

Investigation of the salinization in marine and offshore environment - test methods and challenges

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ABSTRACT: Salinization and contamination of metal surfaces by chloride-containing aerosols is of great importance with regard to corrosion phenomena in the maritime sector and in offshore applications. Especially Offshore Wind Turbines are exposed to extreme corrosive conditions due to high chloride concentrations in the atmosphere and the resulting high chloride deposition rates. It is of great importance to evaluate to what extent salinization of the surface influences the corrosion protection of coatings and pitting occurrence on stainless steels under atmospheric conditions to evaluate the durability of metallic building structures in offshore and marine environments. The evaluation of the scientific literature and regulatory guidelines has shown that there are still many open questions regarding the contamination of metal surfaces by chlorides. This contribution will discuss how salinization of metal surfaces is evaluated and monitored according to current standards and guidelines. Future challenges concerning test methods and the application of evaluated salinization values and deposition rates will be discussed.

1 INTRODUCTION

The salinization and contamination of metal surfaces by chloride-containing aerosols is of great importance with regard to corrosion behavior of metal surfaces in marine and offshore applications. Metallic construction materials react to substances from the surrounding environment and atmosphere due to their thermodynamically instable state. Under atmospheric conditions, a major role in these reactions is played by the supply of humidity, which does not necessarily have to be accompanied by a visible film of water. Visible and non-visible water films are built at a relative humidity above 80 % r. H. at clean metal surfaces and above 25 % r. H. at salt contaminated surfaces. In contrast moistening of the surface can also promote deposition of chlorides at the surface within certain limits. The deposition of chlorides on metal surfaces is strongly dependent on environmental conditions such as humidity, temperature, wind and proximity to the chloride source (distance to the sea) [*Castañeda et al (2018)*]. In addition, the roughness and morphology of a surface influence the humidification, moistening and the resulting chloride deposition. The installation conditions on buildings also play a role. In maritime and offshore areas, roofed areas that are protected from rain as well as sheltered but ventilated facade areas are especially problematic. Chlorides cannot be washed off during rainy periods in these areas and can accumulate on the metal surface. If the humidity of the surrounding atmosphere is high, accumulated chlorides can act as corrosion stimulators again. This effect could be proven in recent weathering tests of different stainless steels on the deep-sea island of Heligoland. The investigations have shown that the test specimen's surfaces from

the sheltered exposure tests significantly differ from the freely weathered test specimens. The corrosion effects were markedly pronounced for the sheltered conditions leading to pitting [Burkert *et al* (2018)].

Chloride and salt contaminations represent a critical factor for the expected durability of coated metals which has been scarcely considered systematically so far. For surfaces which can not be coated at the factory in chloride-free atmospheres or need an on-site maintenance, a certain degree of salinization and higher air humidity have to be expected during surface preparation prior to the coating process. A salinization and contamination of the surface can lead to the decrease of the protection duration of a coating under marine and offshore conditions. The question arises as to what extent salinization and humidity are acceptable to guarantee a sufficient duration of new and repair coatings under the given atmospheric conditions. The DIN SPEC 55684 [DIN SPEC 55684 (2018)] contains tables suggesting upper limits for chloride and salt contaminations on surfaces in order to achieve a required coating durability depending on the corrosivity of the atmosphere. The durability ranges “Low”, “Medium”, “High” and “Very High” are based on ISO 20340 [ISO 20340 (2018)]. Table 1 provides a summary of the suggested chloride and salt contaminations.

Table 1. Amount of chlorides and salt in mg/m² (eluate volume 250 ml) on a surface indicating no risk and low risk, according to [DIN SPEC 55684 (2018)]

Expected durability of a coating	Type of contamination	Corrosivity category			
		≤ C2	C3	C4	C5
Low < 7 years	chloride	350	300	250	200
	salt	560	480	400	320
Medium 7 - 15 years	chloride	300	250	200	150
	salt	480	400	320	240
High 15 - 25 years	chloride	250	200	150	100
	salt	400	320	240	160
Very High > 25 years	chloride	200	150	100	50
	salt	320	240	160	80

The presented values refer to an eluate amount of 250 ml. In highly corrosive atmospheres (C5), fewer chlorides and salt contaminations are tolerable on the surface before the coating process than in less corrosive atmospheres (≤ C2). If a higher protection duration of a coating within a corrosivity category is required, the tolerable amount of chloride and salt decreases accordingly. The values in the table are meant to be a guideline since they are not scientifically proven by long-term tests. Protective coatings on Offshore Wind Turbines must provide an expected durability of more than 25 years in a C5 or CX atmosphere. Thus, a value of 50 mg/m² for chloride and 80 mg/m² for salt is demanded in most guidelines and standards for offshore applications. Table 2 sets an overview of the relevant standards and guidelines that specify threshold values and limits for chloride and salt contamination of metal surfaces prior to a coating process.

