The influence of soluble salts content on the performance of an epoxy coating system via accelerated corrosion tests

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ABSTRACT

It is generally accepted that surpassing a threshold value of water-soluble salts at the substrate/coating interface can impart premature failure in painted structures. The Coatings industry has an identified need in defining a maximum allowable soluble salts content, however, a variety of threshold values are found in published data. Based on that, this work aims at evaluate the effect on epoxy coating performance of three different ranges of soluble salts content taking into account the maximum allowable values specified by NORSOK M-501 and IMO PSPC MSC.215, two important standards of naval and offshore sectors.

Blast-cleaned carbon steel specimens contaminated with sodium chloride solutions diluted in methanol ranging 20, 50 and 100 mg/m² NaCl were painted with two epoxy-amine paint coats. Samples were evaluated by cathodic disbondment, water immersion at 40 ºC, pull-off adhesion strength and cyclic corrosion tests.

Larger blisters and loss of adhesion were observed as the soluble salts content at the interface increased. Although, it was not possible to find a critical level of soluble salts even considering data about similar coating systems. A safe soluble salt content must be chosen based on tests that closer reproduce service and environmental conditions to which a painted structure will be exposed.

Keywords: Carbon steel, Corrosion, Soluble Salts Content, Epoxy, Paint.

1. INTRODUCTION

Water-soluble salts, such as chlorides and sulphates, once deposited on steel structures will be hardly completely removed, even by abrasive blast-cleaning [1-3]. They are considered by the coatings industry all over the world as responsible for the detriment of painted steel structures when a threshold concentration is exceeded [4-8].

The presence water-soluble salts at the metal/coating interface promotes osmosis due to their hygroscopic nature [5, 9, 10]. As water penetrates through the coating, that is a semi-permeable membrane, it dissolves the soluble salts resulting in a strong electrolyte that promotes underfilm corrosion [11-13]. Hence, premature failures such as osmotic blistering, cathodic disbondment, adhesion loss, corrosion and delamination under the film are observed [6, 9, 13-15]. Even a coating with improved barrier characteristics to reduce water diffusion may not be enough to stop corrosion from a contaminated substrate with soluble salts [10].

A big number of specifications and surface preparation procedures were developed trying to prevent such premature failures resulting in a variety of different acceptable levels of soluble salts content [2-4, 16-18]. An example is the Technical Report ISO/TR 15235, developed by the International Standard Organization (ISO) that presents a collection of results from scientific works and data from coatings manufacturers and users. According to this document, there is a wide variation in the existing knowledge regarding soluble salts content and, its effects on the performance of coatings and related products [1]. Nowadays, the problem remains unsolved since the coating industry did not define an acceptable soluble salt content or a global ref-

erence standard with levels that could be easily applied to reduce the risks of failure [4, 17, 18].

It is expected that different coatings systems behave equally different at various soluble salts levels and exposure conditions [19]. In the best of our knowledge, however, there is no coherence for maximum allowable soluble salts content even considering similar coating systems, with similar chemical binder, film thickness, substrate and surface preparation. Consensus cannot be found even in worldwide standards for coating systems approval. The standards IMO PSPC MSC.215 (82) [20] (naval sector) and the NORSOK M-501 [21] (offshore sector) specify allowable soluble salts contents of 50 and 20 mg/m² NaCl, respectively. Considering the published literature, for an epoxy system, which is one of the most important anticorrosion coatings [22], with a dry film thickness within 200 to 300 μm, the soluble salts content considered of low risk vary between <10 and 164 mg/m² NaCl [1, 15, 23, 24].

Lee *et al.* [23], for example, evaluated the effect of soluble salt contents within the range of 0 (virtually) up to 200 mg/m² NaCl on fully-blasted steel. They recommended a maximum soluble salts content of 100 mg/m² NaCl. Axelsen and Knudsen [24] carried out a study based on NORSOK M-501 [22]. They investigated the effect of water-soluble salts on two commercially available epoxy systems and a clear lacquer in an interval of 5 up to 300 mg/m² NaCl. On one hand, they showed that the soluble salts content had little effect on the corrosion around the scribe in cyclic corrosion test and cathodic disbondment. On the other hand, the authors concluded that the soluble salts content should be kept as low as possible and that the value proposed by NORSOK M-501 is suitable. Moreover, Baek *et. al* [15] studied the effect on the performance of one epoxy system from 0 (virtually) up to 660 mg/m² NaCl also based on the NORSOK M-501 [21] specifications. They settled a soluble salt limit of 115 mg/m² NaCl based on results of cyclic corrosion test, approximately 6 times higher than NORSOK M-501 recommended value.

Therefore, based on this diversity of values and ranges found in the literature, this work aims at investigate the influence of soluble salts content on the performance of a two-coat epoxy system applied on blast-cleaned carbon steel based on the limits specified by IMO PSPC MSC.215 (82) [20] and NORSOK M-501 [21] standards and the technical report ISO/TR 15235 [1].

