Organic-inorganic hybrid (OIH) sol-gel coatings based on ureasilicates (U(X)) have promising properties for use as eco-friendly coatings on hot dip galvanized steel (HDGS) and may be considered potential substitutes for pre-treatment systems containing Cr(VI). These OIH coatings reduce corrosion activity during the initial stages of contact of the HDGS samples with highly alkaline environments (cementitious media) and allow the mitigation of harmful effects of an initial excessive reaction between cement pastes and the zinc layer. However, the behavior of HDGS coated with U(X) in the presence of chloride ions has never been reported. In this paper, the performance of HDGS coated with five different U(X) coatings was assessed by electrochemical measurements in chloride-contaminated simulated concrete pore solution (SCPS). U(X) sol-gel coatings were produced and deposited on HDGS by a dip coating method. The coatings performance was evaluated by electrochemical impedance spectroscopy, potentiodynamic polarization curves measurements, macrorole current density and polarization resistance in contact with chloride-contaminated SCPS. The SEM/EDS analyses of the coatings before and after the tests were also performed. The results showed that the HDGS samples coated with U(X) sol-gel coatings exhibited enhanced corrosion resistance to chloride ions when compared to uncoated galvanized steel.

The SEM/EDS analyses of the coatings before and after the tests were also performed. The results showed that the HDGS samples coated with U(X) sol-gel coatings exhibited enhanced corrosion resistance to chloride ions when compared to uncoated galvanized steel. The OIH films are reported to be environmentally friendly alternatives to replace chromate conversion layers. They are widely used as corrosion protective coatings on several metallic alloys, such as aluminum, 27–29 carbon steel, 21–23 stainless steel, 24–26 galvanized steel 27–29 and magnesium. 30,31 These OIH films are reported to be environmentally friendly alternatives to replace chromate conversion layers. Their synthesis is based on the sol–gel process which involves the hydrolysis of metal alkoxides to produce hydroxyl groups in the presence of stoichiometric water (generally catalyzed by an acid or base) followed by polycondensation of the resulting hydroxy groups and residual alkoxyl groups, forming thin, dense and chemically inert films on the metallic substrates with controlled physical shape and dimensions. Precursors containing non-hydrolysable groups are used to incorporate the organic part in the coating. This organic component provides flexibility and reduces defects while the inorganic constituent provides superior adhesion to the metal surface and improves mechanical resistance. 32–36 The sol–gel method is a versatile and simple method to produce silicate based gel materials under room temperature. The gel is aged for a period of time to allow the gel network to strengthen and then it is dried under atmospheric conditions. Materials prepared in this way are called xerogels. 37 Small molecules resulting from the condensation process remain trapped within the formed network even after the post-gelation drying/curing process is completed. 38 The OIH gels exhibit a biphasic structure that combines a rigid and hydrophilic silicate backbone linked to amorphous, malleable and hydrophobic organic (polymeric) spacer. The coexistence of the two distinct phases enhances the dispersion of a large variety of hosted species and allows control of the physical properties of the gel (transparency, porosity, wettability, hydrophobicity, etc.).

The term ureasilicate (U(X)) refers to OIH sol-gel coatings obtained from a reaction between a functionalized siloxane (3-isocyanate propyltriethoxysilane) and a di-amino functionalized polyether (Jeffamine) with different molecular weights (ranging from 230 to 2000 g mol\(^{-1}\)). 27 Since urea bonds are formed between the two precursor molecules, the term U(X) has been used to identify this type of OIH network where “U” refers to the type of bond established and “X” to the molecular weight of Jeffamine used. U(X) coatings have been extensively studied in contact with cementitious media, showing that these coatings provide barrier properties that withstand the high pH of the electrolyte, protecting the HDGS when it first comes into contact with cementitious media. The lowest corrosion rates obtained, after 127 days of contact with a mortar, are given by U(230) and U(400) and are respectively 30 and 31 times lower than the control samples. 29

Several methods to improve the corrosion resistance of RCS have been proposed. 1–5 In the last few years, the use of hot-dip galvanized steel (HDGS) has been recognized as an effective measure to increase the service life of RCS. 6–11 The galvanized coating (zinc layer) acts as a physical barrier, hindering the contact of aggressive agents with the steel substrate and the zinc acts as a sacrificial anode protecting the steel against corrosion. In addition, the formed chlorides in concrete can seriously shorten the service life of RCS. 3,4

The expanded volume of corrosion products deposited in the interface between the concrete and the steel imposes expansive stresses, leading to delamination, cracking or spalling and eventually to the collapse of the RCS. 1 Several methods to improve the corrosion resistance of RCS have been proposed. 1,5–7 In the last few years, the use of hot-dip galvanized steel (HDGS) has been recognized as an effective measure to increase the service life of RCS. 6–11 The galvanized coating (zinc layer) acts as a physical barrier, hindering the contact of aggressive agents with the steel substrate and the zinc acts as a sacrificial anode protecting the steel against corrosion. In addition, the formed chlorides in concrete can seriously shorten the service life of RCS. 3,4