Table 2. Maximum threshold values for the contamination of metal surfaces prior to coating processes from relevant guidelines, according to [Babutzka et al (2018)]

Reference	Title	Threshold value	Type of contamination referred to	application
[NORSOK (2012)]	NORSOK M501: Surface preparation and protective coating	20 mg/m ²	maximum conductivity corresponding to sodium chloride	surface preparation and protective coating: inspection and testing
[GfKORR (2016) ^G]	GfKORR guideline: Korrosionsschutz von Offshore-Windenergieanlagen, Teil 1 - 3	20 mg/m ² up to 35 mg/m ²	water-soluble substances (in particular salts), NaCl equivalent	duplex coating of towers: surface preparation for zinc spraying and coating, corrosion protection of foundation structures: surface preparation
[NORSOK (2012)]	NORSOK M501: Surface preparation and protective coating, Annex A: Coating systems	50 mg/m ²	salt on surface	reduced requirements prior to coating for Coating system no. 8 according to NORSOK M501
[IMO/MSC (2006)]	IMO/MSC 82/24, Annex 1: Performance standard for protective coatings for dedicated seawater ballast tanks in all types of ships and double-side skin spaces of bulk carriers	50 mg/m ²	water soluble salt limit equivalent to sodium chloride	primary and secondary surface preparation for coating systems on seawater ballast tanks and double-side skin spaces of bulk carriers
[VGB/BAW (2018)]	VGB/BAW standard: Corrosion Protection for Offshore Wind Structures – Part 3: Application of Coating Systems	50 mg/m ² (anions), 80 mg/m ² (salt)	water-soluble contaminants	inspection of blast cleaned surfaces prior to coating

^G to date only available in German

The table shows differences for acceptable chloride and salt contaminations depending on the guideline and application. For some demanding applications, lower chloride values are required, deviating from the usual value of 50 mg/m². A comparison of the guidelines reveals differences in the denomination and classification of the type of contamination. In most cases, the threshold values are classified as water-soluble contaminations and salts on the surface. In the offshore sector, the main part of the contaminations are chlorides that is why other contents usually could be neglected regarding corrosion phenomena. The given threshold values are the maximum values of chlorides and salts allowed for the applications presented in the table.

In practice, the contamination of metal surfaces in mg/m² is usually determined by a wipe test, described in DIN SPEC 55684 [DIN SPEC 55684 (2018)], or by the Bresle method according to

ISO 8502-6 [ISO 8502-6 (2006)]. Typically, the amount of chlorides taken from the surface by Bresle method or swipe test are determined by ion chromatography (IC), titration according to Mohr or photometric analysis. Special attention must be paid to the amount of eluate used for washing the chlorides and salts from the surface in order to guarantee comparability of values.

Another way to approach the issue of contamination of metal surfaces is by assessing the amount of aerosol in the surrounding atmosphere. This is achieved by determining chloride deposition rates in $\text{mg}/(\text{m}^2 \text{ d})$. Deposition rates of chlorides are widely investigated for different atmospheres around the world and are given in relevant standards, guidelines and scientific publications. These values enable the classification of the corrosivity of atmospheres and different exposure and weathering sites. Usually, the deposition rates are determined over a period of 30 days by collecting the amount of chlorides from the atmosphere, followed by analysis and calculation of a daily mean value for the deposition rate. The ISO 9225 [ISO 9225 (2012)] describes two methods for determining the deposition rate of chlorides in its appendix: the wet candle method (Annex D) and the dry plate method (Annex E). However, values determined by these two methods do not provide any information on the actual chloride and salt contamination of a metal surface but reflect the supply of these substances in the surrounding atmosphere.

The present paper should be used as a basis for discussion to initiate advanced scientific and practical consideration of the mentioned issues. The following sections characterize the different methods to evaluate surface contaminations as well as deposition rates and discuss limits and applications of the different methods.