2. MATERIALS AND METHODS

2.1 Materials

Sodium chloride (NaCl, ≥99,0%, Anidrol) was used to prepare solutions for the contamination process, salt spray and cathodic disbondment tests. Sodium sulphate (Na$_2$SO$_4$, ≥99,0%, Dinâmica Química) and sodium carbonate (Na$_2$CO$_3$, ≥99,5%, Química Moderna) were used just in cathodic disbondment solution. Deionized water was used in all experiments (MB 400 ion exchange resin, Purolite) if not mentioned otherwise.

2.2 Preparation of specimens for tests

2.2.1 Blast-cleaning

Steel panels were degreased with xylene and blasted with angular and spherical steel grit in the proportion 75:25 to Sa 2 ½ according to ISO 8501-1 [25]. A total of thirty-six specimens of (100 x 150 x 3) mm were prepared for tests of soluble salts content, pull-off adhesion, cathodic disbondment and water immersion, and other fifteen samples of (75 x 150 x 30) mm for cyclic corrosion test.

2.2.2 Contaminating procedure

The procedure for specimens' contamination to achieve the proposed range of soluble salts was based on method described by Flores *et al*. [26], Fuente *et al.* [7, 8, 27] e Baek *et al*. [15].

Three contamination ranges were selected to investigate the effects of soluble salts on steel before painting. The condition A with a soluble salts level measured as sodium chloride up to 20 mg/m² was chosen to evaluate the limit proposed by NORSOK M-501 [22]. The condition B, with a soluble salt level from 21 up to 50 mg/m² was selected to test the IMO PSPC MSC.215(82) [20] specification. And the condition C, with a soluble salt content from 51 up to 100 mg/m² was selected trying to reproduce some of the highest values mentioned by coating manufacturers according to ISO/TR 15235 [1].

Solutions for blast-cleaned specimens' contamination were prepared by dissolving NaCl analytical grade in 10 mL of deionized water in a beaker, at an amount previously weighed on analytical balance according to the required solution concentration presented in Table 1. The soluble salt content generally found on metal surface before the intentional contamination was not subtracted from the desired content as pre-tests

showed that the ranges could be fully met without this subtraction.

Table 1: Data for contamination process

CONDITION	SPECIMEN SIZE (mm)	AREA (m²)	TARGET VALUE (mg/m² NaCl)	NaCl SOLUTION (g/L)	APPLIED VOLUME ON THE SURFACE FOR CONTAMINATION (mL)
A	100 x 150	0.01500	16	0.300	0.8
	75 x 150	0.01125	16	0.300	0.6
B	100 x 150	0.01500	40	0.750	0.8
	75 x 150	0.01125	40	0.750	0.6
C	100 x 150	0.01500	100	1.875	0.8
	75 x 150	0.01125	100	1875	0.6

The content was transferred to a 2 L volumetric flask and diluted with 98% methanol, in which sodium chloride presents a higher solubility compared to ethanol, 13.75×10^{-3} and 0.55×10^{-3}, respectively, by weight fraction [28]. Methanol was used aiming to promote a rapid evaporation and prevent the formation of fast surface corrosion (flash rust) during specimens' contamination, which could compromise the test results [35].

Sodium chloride (NaCl) was used as a reference since it represents the major cause of premature failure of coatings due to its high solubility and hygroscopicity. Furthermore, it is the soluble salt most found on contaminated substrates [5, 12, 16, 29].

Both sample sides were contaminated with the methanolic solutions previously prepared in appropriate concentrations to obtain the target values presented in Table 1. An appropriate volume of solution, Table 1, enough to wet the substrate evenly, without leaving accumulation, was transferred with a 1 mL graduated pipette and deposited on one of the sides to be contaminated. The solution spreading, and the substrate wetting were done with a glass rod.

Samples were dried in an electric oven at 70°C, for 3 minutes. After removal from the oven, we waited until the test specimen reached room temperature (24 ± 2 ºC) to proceed with the contamination of the other side following the same steps.

2.2.3 Determination of soluble salts content

Extraction can be performed by multiple techniques, like swabbing method, Bresle method and the Mayne one, with efficiency between 90 and 100% in analyses on surfaces without corrosion [7, 26]. Similarly, the salts content determination in a water extract can be performed by ion selective electrodes, spectrophotometer, titration or conductivity meter and others [10].

The Bresle extraction method and measurement by a conductometer were chosen because they are specified by the worldwide standards IMO PSPC MSC.215(82) [20] and NORSOK M-501 [21]. Furthermore, is a simple and cheap method, therefore one of the most used [5, 29].

Immediately after abrasive blast-cleaning two samples were randomly chosen for verification of the soluble salts content. According to the industrial practice a total of 10% of prepared samples for performance tests per batch must have the soluble salts content evaluated. Thus, two samples per condition were considered enough as they correspond to 10% of the number of prepared samples.

