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Leaching from coatings pigmented with strontium aluminium polyphosphate inhibitor pigment- evidence for a cluster-percolation model


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Abstract

Model organic coatings were formulated with different volume concentrations of strontium aluminium polyphosphate (SAPH) inhibitor pigment. Leaching measurements were performed from the top surfaces of the coatings. The microstructure of the coatings and the distribution of phosphorus and strontium within the coatings prior to and after exposure to an aggressive environment were characterized by SEM, EDS and EDXRF. The increase in inhibitor pigment volume concentration (PVC) results in the formation of larger clusters of connected inhibitor pigments within the coatings, which coincides with higher leaching rates from the coatings with higher inhibitor PVC. It is revealed that in the presence of the large clusters, the concentrations of inhibitor pigments decreases through the entire thickness of the exposed coating. In contrast, when the inhibitor PVC is low and elongated clusters of inhibitor pigments do not span the thickness of the coating, the reduction of the inhibitor pigment concentration within the exposed coating is limited to regions closer to the coating/environment interface. On the other hand, EDS analysis shows that after exposure, the concentrations of species released from the inhibitor pigments are below the detection limit within the polymeric binder. It is also shown that the diffusion through the polymeric binder would appear to be the limiting factor that retards the leaching from the coating, suggesting that diffusion through the polymeric binder is not the dominant transport mechanism for leaching of species released from the inhibitor pigments. A cluster model appears to describe well the leaching of inhibitive species released from the SAPH inhibitor pigments incorporated into the organic coatings.

Keywords: Organic coating; Corrosion; Inhibitor; Pigment leaching; Cluster model; Percolation

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1. Introduction

Organic coatings are widely used to protect metallic assets, in e.g. aerospace, marine and automotive application. Coating protect against corrosion by providing a barrier between the external environment and the substrate [1], and by increasing the resistance of the ionic transport paths between the local anodes and cathodes on the surface of the metal [2-4]. Nonetheless, organic coatings are not usually perfect and defect-free when deposited. In addition, ageing and interactions with external environmental factors such as electromagnetic radiation, water/moisture, thermal cycles and mechanical impacts will also eventually result in defects within coatings, limiting the performance lifetime [5-7].

To improve protective performance, passive and active inorganic pigments such as aluminium flakes [8], talc [9], strontium chromate [10] and lithium carbonate [11-14] are incorporated into organic coatings. Active inhibitor pigments, e.g. strontium chromate [15-17] and lithium carbonate [18-21], are expected to impart self-healing ability when a defect is formed and the metallic substrate is exposed to the environment. An organic coating should, therefore, act as a reservoir for active inhibitor pigments until a defect is formed. Inhibitive species should then leach out into the defect area and form a passive layer on the metallic substrate retarding the corrosion process [17, 22-26].

Clearly, the leaching kinetics play a key role in the formation and maintenance of the protective film over the service life of coated products [17, 22, 25, 27-29]. At the early stages after the defect formation, the leaching rate need to be sufficiently high to provide adequate concentrations of inhibitive species within the defect to form a protective film, but not so high as to lead to a rapid depletion of inhibitive species at early stages of the product lifetime. After the initial formation of a protective film, a lower concentration of inhibitive species may be required to maintain the protective film during the designated service life. Therefore, the ideal leaching conditions for the passive film formation and its maintenance could be expected to be: relatively high leaching rates immediately after defect formation, followed by lower leaching rates after formation of the protective film [25, 27, 30-34].

Chromate-containing pigments incorporated into organic coatings are proven effective in different environments and on different substrates. However, chromate is carcinogenic, toxic and hazardous to the environment and therefore should be replaced with benign and environmentally friendly inhibitor pigments. In spite of numerous efforts over the past three decades to replace chromate-containing pigments in organic coatings, suitable candidates are yet to be found for demanding applications such as aerospace and coil coated strip steel [17, 35-40]. Successful incorporation of benign and environmentally friendly inhibitor pigments into the organic coating requires a comprehensive understanding of the microstructure of the organic coating, the interactions between different components of the organic coating and their effect on the leaching mechanisms and the protection performance [12, 41]. Therefore, it is vital to characterize the unexposed (as-formulated) and the exposed organic coatings to correlate the performance to the microstructure and chemistry of the organic coatings [10, 12, 18, 34, 42-50]. In addition, leaching behaviour should be investigated to establish the influence of various conditions on the leaching kinetics and to develop leaching models [10, 18, 23, 43, 50], which can be used to optimise formulation and to predict service life.

The objective of this work is to quantify the leachate concentrations as a function of inhibitor pigment volume concentration (PVC) and to characterise the chemistry and microstructure of the organic coatings as a function of inhibitor PVC prior to and after exposure to 0.86 M NaCl solution. This will provide important insights into the effect of inhibitor PVC on the leaching kinetics, and the changes in the microstructure of the organic coatings due to the leaching of species released from the inhibitor pigments.

2. Experimental
2.1. Materials and coating formulation

Model organic coatings were formulated based on a polyester with polyisocyanate as the crosslinker with different volume concentrations of inhibitor pigment [43]. The inhibitor pigment employed in this study was strontium aluminium polyphosphate (SAPH). Density, oil absorption and average particle size of SAPH pigment are 2.9 $\frac{g}{cm^3}$, 40 $\frac{g}{100 g}$ and 2.0-3.5 $\mu m$, respectively. Average elemental composition of SAPH inhibitor pigments is depicted in Table 1.

Table 1. Average elemental composition of the powder SAPH pigment.

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>44.1 ± 1.3</td>
</tr>
<tr>
<td>Sr</td>
<td>21.1 ± 1.5</td>
</tr>
<tr>
<td>Al</td>
<td>6.0 ± 0.2</td>
</tr>
<tr>
<td>P</td>
<td>18.6 ± 0.2</td>
</tr>
<tr>
<td>C</td>
<td>9.1 ± 0.1</td>
</tr>
<tr>
<td>Trace amounts of F, Na, Mg, Si, S, Cl, Ca and Zn</td>
<td></td>
</tr>
</tbody>
</table>

SAPH elemental analysis (Weight%)

Two groups of coatings were formulated for this study; each group comprises a series of different formulations with different volume concentrations of SAPH pigments. The difference between the two groups is that one had a constant volume concentration of titanium dioxide, approximately 4.52% (as an inert pigment and a rheology modifier), whereas the other group had a constant volume concentration of silica, approximately equal to 0.42% (as a rheology modifier). Table 2 shows a list of the different coatings formulated during this study with their corresponding volume concentrations of inorganic pigments and their final thicknesses measured using scanning electron microscopy of cross sections after curing on the substrate. Two formulations of Group 1 (A-SP10-Si and A-SP20-Si) were also applied with lower thicknesses (approximately half) on the substrate compared with the rest of coated systems.

