt, ^daemart@uol.com.br, ^edaraujomelo@gmail.com, ^fvitória@ct.ufrn.br

Keywords: oilwell, cementing, casing, acidizing, corrosion, SAE 1045

Abstract. External corrosion is one of the most common causes of oilwell casing failure. Hostile environments can be due to acidizing treatments. Although it is common to add corrosion inhibitors and oxygen scavengers in acidic solutions to control external casing corrosion, their real efficiency is unknown yet. Therefore, it is important to establish how aggressive to steel are the different hostile environments to help decide which acidic systems can be used. A comparative evaluation of the corrosion of steel immersed in hardened cement slurries submitted to commonly acidizing agents is suggested. The performance of Special Class Portland Cement Slurries reinforced with polished SAE 1045 steel was evaluated by electrochemical measurements as a function of time. Open circuit potential, polarization curves and electrochemical impedance spectroscopy were studied. 15.0 wt% HCl, 12.0 wt% HCl + 3.0 wt% HF (regular mud acid), 10.0 wt% HAc + 1.5 wt% HF and a simulated hardened cement slurry pore solution were used as electrolytes. The most aggressive acid solution to plain Portland hardened cement slurries was the regular mud acid. 10.0 wt% HAc + 1.5 wt% HF electrolytes were the least aggressive ones, showing open circuit potentials around +250 mV compared to -130 mV of the simulated hardened cement slurry pore solution after the first 24 hours of immersion. This behavior was observed during two months at least. Similar corrosion rates were shown between both electrolytes, around $0.01 \mu\text{A}\cdot\text{cm}^{-2}$. Total impedance values, insipient arcs and large polarization resistance capacitive arcs on the Nyquist plots, indicating passivity process, confirmed the behaviour of the system in the 10.0 wt% HAc + 1.5 wt% HF electrolyte.

Introduction

Acidizing is an important oilwell stimulation technique, which increases well production. The injection of acid solutions to remove solid debris from oil wells is a commonly employed technique to increase the flow of oil [1]. The acid is pumped down under pressure through the casing towards the formation. The usual acidizing solution used in oilwells are 10 wt% acetic acid + 1.5 wt% HF, 12.0 wt% HCl + 1.5 wt% HF (mud acid) and 15.0 wt% HCl [2-4].

At the cannonades, the acid comes in contact with the cement sheath, where they react causing severe damage to the cement, eventually exposing the casing to corrosive fluids causing external casing corrosion. The susceptibility of the cement to acid dissolution and its significance to the oil industry has been reported [2-4]. It is important to remember that the aggressive behaviour of acids is controlled in oil fields using oxygen scavengers [5] and corrosion inhibitors [6] in the injected acids. The acid strength is minimized with water after acidizing operations [1]. In a general way, the use of cathodic protection has also been reported [7] to prevent external corrosion.

This work comparatively assess different aggressive acidizing solutions to external corrosion casing, destroying the passive film of the interface of the cement sheath and steel of the casing.

Material and methods

Special Class oil well Portland cement (CIMESA, Laranjeiras, Brazil, density 3.15 g.cm^{-3}) and water (density 0.9969 g.cm^{-3}) were used to prepare the slurries at a water to cement weight ratio of 0.46 according to API Spec 10a and API Spec 10b [8, 9].

The slurries were reinforced with polished SAE 1045 steel to carry out the electrochemical measurements according to a proposed system used in chloride corrosion in steel bars immersed in concrete, as already described in a previous work [10]. 100 mm pieces of 8 mm round steel were submitted to chemical cleaning and painted with two coatings of coal tar epoxy paint, in order to protect its surface from premature oxidation in contact with the environment. A SAE 1045 steel was evaluated in order to minimize the inference of other compounds on the corrosive process.