TQC Bresle adhesive patches were used with a compartmented area of 1250 ± 13 mm², placed in the center of each sample. A 3 mL syringe with needle was used to remove internal air from the patch and then filled with 2.5 mL of deionized water. From this volume, 1.5 mL was injected into the conductometer measuring cell to determine the initial conductivity (blank value).

This volume of deionized water (1.5 mL) was drawn to have again 2.5 mL for injection through the latex membrane and the foam, in the inner compartment of the patch without removing the syringe. The adhesive was massaged for a minute and then proceeded the suction and reinjection of the liquid twice a minute, for 3 minutes. Finally, the water was again collected, and 1.5 mL injected in the measuring cell to determine the final conductivity.

The conversion of conductivity to soluble salts content in mg/m² NaCl was obtained according to

Equation 1, from ISO 8502-9 [30]:

$$\rho_A = c.v. (\gamma_f - \gamma_i).100/A \tag{1}$$

Where ρ_A: soluble salts content; c: empirical constant equal to 5 kg/m^2.s^1 under normal conditions; v: volume injected into the adhesive patch in millilitres; γ_f: final conductivity measurement of solution extracted from the patch; γ_i: initial conductivity measured of deionized water (blank value); A: analysed area (corresponding to the adhesive compartment area) in mm^2.

The same steps were repeated for the three target contamination conditions.

2.2.4 Painting procedure

A coating system suitable for the proposed investigation was selected based on the specifications of coating system 3B of NORSOK M-501 [21]. This is a coating system that acts only as a physical barrier specified for application in ballast water carbon steel tanks, which is one of the most corrosive environments. The coating system is detailed in Table 2.

Table 2: Coating system data

SUBSTRATE	Steel hot rolled, ASTM A36-08 (Usiminas)
SURFACE PREPARATION	Abrasive blast-cleaned at Sa 2 ½ [25]
ROUGHNESS PROFILE (µm)	Between 50 and 80
MANUFACTURER	Weg Tintas LTDA. (Guaramirim, Brazil)
FIRST COAT	Primer-top coat epoxy amine two pack Grey N 6.5
NOMINAL DRY FILM THICKNESS – NDFT (µm)	150
SECOND COAT	Primer-top coat epoxy amine two pack White N 9
NOMINAL DRY FILM THICKNESS – NDFT (µm)	150

Paints were prepared according to the manufacture's technical datasheet. Both coats were applied with a conventional spray gun (DeVilbiss JGA-503) respecting the overcoating period on both panels' sides.

Seven days after the second coat application, the dry film thickness was measured with the magnetic-type thickness gauge Tecnomedição SME-CII PLUS. A reduction factor of 25 μm was considered in each measurement according to ISO 19840 [31] recommendation, as a roughened surface has a higher volume to be completed when compared to a flat one.

The test side of each panel was selected based on measurements of dry film thickness (DFT) in five points considering the acceptance criteria of ISO 19840 [31].

All specimens for the accelerated corrosion tests had their borders protected with the same applied coating.

2.3 Tests

Tests were carried out according to the performance tests listed in the Table 3. All tests were carried out in a laboratory at 23 ± 2 ºC and relative humidity of 55 ± 5%.

Table 3: Performance tests

TEST	STANDARD PROCEDURE FOR TESTING	ESTIMATED LENGTH OF TIME (h)	DIMENSIONS OF SPECIMENS (mm)	NUMBER OF SPECIMENS PER CONDITION
Pull-off adhesion	ISO 2812-2 [32]	24	100 x 150 x 3	1
Cathodic disbondment by impressed current	ISO 4624 [33]	720	100 x 150 x 3	3
Immersion in deionized water at 40° C	ASTM G-8 [34]	3000	100 x 150 x 3	3
Cyclic corrosion	ISO 20340 [35]	4200	75 x 150 x 3	3

Rusting and blistering grades eventually observed in accelerated corrosion tests were classified according to standards ISO 4628-3 [36] and ISO 4628-2 [37], Tables 4 and 5, respectively.

Table 4: Rusting grade classification

DEGREE	RUSTED AREA (%)
Ri 0	0
Ri 1	0.05
Ri 2	0.5
Ri 3	1
Ri 4	8
Ri 5	40 a 50

Table 5: Blistering grade classification

GRADE	QUANTITY	GRADE	SIZE
0	None	S0	Not visible under x 10 magnification
1	Very few	S1	Only visible under magnification up to x 10
2	Few	S2	Just visible with normal corrected vision
3	Moderate	S3	Clearly visible with normal corrected vision (up to 0.5mm)
4	Considerable	S4	0.5 to 5 mm
5	Dense	S5	Larger than 5 mm

2.3.1 Pull-off adhesion test

Adhesion of a protective coating is an important prerequisite for corrosion protection effectiveness [22].