2 METHODS FOR EVALUATION OF CHLORIDE DEPOSITION RATES

The chloride deposition rate in $\text{mg}/(\text{m}^2 \text{ d})$ is determined by the methods described in ISO 9225 [ISO 9225 (2012)]. ISO 9225 defines parameters to enable standardized measurements and a comparability of determined values. Chloride deposition rates are used to estimate the corrosivity of atmospheres according to ISO 9223 [ISO 9223 (2012)]. In Table B.4 in the Annex B of ISO 9223 contamination degrees based on chloride deposition rates determined with the wet candle method according to ISO 9225 are defined which can be used as guiding values for the assessment of the corrosivity of atmospheres and exposure sites. The different limits and levels of pollution by airborne salinity are shown in Table 3.

Table 3. Deposition rates of pollution by airborne salinity represented by chloride according to ISO 9223, Annex B, Table B.4 [ISO 9223 (2012)]

Deposition rate of chloride daily mean value in $\text{mg}/(\text{m}^2 \text{ d})$	Level of pollution
$S_d \leq 3$	S_0
$3 < S_d \leq 60$	S_1
$60 < S_d \leq 300$	S_2
$300 < S_d \leq 1500$	S_3

The wet candle method and the dry plate method described in ISO 9225 lead to different values due to their different shape and type of chloride collecting surfaces. At low deposition rates there is only a small difference between the results of both methods. At higher deposition rates,

the values from the wet candle method are significantly higher than the values from the dry plate method. When looking at annual average values, however, there is a good correlation between the values from both methods. The relationship of the results of both methods to each other is given in Annex F as follows:

$$S_{d,c} = 2,4 S_{d,p} \quad (1).$$

$S_{d,c}$ is the chloride deposition rate from the wet candle method and $S_{d,p}$ is the chloride deposition rate from the dry plate method.

The wet candle method according to ISO 9225, Annex D, is carried out by exposure of a rain-protected textile surface (with a known surface area) for a specified period of time and the subsequent determination of the amount of chloride by chemical analysis. The method involves a candle-like device with a wick immersed in a bottle. The wick itself consists of an inert material over which a gauze tube or gauze bandage is wrapped. The bottle contains a glycerol solution inoculated with octanoic acid to prevent fungal growth. The test set-up is fixed on a frame under a rain-protecting roof.

The dry plate method according to ISO 9225, Annex E, uses a rain-protected two-layer gauze (= dry plate) with a known area. The dry plate is clamped in a collection frame and exposed to the atmosphere in a sheltered or roofed area. After exposure the amount of chloride is chemically analyzed. Figure 1 shows a chloride trap using the dry-plate method on an exposure test rack for standard samples of the Bundesanstalt für Materialforschung und -prüfung (BAM) in Berlin, Germany.



Figure 1. Test rack for exposure studies of standard test samples at the BAM Test Site for Technical Safety TTS equipped with dry plate method.

For evaluation of the amount of chloride after exposure it is important to know that both methods assume an eluate volume of 50 ml for the chemical analysis in the laboratory.

As presented, both methods of ISO 9225 for chloride accumulation in the atmosphere are applied under sheltered conditions. Under free-weathering conditions chloride can be washed away by rain while it can accumulate under protected, sheltered conditions. Both methods are not able to evaluate chloride deposition rates under free-weathering conditions. In addition, the following limits of the two methods must be considered: The results of short-time exposure exhibit large variations and strongly depend on weather conditions and the season of the year.

An extreme contamination in form of chlorides due to splash or spray water at the sea or from de-icing salts at streets is also not in the range of application of these methods. The two methods do not provide surface specific deposition rates. They are mainly utilized to assess the supply of chlorides being as aerosol in the atmosphere and to classify the corrosivity of an atmosphere or an exposure site. Especially for coating applications in the offshore sector it is important to know how much chloride really remains on a metal surface depending on surface structure, weather conditions and tilt angle of the surface. Consequences on the durability of coatings are not caused by the supply of chlorides but the actual deposited and remaining chlorides. Nonetheless, the determination of chloride deposition rates via the methods described in ISO 9225 largely neglect the influence of surface state, situation of installation (orientation, tilt angle) as well as weathering conditions. In order to determine the real amount of chlorides deposited on a metal surface, other methods are applied, which are explained in the following section.