To formulate the coatings, first sufficient weights of the inorganic components were added to the first part of the polymeric binder containing the polyester resin. Then, zirconia beads were added to this mixture to assist in the milling process. The milling process was performed for 5 minutes using a dual axes centrifuge (Speedmixer DAC150) at 2400 rpm. After that, the second part of the polymeric binder containing the curing agent (i.e. polyisocyanate) was added to this mixture. Also, dibasic ester solvent was added at sufficient amount to adjust the non-volatile volume fraction of the liquid phase of each formulation to approximately 0.4, which was followed by 3 minutes of mixing at 1600 rpm. The target fineness of inorganic particles was 10 $\mu m$, which was checked by a Hegman gauge. Further milling was performed if the particles sizes were found to be greater than the target.

Table 2. List of coatings formulated in this study with their corresponding pigment volume concentration and the average thickness.

<table>
<thead>
<tr>
<th>Group</th>
<th>Nomenclature of the coated substrates</th>
<th>SAPH volume concentration (%)</th>
<th>SiO$_2$ volume concentration (%)</th>
<th>TiO$_2$ volume concentration (%)</th>
<th>Thickness of the cured coating ($\mu m$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A-SP10-Si</td>
<td>10</td>
<td>0.42</td>
<td>-</td>
<td>6.5 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>A-SP20-Si</td>
<td>20</td>
<td>0.42</td>
<td>-</td>
<td>6.8 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>B-SP05-Si</td>
<td>5</td>
<td>0.42</td>
<td>-</td>
<td>12.6 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>B-SP10-Si</td>
<td>10</td>
<td>0.42</td>
<td>-</td>
<td>12.6 ± 1.5</td>
</tr>
<tr>
<td></td>
<td>B-SP15-Si</td>
<td>15</td>
<td>0.42</td>
<td>-</td>
<td>13.3 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>B-SP20-Si</td>
<td>20</td>
<td>0.42</td>
<td>-</td>
<td>13.0 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>B-SP25-Si</td>
<td>25</td>
<td>0.42</td>
<td>-</td>
<td>12.7 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>B-SP30-Si</td>
<td>30</td>
<td>0.42</td>
<td>-</td>
<td>12.9 ± 1.3</td>
</tr>
</tbody>
</table>
Wire wound K-bar applicators were used to apply the coatings with nominal wet thicknesses of 20 µm and 40 µm on Galfan (95%Zn-5%Al) coated steel substrate (a widely used material in the coil coating industry), which had a 50 nm pretreatment layer containing Mn, Ti, P, F and Si on its surface. The surface of the substrates was cleaned with acetone and dried in a stream of cold air prior to the coating application. The deposited wet films were immediately cured for 1 minute in an air circulating oven at 300°C followed by quenching in water. Then, the coated panels were touch dried with soft tissue and stored in a desiccator over silica gel prior to any characterization and exposure.

2.2. Sample preparation

A guillotine was used to cut the coated panels into the appropriate size for measurements (2 cm × 2 cm for exposure and 6 cm × 7 cm for leaching experiments). The panels were cut from the organic coating side towards the Galfan coated steel substrate. Then, a waterproof masking tape was used to cover the backs and edges of all the samples before exposure to the testing environment.

2.3. Leaching and exposure measurements

Leaching and exposure measurements were performed in 0.86 M NaCl solution at 30°C. The electrolyte was prepared with analytical reagent grade > 99.9% sodium chloride and deionized water (15 MΩ.cm). The leaching and exposure specimens were placed horizontally at the base of 2 litre beakers filled with 250 ml electrolyte. 2 ml leaching aliquots were removed after 6, 24 hours, 3, 7, 21 and 44 days from the start of immersion, and the cumulative concentrations of P and Sr in the leachate solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Specimens were also removed after different immersion times up to 44 days, rinsed with deionized water, dried with cool air and characterized using electron microscopy.

2.4. Characterization techniques

Elemental analysis on unexposed and exposed coatings was performed from the top surfaces of the coatings by Energy Dispersive X-ray fluorescence (EDXRF) spectrometry. A PANalytical Minipal 4 EDXRF bench-top spectrometer with a rhodium X-ray tube was employed in this study to quantify the strontium concentration within the coatings. Measurement durations of 1500 seconds for each sample were undertaken under a dynamic helium gas purge with a beam size of ~1 cm in diameter at 30 kV with a typical current of 300 µA (optimised by the data collection software and thermal parameters of the X-ray tube) and no filter. Unexposed samples for EDXRF analysis were approximately 1 cm × 1 cm cut from larger panels of the coated substrates with a guillotine. In a similar manner the edges of the exposed samples, which were covered with the masking tape, were cut to only have the exposed area of each sample available for the EDXRF analysis. No further treatment and preparation was required for these measurements. The measurements were repeated three times for each unexposed and exposed coating conditions for statistical averaging. Fityk 1.3.0 software [51] was used to process the EDXRF spectra. The observed background is removed and the Sr Lα (1.806 keV), Sr Kα (14.163 keV) and Ti Kα (4.510 keV) peaks are fitted with Gaussian functions using a least squares fitting technique. To a first approximation, the calculated areas beneath the peaks for the X-ray lines of Sr Lα, Sr Kα and

<table>
<thead>
<tr>
<th>2</th>
<th>C-SP00-Ti</th>
<th>0</th>
<th>-</th>
<th>4.52</th>
<th>11.4 ± 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-SP02-Ti</td>
<td>2</td>
<td>-</td>
<td>4.52</td>
<td>13.5 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>C-SP05-Ti</td>
<td>5</td>
<td>-</td>
<td>4.52</td>
<td>12.7 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>C-SP10-Ti</td>
<td>10</td>
<td>-</td>
<td>4.52</td>
<td>13.2 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>C-SP15-Ti</td>
<td>15</td>
<td>-</td>
<td>4.52</td>
<td>12.2 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>C-SP20-Ti</td>
<td>20</td>
<td>-</td>
<td>4.52</td>
<td>13.4 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>C-SP25-Ti</td>
<td>25</td>
<td>-</td>
<td>4.52</td>
<td>12.3 ± 1.0</td>
</tr>
</tbody>
</table>
Ti Kα correspond to the concentrations of Sr and Ti elements within the sampling volume of each coating.

