

Electrochemical Behaviour of Iron in Chlorinated Alkaline Media. The Effect of Slurries from Granite Processing

Carmen M. Abreu, Alba Covelo, Belén Díaz, Lorena Freire, X. Ramón Nóvoa* and M. Consuelo Pérez

Universidade de Vigo, E. T. S. E. I., Rúa Maxwell, 9, Campus Universitario 36310 Vigo, Spain

O Porriño é uma zona bem conhecida de pedreiras do sudoeste de Galiza, Espanha. Nas operações de processamento do granito são geradas 3×10^5 ton ano⁻¹ de pó nesta área, com consequências graves para o meio ambiente. Este pó resultante comprovou ser um aditivo eficiente do concreto de alta resistência com melhoramento efetivo das suas propriedades mecânicas. Nenhum trabalho foi publicado acerca do efeito desta mistura na passivação de reforços de aço. O objetivo deste trabalho é analisar o comportamento electroquímico dos eletrodos de aço e de ferro em soluções alcalinas resultantes desta lama. O crescimento e evolução das camadas de passivação formadas nos eletrodos testados foram estudados por Voltametria Cíclica e Espectroscopia de Impedância Electroquímica. Foram usadas técnicas de Difração de raios-X e Microscopia de Varrimento por Elétrons para a caracterização morfológica e química dos filmes de passivação gerados. O efeito da presença de íons cloreto também foi considerado.

Porriño is a well known zone of quarry and stone working of the SW of Galicia, Spain. In granite's working processes 3×10^5 ton year⁻¹ of granite powder are generated in this area, causing an important environmental problem. This dust has proved to be an efficient addition to high-strength concrete to improve mechanical properties. Nevertheless, no works have been published concerning the effect of this admixture in the passivation of steel reinforcements. The objective of the present work is to analyze the electrochemical behaviour of iron and carbon steel electrodes in alkaline solutions resulting from these slurries. The growth and evolution of the passive layers formed on the tested electrodes are studied by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy. Scanning Electron Microscopy and X-ray powder Diffraction have been used for the morphological and chemical characterisation of the generated passive films. The effect of the presence of Cl⁻ ions is also considered.

Keywords: granite slurry, corrosion inhibitors, CV, EIS

Introduction

Spain is one of the three major ornamental rock producers and the first European granite producer. 60% of the Spanish production is concentrated in the Porriño district (NW of Spain) with 3×10^5 ton year⁻¹. The granite cutting residues are originated from the sawing process of rock blocks into plates. In this process, 20% to 30% (m/m) of mineral is transformed into dust which mixed with water, shot-blasting particles, lubricants, tensioactives and lime form the so-called granite cutting slurries, GCS. The solid and liquid phases are separated by density difference: the solid fraction remains into a tank while the liquid fraction is recycled at the beginning of process.

The particles present in the solid phase are classified in two sizes: the greater fraction, used as aggregates for concrete, and the finer fraction which nowadays is useless, remains as waste accumulated in landfills. The environmental problem generated urges to find a solution acceptable from the economical and ecological points of view.

The recycling of industrial wastes in concrete manufacturing is a matter of increasing interest worldwide. Indeed, concrete technology can use great amounts of industrial residues as secondary raw materials. For instance, blended cements are normally produced by adding different quantities of coal fly ash, silica fume or ground granulated blast furnace slag to Portland cement clinker. These mineral additions, that have been initially simply used as recycled wastes, turned out to be beneficial with regard to the properties of concrete, especially in relation to its resistance to

*e-mail: movoa@uvigo.es

aggressive agents.^{1,2} Preliminary works suggested the possibility of using GCS as an additive in concrete structures, concluding that small additions of these slurries improved the mechanical resistance of concrete.³ However, the possible effects that granite slurry's additions can have in the passive layer of rebars must be studied prior to the use of GCS as cement additives.

The present paper is aimed to analyse the possible use of Granite Cutting Slurries as additive in reinforcing concrete structures, evaluating the GCS addition effect when chloride ions are present. The study is developed in two parts: A first one where the chemical and morphological properties of GCS are analysed, and a second one focused on the electrochemical behaviour of iron in alkaline solution containing GCS powder and chloride ions.