One of the extremities of the bar was smoothed just before the immersion in the sample, delimitating the surface for study. A metallographic procedure including smoothing and polishing was performed to adjust the surface roughness for corrosion pitting identification. The smoothed area was turned to the lower part of the samples, making it necessary the use of a Luggin capillar. Five samples of 50 mm x 100 mm (diameter x height) were produced for each situation. Samples were prepared in a vibration table and cured in water at 38 degrees Celsius in order to reproduce superficial oil well conditions.

Three-electrode cell systems were used in the measurements. Saturated calomel electrode was used as the reference electrode and a platinum electrode with 1 cm^2 of exposed area was used as the counter electrode. Open circuit potentials (OCP) were obtained in order to determine the necessary time to stabilize the potential in all the samples before potentiodynamic polarization tests. The polarization curves prior to Tafel plot analyses were gathered from - 400 mV to +1200 mV at a scan rate of 1 mV.s^{-1} . A PGP201 Radiometer potentiostat/galvanostat was used in both tests.

Impedance spectroscopy measurements were carried out using a Radiometer potentiostat PGZ100. They were performed from 100 KHz to 10 mHz with a peak to peak amplitude of 10 mV immediately after the immersion and after 1 h, 2 h, 3 h, 4 h, 1 day, 2 days, 3 days, 4 days, 15 days, 1 month and 2 months.

Results and Discussion

Open circuit potential measurements are shown in Fig. 1. As it can be seen, samples immersed in 10.0 wt% HAc + 1.5 wt% HF solution showed the most positive open circuit potentials. Also, an increase in the OCP values is observed with the time in 10.0 wt% HAc + 1.5 wt% HF and simulated pore solution samples. This behavior suggests the formation of a thermodynamically stable passive layer [11, 12]. Similar behavior was observed after 2 months of exposition to the acids. Oppositely, 15.0 wt% HCl and regular mud acid samples, shown a decrease in the OCP values with the time indicating a higher corrosion tendency.

The long time required to stabilize the OCP is associated to the presence of hardened cement around the electrode. Chemical changes on the double electrical layer due to H^+ evolution from the acidic electrolytes may also contribute [13]. Although some samples presented smaller OCP stabilization times, 24 hours was established as the standard period for all systems. This is important because the

initial corrosion rates are larger than those after stabilization, once the new chemical composition of the double layer was not adjusted for each new potential [13].

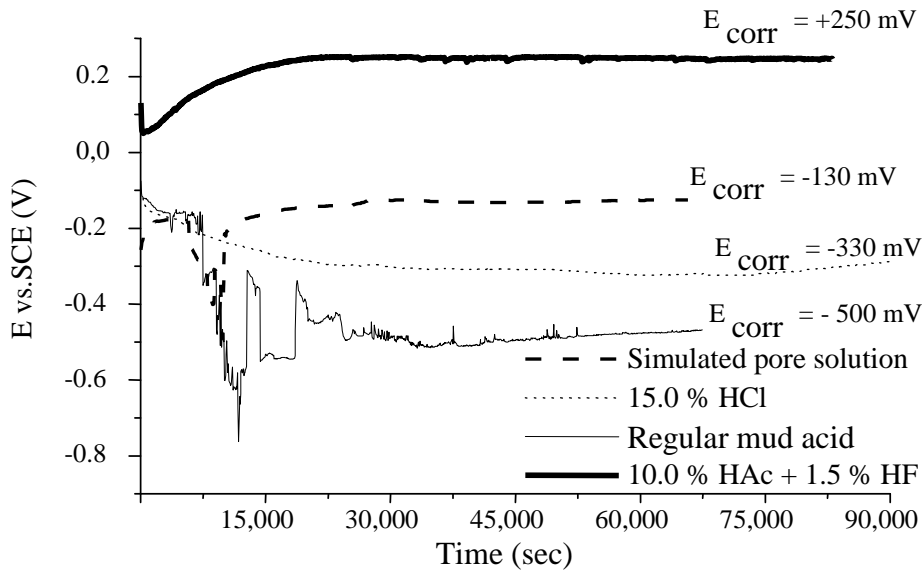


Figure 1. Open circuit potential curves as a function of time for the first 90,000 seconds.