The pH of this medium is typically above 12.5. This initial corrosion process, which may vary from hours to days, may lead to zinc consumption until either the formation of a passivation layer or until all the zinc layer is consumed. 8,13–16 To minimize this corrosion process, measures such as increasing the chromate content by adding water-soluble chromates into the concrete mixture or the use of chromate conversion layers have been widely implemented. Nevertheless, due to the adverse health effects of the hexavalent chromium ions (Cr(VI)), hard restrictions on the use of chromates have been imposed. Neverthe-

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Later and considering these promising results, 77,39 studies on the influence of the residence time, curing process between each dipping step and thickness of U(230) and U(400)40 were performed in highly alkaline environments. The glow discharge optical emission spectroscopy results show that the coating thickness of U(400) globally increases both with the number of dipping steps and with residence time. However, the SEM/EDS results point to the conclusion that full coverage is seldom achieved even when three layers are deposited on HDGS with residence time with the curing process between each deposition.40,41

The present work is focused on study the corrosion performance of five U(X) sol-gel coatings (U(230), U(400), U(600), U(900) and U(2000)) in chloride-contaminated alkaline solutions which simulate the aqueous phase present in concrete pores. This paper describes the modifications that the presence of chloride ions has on the corrosion behavior of coated HDGS samples in highly alkaline solutions. Bare HDGS samples were used for comparison purposes. The OIH coatings were prepared according to the literature.25,39,40 The coatings were deposited on HDGS surfaces by dip-coating using one or three consecutive dip steps. The novelty of the proposed work relies on the fact that, to the best of the authors’ knowledge, no study is available in the literature where U(X) OIH sol-gel coatings deposited on HDGS have been tested in chloride-contaminated SCPS. The morphology of the OIH films was assessed by scanning electron microscopy (SEM). The corrosion properties of the OIH coatings were evaluated by macrocell current density (i_{mcd}), polarization resistance (R_p), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization methods in chloride-contaminated simulated concrete pore solutions (SCPS). i_{lpg} and R_p measurements were carried out since they offer several advantages for corrosion monitoring in new and repaired RCS.42–45 i_{lpg} measurements allowed for real-time and continuous monitoring, providing semi-quantitative information about the corrosion rate and detected the instant where the construction steel depassivates.44,46 The R_p measurements were performed periodically since these allowed for measurement of instantaneous corrosion current density in order to assess the condition of the embedded steel reinforcement related to its corrosion.47 EIS is a reliable, non-destructive and fast method providing accurate results about corrosion protection behavior of the OIH sol-gel coatings. EIS data were interpreted on the basis of electrical equivalent circuits consisting of a combination of resistances and capacitances associated in series or in parallel providing the same electrical response as the studied electrochemical interface.25,48–51 The potentiodynamic polarization curves were used to compare the corrosion resistance of coated HDGS samples.52

### Experimental

**Materials.—** Five di-amino functionalized polyethers (hereafter referred to as Jaffamine) with different molecular weights (MWs) were used. Jaffamine with five different molecular weights provided by Fluka (Jaffamine D-230, Jaffamine D-400, Jaffamine 600, Jaffamine ED-900 and Jaffamine ED-2000) and 3-isocyanate propyltriethoxysilane (ICPTE, 95%, Aldrich) were stored, protected from light and used as supplied. Absolute ethanol (EtOH, absolute 98%, Riedel-de-Haën) and citric acid monohydrate (Merck) were also used as delivered. Ultra-pure water (0.055–0.060 μS/cm) obtained from a Purelab Ultra System (Elga) was used.

**Sol-gel synthesis procedure of OIH ureasilicate coatings.—** The experimental steps involved in the synthesis of ureasilicate matrices to produce the coatings on HDGS samples were performed according to the literature.25,39,40 Five different materials were prepared as coatings on HDGS, i.e. U(230), U(400), U(600), U(900) and U(2000). The matrices were obtained using 1:2 stoichiometric molar ratio of each Jaffamine molecular weight and 3-isocyanate propyltriethoxysilane. These two reagents were mixed and stirred at 700 rpm for 20 min in a glass container. In the second step, 0.22 M of citric acid ethanolic solution was added, setting the citric acid/3-isocyanate propyltriethoxysilane molar ratio equal to 0.094. The mixture was stirred and after 15 min distilled water was added until the total volume of reaction media equaled 8 mL. The final mixture was left to react for a further 15 min.

**Preparation of the coatings.—** The HDGS samples were obtained from commercially available plates and cut with dimensions of 5.0 × 1.0 × 0.1 (in cm). The HDGS samples with an average Zn thickness of 16 μm on both sides were degreased with acetone. Coated HDGS samples were prepared by dipping the metallic plates of HDGS in the synthesized sol mixture using a dip coater (Nima, model DC Small). The OIH coatings were deposited by one and three consecutive dip steps at a withdrawal speed of 10 mm min−1 without residence time. Previous studies have shown that the thickness of the U(X) deposited on HDGS by one and three dip steps ranged between 2.5–12.7 μm and 3.6–24 μm, respectively.39 depending on the MW of Jaffamine used. Therefore, the choice in producing samples coated by one and three consecutive dip steps was mainly to assess the corrosion performance of thinner and thicker coatings in chloride contaminated simulated concrete pore solutions. Coated HDGS samples were subsequently placed in an incubator-compressor (IPC-400, Memmert) and kept at 40 °C for 15 days.