Experimental

Characterization of GCS

Granite Cutting sludge samples were obtained in Porriño (Pontevedra, Spain). The chemical characterization was done by chemical analysis of cations, X-Ray diffraction and titrations with HCl 0.1 mol L⁻¹.

Electrochemical tests

Granite Cutting suspensions were prepared by adding 0.2 g of slurry to 150 mL of NaOH 0.1 mol L⁻¹ solution. The electrochemical behaviour of iron in this suspension was compared with that of a reference without added GCS. Moreover, alkaline suspensions were used with two chloride concentrations: 0.2 mol L⁻¹ and 0.5 mol L⁻¹.

Electrochemical experiments were performed in a convectional three-electrode cell, where the tested material was corrugated carbon steel having 0.54 cm² exposed area. The reference electrode was Hg/HgO 0.1 mol L⁻¹ KOH and the counter electrode, a Pt mesh. When chloride ions were added to the solutions, a saturated calomel electrode (SCE) was employed as reference electrode. Before each experiment, the working electrode surface was freshly polished and rinsed with distilled water. All electrochemical tests were performed at room temperature and open to the air, using an AUTOLAB 30 Potentiostat (from EcoChemie). Two different electrochemical techniques were employed: Cyclic Voltammetry and Electrochemical Impedance Spectroscopy.

The scanned potential region for Cyclic Voltammetry tests was from hydrogen evolution (-1.4 V vs. SCE) to oxygen evolution (+ 0.6 V vs. SCE) reactions at 1 mV s⁻¹ scan rate, which allows relaxation of the redox process that take place in the passive layer.⁴

EIS tests were conducted at different immersion times (1, 2, 4 and 8 days). They were carried out at the corresponding Open Circuit Potential (OCP). The scanned frequencies interval was from 10 kHz to 1 mHz. Similar experiments were carried out in solutions contaminated with chloride ions.

Results and Discussion

Characterisation of the GCS

X-ray Diffraction analysis shows the existence of different crystallographic forms. Figure 1 corresponds to the obtained diffraction spectrum Quartz (SiO₂), Biotite (K⁺(Mg²⁺, Fe²⁺)(Al³⁺, Fe³⁺)Si₃O₁₀(OH⁻, F⁻)₂), Albite (NaAlSi₃O₈ or CaAl₂Si₂O₈) and an iron oxide, maghemite (Fe₂O₃) can be identified. All those compounds are typical for granite rocks, and are considered to be alkaline in nature; this characteristic, chemical compounds in crystalline form, is typical of chemically stable compounds, therefore having low pozzolanic activity.

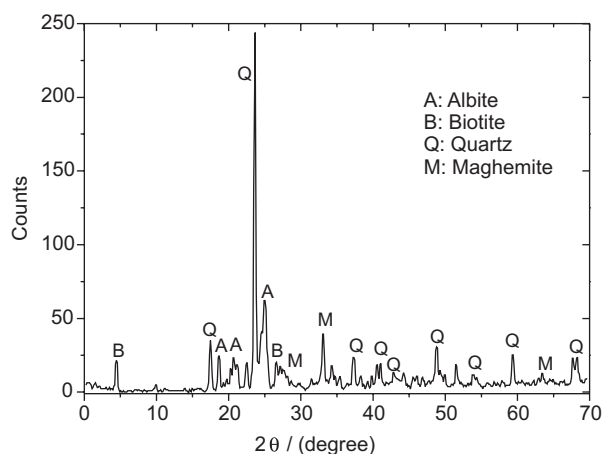


Figure 1. X-ray diffraction analysis of Granite Cutting Slurries showing the identified species present. X-axis corresponds to Bragg's angle 2θ.

The elemental analysis performed on granite slurries allows obtaining the quantitative results that, given as upper oxides, are summarised in Table 1.