The cross sections of unexposed and exposed coated substrates were characterized with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). A Zeiss Ultra 55 field emission gun (FEG) SEM and a Zeiss EVO50 SEM both equipped with EDS detectors were employed for this study. To prepare samples for microscopy, unexposed and exposed specimens were mounted in araldite resin and hardener (10:1 ratio). Then, traditional grinding and polishing was used to prepare the cross sections of the mounted specimens (details can be found in [43]). The polished samples were coated with 15 nm carbon layer. Conductive silver paint was used to connect the top surface of the specimens to the SEM stub.

Energy dispersive X-ray spectroscopy (EDS) was used to characterize the chemical distribution of strontium and phosphorus through the thickness of the initial and exposed coatings. The Zeiss EVO50 SEM was used for these measurements and the SEM settings during the acquisition of the EDS spectra were adjusted to: Electron beam accelerating voltage = 10 kV; Working distance = 8 mm; Probe size = 707 pA (Spot size = 500); X-ray counts obtained per EDS spectrum (spectrum area) = 200000 cts; Process time = 3. The addition of inhibitor pigments results in the formation of a heterogeneous microstructure. Therefore, single point EDS analyses through the thickness of the coatings cannot provide a representative estimate of the elemental concentrations and variations through the thickness of the coatings. A procedure was instead developed to systematically characterize P and Sr concentrations through the thicknesses of the coatings using EDS; 96 EDS points were obtained in two rows (each row consists of 48 EDS points) over approximately 240 μm length (illustrated in Figure 1). The top row (i.e. closer to environment/coating interface) was approximately 2-3 μm below the surface while the bottom row (i.e. closer to the substrate/coating interface) was approximately 7-8 μm below the surface. The distance between the neighbouring EDS points in each row was 5 μm. The spectra of the 48 EDS points for each row were averaged to obtain a single spectrum characterizing the elemental concentrations in the corresponding row. The final spectra were processed as per the EDXRF data, using Fityk 1.3.0 software [51]. The areas beneath peaks fitted to the Sr Lα (1.80 keV), P Ka (2.01 keV) and Ti Kα (4.51 keV) signals for averaged spectra are considered to be the intensities of the characteristic X-ray lines of Sr Lα, P Kα and Ti Kα for each row. This corresponds to the concentrations of P, Sr and Ti elements at 2 different depths through the thickness of the coatings. Three replicates for each coating conditions were measured and averaged to assign a single intensity value to each row of different coatings conditions.

EDS is also used to probe different regions of B-SP05-Si coating, which was exposed to 0.86 M NaCl solution for 44 days, to investigate transport of species released from the inhibitor pigments through the polymeric matrix. The Zeiss Ultra 55 field emission gun (FEG) SEM was used for these measurements. First, a backscattered electron (BSE) image was obtained at 30 kV electron beam accelerating voltage. Then, lower electron beam accelerating voltage (6 kV) was utilized to acquire another BSE image and several EDS point spectra from different regions of the same location. Based on the information acquired from the BSE images taken at 30 kV and 6 kV and the EDS spectra acquired with 6 kV accelerating voltage, the cross section of B-SP05-Si coating is classified into different regions. Then,
several different EDS spectra, which meet the criterion for each region, were acquired from different areas of the cross section of the exposed B-SP05-Si coating. The EDS spectra assigned to each criterion were then averaged to enhance the signal to noise ratio and to obtain a single spectrum representing that criterion.

3. Results

3.1. Microstructural characterization of the coatings

Characterization of the powder SAPH pigments shows that it comprises different particles with different chemical compositions (Figure 2), which are broadly categorized into strontium-rich, phosphorus-rich and aluminium-rich particles [43, 52]. The bright particles are strontium-rich, whereas the grey particles are the mixture of phosphorous-rich and aluminium-rich.

![Figure 2](image)

Figure 2. (a) Backscattered electron (BSE) image from the powder SAPH pigment; (b), (c) and (d) corresponding EDS maps of Sr, Al and P, respectively.

The cross sections of the coatings were characterized by SEM (Figure 3 and Figure 4) to investigate the effect of inhibitor PVC on the initial microstructure, and its evolution after exposure to an aggressive environment. The different types of particle which comprise the SAPH pigment are evident in the backscattered electron (BSE) micrographs obtained from cross sections of the coatings (Figure 3 and Figure 4). It is evident that the SAPH pigments are distributed randomly within the organic coatings, and increasing in SAPH pigment volume concentration results in the reduction of the distance between the neighbouring particles. This leads to the formation of larger clusters of connected SAPH particles in the coatings with higher PVC (Figure 3, Figure 4 and Figure 5). The frequency and the size of these clusters appear to be a function of SAPH PVC. Figure 4 compares the pigment distribution in two
coating systems with approximately equal weights of SAPH pigment per unit area of the substrates but with different SAPH PVC, i.e. different coating thickness. The thickness of A-SP20-Si is approximately half the thickness of B-SP10-Si while the inhibitor PVC in A-SP20-Si is approximately double the inhibitor PVC in B-SP10-Si. This resulted in a difference in spatial distribution of the SAPH pigments within the two coatings. Larger distances exist between the particles and clusters of connected inhibitor pigments in the system with a lower PVC. This distance is filled with the polymeric binder as long as the coating pigmentation is below the critical pigment volume concentration (CPVC).

Figure 3. Backscattered electron (BSE) images obtained at 3 kV accelerating voltage from the cross section of unexposed B-SP05-Si and B-SP30-Si coatings. Red dashed lines follow particles that formed clusters of inhibitor pigments.

Figure 4. Backscattered electron (BSE) images obtained at 3 kV accelerating voltage from the cross section of unexposed B-SP10-Si and A-SP20-Si coatings. Red dashed lines follow particles that formed clusters of inhibitor pigments.

