Cerium modified minerals for eco-friendly anticorrosive paints

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Summary

This paper deals with the replacement of zinc phosphate by a natural zeolite, modified with Ce(III) ions. The inhibitive properties of rare earth metals are very well known and the zeolite would act as a "carrier" for these ions. Alkyd paints were formulated replacing totally and partially zinc phosphate by the Ce-exchanged zeolite. Paints anticorrosive performance was evaluated by electrochemical impedance (EIS) and electrochemical noise measurements (ENM). Results showed that zinc phosphate could be partially replaced by the modified zeolite maintaining acceptable anticorrosive properties.

1. Introduction

Zinc phosphate and related substances became the leading substitutes for toxic inhibitors commonly employed in paints. Three generations of phosphates were introduced in the market, being zinc phosphate the precursor [1-3]. However, zinc phosphate is also being questioned by its negative impact on the environment and new replacements were proposed.

More recently, the challenge in the field of paint technology is to formulate smart coatings to provide an optimum selective response to some external stimulus; for instance corrosion. Ideally, a smart corrosion inhibitive coating will generate or release an inhibitor only when demanded by the initiation of corrosion [4].

The objective of this research was to develop a modified zeolite which is intended to replace phosphate pigments in anticorrosive paints. The modified zeolite was obtained by ionic exchange with Ce(III) ions. The anticorrosive properties of Ce(III) were studied by electrochemical techniques and formulating anticorrosive coatings with the Ce-exchanged zeolite. Coatings performance was evaluated by the salt spray test, EIS and ENM. It was demonstrated that the employment of this modified zeolite allowed to reduce the zinc phosphate content to one third with respect to the value recommended in the literature [1-3].

2. Experimental

2.1 Pigment preparation and characterization

A zeolitic rock from San Andrés, Cuba, was crushed to obtain a fine grain powder with particle size $\leq 10\mu m$. Iron was eliminated from the zeolite by boiling in HNO_3 0,2 M; then the zeolite was put into the Na-form by exchanging with 2M CH_3COONa. Finally, the zeolite was exchanged with Ce(III) ions from 1M $Ce(NO_3)_3$ in $1x10^{-3}$ M HNO_3. The sorbed Ce(III) was extracted with 100 ml 1M CH_3COONH_4

solution from 1g of the treated zeolite and determined by a gravimetric technique with 8-hydroxyquinoline (C_9H_7NO) in ethyl alcohol.

The anticorrosive properties of Ce(III) salts were assessed through the measurement of the corrosion potential (Ecorr) of SAE 1010 steel (surface abraded with SiC paper Nº 600) in $Ce(NO_3)_3$ solutions, of different concentrations, in NaCl 0,025 M. The concentration of the solutions was chosen on the basis of the exchange capacity of the modified zeolite. The reference electrode for all measurements was the saturated calomel electrode (SCE). The characteristics of the protective layer formed on steel were studied by scanning electron microscopy (SEM). Steel corrosion rate (icorr) was also determined by the polarization resistance technique employing a conventional three electrode cell. The working electrode was a SAE 1010 steel rod (cross section: 0.28 cm^2) and the counterelectrode a Pt mesh. The supporting electrolyte was 0.1 M NaCl. The sweep amplitude was $\pm$ 20 mV o.c. and the scan rate 0.1661 mVs^{-1}. All electrochemical measurements were carried out in normally aerated stirred solutions (300 rpm).

2.2 Paints composition, manufacture and application

The resin used to form the paint films to carry out this research was a medium oil alkyd and the solvent white spirit. Paints composition could be seen in Table 1. The PVC/CPVC relationship was 0.8.

SAE 1010 steel panels (15.0 x 7.5 x 0.2 cm) were sandblasted to Sa 2 1/2 (SIS 05 59 00), degreased with toluene and then painted, by brush, up to a thickness of 80 $\pm$ 5 μm. Panels were kept indoors for 7 days before testing.

Table 1. Paint composition as percentage by volume

Components (% by volume)	Paint 1	Paint 2	Paint 3
Zinc phosphate	7.5	---	2.5
Ce-exchanged zeolite	---	7.7	5.0
Barite	7.6	7.2	7.2
Titanium dioxide	2.9	2.9	2.9
Talc	7.6	7.2	7.2
Alkyd resin	35.7	36.0	37.3
Solvent (White spirit)	38.8	39.1	38.1

2.3 Accelerated laboratory tests for paints

A set of three panels was put in the salt spray chamber to evaluate the rusting degree at different exposure times (ASTM D 610).