Dollies of 20 mm diameter were bonded with Scotch Weld epoxy adhesive DP-460 3M® on the specimens' surface. The coating and dollies surfaces were previously sanded with sandpaper grade 240. After the epoxy adhesive curing of 24 h, the pull-off adhesion test was carried out with a hydraulic tester device Positest AT-A applying a tensile stress rate of 1 MPa/s.

Failures percentage by type (adhesion/ cohesion) were determined according to ISO 4624 [33] as illustrated in Figure 1, using the software DraftSight 2013 for area calculation.
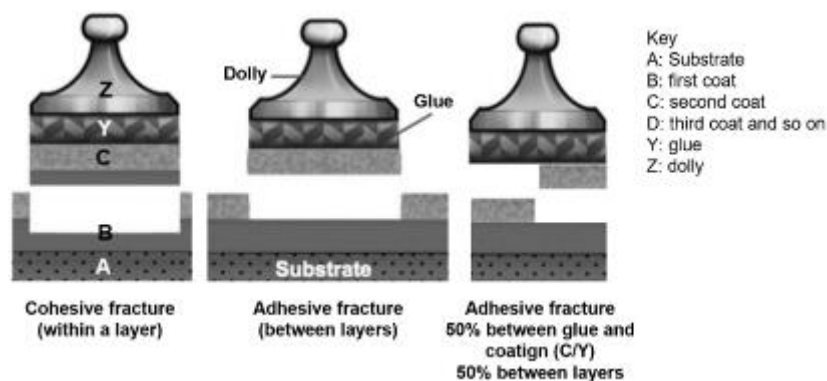

Figure 1: Evaluation and classification of failure types developed in pull-off test. An adhesive failure is reported by a bar between the letter that indicate the coats where the failure happened. A cohesive failure is reported by the coat letter where the failure happened.
Source: Adapted from [38].

2.3.2 Cathodic disbondment by impressed current

The cathodic disbondment test is a powerful way to evaluate the synergic effect of cathodic protection and

the presence of soluble salts [23]. The explanation for the cathodic disbondment effect is unclear [24, 39]. It is suggested that the integrity of the interaction between metal-polymer is compromised by pH increasing due to the reactions 2 and 3 [12]:

In the anode:

$$Fe \rightarrow Fe^{2+} + 2\ e^{-} \tag{2}$$

In the cathode, in non-aerated medium:

$$2\ H_2O + 2\ e^{-} \rightarrow H_2 + 2\ OH^{-} \tag{3}$$

The oxygen reduction reaction in the coating pores (reaction 2) and the migration of Na^+ ions present in the test solution leads to the accumulation of NaOH. Alkalinization can hydrolyses the interfacial bonds between substrate/coating or even the paint itself, degrading it [40]. Another adverse effect is the generation of hydrogen gas (reaction 2) arising the pressure and consequently causing disbondment [23].

The cathodic disbondment by impressed current was performed as mentioned in Table 3, by applying a voltage between minus 1.378 to 1.478 V based on saturated calomel reference electrode (SCE). The voltage was adjusted individually using potentiometers.

Specimens were prepared for test by performing a circular defect with a cutter up to the interface metal/coating, with initial diameter (d_i) of 7 mm, centred in relation to width and 50 mm from the bottom edge. Specimens had $^2/_3$ of their test area immersed in saline solution consisting of 1% by weight of sodium chloride, sodium sulphate and sodium carbonate in freshly potable water as recommended by ASTM G-8 [34].

After 30 days, the specimens were rinsed with potable water at ambient temperature and reconditioned for 24 hours at 23 ± 2 ºC and relative humidity of $55 \pm 5\%$, before detachment process.

To proceed with the delamination around the defect, four incisions were made crossed over the original defect and the disbondment was conducted with a sharp, thin-bladed knife.

The equivalent circular diameter (ECD) in mm was calculated according to the equation 4 based on ASTM G-8 [34].

$$ECD: ((A_t / (\pi / 4))^{1/2}) - d_i \tag{4}$$

The total area (A_t) detached was determined with the software DraftSight 2013.

2.3.3 Immersion in deionized water at 40 °C

Water immersion test is a common practice for accelerate adhesive failures and to estimate the blistering resistance [16, 23].

Water immersion resistance test was carried out by immerging $^2/_3$ of specimens' length at an angle of $20 \pm 5°$, 3 cm apart from each other and from the walls, in a fiberglass tank (EQUILAM EQTI-120) made of inert material. A submerged aquarium pump (Sarlo Better, SB1000a) was used for mechanical circulation at a flow rate of 1000 L/h, maintained at $40 \pm 1°C$.