The potentiodynamic polarization curves of the samples after 24 hours in different electrolytes are shown in Fig.2. Zero current potential ($E_{(i=0)}$) and corrosion current density (i_{corr}) values can be seen in Table 1. 10 wt% HAc + 1.5 wt% HF and the simulated hardened cement slurry pore solution were the least aggressive environments, confirming the open circuit potentials results. They showed similar corrosion current densities, around $0.01 \mu\text{A}\cdot\text{cm}^{-2}$. Besides, the corrosion potential of the 10 wt% HAc + 1.5 wt% HF is greater than that of the simulated pore solution (Table 1), indicating a likely formation of a passive film in that last sample. On the other hand, the negative effects of the halogen ions to carbon steel [12] duplicated the corrosion rates to 15.0 wt% HCl and increased a hundred times in mud acid, as it can be seen from Table 1.

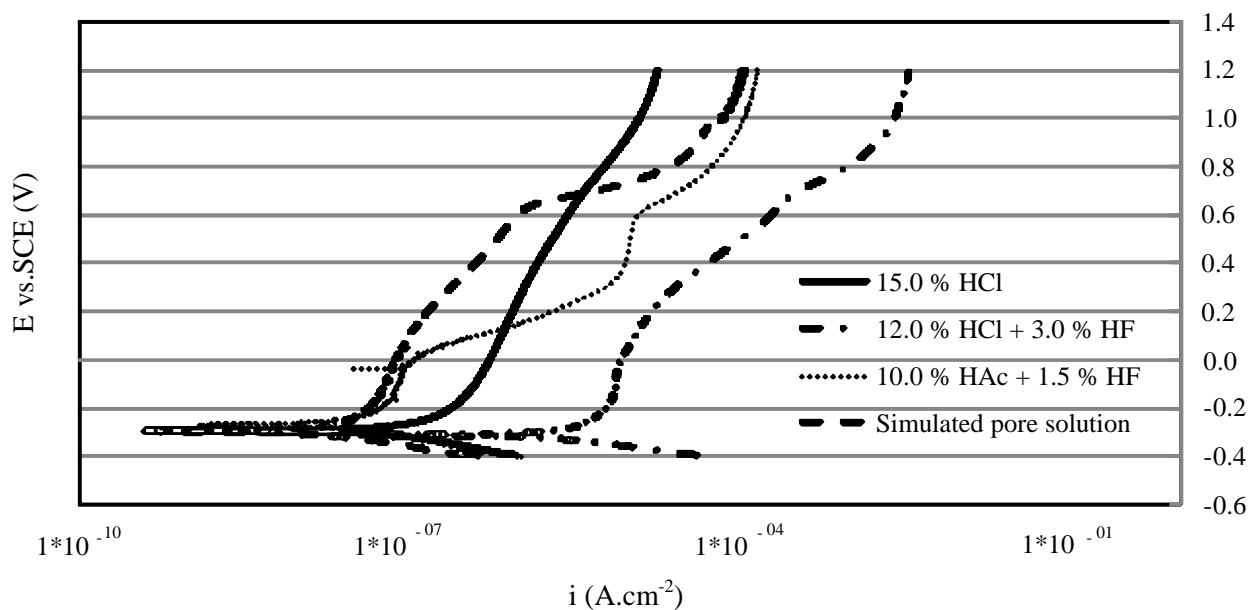


Figure 2. Potentiodynamic polarization curves of the samples after 24 hours.

Table 1. Electrochemical parameters of the samples after 24 hours.