The inhibitor pigments within coatings are supposed to leach out upon direct exposure to electrolyte. Therefore, it is expected that voids and cavities form within the exposed coatings. The formation of voids and cavities can be observed from the top view of the exposed coatings and this has previously been reported in detail [43, 50]. Cross sectional microscopy did not, however, reveal any voids or cavities within the interior of exposed coatings. This is attributed to the smearing of the polymeric binder over the voids and cavities due to the sample preparation method employed in this study. In addition, residues of grinding and polishing may fill the voids and cavities, which could prevent clear observation of them. Nonetheless, differences between the microstructure of the exposed coatings, when compared to the microstructure of unexposed coatings, are clearly evident, as shown in Figure 5. These changes are more profound and most easily observed for coatings with higher inhibitor pigment volume concentrations. For the two coatings containing 5% and 30% SAPH PVC shown in Figure 5, exposure to electrolyte clearly resulted in a reduction of the pigment population density, which is attributed to the leaching of inhibitor pigments. In both cases, the reduction of the SAPH pigment density is more significant in regions closer to the environment/coating interface. In the B-SP30-Si system, areas could be found where the microstructural variation is apparently propagated through the entire thickness of the coating (indicated by oval markers in Figure 5 (d)), whereas adjacent areas could be detected where the apparent microstructural variation is limited to the outer region of the coating.
i.e. closer to environment/coating interface, indicated by rectangles in Figure 5 (d). In comparison, for all the coatings with lower inhibitor pigment PVC, based on the SEM images, it was not possible to identify whether the microstructural variations due to the leaching of inhibitor pigments are propagated through the entire thickness of the coatings or not. However, in general it appears that the inhibitor pigment concentration is reduced within the outer region of the coating.

Figure 5. Backscattered electron (BSE) images obtained at 3 kV accelerating voltage from the cross sections of: (a) unexposed B-SP05-Si; (b) B-SP05-Si after immersion in 0.86 M NaCl solution for 44 days; (c) unexposed B-SP30-Si and (d) B-SP30-Si after immersion in 0.86 M NaCl solution for 44 days. Red dashed lines follow particles that formed clusters of inhibitor pigments. Rectangles and ovals indicate areas where microstructure appears to be modified compared with the unexposed coating.

3.2. Leaching measurements

Leaching measurements were performed for all the formulated coatings as a function of inhibitor pigment volume concentrations, irrespective of the concentration of the inert pigments (TiO₂ and SiO₂). Comparison of the leaching data for the systems with comparable thicknesses and equal volume concentration of inhibitor pigments (with and without TiO₂) reveals a reduction of the leachate concentrations for systems containing TiO₂. Nonetheless, as shown in Figure 6, the release trends of strontium for the two groups of coatings as a function of inhibitor pigment volume concentration are similar. It is evident that the increase in the volume concentration of inhibitor pigments results in higher leachate concentrations. However, the leaching rates increased disproportionately relative to the increase in SAPH PVC and higher leaching rates are observed for the systems with higher inhibitor pigment volume concentration (Figure 7). Similar release trends are also observed for phosphorus (not shown) but at lower leachate concentrations compared with strontium. The higher leaching rates of strontium compared with phosphorus are attributed to higher dissolution rate of strontium-rich particles (i.e. the bright particles in SEM micrographs) and cationic exchange processes replacing Sr²⁺ with other cations in the system (e.g. Na⁺) [43].
Figure 6. Cumulative release of strontium per cm$^2$ of the coating: (a) B-SPxx-Si coatings and (b) C-SPxx-Ti coatings. The missing data of B-SP25-Si and C-SP15-Ti are corresponding to leachate aliquots that were not sent for ICP-AES analysis. The error bars are less than the marker size.

Figure 7. Cumulative release of strontium leached out from (a) B-SPxx-Si coatings and (b) C-SPxx-Ti coatings after 44 days of immersion as a function of initial inhibitor pigment volume concentration. The error bars are less than the marker size. Dashed black lines show expected concentrations of strontium in the leachate solutions if the increase in the inhibitor PVC to more than 5% for B-SPxx-Si group and to more than 10% for C-SPxx-Ti group had a linear relationship with the increase in the leaching rate. The proportionately higher increase in the leaching rates compared with the increase in the inhibitor PVC (Figure 7) indicates that leaching is not merely a linear function of the inhibitor pigment concentration but also it is affected by the microstructure and pigmentation. Therefore, the higher leaching rates are attributed to the variations of the spatial distribution of inhibitor pigments within the coatings, and the increase in the frequency and sizes of the clusters of connected inhibitor pigments in the coatings with higher inhibitor PVC. To check this is not solely a result on the increased concentration of pigments per sample, a comparison of the leachate concentrations released from the coatings with similar mass of SAPH pigments per unit area of the substrates but with different spatial distribution (associated with PVC) of the SAPH pigments was made. This shows significantly higher release rates for systems that are more densely packed and have higher inhibitor PVC (Figure 8). This further confirms that the pigment distribution and formation of the larger clusters of inhibitor pigments have a significant influence on the leaching rate, i.e. the transport of species released from the inhibitor pigments within the coating. This also suggests that the dominant transport paths for the leaching of inhibitive species is not through the polymeric binder, that the polymeric binder significantly retards the leaching kinetics, and that transport through the binder does not significantly contribute to the total leachate concentrations of strontium and phosphorus. The cumulative concentrations of Sr released from thicker coatings with lower inhibitor PVC (i.e. B-SP05-Si and B-SP10-Si) plateaus after 21 days of immersion, while the cumulative concentrations of Sr released from thinner coatings with higher inhibitor PVC (i.e. A-SP10-Si and A-SP20-Si) does not, even after 44 days of immersion.
Figure 8. Comparison of the cumulative concentrations of strontium ((a) and (c)) and phosphorus ((b) and (d)) released per cm$^2$ of the coating. The coatings, which are compared together, have approximately equal mass of SAPH pigments per cm$^2$ of the substrate although the spatial distributions (associated with PVC) of the SAPH pigments are different since the thickness of one is twice the thickness of the other one, whereas the volume concentration of SAPH pigment in the thicker coating is half of the thinner coating. The error bars, which are not evident, are less than the marker size. The concentration of phosphorus released from B-SP05-Si at early stages of measurements is below the detection limit of ICP-AES, which has resulted in a very large uncertainty in the measured values. Therefore, the data points are not plotted.

3.3. Energy dispersive X-ray fluorescence spectrometry

Energy dispersive X-ray fluorescence spectrometry (EDXRF) was employed to: (a) establish the relationship between the intensities of characteristic X-ray lines of Sr K$_\alpha$ and Sr L$_\alpha$, and the inhibitor pigment volume concentrations incorporated into the coatings and (b) monitor the concentration change of strontium within the C-SP10-Ti, C-SP15-Ti, C-SP20-Ti and C-SP25-Ti coatings after 44 days of immersion in electrolyte.