**Preparation of chloride-contaminated simulated concrete pore solution.—** The corrosion behavior of HDGS coated samples with the different OIH coatings was studied in solutions simulating the concrete interstitial electrolyte (simulated concrete pore solutions - SCPS) and contaminated with 1 wt% of chlorides (SCPS + 1 wt% Cl−). SCPS were prepared according to the literature10,53 by the addition of analytical reagent grades 0.2 M KOH to a Ca(OH)2 saturated solution previously prepared with distilled water. A final solution with a pH = 13.2 was obtained and 1 wt% of chlorides was added as sodium chloride. This medium was prepared in order to induce the corrosion of the substrate. According to the literature,54 the critical chloride concentration reported to induce corrosion of reinforcing steel in SCPS, with pH values of 12.5 and 13.9, was of 0.02 and 1 wt%, respectively. Considering that the pH of the SCPS prepared in this work was above 12.5, a value of 1 wt% was used to ensure that the chloride content was above the critical chloride concentration.

**Electrochemical studies.—** In this work different electrochemical techniques were used, namely: electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curve, polarization resistance (R_p) and macrocell current density (i_{mcd}). Two distinct approaches were used to assess the electrochemical behavior of the OIH sol-gel coatings applied on HDGS. In the first approach, short-term studies on HDGS coated with the different OIHs were conducted in chloride-contaminated simulated concrete pore solutions (SCPS + 1 wt% Cl−) using EIS and potentiodynamic polarization measurement. In the second approach, the barrier stability of the OIH coatings was monitored through i_{lpg} and R_p measurements during 16 days in SCPS and on the 8th day 1 wt% of Cl− was added as sodium chloride. For comparison purposes, uncoated samples (control) were also studied.

**Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves measurements.—** EIS and potentiodynamic polarization curves measurements were carried out on HDGS coated samples by one and three consecutive dip steps without residence time in SCPS + 1 wt% Cl−. All the measurements were made in triplicate to check data reproducibility. These measurements were conducted in order to study the influence of the number of dip steps used to coat the HDGS samples on the barrier protection in the presence of aggressive species such as chloride ions. The EIS measurements on HDGS coated samples were performed in the first instants of immersion in SCPS + 1 wt% Cl−. The potentiodynamic curves measurements were performed after 2h of exposure to SCPS + 1 wt% Cl−. The EIS and potentiodynamic polarization curve measurements were performed at room temperature in a Faraday cage. A glass cell
with a saturated calomel electrode (SCE) and a platinum foil (exposed area ≈ 8 cm²) were used respectively as reference electrode (RE) and counter electrode (CE). The exposed surface area of the working electrode (WE) (HDGS coated sample) in the electrolyte was ≈2 cm². EIS studies were accomplished by applying a 20 mV (peak-to-peak, sinusoidal) electrical potential within a frequency range from 1 × 10² Hz to 0.01 Hz (10 points per decade) at open circuit potential (OCP). Measurements were performed using an Impedance/Gain-Phase Analyzer (Model 1260A, Solartron-Schlumberger) and a potentiostat/galvanostat (Model 1287A, Solartron-Schlumberger) controlled by a PC using Zplot software (Solartron-Schlumberger, version 2.9c). The frequency response data of the studied electrochemical cells were displayed in a Nyquist plot, using ZView software (Solartron-Schlumberger, version 2.9c) that was also used for data fitting purposes. For comparison purposes, cells prepared with uncoated HDGS WE electrodes were used as the control.

Polarization resistance ($R_p$).— The $R_p$ values were estimated from the potentiostatic method using a potentiostat/galvanostat (Voltalab PGZ 301) using a three-electrode electrochemical cell system.45,46,55 The $R_p$ values were calculated from the transients due to the application of a 10 mV anodic potential step for 100 s. A stainless steel (SS, type 316L) plate was used as a CE and HDGS coated with the different OIHs was used as WE. Both electrodes had an active average area of 2 cm². The edges of both the CE and WE plates, as well the non-active areas and connecting zones were protected with a dual-component epoxy resin (Araldite). Titanium-activated wire (Ti/TiO₂) with a length of 1 cm was chosen to be used as RE due to its low cost and suitability to be embedded in real RCS. The electrodes were connected to an isolated copper cable and the cutting zone of the tip of the RE was covered with epoxy resin. For comparison purposes, cells with non-coated HDGS WE electrodes were prepared and used as the reference (hereafter referred generically as control) and to check data reproducibility triplicate cells were assembled. The $R_p$ measurements were performed once a day during 16 days on samples coated by one dip step of U(X). After the first eight days of exposure to SCPS, 1 wt% of chloride ions were added as sodium chloride. The measurements were performed at the same periodicity for more eight days.