Electrolyte	Simulated pore solution	15.0 wt% HCl	Regular mud acid	10.0 wt% HAc + 1.5 wt% HF
$E_{(i=0)}$ [mV/SCE]	-300.5	-299.2	-316.5	+95.6
i_{corr} [μAcm^{-2}]	0.01	0.03	1.37	0.01
OCP [mV/SCE]	-130	-243	-480	+240

Samples immersed in simulated pore solution have passive films related with high alkalinity [12]. Several authors have mentioned that high concentrations of fluoride inhibit the corrosion of carbon steel [14]. This phenomenon has been observed for ionic concentrations ≥ 100 ppm. In the present study, the fluoride concentrations are around 15,000 ppm and 30,000 ppm in 10 wt% HAc + 1.5 wt% HF and regular mud acid solutions, respectively. However, the negative effect of chloride ions is predominant. Singh et al. [14] reported that the most devastating effect of fluoride ions is the simultaneous combination with chloride ions.

Zero current potentials ($E_{(i=0)}$) were more negative than corrosion potentials (E_{corr}) for 10 wt% HAc + 1.5 wt% HF and simulated hardened cement pore solution (Table 1). This phenomenon can be explained by the potentiodynamic polarization that started on the cathodic region from values significantly different than E_{corr} . When E_{corr} was the same order of magnitude or lower than the potential applied for the polarization on the cathodic branch, a coherent behavior was observed. A possible explication for the phenomenon is that the polarization can change the chemical composition of the electric double layer due to reduction reactions of the metal ions on the passive oxide film. As a consequence, there are situations where the open circuit potential does not match the inflection point between the anodic and cathodic branches of the Tafel curves [13].

Electrochemical impedance spectroscopy measurements were carried out only until 15 days due to the degradation of the hardened cement slurries in regular mud acid and 15.0 wt% HCl. After 1 month of immersion, some samples depicted total exposure of the steel surface to the acid solutions. In this case, no physical or chemical protection of the cement could be considered. Several calcium acetate crystals were encountered on the surface of these samples as well as on the exposed electrical contact of the working electrode, impairing electrical contact. Even cleaning the salt, the electrical contact could not be established.

The impedance plots of the samples after 3 hours of immersion can be seen in Fig. 3. A similar behavior was observed after 1 or 2 hours. Low frequency diffusion processes can be observed, probably caused by transport processes of chemical species through the hardened bulk. As a consequence, it was not possible to obtain coherent measurements from samples immersed in regular mud acid until 4 hours of immersion, due to bulk colmatation.

There is a high frequency capacitive arc in addition to an intermediate frequency arc both visible in Fig. 3. These arcs are due to the presence of a passive layer on the steel working electrodes when in alkaline environment as the hardened cement slurry, as well as due to responses associated with the dynamic of the active dissolution process on the steel surface. High impedance values, including higher arc diameters extrapolated in the real impedance axis were detected from samples immersed in simulated pore solution, indicating more resistant passive films, followed by 10 wt% HAc+ 1.5 wt% HF and 15.0 wt% HCl. Active corrosion is commonly reported as small diameter flattened circles along the real axis of Nyquist diagrams [15, 16], as it can be seen from samples immersed in 15.0 wt% HCl. This way, electrochemical impedance measurements on the first, second and thirty hours after immersion also confirmed the results of the open circuit potential and potentiodynamic polarization curves.

Although diffusion processes hinder the extrapolation of the high frequency arcs, it is inferred that the systems present similar behaviour related with charge transference. This behavior can be confirmed using Bode's impedance plot, where higher impedance values are associated with more electrochemical systems. Using the same analysis, impedance measurements obtained after 4 days and 15 days of immersion showed better behavior of samples immersed in 10 wt% HAc+1.5 wt% HF than in simulated pore solution.

Although this phenomenon was shown by the open circuit potentials since the first immersion hours, it was only observed after 4 days of immersion, using impedance spectroscopy. This is probably due to the high dissolution of the metallic material in the electrolytic environment. When the metallic concentration gradient increases in solution and consequently around the working electrode, it can act as a protective barrier obstructing the contact of the steel with the aggressive solution, decreasing the corrosive rate and the continuity of the corrosive process.