2.3.4 Cyclic corrosion test

The cyclic corrosion test combining saline fog and exposure to UV-A artificial weathering (340 nm) was chosen because it provides the best correlation with the natural severe marine environment as already demonstrated elsewhere [41]. Since it includes environmental variations such as wet and dry periods, with and without UV rays, it is closer to what happens in the natural environment, without maintaining a corrosive environment on a permanent basis [42].

Cyclic corrosion test was carried out complying with ISO 20340 [35], composed by:

- 72 hours of neutral salt spray, according to 9227 [43];
- 24 hours at -20 °C in a climatic chamber (ESPEC EPL-2H) and;
- 72 hours of accelerated weathering cycles complying with ISO 16474-3 [44], in a weathering chamber (Q-LAB, model QUV/SE) with UV-A 340 nm lamps (Philips) of 40 W. One cycle consists of 4 h of UV-A light at 60 °C and irradiance of 0.89 W/m² plus 4 h of condensation at 50°C.

Specimens received a scribe line made manually using a suitable scratcher and a metal ruler, immediately before starting test. The scribe line was made parallel to its short dimension, 25 mm far from one of the

short edges e 12.5 mm from the long edges, and 2 mm width.

After the exposure time, specimens were rinsed with potable water at ambient temperature and reconditioned for 24 hours at 23 ± 2 ºC and relative humidity of $55 \pm 5\%$, before detachment process using a sharp, thin-bladed knife.

3. RESULTS

3.1 Soluble salts content

Soluble salts contents obtained by the Bresle extraction method and conductometer for the three conditions proposed is presented on the Table 6.

Table 6: Soluble salts levels obtained after contamination of specimens

CONDITION	TARGET OF SOLUBLE SALTS CONTENT (mg/m² NaCl)	SOLUBLE SALTS CONTENT AVERAGE (mg/m² NaCl)
A	Up to 20	13.4 ± 0.8
B	From 21 up to 50	48.4 ± 0.8
C	From 51 up to 100	96.2 ± 8.1

The amounts of soluble salts attended the ranges proposed for comparative performance of test specimens.

The soluble salt content measured immediately after surface preparation was 13.4 mg/m². To avoid that the largest value of the proposed range for condition A (20 mg/m² NaCl) was extrapolated, an additional surface contamination of the specimens belonging to this group was not carried out.

3.2 Pull-off adhesion test

Adhesion strength results and percentages of fractures types developed in the coating system are shown in Table 7.

Table 7: Adhesion strength values and percentages per failure type

CONDITION	DFT (µm)	PULL-OFF STRENGTH		
		DOLLY 01	DOLLY 02	DOLLY 03
A	290 – 305	5.68 MPa 98.2% C/Y, 1.8% Y/Z	5.26 MPa 100% C/Y	5.17 MPa 0.4% B/C; 99.6% C/Y
B	285 – 305	10.66 MPa 100% C/Y	9.05 MPa 100% C/Y	9.69 MPa 100% C/Y
C	245 – 300	8.65 MPa 100% C/Y	8.81 MPa 0.2% A/B; 0.5% B/C; 99.3% C/Y	7.49 MPa 100% C/Y

Key: A: substrate; B: first coat; C: second coat; Y: glue; Z: dolly.

3.3 Cathodic disbondment by impressed current

The specimens' assessments after the test ending are shown in Table 8.

Table 8: Results of cathodic disbondment test after 720 h

CONDITION	DFT (µm)	RUSTING DEGREE	BLISTERING DEGREE	ECD (mm)	PULL-OFF STRENGTH AFTER TEST
A	310 – 355	Ri 0	0 (S0)	10.1	9.4 MPa 100% C/Y
	265 – 330	Ri 0	0 (S0)	11.3	8.00 MPa 100% C/Y
	270 – 330	Ri 0	0 (S0)	5.7	11.09 MPa 100% C/Y
B	285 – 310	Ri 0	0 (S0)	13.0	6.19 MPa 33.2% A/B; 66.8% C/Y
	295 – 325	Ri 0	0 (S0)	12.7	5.14 MPa 91.1% A/B; 8.9% C/Y
	300 – 330	Ri 0	0 (S0)	13.7	5.59 MPa 16.0% A/B; 84.0% C/Y
C	300 – 340	Ri 0	0 (S0)	Total disbondment	3.59 MPa 100% A/B
	295 – 355	Ri 0	0 (S0)	Total disbondment	4.94 MPa 100% A/B
	305 – 340	Ri 0	0 (S0)	Total disbondment	5.06 MPa 100% A/B

Key: A: substrate; B: first coat; C: second coat; Y: glue; Z: dolly.