Scanning electron microscopy (SEM/EDS).— The morphology of the OIH sol-gel coating surface applied on HDGS specimens was analyzed with a scanning electron microscope (SEM, JEOL JSM-6400) coupled with an EDS detector (Inca-xSight Oxford Instruments). The surface of the samples was covered with an ultrathin coating of gold deposited by sputter coating. SEM investigations of the surfaces were carried out by using the back-scattered electron (BSE) detector in order to emphasize the contrast for the different metallic phases. The SEM/EDS studies of the HDGS coated samples were performed on the substrate before and after 16 days in contact with chloride-contaminated SCPS.

Results and Discussion

Electrochemical impedance spectroscopy (EIS).— EIS measurements were performed in order to assess the electrochemical behavior of HDGS coated by one (1 layer) and three (3 layers) consecutive dip steps of OIH sol-gel coatings in chloride-contaminated SCPS (highly alkaline media, pH = 13.2). Figure 2 shows representative Bode plots obtained for control, U(230) and U(400) in the instant of exposure (≈ 10 minutes once the OCP has been established in SCPS + 1 wt% Cl⁻).

The Nyquist plots obtained for control samples (Figure 3a) in the instant of exposure consist of one depressed capacitive loop (one time-constant). The high frequency (HF) capacitive loop is associated to the charge transfer process of the metal corrosion and the double layer behavior.38,49 For the coated HDGS samples, the impedance spectra consist of two partially overlapped capacitive semicircles (two time-constants). Samples coated by one or three layers, with the lowest MWs of Jeffamine (U(230) and U(400) – Figures 2 and 3) reveal the presence of two time-constants in first instants of immersion. The loop at HF, between 10⁴ and 10⁵ Hz, is generally assigned to the OIH sol–gel film capacitance56,57 and the one at low frequency (LF) can be assigned to the corrosive process by charge transference.21,22

The Nyquist plots obtained for samples coated with OIHs synthesized using higher MWs of Jeffamine, namely U(600), U(900)
and U(2000) exhibited also two time-constants at high and medium frequency indicating at least two electrochemical processes with similar relaxation time constants, while one inductive loop was observed at the LF end (Figure 4). This type of impedance spectra have been reported for galvanized surfaces due to the surface relaxation processes of adsorbed species (such as corrosion products) on the HDGS surface. Considering the high pH of the chloride-contaminated SCPS and the mechanism proposed by Liebau, the results suggest that the adsorbed species (such as Zn$^{2+}$, Zn(OH)$_2$, Ca(Zn(OH)$_3$)$_2$·2H$_2$O) may possibly be the reason for the LF inductive loop found in all HDGS samples coated with U(600), U(900) and U(2000).

According to the literature, the inductive loop found in the Nyquist plots (Figure 4) can be explained by considering the anodic reaction separately from the cathodic. A possible cause could be the adsorption or desorption of activating or blocking species with increasing overpotential of each process. Two situations can be considered: (i) If the anodic adsorption (therefore cathodic desorption) of a blocking species occurs the inductive loop appears due to the dominant effect in the cathodic process; or (ii) if the anodic desorption (therefore cathodic adsorption) of a blocking species for the reactions (OIH layer) occurs then the observed inductive loop results as the dominant effect in the anodic component. This behavior at LF range suggests that these OIH coatings are not entirely protective and may change when in contact with the electrolyte, thus exhibiting defects. Barely coated regions also allow the electrolyte to penetrate across coating cracks and reach the substrate. Additionally, in a chloride environment, corrosion products such as zinc hydroxychlorides are formed on the surface of zinc. The LF capacitive loop can be also attributed to the diffusion of the electrolyte in the pores of the coatings and the dissolution of the zinc layer. For samples coated with U(230) and U(400), no inductive loops in the LF region were found. This indicates that these OIH coatings confer good corrosion protection and that the corrosion processes in the first instants of contact with chloride-contaminated SCPS are effectively delayed comparatively to U(600), U(900) and U(2000) coatings. This behavior can be related either to the breakdown of the former protective surface film or relaxation of adsorbed species in the mechanism of zinc dissolution.

![Figure 2](image1.png)  
**Figure 2.** Representative Magnitude and Phase angle Bode plots obtained for control, U(230) and U(400) in the instant of exposure ($\approx$ 10 minutes once the OCP has been established in SCPS + 1 wt% Cl$^-$.)

![Figure 3](image2.png)  
**Figure 3.** Representative Nyquist plots and the respective fitting results obtained for a) control (uncoated HDGS); b) U(230) 1 layer; c) U(230) 3 layers; d) U(400) 1 layer in the instant of exposure to SCPS + 1 wt% Cl$^-$, ($\approx$ 10 minutes once the OCP has been established). EECs used for the numerical fitting of the: e) control sample; f) samples coated with OIHs.

![Figure 4](image3.png)  
**Figure 4.** Nyquist plots obtained for U(600), U(900) and U(2000) in the instant of exposure to SCPS + 1 wt% Cl$^-$, ($\approx$ 10 minutes once the OCP has been established).
Detailed information on the behavior of the different OIH sol-gel coated samples can be extracted from the fitting of the spectra using electrical equivalent circuits (EEC). The selected EECs have been widely used for analysis of impedance spectra of metals coated with sol-gel films. The interpretation of impedance spectra was based on the EECs that include contributions from the sol-gel coating and the corrosion process itself. Capacities were replaced by CPEs to improve the quality of the fitting. The physical origin of the CPE behavior is not completely understood, however, it is generally accepted that it is assigned to inhomogeneous physical properties. CPE behavior is not completely understood, however, it is generally accepted that it is assigned to inhomogeneous physical properties.