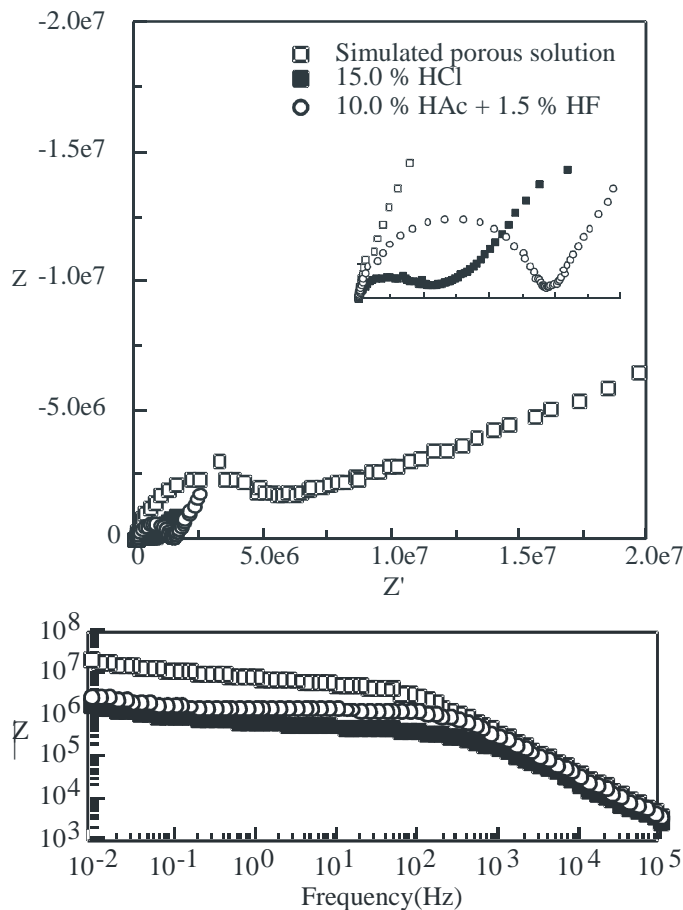


Figure 3. Complex plane and Bode impedance plots of impedance obtained in carbon steel immersed in hardened cement slurry after 3 hours immersed in 15.0 wt% HCl, 10.0 wt% HAc + 1.5 wt% HF and a simulated hardened cement slurry pore solution.

It was not possible to model an equivalent circuit to adequately represent the complex impedance measurements obtained for these systems. This difficulty is mainly related with the heterogeneity of the bulk cementitious material, its degradation along the time of immersion, which changes the microstructure of the material, as well as due to the weak adherence of the smoothed metallic surface-hardened cement slurry interface.

The determination of dissolved iron in all solutions was carried out by atomic absorption after two months of immersion. The concentrations of iron in 10 wt% HAc + 1.5 wt% HF solutions was 50 to 60 times lower than in 15.0 wt% HCl and 100 times lower than in regular mud acid. This behavior confirms the reduced corrosion rate of the carbon steel immersed in hardened cement slurry in 10 wt% HAc + 1.5 wt% HF.

Conclusions

The 10 wt% HAc + 1.5 wt% HF electrolyte was the least aggressive for the external corrosion of the simulated SAE 1045 steel casing, showing open circuit potentials around +250 mV compared to -130 mV of the simulated hardened cement slurry pore solution (to simulate the alkaline environment of a cementitious material) after the first 24 hours of immersion. Similar behavior was

observed along two months of immersion. Similar corrosion rates were measured using either 10 wt% HAc + 1.5 wt% HF or simulated hardened cement slurry pore solution as electrolyte, around $0.01 \mu\text{A.cm}^{-2}$. Total impedance values, insipient arcs and high polarization resistance capacitive arcs on the Nyquist plots, indicating passivity, confirmed the good behaviour of the 10 wt% HAc + 1.5 wt% HF. On the other hand, 15.0 wt% HCl and 12.0 wt% HCl + 1.5 wt% HF (mud acid) solutions are very aggressive to the immersed in hardened Portland slurry, probably due to the presence of chloride ions. It was not possible to adjust an equivalent circuit due to the complex cementitious matrix degraded along the time and the changing resulting interfaces.