It is verified that, from the chemical point of view, the residue is composed mainly of SiO₂, Al₂O₃ and Fe₂O₃ that corresponds to nearly 86%. The high percentages of SiO₂ and Al₂O₃ obtained are typical of igneous granitic rocks.

Table 1. Chemical composition of the granite slurries

Compounds % (m/m)	SiO ₂ 65.840	Al ₂ O ₃ 13.0	Fe ₂ O ₃ 7.118	CaO 5.540	K ₂ O 3.470	Na ₂ O 3.140	MgO 0.871	TiO ₂ 0.332	P ₂ O ₅ 0.280	SO ₃ 0.089	MnO 0.089
Compounds % (m/m)	Cl 0.070	BaO 0.057	SrO 0.027	ZrO ₂ 0.021	Cr ₂ O ₃ 0.016	CuO 0.009	NiO 0.008	ZnO 0.006	N 0.005	C 0.73	H 1.12

The presence of Fe₂O₃ and CaO is probably related to foreign additions, like the addition of steel shot and lime as abrasive in the process of rock cutting /sawing.

In order to homogenize and mix slurries powder, a planetary ball mill was employed. Before milling, the particles size was 1 to 30 μm and, after milling during 45 min, the size was diminished to 1-5 μm. These results are coincident with the bibliography where the size of particles was estimated by laser granulometry, obtaining 3.92 μm average diameter after 80 min milling.⁵

In Figure 2 a SEM micrograph of these particles after the milling process is presented. It can be observed that particles are irregular in shape and size, with about 3 μm average size. SEM-EDX analyses of a GCS powder sample show that chemical composition is particle size dependent. The smallest particles (<1μ) are spherical and Si rich. The remaining particle sizes are irregular shape and rich in Fe, Ca and Al.

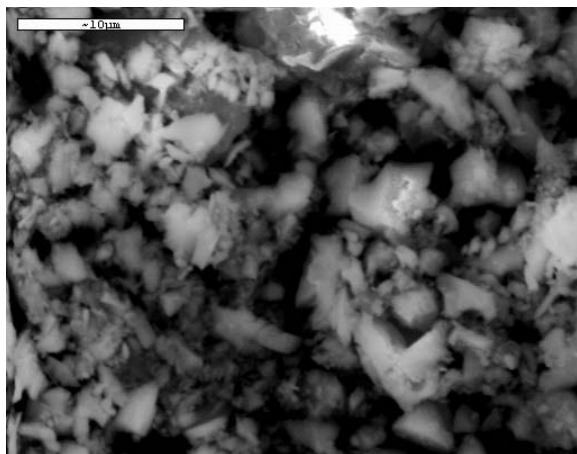
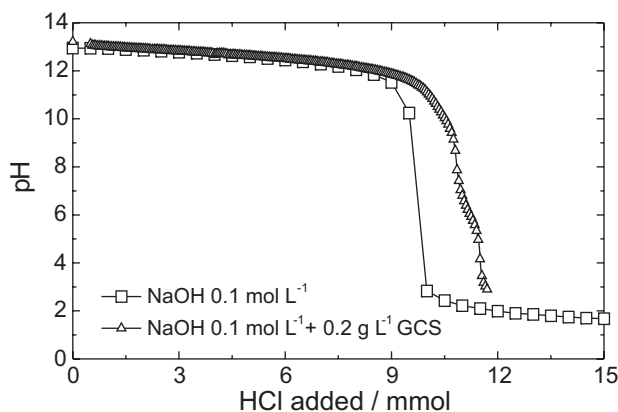
**Figure 2.** SEM micrograph obtained on a sample of GCS after 45 min milling.

Figure 3 presents the titration curve in alkaline media of a GCS suspension (with 2 g L⁻¹ in 100 mL of NaOH 0.1 mol L⁻¹) having as a reference a NaOH 0.1 mol L⁻¹ solution.