Specimens for B and C conditions presented underfilm corrosion as shown in Figure 2, in regions of adhesion failure and disbondment in the specimens, endorsing the development of subcutaneous oxidation in the presence of chlorides.
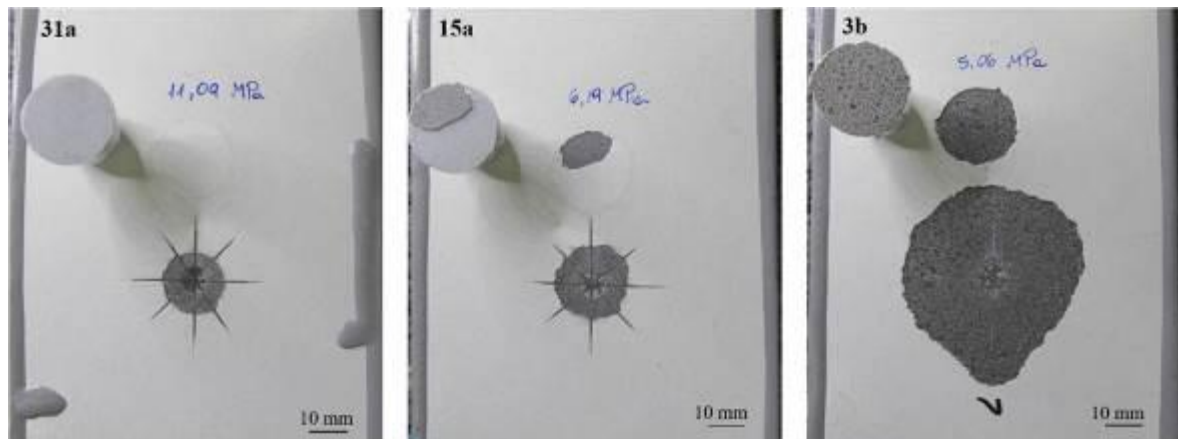

Figure 2: Specimens 31a (condition A), 15a (condition B) and 3b (condition C), respectively after delamination around the circular defect and the pull-off adhesion test.

3.4 Immersion in deionized water at 40 ºC

Table 9 shows the performance results of the test specimens obtained in the immersion test in deionized water at 40 ºC.

The pull-off adhesion after immersion ending was not performed due to the high quantity of blisters and consequent absence of a flat surface, as recommended by ISO 4624 [33].

Table 9: Results of specimens immersed in deionized water at 40°C for 480 hours

CONDITION	DFT (µm)	RUSTING DEGREE	BLISTERING DEGREE
A	295 – 320	Ri 0	4 (S3)
	300 – 330	Ri 0	4 (S3)
	280 – 340	Ri 0	4 (S3)
B	275 – 310	Ri 0	3 (S5)
	285 – 320	Ri 0	3 (S5)
	295 – 340	Ri 0	3 (S5)
C	295 – 335	Ri 0	3 (S5)
	255 – 305	Ri 0	4 (S5)
	290 – 330	Ri 0	3 (S5)

Underfilm corrosion was observed after removing the paint film as shown in Figure 3.
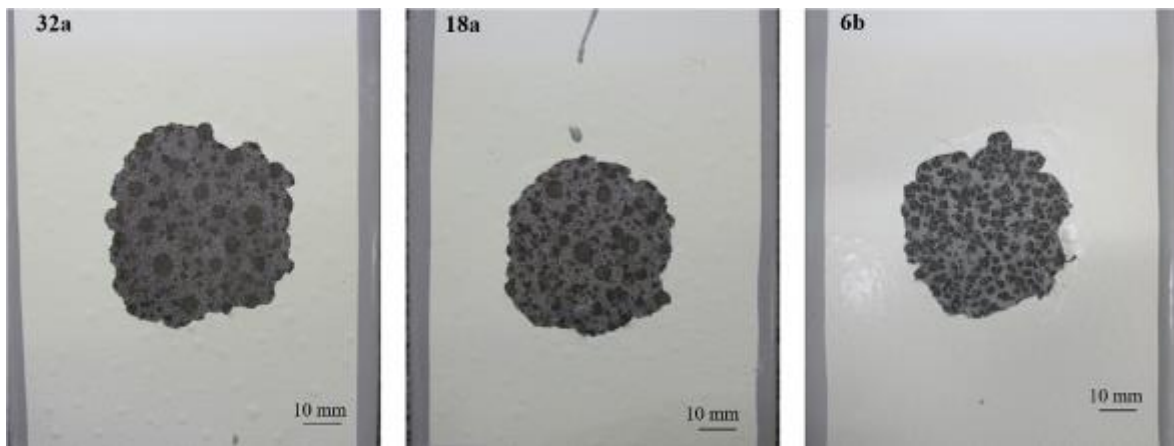
Figure 3: Underfilm corrosion in specimens 32a (condition A), 18a (condition B) and 6b (condition C), respectively.

3.5 Cyclic corrosion test

The results of cyclic corrosion test are shown in Table 10.