3 METHODS FOR EVALUATION THE SALINIZATION OF METAL SURFACES

In order to determine the chloride and salt contamination of a metal surface, test methods are required which allow the deposits to be removed directly from the surface and to be analyzed afterwards. The result of such investigations is a chloride or salt contamination of a surface in mg/m^2 . However, the eluate volume with which the chlorides and salts were removed or rinsed from the surface must always be considered in order to guarantee comparability of values. The ISO 8502 series of standards describes various methods to determine chloride and salt contaminations of surfaces directly at the object or in the laboratory. The series includes the parts:

- ISO 8502, Part 2: Laboratory determination of chloride on cleaned surfaces [*ISO 8502-2 (2017)*],
- ISO 8502, Part 5: Measurement of chloride on steel surfaces prepared for painting (ion detection tube method) [*ISO 8502-5 (1998)*],
- ISO 8502, Part 6: Extraction of soluble contaminants for analysis - The Bresle method [*ISO 8502-6 (2006)*] (currently under review),
- ISO 8502, Part 9: Field method for the conductometric determination of water-soluble salts [*ISO 8502-9 (1998)*] (currently under review),
- ISO 8502, Part 10: Field method for the titrimetric determination of water-soluble chloride [*ISO 8502-10 (1999)*] (withdrawn).

The most widely used method in practice for determining the salt contamination of metal surfaces is the Bresle test according to ISO 8502-6 [*ISO 8502-6 (2006)*]. This method is used as standard to determine the chloride and salt contamination on metal surfaces prior to a coating process and makes it possible to dissolve soluble pollutants such as chlorides and salts and to analyze them quickly on site. A self-adhesive patch is used, into which a defined amount of eluate is injected to dissolve the pollutants. The eluate containing the dissolved contaminants is then sucked out of the patch and placed in a suitable vessel or measuring instrument for analysis. Most measuring instruments determine the chloride or salt content via the conductivity of the eluate. The test can be carried out on any planar surface, regardless of the orientation of a component, as the self-adhesive patch prevents the eluate from leaking. The Bresle test enables rapid assessment of surface contamination by chlorides. However, only water-soluble components can be determined. Repeated rinsing with eluate can solve almost 100% of the

water-soluble chlorides and salts. Separation of chlorides from other salts is not possible using this method, since all dissolved ions are included in the conductivity value. Figure 2 shows the principle of the Bresle test and an exemplary measuring device for determining the conductivity of the eluate.

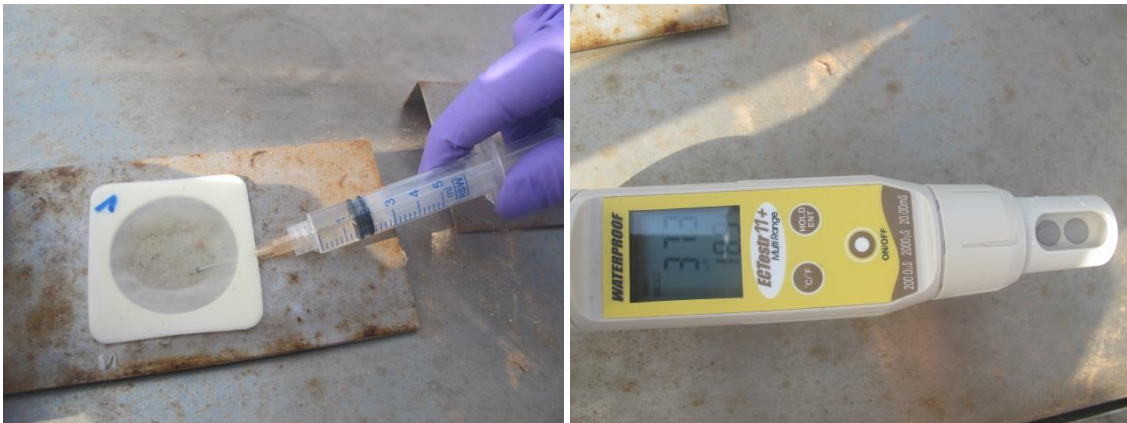


Figure 2. Example of a Bresle Test. Left: Removal of the eluate from Bresle patch on a metal surface, Right: Device for evaluation of the ionic conductivity of the eluate

A kind of wipe test for the removal of chlorides and salt contaminations from metal surfaces is described additionally in DIN SPEC 55684 [DIN SPEC 55684 (2018)]. However, the eluate removed by this method can only be examined in the laboratory and not on site on the component. In advantage, the chloride components can be separated from other conductive ions. Some advantages of wipe tests on metal surfaces are presented in [Babutzka et al (2018)]. With the help of field tests performed under real maritime conditions on the Island of Heligoland it was shown that chloride deposition and salinization depend on the surface structure (roughness), orientation of the specimen (tilt angle) and the weathering conditions (free-weathering, sheltered).