Table I. EIS data fitting parameters and errors in percentage obtained in SCPS + 1 wt% Cl− for control and samples coated with U(230) and U(400) using the EECs shown in Figures 4e) and 40.

| Samples    | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) |
|------------|------------|------------------------|------------------|------------|------------------------|------------------|------------|------------------------|------------------|------------|------------------------|------------------|------------|------------------------|------------------|
| Control    | 4.2 (± 5.2%) | 3.9 × 10⁻⁶ (± 3.0%)    | 0.70             | 2.0 × 10³ (± 9.3%) | 1.7 × 10⁻⁴ (± 20%) | 0.69             | 1.5 × 10² (± 16%) | 6.3 × 10⁻² | 0.69          | 1.5 × 10² (± 16%) | 6.3 × 10⁻² | 0.69          | 1.5 × 10² (± 16%) | 6.3 × 10⁻² |
| U(230) 1 Layer | 12 (± 8.3%) | 3.9 × 10⁻⁶ (± 3.0%)    | 0.70             | 2.0 × 10³ (± 9.3%) | 1.7 × 10⁻⁴ (± 20%) | 0.69             | 1.5 × 10² (± 16%) | 6.3 × 10⁻² | 0.69          | 1.5 × 10² (± 16%) | 6.3 × 10⁻² | 0.69          | 1.5 × 10² (± 16%) | 6.3 × 10⁻² |
| 3 Layers   | 23 (± 3.5%) | 4.3 × 10⁻⁶ (± 2.0%)    | 0.67             | 2.0 × 10³ (± 8.1%) | 1.8 × 10⁻⁴ (± 14%) | 0.81             | 1.0 × 10² (± 1.8%) | 4.0 × 10⁻³ | 0.81          | 1.0 × 10² (± 1.8%) | 4.0 × 10⁻³ | 0.81          | 1.0 × 10² (± 1.8%) | 4.0 × 10⁻³ |
| U(400) 1 Layer | 10 (± 6.1%) | 9.4 × 10⁻⁶ (± 5.0%)    | 0.67             | 1.1 × 10³ (± 7.2%) | 2.6 × 10⁻⁵ (± 16%) | 0.86             | 1.2 × 10² (± 1.0%) | 3.0 × 10⁻⁴ | 0.86          | 1.2 × 10² (± 1.0%) | 3.0 × 10⁻⁴ | 0.86          | 1.2 × 10² (± 1.0%) | 3.0 × 10⁻⁴ |
| 3 Layers   | 18 (± 6.4%) | 4.9 × 10⁻⁶ (± 5.3%)    | 0.76             | 4.4 × 10³ (± 7.1%) | 3.4 × 10⁻⁶ (± 17%) | 0.96             | 3.4 × 10⁵ (± 1.1%) | 7.0 × 10⁻⁶ | 0.96          | 3.4 × 10⁵ (± 1.1%) | 7.0 × 10⁻⁶ | 0.96          | 3.4 × 10⁵ (± 1.1%) | 7.0 × 10⁻⁶ |

Table II. EIS data fitting parameters and errors in percentage obtained in SCPS + 1 wt% Cl− for samples coated with U(600), U(900) and U(2000) using the EECs shown in Figure 5d.

| Samples     | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) | Rs (Ω cm²) | CPEcoating (sΩ⁻¹ cm⁻²) | Rcoating (Ω cm²) |
|-------------|------------|------------------------|------------------|------------|------------------------|------------------|------------|------------------------|------------------|------------|------------------------|------------------|
| U(600) 1 Layer | 7.9 (± 1.3%) | 2.0 × 10⁻⁵ (± 10%)     | 0.84             | 2.4 × 10² (± 9.5%) | 3.6 × 10⁻² (± 21%) | 0.95             | 56 (± 17%) | 3.8 × 10⁻² |
| 3 Layers    | 8.1 (± 2.6%) | 8.7 × 10⁻⁶ (± 9.6%)    | 0.88             | 3.4 × 10² (± 8.2%) | 1.5 × 10⁻⁵ (± 16%) | 0.97             | 26 (± 14%) | 4.6 × 10⁻⁴ |
| U(900) 1 Layer | 6.5 (± 1.6%) | 3.2 × 10⁻⁵ (± 5.1%)    | 0.82             | 2.4 × 10² (± 4.3%) | 1.6 × 10⁻⁴ (± 27%) | 0.91             | 25 (± 23%) | 1.9 × 10⁻⁲ |
| 3 Layers    | 5.5 (± 1.9%) | 2.1 × 10⁻⁵ (± 5.9%)    | 0.84             | 2.9 × 10² (± 7.2%) | 6.1 × 10⁻⁵ (± 14%) | 0.88             | 78 (± 29%) | 2.4 × 10⁻² |
| U(2000) 1 Layer | 8.2 (± 6.0%) | 3.3 × 10⁻⁵ (± 13%)     | 0.82             | 1.6 × 10² (± 9.5%) | 6.4 × 10⁻⁴ (± 9.4%) | 0.92             | 58 (± 24%) | 2.8 × 10⁻² |
| 3 Layers    | 7.5 (± 1.9%) | 4.3 × 10⁻⁵ (± 6.5%)    | 0.79             | 2.4 × 10² (± 5.7%) | 1.7 × 10⁻⁴ (± 28%) | 0.99             | 37 (± 24%) | 7.0 × 10⁻³ |
coating is higher for U(600), U(900) and U(2000) materials when compared to U(230) and U(400). In highly alkaline environments, the results suggest that the organic chains are partially damaged by the electrolyte leading to rupture of the coating in certain areas. This rupture is significantly higher in samples coated with OIHs prepared with higher MWs of Jeffamine. Yet, the role of Jeffamine is crucial to minimize cracking of the deposited gels during the curing process due to network stress as the formation of silicate regions involves the release of ethanol molecules. Therefore, in highly alkaline environments, a settlement between the organic and inorganic components should be taken in account.