As mentioned in section 2.1, TiO$_2$ was added at a constant volume concentration to all the coatings of C-SPxx-Ti group. The concentration of Ti in the leachate solutions was not within a detectable range of ICP-AES. Therefore, it is considered that the TiO$_2$ does not leach out during immersion and, hence, the volume concentration of TiO$_2$ within the coatings is unchanged (approximately 4.52 volume%). Therefore, the intensity of Ti K$_\alpha$ (i.e. calculated area beneath the peak for the X-ray line of Ti K$_\alpha$) for each sample is used to normalize the intensities of Sr L$_\alpha$ and Sr K$_\alpha$ (i.e. calculated areas beneath the peaks for the X-ray lines of Sr L$_\alpha$ and Sr K$_\alpha$). The normalized intensities of Sr K$_\alpha$ and Sr L$_\alpha$ correlate directly to the concentrations of Sr within the coatings. Figure 9 shows the normalized intensities of Sr K$_\alpha$ and Sr L$_\alpha$ determined from the EDXRF spectra for the unexposed and exposed coatings as a function of the initial inhibitor pigment volume concentration. As expected a linear correlation exists between the initial inhibitor pigment volume concentrations and the normalized intensities of Sr characteristic X-ray lines. Therefore, as shown on the graphs (Figure 9), linear functions are used to fit the data, and these are then used as calibration curves to calculate the concentrations of Sr within the coatings after
exposure to the electrolyte. Figure 9 shows that the normalized intensities of Sr $K_\alpha$ and Sr $L_\alpha$ obtained from the exposed coatings are reduced compared with the initial coatings. This is attributed to leaching of Sr into the environment, leading to the reduction of Sr concentrations within the exposed coatings. Figure 9 also shows more significant reductions for the coatings with the higher initial SAPH PVC, indicating enhanced leaching rates for coatings with higher inhibitor PVC, leading to faster depletion of Sr from the coatings, which is consistent with the leaching measurements presented in section 3.2.

![Figure 9. Normalized intensities of characteristic X-ray lines of (a) Sr $K_\alpha$ and (b) Sr $L_\alpha$ measured from the EDXRF spectra for unexposed coatings pigmented with different volume concentrations of SAPH inhibitor pigment, and for C-SP10-Ti, C-SP15-Ti, C-SP20-Ti and C-SP25-Ti coatings after 44 days immersion in 0.86 M NaCl solution. The dotted lines are the trend lines fitted with a linear function to the intensities of Sr $K_\alpha$ and Sr $L_\alpha$ of the unexposed coatings. The data points are average between three independent measurements.](image)

A more significant reduction in the normalized intensities is evident for Sr $L_\alpha$ characteristic X-ray lines compared with the reductions of Sr $K_\alpha$ characteristic X-ray lines. The fractions of Sr released into the environment after 44 days of immersion were calculated using both the Sr $L_\alpha$ and Sr $K_\alpha$ characteristic X-ray lines (Table 3). For comparison, the leaching data was also used to calculate the fractions of strontium released into the environment according to Equation 1. The data presented in Table 3 shows that the released fractions of Sr calculated based on the Sr $K_\alpha$ characteristic X-ray lines and the values calculated based on the leaching data lie within comparable ranges. Note that since the leaching data correspond to the average concentration released from the entire thickness of the coatings, the released fractions of Sr calculated based on the Sr $K_\alpha$ characteristic X-ray lines also represent the released fractions from the entire thickness of the coating. In contrast, significantly higher released fractions are estimated based on the Sr $L_\alpha$ characteristic X-ray lines. This can be explained by consideration of the detection mechanism; the energy of the Sr $L_\alpha$ peak (1.80 KeV) is significantly lower than the Sr $K_\alpha$ peak (14.16 KeV) and, hence, the relative escaping depths of the two emission lines differ. Thus, it is believed that the released fractions of Sr calculated based on the Sr $K_\alpha$ characteristic X-ray lines only represent the fractions of strontium released from the outer region of the coatings (i.e. closer to environment/coating interface), and are not representative of the average fractions of strontium released from the entire thickness of the coatings.

The relative intensities of the two peaks therefore constitutes a convenient method to discriminate between species leached from the outer region of the coating (represented by both Sr characteristic peaks) and species leached from deeper inside the coating (represented by the Sr $K_\alpha$ peak only) as the EDXRF was performed on the coating surface. The results suggest that, after the immersion, the strontium concentrations within the outer region of the coatings are lower than the strontium concentrations within the inner region of the coatings (i.e. closer to the substrate/coating interface). This explains the more significant reductions of the normalized intensities of Sr $L_\alpha$ characteristic X-ray lines.
compared with Sr Kα characteristic X-ray lines. Furthermore, this is consistent with microstructural characterization of the cross sections of the coatings, which revealed more significant changes within the outer region of the exposed coatings compared with the inner region of the exposed coatings.

It should be noted that similar calculations were also performed for phosphorus concentration within the coatings based on the EDXRF and ICP-AES data (available in electronic supplementary information). Similar to Sr Lα, higher released fraction of phosphorus were calculated based on the EDXRF data compared with the ICP-AES data. The energy of P Kα (2.01 KeV) characteristic X-ray line is in comparable ranges to Sr Lα (1.80 KeV). Therefore, it is believed that phosphorus concentrations calculated based on the EDXRF data also do not represent an average of the phosphorus concentrations within the coatings and only represent phosphorus concentrations within the regions closer to the environment/coating interface. The released fractions calculated for P based on the EDXRF data showed lower values compared with the released fractions of Sr calculated based on the Sr Lα, which indicates that the leaching rate of phosphorus is slower than the leaching rate of Sr. This is again consistent with the leaching measurement data.

The reduction of Sr concentrations within the C-SP20-Ti and C-SP25-Ti coatings is more profound than those within the C-SP10-Ti and C-SP15-Ti coatings. It is believed that the inhibitor pigment volume concentrations within C-SP20-Ti and C-SP25-Ti coatings are above the percolation threshold (Pc) while the inhibitor concentrations within C-SP10-Ti and C-SP15-Ti coatings are below the Pc. The significantly higher leaching rates from C-SP20-Ti and C-SP25-Ti are attributed to this phenomenon and are discussed in detail in [43, 50].