Acknowledgements

The authors acknowledge FACEPE and PRH30/ANP/MCTPETROBRAS for the financial support.

References

- [1] L. Kalfayan, Production Enhancement with Acid Stimulation, PennWell Corp., 2008, pp. 270.
- [2] E.P. Motta, C.R. Miranda, S.M.C. Anjos, J.A. Ribeiro, E.C. Jr., Acidizing Wells With Acetic/HF Acid Mixtures to Minimize Cement Dissolution, in: SPE Formation Damage Control Symposium, Society of Petroleum Engineers, Lafayette, Louisiana, 1996.
- [3] C.R. Miranda, J.S. Gold, Study of Cement Resistance to the Attack of Acid Solutions, in: International Symposium on Oilfield Chemistry, 1997 Copyright 1997, Society of Petroleum Engineers, Inc., Houston, Texas, 1997.
- [4] A.A. Al-Taq, H.A. Nasr-El-Din, T.A. Al-Shafei, A New Technique to Enhance Cement Resistance to Mud Acids, in: 8th European Formation Damage Conference, Society of Petroleum Engineers, Scheveningen, The Netherlands, 2009.
- [5] F.W. Schremp, J.F. Chittum, T.S. Arczynski, Use of Oxygen Scavengers To Control External Corrosion of Oil-String Casing, SPE Journal of Petroleum Technology, 13 (1961) 703-711.
- [6] J. Cassidy, Design and Investigation of a North Sea Acid Corrosion Inhibition System, in: CORROSION 2006, NACE International, San Diego Ca, 2006.
- [7] C. Brelsford, C. Rounding, C.A. Kuiper, Well Casing Cathodic Protection Evaluation Program in the Spraberry (Trend Area) Field, in: CORROSION 2003, NACE International, San Diego Ca, 2003.
- [8] API, Specification for Cements and Materials for Well Cementing, American Petroleum Institute, pp. 46.
- [9] API, Recommended Practice for Testing Well Cementing, American Petroleum Institute, pp. 175.
- [10] D.R. Silva, H. Scatena Junior, A.C.V. Nóbrega, M.V.A. Sá, Use of sodium molybdate in reinforced concrete exposed to chlorides, in: R.M. Ferreira, J. Gulikers, C. Andrade (Eds.) International RILEM Workshop on Integral Service Life Modelling of Concrete Structures Guimarães, 2007.
- [11] S. Wolyneć, Técnicas eletroquímicas em corrosão, Editora da Universidade de São Paulo, São Paulo, 2003.
- [12] V. Gentil, Corrosão, LTC (Grupo GEN), Rio de Janeiro, 2011.
- [13] W.S. Tait, An Introduction to Electrochemical Corrosion Testing for Practicing Engineers & Scientists, Pair O Docs Pubns, 1994.
- [14] D.D.N. Singh, R. Ghosh, B.K. Singh, Fluoride induced corrosion of steel rebars in contact with alkaline solutions, cement slurry and concrete mortars, Corrosion Science, 44 (2002) 1713-1735.
- [15] P. Gu, J.J. Ping Xie, Beaudouin, Characterization of surface corrosion of reinforcing steel in cement paste by low frequency impedance spectroscopy, Cement and Concrete Research, 24 (1994) 231-242.
- [16] D. Jolivet, D.M. Bonen, S.P. Shah, The corrosion resistance of coated steel dowels determined by impedance spectroscopy, Cement and Concrete Research, 37 (2007) 1134-1143.