Table 10: Cyclic corrosion test results after 4200 hours

CONDITION	DFT (µm)	RUSTING DEGREE	BLISTERING DEGREE	CORROSION AROUND THE SCRIBE (mm)	PULL-OFF STRENGTH AFTER TEST
A	268 – 321	Ri 0	0 (S0)	11.83	9.84 MPa 100% C/Y
	255 – 323	Ri 0	0 (S0)	11.65	9.64 MPa 100% C/Y
	278 – 307	Ri 0	0 (S0)	15.53	9.24 MPa 100% C/Y
B	291 – 310	Ri 0	0 (S0)	15.15	6.75 MPa 100% C/Y
	293 – 317	Ri 0	0 (S0)	13.83	7.15 MPa 100% C/Y
	291 – 333	Ri 0	0 (S0)	14.49	8.60 MPa 100% C/Y
C	298 – 355	Ri 0	0 (S0)	16.03	6.60 MPa 36.5% A/B; 63.5% C/Y
	301 – 360	Ri 0	0 (S0)	12.38	6.21 MPa 22.8% A/B; 77.2% C/Y
	299 – 340	Ri 0	0 (S0)	17.35	9.68 MPa 21.6% A/B; 78.4% C/Y

Key: A: substrate; B: first coat; C: second coat; Y: glue; Z: dolly.

4. DISCUSSION

4.1 Soluble salts contents

An initial value of 13.4 mg/m² NaCl even before intentional contamination can be attributed to atmospheric contaminants deposition on the surface of the test specimens prior to blasting, or even to steel grit used as abrasives [1,44]. Abrasives themselves can contain salts at their sources, transport vessels, storage environments and so on, which contributes to the amount of soluble salts deposited on surface [45].

According to Appleman [14], dry abrasive blasting is only a mechanical technique incapable of removing the microcrystals from the salts deposited in the steel. Johnson [46] explains that chloride ions form strong electrochemical bonds with the metal surface, so it is difficult to extract them. Fuente *et al.* [7] states that the percentage of soluble salts extraction from a dry sandblasted surface to the Sa 2 ½ degree is about 84%, i.e., this surface preparation method does not completely remove the present salts.

For the Condition (C), the sample standard deviation was relatively higher which can be ascribed to some local accumulation of salts during the spreading of the contamination solution, or even by the blasting process.

On one hand, the droplet and spreading method for laboratory contamination is the most convenient and safe way to obtain pre-established levels of salts in a sample comparing to the exposure procedure in natural weathering or corrosion test chamber, i.e., salt spray chambers [7, 47]. On the other hand, this method provides crystal size and distribution less homogeneous than by spraying [19]. The slight deformation suffered by some specimens during the blast-cleaning may have affected the spreading of the contamination solution on the surface and contributed to a greater heterogeneity between the salt contents measured, as in Condition C, with a larger standard deviation.

Moreover, the extraction method itself presents a considerably varied percentage of extraction, from 22 to 150%, according to literature data collected by Appleman [48], what could contribute to the variation in the values collected, even though ISO 8502-6 [29] states that approximately 95% of soluble salts are satisfactorily dissolved by re-injecting the solvent into the compartment for just four times.

4.2 Pull-off adhesion test

Failures were predominantly of adhesive nature between the topcoat and the adhesive used to glue dollies. So, the strength magnitude was not a response to the contamination level, just of the interaction/compatibility between glue and paint, which fully corroborate with Lee *et al.* [23]. However, in Condition (C), it was observed a small failure of type A/B (first coat/substrate), due to a likely accumulation of salts as explained below.

The difference between the soluble salts levels did not affect the adhesion of the coating system. Exposure to moisture and occurrence of osmosis are need so that the effects of salt contamination will be noted [19, 44].

4.3 Cathodic disbondment by impressed current

Increasing the soluble salts content also raised the disbondment around the circular defect and the A/B (substrate/ coating) failure percentage. As observed (Table 8) the adhesion strength decreased as the soluble salts level increased, in agreement with Morcillo [6] and with the results of a linear tendency found by Axelsen and Knudsen [24].

Based on cathodic disbondment results the maximum allowable salt contamination level for the coating system used might be within the range of approximately 13 to 50 mg/m² NaCl.

The presence of soluble contaminants increases the conductivity of the electrolyte in the region where the paint is displaced, intensifying the reaction process with proportional decreasing of the adhesion and delamination increasing [24].

There was water penetration through the film evidenced by the formation of underfilm corrosion, but blistering was not observed because the hydraulic pressure caused by water was not enough to cause a perceptible deformation in the bubble form. Although, Lee *et al.* [23] have observed blisters for all contamination ranges considering the results of "system C" like the one applied on the present work. Thus, even similar paint systems can present anticorrosive performance completely different once blisters development is either

a response of paint viscoelasticity or its deformation mechanism [19].

4.4 Immersion in deionized water at 40 ºC

In the immersion test, unexpectedly all specimens showed blisters within 480 hours of test, ending it ahead of scheduled. This behaviour can be explained by the high concentration gradient, elevated temperature and the coating system porosity that facilitates water diffusion. The safe soluble salts content based on these results might be lower than 13 mg/m² NaCl.