Equation 1. \[ F = \frac{m}{MPV \rho} \times 100 \]

Where

F: Fraction of Sr (%) released per unit area of the coated substrate during exposure; m: Cumulative concentration of the Sr released per cm² of the substrate obtained from the leaching measurements; p: Density of SAPH pigment = 2.9 g/cm³; V: Volume of coating (cm³) per unit area of the substrate (cm²); P: SAPH pigment volume concentration (%) × \( \frac{1}{100} \); M: Weight concentration of Sr (Sr ≈ 21.1 ± 1.5 %) within the SAPH pigments (%) × \( \frac{1}{100} \).

Table 3. Fractions of Sr released from C-SP10-Ti, C-SP15-Ti, C-SP20-Ti and C-SP25-Ti coatings after 44 days of immersion in 0.86 M NaCl solution at 30°C calculated based on the EDXRF and ICP-AES data.

<table>
<thead>
<tr>
<th>Coating Nomenclature</th>
<th>Released Fraction (%)</th>
<th>EDXRF</th>
<th>ICP-AES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated based on</td>
<td></td>
<td>Calculated according to Equation 1</td>
</tr>
<tr>
<td></td>
<td>the characteristic X-</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ray line of Sr Lα</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-SP10-Ti</td>
<td>28.4 ± 3.6</td>
<td>6.4 ± 1.0</td>
<td>6.8 ± 1.2</td>
</tr>
<tr>
<td>C-SP15-Ti</td>
<td>29.9 ± 2.1</td>
<td>8.1 ± 0.3</td>
<td>11.5 ± 1.5</td>
</tr>
<tr>
<td>C-SP20-Ti</td>
<td>44.0 ± 1.3</td>
<td>25.4 ± 1.3</td>
<td>29.0 ± 3.2</td>
</tr>
<tr>
<td>C-SP25-Ti</td>
<td>59.3 ± 1.1</td>
<td>44.4 ± 1.7</td>
<td>49.5 ± 5.5</td>
</tr>
</tbody>
</table>

3.4. Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy (EDS) was used to characterize the chemical distribution of strontium and phosphorus through the thickness (i.e. at different depths) of the unexposed and exposed coatings according to the procedure described in section 2.4. Similar to the EDXRF data, these
measurements were performed for C-SPxx-Ti coatings and the intensities of Sr L$_{\alpha}$ and P K$_{\alpha}$ at different depths are normalized to the intensity of Ti K$_{\alpha}$ for the corresponding depth.

Figure 10 shows the normalized intensities of Sr L$_{\alpha}$ and P K$_{\alpha}$ for the top and bottom rows of unexposed coatings. It is evident that when the concentrations of P and Sr increase within the coatings due to the increase in volume concentration of inhibitor pigment, the normalized intensities of Sr L$_{\alpha}$ and P K$_{\alpha}$ increase as well. As shown on the graphs (Figure 10), a linear relationship exists between the normalized intensities of the elements and the increase in inhibitor pigment volume concentration. Therefore, normalized intensities can be considered as a direct indication of P and Sr concentrations within the coatings. The intensities measured for the top and bottom rows of unexposed coatings are very close to each other and are in comparable ranges. This indicates that the average distributions of P and Sr within the sampling volume for each row is almost uniform through the thicknesses of the coatings in spite of the formation of different microstructural heterogeneities within the coatings due to the incorporation of the SAPH pigments.

![Figure 10](image1.png)

**Figure 10.** Normalized intensities of characteristic X-ray lines of (a) Sr L$_{\alpha}$ and (b) P K$_{\alpha}$ calculated from the EDS spectra acquired from the cross sections of unexposed coatings (from 2 different rows at different depths through the thicknesses of the initial coatings).

As demonstrated in previous sections, leaching of Sr and P occurs during immersion of coated substrates in 0.86 M NaCl solution and, as a result of this, the concentrations of Sr and P drop to lower levels within the coatings. Therefore, EDS analysis was employed to monitor the variations of normalized intensities of Sr L$_{\alpha}$ and P K$_{\alpha}$ through the thicknesses of the exposed C-SP10-Ti and C-SP25-Ti coatings after different immersion times. Figure 11 shows that P and Sr concentrations are reduced at different depths through the thickness of the exposed C-SP25-Ti coatings. Strontium concentration is reduced significantly within the top row of C-SP25-Ti coating after 7 days of immersion, whereas the concentration of Sr within the bottom row is comparable to its unexposed condition. However, after 21 days of immersion, a reduction in concentration of Sr within the bottom row of C-SP25Ti is evident as well as further reduction of the Sr concentration within the top row of this coating. The reduction in concentrations of Sr at different depths through the thickness of C-SP25-Ti coating continues up to 44 days, where the immersion was terminated, although the rates of reduction slow down as immersion progresses. This suggests that the strontium detected in the leachate solution during the first few days after the start of immersion mainly leached out from the outer regions of the coating (i.e. closer to the environment/coating interface), whereas at prolonged immersion times, the strontium in the leachate solution leached out from the inner regions (i.e. closer to the substrate/coating interface) as well as the outer regions of the C-SP25-Ti coating. This indicates that transport paths exist within the C-SP25-Ti coating to support a relatively fast transport of Sr towards the environment from the inner regions of
the coating, which leads to a significant reduction of Sr concentration within the inner regions of the coating to levels that could be resolved by the EDS analysis.

The trends for normalized intensities of phosphorus obtained from the exposed C-SP25-Ti coatings are similar to Sr but less significant, due to the lower leaching rates of phosphorus-containing species. This is in keeping with the leaching results and X-ray fluorescence data. Reduction in the phosphorus concentration at different depths through the thickness of C-SP25-Ti coating is not detected after 7 days of immersion, despite leaching data, which revealed that phosphorus leached out into the environment from the beginning of immersion. This indicates that the employed EDS methodology is not sufficiently sensitive to resolve the variations of phosphorus concentration within the first few days after the start of immersion. However, continuous leaching of P-containing species from the coating lowers the concentration of P to levels at which its variation is detected by EDS within the top row of the coating after 21 days of immersion, and within both the top and the bottom rows of the C-SP25-Ti coating after 44 days of immersion.