The initial pH value (about 13) is similar for both solutions. Nevertheless, it can be seen that the GCS suspension needs 2 mmol HCl more than NaOH solution to neutralise. Thus, GCS show some “buffering power”, similar to that found in red muds.⁶

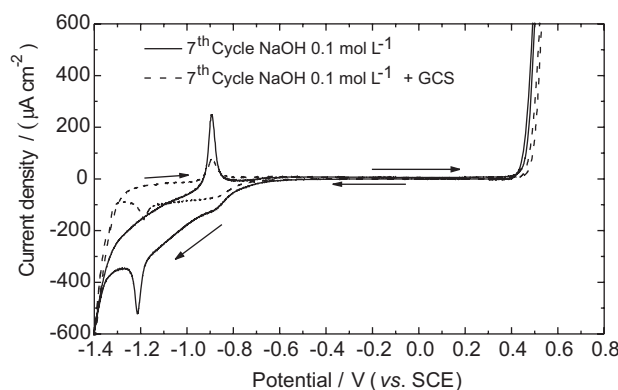
**Figure 3.** Titration curve corresponding to 100 mL of NaOH 0.1 mol L⁻¹ suspension containing 2 g L⁻¹ of GCS and NaOH 0.1 mol L⁻¹.

Electrochemical behaviour of iron in alkaline solutions containing GCS

Solutions without chloride ions

Carbon steel behaviour in alkaline solutions with GCS was analysed by Cyclic Voltammetry and Electrochemical Impedance Spectroscopy. These data were compared with those obtained for an iron electrode in 0.1 mol L⁻¹ NaOH solution.

Oxide films were grown by cyclic voltammetry (seven cycles) on carbon steel electrodes in the different solutions (NaOH 0.1 mol L⁻¹ without additives and with 2 g L⁻¹ GCS). The voltammograms corresponding to the last cycle are depicted in Figure 4. Both forward scans show the activity peak at -0.9 V vs. SCE, typical of magnetite

**Figure 4.** Comparison of the seventh cycles of carbon steel in NaOH 0.1 mol L⁻¹, without and with 2 g L⁻¹ GCS added.

formation, observed for iron electrode in alkaline media.⁷ Nevertheless, in presence of GCS both the peak current and current in the cathodic domain are lower. Moreover, the potential of oxygen evolution is shifted anodically. Those effects can be attributed to blockage of the carbon steel surface due to GCS.

Electrochemical Impedance Spectroscopy, EIS, was used in order to obtain additional information on the electrode processes involved. Figure 5 depicts the typical Bode impedance spectra obtained at 4 and 8 days immersion. The impedance spectra were recorded at the corresponding OCP values, which vary between -200 mV and -100 mV up to 8 days immersion time.

All plots reveal the presence of two time constants that can be attributed to the double layer capacitance-charge transfer resistance and the redox processes developing in the passive layer.⁸ Thus, the impedance can be modelled using equation 1 where R_e represents the high frequency (electrolyte) resistance; R_1 and C_1 correspond to the double layer capacitance and charge transfer resistance; and the R_2C_2 time constant is associated to the redox processes developing in the passive layer. Good agreement is found between this model and the experimental data as illustrated in Figure 5A. The best fitting parameters for the data depicted in Figure 5 are given in Table 2.

$$Z(\omega) = R_e + \frac{R_1}{(j\omega R_1 C_1)^{\alpha_1} + 1/(1 + (Z_2(\omega)/R_1))}; \quad Z_2(\omega) = \frac{R_2}{1 + (j\omega R_2 C_2)^{\alpha_2}} \quad (1)$$

It can be seen in Figure 5 that the overall impedance is higher for the solution containing GCS. Moreover, the high frequency resistance (see R_e parameter in Table 2) is also higher for this solution. Variations in R_e have been related to changes in the dielectric properties of passive films.^{9,10} In the present case, GCS could induce either the formation of an adsorbed layer which blocks the electrode surface, or a chemical modification of the passive layer, with similar result.