Lee *et al.* [23] observed failure of the epoxy coating system fully blasted only at 200 mg/m² NaCl in immersion condition at 40 ºC, using natural seawater, after testing for 5 months. This completely different performance compared to the results of this work can be easily explained by the concentration of salts in the test media. Since osmosis happens due to a concentration gradient, a media like natural seawater that already contains a salts concentration creates a smaller driven force than deionized water [16].

Low cross-linked regions in the paint film, even after the curing time specified by the manufacturer may had become percolating pathways for water and O_2 through the coating during test, as suggested for Lyon *et al.* [10].

For Conditions B and C (Table 9), the blistering development in the same quantity and size suggests that the formation rate for levels above 13 mg/m² NaCl is similar, in this case.

The barrier protection effect is clearly observed in the second specimen of condition C (Table 9), given the development of larger and bigger number of blisters in a smaller dry film thickness (255 – 305 μm) when compared to the others of the same group (condition C).

Axelsen and Knudsen [24] found a defined time interval of 85, 60 and 5 days, respectively, for the development of blistering between test specimens applied with clear epoxy and with contamination levels of approximately 6, 40 and 127 mg/m² NaCl. Conversely, in this work blisters appeared at all levels of salt contents within the inspection interval, between 14 and 20 days of testing. This fact suggests that the level of acceptable contamination on a surface is particularly dependent of the coating formulation and its intrinsic polymeric heterogeneity [9, 18]. Lee *et al.* [23] corroborate by concluding in their work that a reliable value of soluble salt depends on applied coating system, environmental and substrate condition.

There are significant differences in the maximum allowable levels of soluble salts according to the data for two coats epoxy systems in water immersion tests presented by ISO/TR 15235 [1]. In table A.1 of this standard, the level of soluble salts considered safe is 115 mg/m² NaCl. In Tables C.1 and C.2, nine of thirteen coating manufacturers recommend values between 82 and 115 mg/m² NaCl, two other manufacturers up to 49 and only one up to 16 mg/m² NaCl. On the other hand, the results found in the present study shows that there was a failure even at the lowest evaluated value, about 13.4 mg/m² NaCl.

Additionally, it is observed that the safety values recommended in these same tables for immersion situations are lower, less than half to the levels indicated for structures exposed to atmospheric conditions, probably due to the criticality of the immersion condition, as evidenced by this study and states by Tator [49].

4.5 Cyclic corrosion

Again, the corrosion around the scribe increased as soluble salts content also increased. But, underfilm corrosion affected the coating system adhesion just for the highest level considered in this study (100 mg/m² NaCl). So, the allowable soluble salt content for this test might be between 50 and 100 mg/m² NaCl.

Axelsen and Knudsen [24] otherwise, reported that the salt content had little or no effect on coating system with two coats of modified epoxy coating and a total coat thickness of 284 ± 35 μm, exposed in a cyclic corrosion test.

The development of underfilm corrosion for condition C, is different of what was reported by Baek *et al.* [15]. The authors did not observe this phenomenon in contaminated specimens with around 115 mg/m² NaCl, exposed in cyclic corrosion test. In their study, the corrosion around the scribe was smaller than 3 mm, within the contamination range mentioned above, contrasting our findings as shown in Table 10.

Lee *at al.* [23] have suggested the cathodic disbondment test is the most reliable way to find the maximum allowable soluble salt level. Nevertheless, it is more reasonable to expose a coating system to determine a permissible level based on tests that closely simulate the real service conditions. If a system will not be used together with cathodic protection and it will be exposed in natural weathering conditions, the maximum allowable limit can be higher as discussed this work.

5. CONCLUSIONS

In the present study, we demonstrated that pull-off adhesion strength without any exposure to a corrosive atmosphere, in order to promote osmosis, was not able to provide results in response to the levels of the substrate contamination with soluble salts.

The results show that, for the coating system studied, NORSOK M-501 3B, a soluble salts content above 20 mg/m² NaCl significantly compromises the performance in accelerated corrosion tests. In cathodic disbondment and cyclic corrosion tests, adhesion failures due to water penetration and underfilm oxidation occurred proportionally to the salt content used.

Considering the bibliographical survey carried out, as well as the results of this work, it was not possible to define a critical soluble salts content, satisfactory and safe, for different corrosive atmospheres to which a painted steel structure may be exposed in service, even for an epoxy coating system worldwide studied on similar conditions of preparation and tests.

In addition, it is important to mention that different coating systems behave equally in a differentiated manner on salts residues and exposure conditions. In this way, the choice and specification of a maximum soluble salts content should be made with great caution, considering a test protocol as closer as possible to the actual service conditions in which a coating system will be exposed.

The most recommended and safe practice is to work at the lowest soluble salt content as possible.

6. ACKNOWLEDGEMENTS

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