As shown in sections 3.2 and 3.3, the leaching rates from the C-SP10-Ti coating are significantly lower than the leaching rates from C-SP25-Ti coating. This is also evident in the EDS data (Figure 11). The variations of the normalized intensities of Sr Lα and P Kα are not differentiated for the C-SP10-Ti coating that was immersed for 7 days. This indicates that the resolution of the developed EDS methodology is a limiting factor for characterizing the concentrations of elements through the thickness of the coatings. Nonetheless, after 21 days of immersion, the normalized intensities of P Kα and Sr Lα acquired from the top row are reduced. Increasing the immersion time up to 44 days resulted in further reduction of the normalized intensities of P Kα and Sr Lα acquired from the top row, whereas a reduction in the normalized intensities of P Kα and Sr Lα acquired from the bottom row is not evident up to 44 days of immersion, which suggests that the concentrations of Sr and P within the sampling volume of the bottom row for the exposed and unexposed coatings are in comparable ranges, while the concentrations of P and Sr are reduced within the sampling volume of the top row. These results would again suggest that both P and Sr detected in the leaching solutions of C-SP10-Ti coatings are mainly released from the outer region of this coating (i.e. closer to the environment/coating interface), and the transport of Sr and P from the inner region towards the environment is highly restricted for C-SP10-Ti coating.

In general, reduction of normalized intensities of P Kα and Sr Lα are evident within the exposed coatings compared with the unexposed coating indicative of lower concentrations of P and Sr. However, the rate and extent of reduction in the normalized intensities appears to be a function of the initial SAPH PVC and the measurement position within the coating. The EDS data are consistent with the EDXRF data, which reveals lower concentrations of Sr within the outer regions of the exposed coatings (irrespective of the initial volume concentration of inhibitor pigment). These measurements confirmed that after the immersion the distributions of P and Sr through the thickness of the coatings are no longer uniform and lower concentrations of P and Sr exist within the outer regions (i.e. closer to the environment/coating interface). Also, these measurements suggest that inhibitor pigmentation significantly affects the transport properties within the coatings. This is attributed to the formation of clusters of connected inhibitor pigments in the coating with higher inhibitor PVC that provides easy transport paths for leaching of inhibitive species released from pigments located further away from the environment/coating interface. This accelerates the leaching process as leaching of species released from pigments located further away from the environment/coating interface is no longer hampered by transport through the polymeric binder. Leaching of these species takes place through the voids and cavities formed after leaching of connected inhibitor particles.
Figure 11. Variations of normalized intensities of characteristic X-ray lines of (a) Sr \( \text{L}_\alpha \) and (b) P \( \text{K}_\alpha \) as a function of immersion time, which are calculated from the EDS spectra acquired from the cross sections of C-SP10-Ti and C-SP25-Ti coatings (from 2 different rows at different depths through the thicknesses of the C-SP10-Ti and C-SP25-Ti coatings).

An increase in inhibitor PVC results in a reduction of the polymer to inhibitor ratio, and coincides with a proportionately higher increase in the leachate concentrations than the increase in inhibitor PVC. This suggests that the transport through the polymeric binder is a restricting factor that controls the leaching from the coatings with lower SAPH PVC. If diffusion happens through the polymeric binder, higher concentrations of the species released from the inhibitor pigments should be detected in the polymer matrix at locations close to embedded inhibitor particles after exposure [10, 45]. To investigate this, EDS point analysis is used to probe different regions of the B-SP05-Si coating, which was immersed in 0.86 M NaCl solution for 44 days. B-SP05-Si has a relatively low concentration of SAPH pigments, which provides sufficient polymeric binder between the inhibitor particles to investigate the diffusion of strontium and phosphorus containing species through the polymeric binder. Based on the information acquired from the BSE images taken at 30 kV and 6 kV and the EDS spectra acquired with 6 kV accelerating voltage, 5 different criteria are defined to classify the cross section of B-SP05-Si coating into different regions. These criteria are described in Table 4. Figure 12 shows a typical example of the BSE images and the EDS spectra that meet the defined criteria. Several different EDS spectra, which meet the criterion for each category, were acquired from different areas of the cross section of the exposed B-SP05-Si coating. Then, the EDS spectra assigned to each criterion were averaged to obtain a single spectrum representing that criterion. The averaged spectra are presented in Figure 13. The only elements that were detected within the polymeric binder, irrespective of its distance from an inhibitor particle, were Si and Cl. Nano size powder SiO\(_2\) was added to the formulation of B-SP05-Si coating at approximately 0.42 volume% concentration, which resulted in the appearance of Si \( \text{K}_\alpha \) peak, whereas exposure to electrolyte resulted in the penetration of low concentrations of chloride ions from the environment into the polymeric binder after 44 days of immersion. On the other hand, the intensity of the characteristic X-ray lines of Sr and P acquired from areas that meet the R-3, R-4 and R-5 criteria are negligible and lower than the characteristic X-ray lines of chlorine and silicon (Figure 13 (c)). As discussed, if Sr\(^{2+}\) and phosphorus containing species released from the inhibitor pigments were able to diffuse through the polymeric binder, the concentration of Sr and P within a close vicinity (1 \( \mu \text{m} \) to 2 \( \mu \text{m} \)) of inhibitor pigments would be expected to be higher than the other areas of the polymeric binder further away (> 2 \( \mu \text{m} \)) from the inhibitor pigments [10, 45]. Therefore, the very low intensities of characteristic X-ray lines of Sr and P suggest that: 1- the concentrations of Sr and P that may exist within the polymeric binder are below the detection limit; and 2- transport through the polymeric binder
is negligible and does not contribute considerably to the total leachate concentrations of Sr and P detected within the leachate solutions. Similar conclusions have previously been made by Sellaiyan et al. [10] and Hughes et al. [45] regarding the transport of chromate through an epoxy polymeric binder.

Table 4. Five different criteria defined based on the SEM and EDS information acquired from the cross section of B-SP05-Si coating to classify different areas of the cross section.

<table>
<thead>
<tr>
<th>Defined criteria for classification of the cross section of B-SP05-Si coating</th>
<th>Nomenclatures of the criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. SAPH particles on the surface, which are observed in BSE image taken at 6 kV accelerating voltage.</td>
<td>R-1</td>
</tr>
<tr>
<td>2. SAPH particles beneath the surface that could not be observed with 6 kV accelerating voltage but their presence is confirmed by the EDS analysis and the BSE image, which is taken at 30 kV.</td>
<td>R-2</td>
</tr>
<tr>
<td>3. SAPH particles further below the surface that their presence is only confirmed by the BSE image taken at 30 kV accelerating voltage (Neither the EDS spectrum nor the BSE image acquired at 6 kV electron beam accelerating voltage could reveal their presence).</td>
<td>R-3</td>
</tr>
<tr>
<td>4. Polymeric areas which are 1 μm to 2 μm away from a SAPH particle.</td>
<td>R-4</td>
</tr>
<tr>
<td>5. Polymeric areas which are &gt; 2 μm away from a SAPH particle.</td>
<td>R-5</td>
</tr>
</tbody>
</table>

Figure 12. (a) - (b) BSE images taken at 30 KeV and 6 KeV accelerating voltage respectively from the same location of the cross section of B-SP05-Si coating that was exposed to 0.86 M NaCl solution at 30°C for 44 days. (1), (2), (3), (4) and (5) are
the EDS spectra acquired from R-1, R-2, R-3, R-4 and R-5 points, respectively, indicated by crosses on image (b), which meet the criteria defined for 5 different regions on the cross section of B-SP05-Si coating (Table 4).