**Potentiodynamic polarization studies.—** The potentiodynamic polarization methods can provide a direct measure of the corrosion current, which can be related to corrosion rate and can be used to examine the passivation of a metal in an electrochemical system. Figure 7 shows the polarization curves for uncoated and coated HDGS with one (1 layer) and three (3 layers) dip steps of U(230), U(400), U(600), U(900) and U(2000) recorded after 2 h of immersion in chloride-contaminated SCPS (1 wt% of Cl\(^-\) was added to SCPS).

The potentiodynamic polarization curves obtained for HDGS coated samples with U(230) and U(400) are appreciably different from the control (Figure 7). First, the OCP of this OIH sol–gel coatings is significantly higher than that of the bare HDGS. Secondly, a passivation region with a rather low passivation current densities is observed, which indicates that U(230) and U(400) coatings provide a physical barrier by blocking the electrochemical process. HDGS coated by one or three consecutive dip steps of U(600), U(900) and U(2000) show OCP values very similar to the control, yet low passivation current densities were recorded. Moreover, the control exhibited a polarization curve with a passive region comparatively narrower than all the OIH-coated HDGS.

Quantitative information on corrosion currents and corrosion potentials can be extracted from the slope of the curves, using the Stern-Geary equation,\(^7\) as follows:

\[
\begin{align*}
\text{icorr} &= \frac{1}{2.303} R_p \left( \frac{\beta_c \times \beta_a}{\beta_a + \beta_c} \right) \quad [1] \\
\end{align*}
\]

Table III shows representative electrochemical parameters obtained namely the Tafel slopes (\(\beta_c\) and \(\beta_a\)) and the polarization resistance (\(R_p\)). The corrosion current density (\(i_{corr}\)) and corrosion potential (\(E_{corr}\)) were determined by analysis of Tafel curves and are shown in Figures 8 and 9, respectively. The protection efficiency (PE\%) was calculated by using the following equation:

\[
\text{PE (\%)} = \frac{i_{corr} - i_{corr}^*}{i_{corr}} \times 100 \quad [2]
\]

where \(i_{corr}\) and \(i_{corr}^*\) are the corrosion current densities obtained for uncoated and coated HDGS, respectively and is shown in Figure 8.

Generally, coated HDGS samples in the presence of 1 wt% of Cl\(^-\) show improved results when compared to the control (Table III and Figure 7).

![Figure 6](image_url) Variation of the a) \(R_{Coating}\) and \(CPE_{Coating}\) and b) \(R_{dl}\) and \(CPE_{dl}\) values obtained from impedance data for HDGS coated by one dip step (one layer) and three consecutive dip steps (three layers) according to the MW of Jeffamine in the instant of exposure to SCPS + 1 wt% Cl\(^-\).

![Figure 7](image_url) Representative potentiodynamic polarization curves of the HDGS coated by: a) one dip step (one layer); b) three consecutive dip steps (three layers) of U(230), U(400), U(600), U(900) and U(2000) after being exposed in SCPS + 1 wt% Cl\(^-\) during 2h. The curve for uncoated HDGS was included for comparison purposes.
Table III. Representative electrochemical parameters (Tafel slopes), polarization resistance values and respective errors in percentage obtained from potentiodynamic polarization curves of HDGS coated with the different OIH exposed to SCPS + 1 wt% Cl\(^{-}\) during 2h.

