

# INVESTIGATION OF DE-ICING AGENT IMPACTS THROUGH MATERIAL AGING TESTS

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**Abstract** - The maintenance of secure traffic conditions during winter is ensured by the use of de-icers. The type of de-icers used depends on the surfaces that need to be treated. However, these products can have important impacts provoking corrosion or aging appearance of materials surrounding the surfaces that are treated.

In this work, we present a set of tests developed for the evaluation of the de-icer impacts on infrastructure materials, impacts investigated through aging tests.

**Keywords:** de-icing solutions, infrastructures, aging tests, corrosion

## 1. INTRODUCTION

Winter maintenance is based on the spreading of de-icing chemicals on pavements in order to ensure the maintenance of secure conditions for the traffic [1]. The role of these chemicals is to prevent the formation of ice and to provoke its melting [2] thanks to their capacity of reducing the water/ice mixture's freezing point [3].

The type of de-icer used depends on the surfaces that need to be treated, but also on country policies. In France, on the road network, it is mainly sodium chloride that is employed. On airport areas, on the other hand, other products have to be used since the chlorides are highly corrosive and therefore possibly dangerous for airplanes [4]. Therefore, it is mainly chemicals based on sodium or potassium acetates and formates that are spread over the runways. The corrosion inhibitors that these products contain permit to reduce the airplane risks [5]. However, it is not known whether they can have other impacts on the aeronautical materials such as the airplane composites. The materials surround the surfaces that are treated with de-icing products are then exposed to these products as well and can thus be submitted to aging or corrosion risks that need to be investigated.

As the exposure of infrastructure and aeronautical materials to de-icing products during winter differs, two types of tests were developed. The first type concerns the infrastructure materials exposed to road de-icers. This exposure is on periodical basis, the de-icers (sodium chlorides) being splashed by the wheels of the vehicles. To simulate that kind of exposure, tests with immersion-emersion cycles were thus developed and performed on the infrastructure materials. On the other hand, the aeronautical materials, such as aircraft composites, are constantly exposed to de-icing fluids (mainly glycols) which

are directly applied on the aircraft surface. To simulate this kind of exposure, tests with full immersion of aeronautical composites were developed. In this paper, the focus is made on the tests performed on infrastructure materials that are highly exposed to sodium chloride.

Between 800 000 and 2 millions of tons of this sodium chloride de-icer are applied each year on the road throughout the France. Due to several meteorological conditions and to traffic, these chemicals are transported out of the roads. Large quantities hence end up either in the surrounding environment (splashed out by the vehicles or blown away by the wind) [6] or in ponds used for road water runoff remediation and flow control (by flows after precipitations) [7], [8]. The environmental impacts and the possibilities of depollution of road de-icers have been studied and reported in the literature [9], [10].

Nevertheless, the de-icers are not only transported out of the roads into the environment, but also on the surrounding infrastructure structures which are often metallic and therefore possibly sensitive to corrosion [11]. An example of a metallic structure severely attacked by corrosion is presented Fig. 1.



Fig. 1. Example of corrosion appearing on a metallic bridge (Fades viaduct).

The maintenance of these structures against the corrosion requires technical solutions that are often expensive and nocuous for the environment. Another option is to adapt the material choice on the exposition conditions, which can permit the limitation of corrosion risks [12].

For that purpose, a system and a methodology for the evaluation of the corrosion risks for the infrastructure materials, inspired by standards [13], were developed. This paper describes them, as well as the tests including an immersion of different materials in de-icing solutions that were performed. During the tests, a follow-up of the corrosion appearance and evolution is put in place through

a monitoring of different physicochemical properties. The aim of this study was to validate the methodology before developing a prototype for the study of corrosion process. The final aim is to study the corrosion kinetics in order to permit a preventive management of the transportation infrastructures.

## 2. MATERIALS AND METHODS

### 2.1. De-icing agents

The de-icing product chosen for this study is the main product that is used on the French road network, sodium chloride. This de-icer is mainly present in its liquid form (called brine): it is either applied directly as a brine or, when applied in solid form, ends up being dissolved in the water coming from the precipitations.

The effect of two different concentrations were studied: one at 300 g/L (the main concentration being applied on the roads) and one at 10 g/L (the brine applied being diluted by the meteorological precipitations such as rain or snow). For comparison reasons, for each set of tests, one material was analyzed while in contact with pure water and one while in contact with a diluted 10% acetic acid.

### 2.2. Infrastructure materials

The infrastructure materials tested were the main materials constituting the infrastructures, such as steel and aluminum. To assure a better homogeneity of the material composition, only standardized metals were chosen. Rectangular  $90 \times 60 \times 6$  mm test specimens of different materials were analyzed:

- EN 10025-2 - S355 K2+N steel,
- EN 10025-2 - S355 K2+N steel galvanized by the NF ISO 1461 standard, with a  $70 \mu\text{m}$  zinc layer,
- EN AW 5754 aluminum.

The effect of the presence of a covering was investigated. For that purpose, two samples of the S355 steel were tested: one without covering, and the other one with a geomet covering.