![EDS spectra images](image)

**Figure 13.** The EDS spectra acquired from the cross section of B-SP05-Si coatings that were exposed to 0.86 M NaCl solution at 30°C for 44 days. The cross section of the coating is classified into five different regions (see Table 4) and several EDS-point spectra were acquired from different areas that met the criterion for each region. Then, the spectra assigned to each region were averaged to enhance the signal to noise ratio and to obtain a single spectrum representing that region, which are illustrated in these graphs.

### 4. Discussion

The incorporation of inhibitor pigments into the coating is known to result in microstructural heterogeneities and clusters of connected inhibitor pigments within the polymeric matrix. The increase in inhibitor PVC results in an increase in the frequency and size of the clusters of connected inhibitor pigments while clusters of connected inhibitor pigments form that span the entire thickness of the coating at relatively high volume concentration of inhibitor pigments [43-45, 50]. Concomitantly, the increase in inhibitor PVC also results in proportionately higher increases in the leaching rate compared
with the increase in the inhibitor PVC, which indicates that the leaching is not only affected by the inhibitor concentration but also it is affected by the coating microstructure; i.e. the internal arrangement of pigments in 3D. It is shown that after exposure to electrolyte, the inhibitor concentration is significantly reduced through the entire thickness of the coatings containing a relatively high initial inhibitor PVC, within which large clusters of connected inhibitor pigments exist. The change in inhibitor concentration is only superficial and limited to the areas just below the surface (i.e. coating/environment interface) when the inhibitor concentration is low and elongated clusters of connected inhibitor pigments do not form within the coating. Moreover, the concentrations of species released from inhibitor pigments are below detection limit within the exposed polymeric binder and leaching is retarded when relatively long distances, which are filled with polymeric binder, exist between the neighbouring inhibitor particles. These results suggest that transport through the polymeric binder is negligible and does not significantly contribute to the total leachate concentrations. Therefore, the cluster model, which is proposed by Sellaiyan et al. [10] and Hughes et al. [44, 45] for leaching of chromate from epoxy organic coatings, can be used to explain the leaching of species released from strontium aluminium polyphosphate inhibitor pigment. In this model, diffusion through the polymeric binder is not considerable. Leaching only starts when an inhibitor pigment is in direct contact with the environment via a defect, and continues until the cluster of connected inhibitor particles becomes depleted of species that could be released from the inhibitor pigments. A void/cavity forms when the first inhibitor pigment, which is in direct contact with the environment, dissolves and leaches out into the environment. The void, which is connected to the next neighbouring particle, becomes filled with electrolyte. Therefore, the environment becomes in direct contact with the next neighbouring particle via the void/cavity, which facilitates the dissolution and transport of a second inhibitor particle. This continues until the cluster becomes depleted from inhibitor pigments. Note that local fluctuations of the inhibitor PVC within a coating changes the local sizes of the clusters and therefore can lead to the observation of non-uniform depletion fronts within a coating, such as those that have been observed here and reported in [10, 45].

The cluster model suggests that at the beginning of immersion the leaching profile and the leaching rate depend on the solubility and dissolution rate of the inhibitor pigments that are in direct contact with the environment via defects, whereas at prolonged immersion times leaching profile depends on the fractal dimension of voids and cavities formed due to dissolution and removal of inhibitor particles. It should be noted that the network of connected voids and cavities follows the structure of connected inhibitor particles. Therefore, the leaching profile at later stages of immersion will be a time dependent parameter as the dissolution and removal of inhibitor pigments change the fractal dimensions of the connected voids and cavities (i.e. changes the size, tortuosity and the nature of the interconnected voids). Also, several of connected clusters of inhibitor pigments with different sizes could potentially become active simultaneously due to the formation of a defect through the thickness of the coating. Each one will have a different leaching profile depending on its fractal dimension, which makes the analysis of leaching profile and behaviour very complicated [41, 44, 45].

5. Concluding Remarks

Organic coatings with different volume concentrations of strontium aluminium polyphosphate inhibitor pigments were formulated to investigate the effect of inhibitor PVC on leaching rates and to characterize the chemistry and microstructure of the coatings as a function of inhibitor PVC prior to and after exposure to 0.86 M NaCl solution at 30°C. It is shown that a non-linear relationship exists between the leachate concentrations and the increase in inhibitor pigment volume concentration. Microstructural characterization revealed formation of clusters of connected inhibitor pigments within the organic coatings, where the size and frequency of clusters increase with the increase in inhibitor PVC. Therefore, the non-linear relationship is attributed to the formation of clusters of connected inhibitor
pigments generated after the addition and the increase in inhibitor PVC. This is supported by the EDXRF and EDS analysis, which confirm that the transport properties change through the bulk of the coatings when large clusters of connected pigments span the thickness of the coating. It is shown that the concentration of inhibitor pigments decreases through the entire thickness of the coating when the inhibitor pigment volume concentration is 25% (i.e. above the 3D percolation threshold) and elongated clusters of connected inhibitor pigments are extended through the thickness of the coating, whereas the inhibitor pigment concentration only decreases within the regions that are closer to the coating/environment interface (i.e. the reduction of the concentration of inhibitor pigment does not propagate through the entire thickness of the coating) when the inhibitor pigment volume concentration is 10% . On the other hand, EDS analysis showed that the concentrations of species released from the inhibitor pigments are below the detection limit within the exposed polymeric binder. Also, leaching data from coatings with different inhibitor PVC but comparable weights of inhibitor pigment per unit area of the coated substrates showed that the leaching is highly disrupted when long distances filled with polymeric binder exist between the neighbouring inhibitor particles. The system with higher PVC, which is more densely packed, showed significantly higher leaching rates compared with the system with lower PVC although the two coatings had almost equal weights of inhibitor pigments per unit area of the substrate. Based on these observations, a cluster model is used to describe the leaching of species released from strontium aluminium polyphosphate inhibitor pigment.

Acknowledgments

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

References