| Sample | \(\beta_a\) (10 mV vs SCE) | \(\beta_c\) (mV vs SCE) | \(R_p\) (\(\Omega\ cm^2\)) |
|--------|-----------------|-----------------|-----------------|
| Control | 9.3             | 49              | \(3.6 \times 10^{2}\) (\(\pm\) 2.4%) |
| U(230) 1 Layer | 1.5             | 41              | \(1.9 \times 10^{1}\) (\(\pm\) 6.1%) |
| U(230) 3 Layers | 2.5             | 62              | \(8.3 \times 10^{4}\) (\(\pm\) 1.6%) |
| U(400) 1 Layer | 3.6             | 46              | \(3.2 \times 10^{2}\) (\(\pm\) 7.3%) |
| U(400) 3 Layers | 2.3             | 28              | \(6.9 \times 10^{4}\) (\(\pm\) 2.3%) |
| U(600) 1 Layer | 13              | 51              | \(4.3 \times 10^{2}\) (\(\pm\) 2.7%) |
| U(600) 3 Layers | 14              | 45              | \(4.8 \times 10^{2}\) (\(\pm\) 7.0%) |
| U(900) 1 Layer | 12              | 31              | \(7.3 \times 10^{2}\) (\(\pm\) 2.7%) |
| U(900) 3 Layers | 9.9             | 19              | \(5.0 \times 10^{4}\) (\(\pm\) 6.2%) |
| U(2000) 1 Layer | 11              | 26              | \(5.5 \times 10^{2}\) (\(\pm\) 2.8%) |
| U(2000) 3 Layers | 10              | 51              | \(4.3 \times 10^{2}\) (\(\pm\) 3.4%) |

Coatings based on low MWs of Jeffamine (U(230) and U(400)) show enhanced corrosion protection compared to OIHs based on high MWs of Jeffamine. The \(i_{\text{corr}}\) values (Figure 8) obtained for control (uncoated HDGS) were about 1–3 orders of magnitude higher than coated samples. Figure 8 shows that the \(i_{\text{corr}}\) values obtained for coated samples ranged between 0.03–24.27 \(\mu\)A cm\(^{-2}\). The highest \(i_{\text{corr}}\) value (Figure 8) was given by samples coated with three consecutive dip steps of U(2000) and the lowest by samples coated by one dip step of U(230). Figure 8 also shows that the highest and lowest PEs were given by samples coated with U(230) and U(2000), respectively. Figure 9 clearly shows that the \(E_{\text{corr}}\) values obtained for coated samples coated with U(230) and U(400), either by one or three layers, was significantly higher than that of the bare HDGS. This might be due to the effective suppression of the cathodic reaction from water hydrolysis. It can also be observed that the \(E_{\text{corr}}\) reduces as the MW of Jeffamine increases which indicates that coatings synthesized with higher MWs of Jeffamine are not so effective in suppressing the cathodic reaction when compared to coatings produced with lower MWs of Jeffamine. Although the Cl\(^{-}\) is a strong anodic activator due to its small radius and volume the results obtained for samples coated with U(230) and U(400) indicate that the Cl\(^{-}\) cannot reach the surface of the substrate after 2h of immersion. These findings suggest that the diffusion of Cl\(^{-}\) ions across the coating layer is prevented and the Cl\(^{-}\) ions remain entrapped within the OIH network being unable to reach the surface of the metallic substrate. Furthermore, the potentiodynamic polarization curves are in agreement with ECS measurements.

**Macrocell current density** (\(i_{\text{gal}}\)).—Figure 10 shows the \(i_{\text{gal}}\) collected from the different prepared electrochemical cells involving the HDGS coated samples and the control that were immersed in SCPS during 16 days. After 8 days of immersion, 1 wt% of Cl\(^{-}\) was added.
Anodic dissolution of zinc:

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad [3]
\]

Cathodic reaction from water hydrolysis:

\[
2\text{H}^+ + 2e^- \rightarrow \text{H}_2(g) \uparrow \quad [4]
\]

The global process can be described as:

\[
\text{Zn} + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_2 + \text{H}_2(g) \uparrow \quad [5]
\]

After 5 days of immersion, samples coated with U(600) and U(2000) dropped to lower \(i_{\text{gal}}\) values compared to samples coated with U(230) and U(900) which showed steady behavior until the addition of chloride ions. Lower values for samples coated with U(230) were expected after 5 days of immersion. This behavior suggests that the oxide layer formed did not fully cover the HDGS leading to the passivation of the working electrode surface; however, no further conclusion can be drawn. The comparison of the \(i_{\text{gal}}\) values before and after Cl\(^{-}\) addition shows that for the coating U(2000) the \(i_{\text{gal}}\) values increased remarkably compared to the other coated samples. A similar behavior, however, less obvious, was found for samples coated with U(400) and U(600). Samples coated with U(230) and U(900) showed a slight decrease of the \(i_{\text{gal}}\) values after Cl\(^{-}\) addition. Excluding samples coated with U(400), which reached lower \(i_{\text{gal}}\) values on the 12th day increasing after that to higher values, the \(i_{\text{gal}}\) measurements (Figure 10) showed that after Cl\(^{-}\) addition a steady behavior along time was found for each OIH coating. Lower \(i_{\text{gal}}\) values represent improved corrosion behavior.

Coated HDGS samples showed lower values than the control during all the study period, therefore showed improved corrosion behavior. The results also indicated that the \(i_{\text{gal}}\) cells in SCPS were sensitive to the external laboratory temperature variation, to the presence of chloride ions and to the composition of the OIH material deposited which is also according to the literature.44,46

**Polarization resistance \((R_p)\).—** Figure 11 shows the \(R_p\) values obtained for the different electrochemical cells prepared with HDGS coated by one dip step (1 layer), that were immersed in SCPS during 16 days. Results for control samples are also presented. After 8 days of immersion, 1 wt% of Cl\(^{-}\) was added into the SCPS. The \(R_p\) measurements were performed once a day.