Impedance spectra of painted panels (frequency range 1.10^5 Hz $\leq$ f $\leq$ 1.10^{-3} Hz) were performed in the potentiostatic mode, at the Ecorr. Measurements were carried out as a function of the exposure time in 0.5 M NaCl, using the 1255 Solartron FRA and the 1286 Solartron EI. The amplitude of the applied AC voltage was 0.010 V peak to peak. Two acrylic tubes were attached to each coated panel (working electrode) with an epoxy adhesive; the geometric area exposed to the electrolyte, in each cell, was 15.9 cm^2. A large area Pt-Rh mesh of negligible impedance and the SCE were employed as auxiliary and reference electrodes, respectively. The experimental impedance spectra were interpreted on the basis of

equivalent electrical circuits [5], using a suitable fitting procedure developed by Boukamp [6]. This electrochemical experiments were carried out at 20±2ºC, using a Faraday cage. Simultaneously, corrosion potential values were recorded as a function of immersion time.

The experimental arrangement for electrochemical noise measurements was a computer-controlled, automated digital system for the simultaneous measurement of electrochemical voltage and current as described elsewhere [7]. The edges of the specimens were blanked off leaving 50 cm^2 of the painted panel exposed to a 0.5M NaCl solution. The sampling frequency was 5 Hz. Statistical analysis of data was performed in the time domain while the analysis in the frequency domain was done by the Fast Fourier Transform.

3. Results and discussion

3.1 Pigment preparation and characterization

The zeolitic rock was mainly composed by mordenite (50-80%) and heulandite (30-50%); clay and quartz were also encountered in low proportions. The Exchange capacity of the zeolite varied significantly; it was 22,00 mg/g$_{mineral}$ when the zeolite is in its Na-form and diminished till 5.85 mg/g$_{mineral}$ when Na was replaced by Ce(III).

The Ecorr of SAE 1010 steel was displaced to more negative potential as time elapsed (Figure 1). This displacement was more noticeable for the highest concentrations of cerium nitrate. Pitting was observed for the highest tested concentrations. Pitting was confirmed by a cyclic polarization test (Figure 2). The critical pitting potential was ~0.300 V and the protection potential was found to be ~0.570 V. The protective film was mainly composed by a layer of iron oxyhidroxides (Figure 3) with low proportions of Ce (~1.3%); however Ce tended to accumulate in certain regions, in great amounts; higher than 50% (Figure 4).

The steel corrosion current density, after 2 hours of exposure was 2.35 µAcm^{-2} when the concentration of cerium nitrate was 2.30 x 10^{-4} M and it did not decrease for higher concentrations. The corrosion current density did not change significantly after 24 hours of exposure. The icorr in the supporting electrolyte was 84.2 µAcm^{-2}.

3.2 Accelerated laboratory tests for paints

Results obtained in the salt spray test showed that paint 1 and paint 3 had similar anti-corrosion performance (Table 2); but that of paint 2 was poor. The partial replacement of zinc phosphate by the Ce-exchanged zeolite resulted possible without loosing the paint anti-corrosion performance.

EIS measurements showed that paint 1 and paint 3 actually protected steel against corrosion. They possessed an important barrier effect as it was revealed by the value of the ionic resistance; as an average, >10^6 Ωcm^2 (Figure 5). The corrosion reaction was also inhibited as it could be appreciated by the charge transfer resistance (Figure 6). These results indicated that two thirds of the zinc phosphate pigment could be replaced by the Ce modified zeolite. Full replacement of zinc phosphate by the modified zeolite led to poor results (paint 2). The noise resistance resulted similar to the charge transfer resistance as expected. The mean value of the noise impedance approached the noise resistance.