Table 2 shows also that double layer capacitance is smaller for the solution containing GCS. If the hypothesis of adsorbed layer applies, the result will be C_1 decreasing

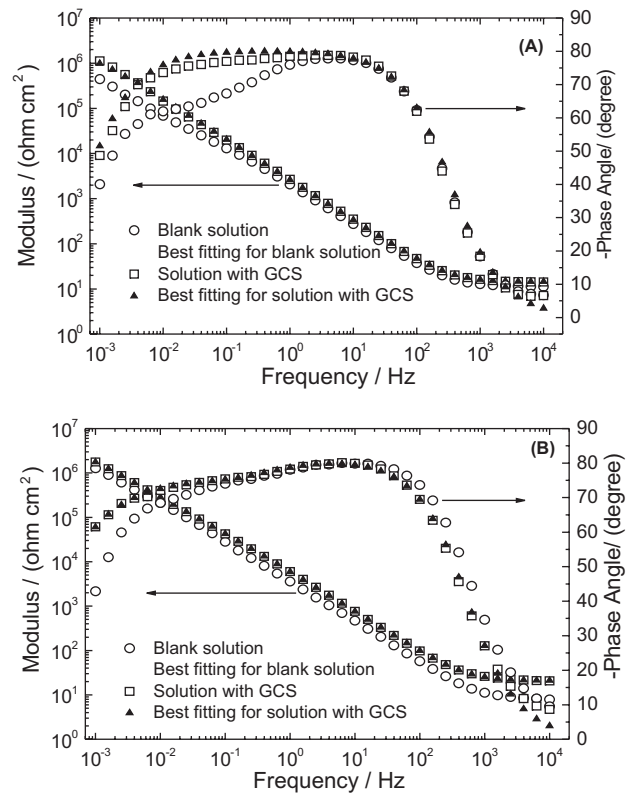


Figure 5. Bode diagrams obtained for carbon steel electrode at (A) 4 and (B) 8 days of immersion time in NaOH 0.1 mol L⁻¹ solution and in the same solution contaminated with GCS.

due to series combination of double layer capacitance and the dielectric capacitance corresponding to this adsorbed layer. Nevertheless, if the double layer capacitance is about $100 \mu\text{F cm}^{-2}$ and the measured C_1 $30 \mu\text{F cm}^{-2}$, the series capacitance shall be $40 \mu\text{F cm}^{-2}$, which gives film thickness about 10^{-10} m, value not compatible with any physical film.

An alternative to explain the observed C_1 decreasing is that GCS change the passive film's zero charge potential (ZCP) by modification of the outermost layer. The OCP shifts cathodically with time in presence of GCS and is globally more cathodic than in the blank solution. According to the literature concerning the electrochemical behaviour of steel in alkaline media, more cathodic potentials means more hydrated passive

Table 2. Best fitting parameters corresponding to data in Figure 5 using equation 1 as equivalent model

	Immersion time / days	$R_e / (\Omega \text{ cm}^2)$	$R_1 / (\text{k}\Omega \text{ cm}^2)$	$C_1 / (\mu\text{F cm}^{-2})$	α_1	$R_2 / (\text{k}\Omega \text{ cm}^2)$	$C_2 / (\mu\text{F cm}^{-2})$	α_2	OCP / mV (SCE)
NaOH 0.1 mol L ⁻¹	4	11.5	28	100	0.9	500	188	0.7	-176
	8	14.8	89	87	0.9	8800	55	0.7	-148
NaOH 0.1 mol L ⁻¹ + GCS	4	19.7	260	32	0.9	8500	35	0.6	-168
	8	21.5	272	33	0.9	8900	55	0.7	-190