4 CONCLUSION AND FUTURE CHALLENGES

In this paper, the problem of chloride and salt contaminations on metal surfaces in marine and offshore applications was presented. Based on relevant standards and guidelines, measuring methods for the assessment of chloride and salt contaminations on surfaces and the chloride supply of the atmosphere were presented. Relevant guidelines are often based solely on observations and empirical values rather than on significantly confirmed scientific results. With regard to the measurement methods for chloride and salt assessment, a distinction must be made between methods that provide information on the actual chloride and salt contamination of a metal surface and methods to assess the supply of chlorides being as aerosol in the atmosphere and to classify the corrosivity of an atmosphere or an exposure site. Depending on what needs to be examined, special examination methods have to be applied.

Up to now, the existing measuring methods have not enabled smart monitoring of chloride supply and chloride loading of surfaces. All sampling methods are based on manual work and sampling on site and are faulty due to their specific peculiarities, so that sometimes high inaccuracies have to be expected. Especially for offshore applications, automated methods for

chloride determination would be advantageous, as chloride load testing on the towers prior to a repair coating are both expensive and difficult to perform.

5 REFERENCES

Castañeda, A., Valdés, C. and Corvo, F., 2018, Atmospheric corrosion study in a harbor located in a tropical island. *Materials and Corrosion*, 69, 1462.

Burkert, A., Müller, T., Lehmann, J., and Mietz, J., 2018, Long-term corrosion behaviour of stainless steels in marine atmosphere. *Materials and Corrosion*, 69, 20.

DIN SPEC 55684:2018-07, 2018. Corrosion protection of steel structures by protective paint systems - Testing of surfaces before application of coating materials for containments that cannot be detected visually, DIN Deutsches Institut für Normung e. V., Beuth Verlag GmbH, Berlin.

ISO 20340:2009, 2009. Paints and varnishes – Performance requirements for protective paint systems for offshore and related structures, International Organization for Standardization.

Babutzka, M., Mietz, J, and Burkert, A., 2018, Investigation of the salinization of steel surfaces in marine environment. *Materials and Corrosion*, Early View, DOI: 10.1002/maco.201810636.

NORSOK M501, 2012. Surface preparation and protective coating, Standards Norway, Lysaker, Norway.

GfKORR guideline, 2016. Korrosionsschutz von Offshore-Windenergieanlagen, Part 1-3, GfKORR – Gesellschaft für Korrosionsschutz e.V., Frankfurt, Germany.

IMO/MSC/82/24, 2006. Performance standard for protective coatings for dedicated seawater ballast tanks in all types of ships and double-side skin spaces of bulk carriers, International Maritime Organization – Maritime Safety Committee.

VGB/BAW-Standard, 2018. Corrosion Protection for Offshore Wind Structures, Part 1-3, VGB PowerTech Service GmbH.

ISO 8502-6:2006, 2006. Preparation of steel substrates before application of paints and related products - Tests for the assessment of surface cleanliness - Part 6: Extraction of soluble contaminants for analysis - The Bresle method, International Organization for Standardization.

ISO 9225:2012, 2012. Corrosion of metals and alloys - Corrosivity of atmospheres - Measurement of environmental parameters affecting corrosivity of atmospheres, International Organization for Standardization.

ISO 9223:2012, 2012. Corrosion of metals and alloys - Corrosivity of atmospheres - Classification, determination and estimation, International Organization for Standardization.

ISO 8502-2:2017, 2017. Preparation of steel substrates before application of paints and related products - Tests for the assessment of surface cleanliness - Part 2: Laboratory determination of chloride on cleaned surfaces, International Organization for Standardization.

ISO 8502-5:1998, 1998. Preparation of steel substrates before application of paints and related products - Tests for the assessment of surface cleanliness - Part 5: Measurement of chloride on steel surfaces prepared for painting (ion detection tube method), International Organization for Standardization.

ISO 8502-9:1998, 1998. Preparation of steel substrates before application of paints and related products - Tests for the assessment of surface cleanliness - Part 9: Field method for the conductometric determination of water-soluble salts, International Organization for Standardization.

ISO 8502-10:1999, 1999. Preparation of steel substrates before application of paints and related products - Tests for the assessment of surface cleanliness - Part 10: Field method for the titrimetric determination of water-soluble chloride, International Organization for Standardization.