Tabla 2. Corrosion degree (ASTM D 610) of painted panels in the salt spray cabinet (ASTM B 117)

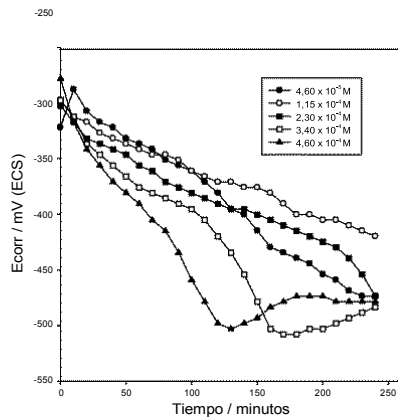| Paints	Exposure time (hours)			
	360	504	670	720
1	10	10	8G	8G
2	8G	8G	7G	--
3	10	9G	8G	9G

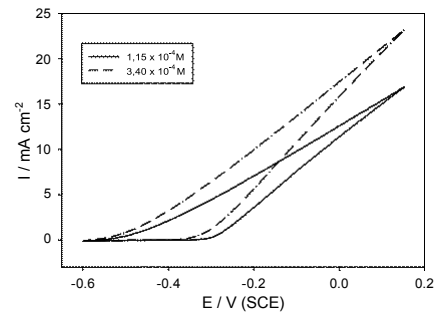Figure 1. Corrosion potential of the SAE 1010 steel in $Ce(NO_3)_3$ solutions as a function of time

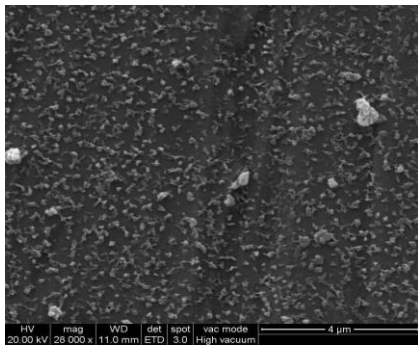Figure 2. Cyclic polarization test of the SAE 1010 steel in $Ce(NO_3)_3$ solutions. Scan rate 0.5 Vs^{-1}.

Figura 3. Morphology of the protective layer on SAE 1010 steel in $Ce(NO_3)_3$ $4,60 \times 10^{-5}$ M
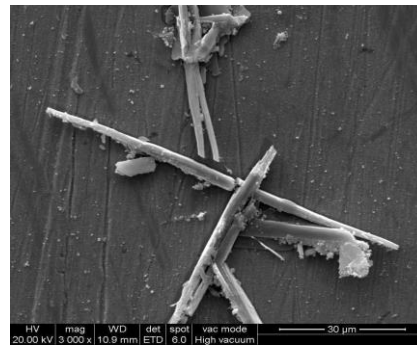

Figura 4. Ce-enriched formations on the protective layer on SAE 1010 steel in $Ce(NO_3)_3$ $4,60 \times 10^{-5}$ M

4. CONCLUSIONS

Zinc phosphate could be partially replaced by the Ce-exchanged zeolite up to two thirds without impairing paints anti-corrosion performance.
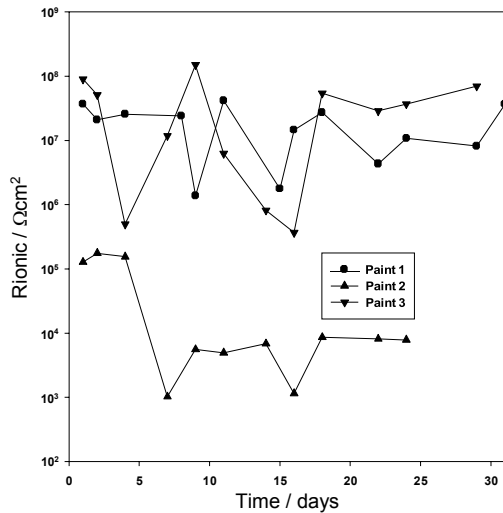
Figure 5. Paints ionic resistance
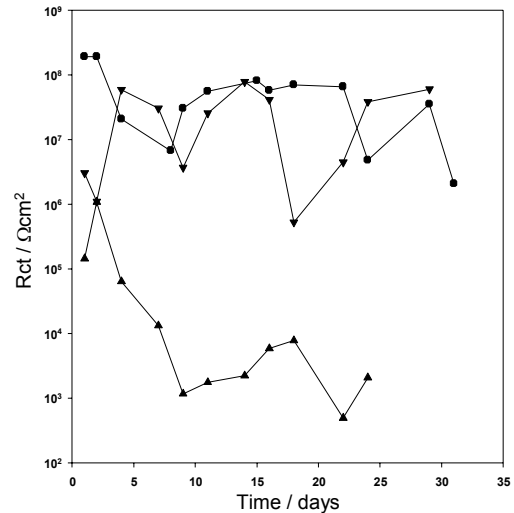in 0.5 M NaCl, as a function of time

Figure 6. Paints charge transfer resistance
in 0.5 M NaCl, as a function of time

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