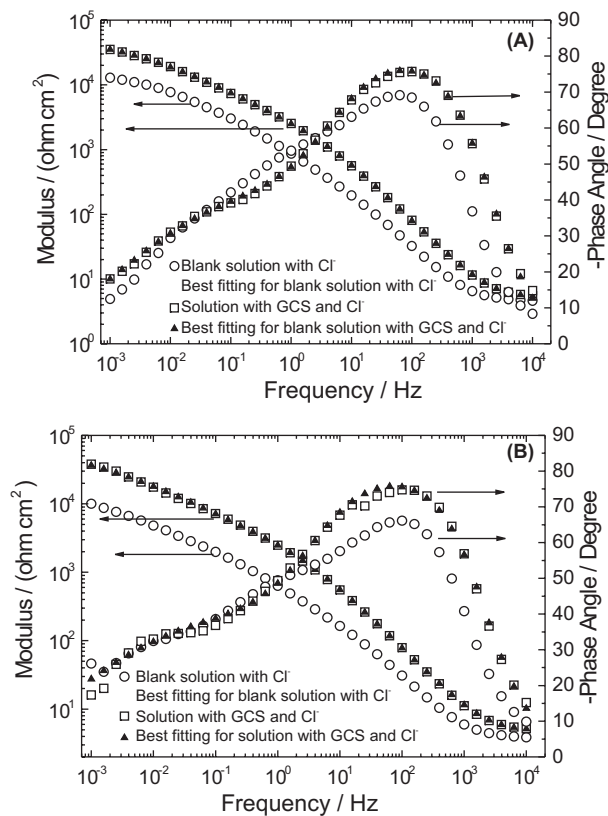


Figure 8. Bode diagrams obtained for carbon steel electrode at (A) 4 and (B) 8 days of immersion time in NaOH 0.1 mol L⁻¹ + 0.5 mol L⁻¹ NaCl solution with and without GCS.

in the reference solution can only be attributed to local loss of passivity with alternate cathodic reaction (H^+/H_2 instead of O_2/OH^-). In fact, pitting is visually observable after 10 days immersion in absence of GCS.

Conclusions

Small additions of Granite Cutting Slurries to alkaline solutions modify the natural passive layer formed on carbon steel. The peak current of the magnetite formation peak decreases in presence of GCS, indicating a corrosion rate reduction; moreover, the high frequency capacitance

decreases, which has been attributed to modifications in the outermost level of the passive layer.

GCS are able to inhibit pitting of carbon steel in presence of chlorides. The steel remains passive after at least 10 voltammetric cycles while without GCS pitting occurs at the first cycle.

Acknowledgment

The authors wish to acknowledge the Spanish "Ministerio de Educación y Ciencia" for financial support under contract no. MAT2004-06435-C02-01.

References

1. Neville, A.M.; *Properties of Concrete*, Longman: Harlow, GB, 1995.
2. Sousa, J.; *Cem. Concr. Compos.* **2003**, *25*, 51.
3. Gonçalves, J.P.; Moura, W.A.; Coitinho Dal Molin, D.C.; *Ambiente Construído* **2002**, *2*, 53.
4. Andrade, C.; Merino, P.; Nóvoa, X. R.; Pérez, M. C.; Soler, L.; *Mater. Sci. Forum* **1995**, *192-194*, 891.
5. Moura, W.A.; Gonçalves, J.P.; Da Silva Leite, R.; *Sittientibus* **2002**, *26*, 49.
6. Díaz, B.; Joiret, S.; Keddad, M.; Nóvoa, X. R.; Pérez, M.C.; Takenouti, H.; *Electrochim. Acta* **2004**, *49*, 3039.
7. Joiret, S.; Keddad, M.; Nóvoa, X.R.; Pérez, M.C.; Rangel, C.; Takenouti, H.; *Cem. Concr. Compos.* **2002**, *24*, 7.
8. Andrade, C.; Keddad, M.; Nóvoa, X.R.; Pérez, M.C.; Rangel, C.M.; Takenouti, H.; *Electrochim. Acta* **2001**, *46*, 3905.
9. Abreu, C.M.; Cristóbal, M.J.; Montemor, M.F.; Nóvoa, X.R.; Pena, G.; Pérez, M.C.; *Electrochim. Acta* **2002**, *47*, 2271.
10. Collazo, A.; Cristóbal, M.J.; Nóvoa, X.R.; Pena, G.; Pérez, M.C.; *J. ASTM International (JAI)* **2006**, *3*, 2.
11. Alonso, C.; Castellote, M.; Andrade, C.; *Electrochim. Acta* **2002**, *47*, 3469.

Received: January 26, 2007

Web Release Date: September 12, 2007