Figure 11 shows that the \(R_p\) data are generally in agreement with \(i_{\text{gal}}\) measurements. The results also indicate that the \(R_p\) cells in SCPS are sensitive to the presence of chloride ions and to the composition of the OIH material deposited which is also according to the literature.44,46 HDGS coated samples during all the period of study, in general, displayed higher values than the control. Therefore, showed improved corrosion behavior. During the first days of immersion, the \(R_p\) values decreased suggesting that zinc corrosion occurred, which is also in agreement with the \(i_{\text{gal}}\) results and literature.44 After chloride addition (on the 8th day) the \(R_p\) values of samples coated with U(600), U(900) and U(2000) dropped to lower values, however, remained always above the control.

Improved results were obtained by samples coated with U(230) and U(400) when compared to the other samples and the \(R_p\) values are also in agreement with the EIS, potentiodynamic measurements, and \(i_{\text{gal}}\) data.
Additionally, during the curing process the action of gravity led to the displacement of the gel from the top to the bottom. This is particularly significant for samples coated with U(230) and U(400). Figure 12a clearly demonstrates that samples coated by one dip step of U(400) have several regions, barely coated within the same sample, when compared to samples coated by one dip step of U(2000). The EDS analysis shows that the OIH coating correspond to high peaks of C, Si and O. Uncoated areas only show the presence of high peaks of Zn (Figure 12).

The preliminary observations of the HDGS surface (working electrode used for Igal measurements) after being in chloride-contaminated SCPS during 16 days (1 wt% of chloride ions were added on the 8th day) were performed using a stereo-zoom microscope. The images obtained for the control sample, and samples coated by one dip step of the different OIHs are shown in Figure 13. The control samples were HDGS samples where no OIH coating was deposited. The visual observation clearly shows a difference between coated and uncoated (control) samples. The control sample shows severe corrosion regions where the presence of iron oxide (rusty deposits) is clear. White deposits (zinc oxide) and calcium hydroxide zincate (CaHZn) crystals are also visible. However, due to the high pH of SCPS the size of CaHZn crystals are so large that they cannot completely cover the HDGS surface. As a consequence of this, small regions of the steel underneath.

Figure 13. Stereomicroscopic observation of uncoated and coated HDGS surfaces, magnified twenty times, after being immersed in SCPS for 16 days (1 wt% of chloride was added on the 8th day).

In summary, the electrochemical results obtained (Igal, Rp, EIS and potentiodynamic curves) are generally in agreement and point to the same outcome showing that improved anti-corrosion performance was given by samples coated with U(230) and U(400) (produced with lower MWs of Jeffamine). Inferior results were provided by samples coated with U(600), U(900) and U(2000) (produced with high MWs of Jeffamine). This behavior may be explained by the increase of the organic chains, which increase when the MW of Jeffamine increases. In highly alkaline environments, as mentioned previously the organic chains are partially damaged by the electrolyte leading to rupture of the coating in certain areas. This rupture is significantly higher in
Figure 14. SEM images of: a) control (HDGS without any OIH coating); and HDGS coated by one dip step of b) U(230) and c) U(400) with the localization of EDS analysis including semi-quantitative analysis after being immersed in SCPS for 16 days (1 wt% of Cl\(^-\) was added on the 8th day).

Figure 15. SEM images of: HDGS coated by one dip step of a) U(600) and b) U(2000) with the localization of EDS analysis including semi-quantitative analysis after being immersed in SCPS for 16 days (1 wt% of Cl\(^-\) was added on the 8th day).

samples coated with OHMs prepared with higher MWs of Jeffamine leading to inferior results compared to samples coated with lower MWs of Jeffamine. The SEM/EDS results are also in agreement with these findings.

Conclusions

The present work reported the electrochemical study of U(X) sol-gel based coatings on HDGS in chloride-contaminated SCPS. It was demonstrated that the U(X) coatings prevent chloride ions reaching by diffusion to the surface of the metallic substrate by immobilizing them within the most exterior regions of the OIH network of the coating.

The analysis of the results obtained from electrochemical studies (i\(_{gal}\), R\(_p\), EIS and potentiodynamic curves) allowed to conclude that improved anti-corrosion performance was given by samples coated with U(230) and U(400). The poorer results, still better than the control, were given by samples coated with U(2000). SEM/EDS results, in agreement with the i\(_{gal}\) and R\(_p\) results, pointed to the conclusion that full coverage was seldom achieved which is consistent with the literature.

In conclusion, besides the barrier effect introduced by U(X) coatings by hindering the zinc corrosion activity during the initial stages of contact of the HDGS samples with SCPS (highly alkaline environment), these coatings protect the HDGS from Cl\(^-\) attack and may be considered potential substitutes for chromate conversion layers and systems containing Cr(VI). Therefore, these U(X) sol-gel coatings can be employed as pre-treatments to reduce the corrosion in the first instants of immersion in SCPS and protect the HDGS from a further attack of Cl\(^-\).

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