### 2.3. Aging tests (Immersion - emersion cycles)

The infrastructure materials are exposed to road de-icers on periodical basis, the de-icers being splashed by the wheels of the vehicles. To simulate that kind of exposure, the samples of the infrastructure materials were exposed to de-icing agents at different concentrations with immersion-emersion cycles. It is important to note that the metal samples were not completely immersed, but only semi-immersed in the de-icing solution.

The experimental setup developed for these tests was named PORC-EPIC (for "Prototype of corrosive reactions - studies by cyclic immersions" in French). Beakers with de-icing solutions were placed in a tank underneath the metal samples. These samples were hung on a plate submitted to cyclic vertical translation by a rotative device connected to an engine which is controlled by a timer with programmed cycles. The schematic representation of the

entire experimental setup is shown in Fig. 2.

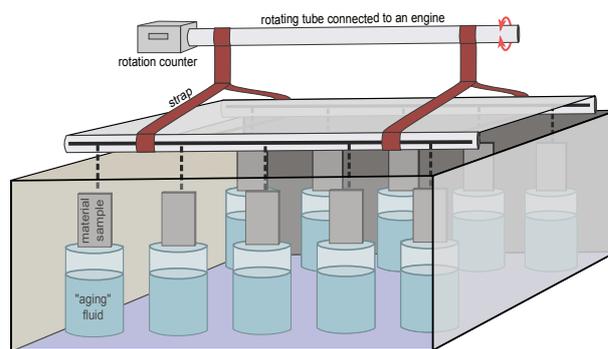


Fig. 2. Experimental setup for the immersion-emersion tests.

The vertical translation permits to the samples to be semi-immersed in the de-icing solutions and then emerged. The immersion and emersion were 15 minutes long each, and the metal samples were submitted to the cyclic semi-immersion - emersion during 2 months. During the tests, several physicochemical properties were measured once a week (presented in Table 1).

Table 1. Physicochemical measurements monitored.

Sample	Analysis made
De-icing solutions	- pH, - conductivity, - Raman analysis.
Metal sample	- Raman surface analysis, - optical microscopy, - photography, - sample weight.

## 3. PRELIMINARY RESULTS

### 3.1. Qualitative approach

During the tests, a development of a cristallisation on the metal surface can be observed (Fig. 3). This cristallisation is a fonction of the surface porosity and roughness, as well as of the material chemical composition.

As it can be seen in Fig. 3, the cristallisation is much more pronounced on the steel that has no covering (picture in the middle) and its color shows that the steel is more corroded than the steel with geomet covering. Furthermore, for the same steel sample, the cristallisation is much more pronounced on the interface (picture on the right) than on the immersed part of the sample that was semi-immersed (picture on the left).

After the 2-months-long tests, the metal surface is cleaned (all residual traces of corrosion are removed and the



Fig. 3. Surface impact on the cristallisation form: immersed areas of a steel without covering (middle) and with a geomet covering (left), interface of steel with geomet covering (right).

surface is thoroughly rinsed with deionized water) and dried before observation with optical microscopy. The pictures obtained, presented in Fig. 4, show different types of corrosion that occurred after immersion of steel samples in different aging solutions.

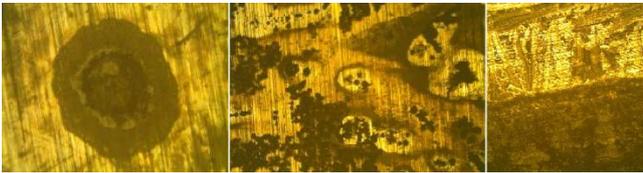


Fig. 4. Examples of fluid impact on the corrosion type after immersion in: water (left), a brine (middle) and an acetate (right).

The Fig. 4 shows that it is possible to differentiate the pitting corrosion occurring while steel is immersed in water, from the differential aeration occurring when it is immersed in a brine and the uniform corrosion when the immersion solution is a 10% diluted acetic acid.

### 3.2. Quantitative approach

In order to estimate the corrosion rate of each sample, the weight of each metal sample was measured before and after the 2-months-long essays. At the end of the essays, the sample surface was cleaned before the weighing. This permitted to evaluate the sample weight loss provoked by the immersion - emersion cycles, and the associated corrosion rate calculated. The corrosion rate conventionally being expressed in  $\mu\text{m}/\text{year}$ , it is calculated with the following equation:

$$C_{rate} = \frac{M_f - M_i}{\rho \times S} \times 6,518 \times 10^4 \quad (1)$$

where  $M_f$  and  $M_i$  are, respectively, the final and initial mass of the metal sample (expressed in g),  $S$  the active surface of the sample (in  $\text{cm}^2$ ),  $\rho$  the density of the metal under test (in  $\text{g}/\text{cm}^3$ ).

The densities of the three reference metals analyzed are:

- 7,85  $\text{g}/\text{cm}^3$  for steel,
- 7,20  $\text{g}/\text{cm}^3$  for galvanized steel,
- 2,81  $\text{g}/\text{cm}^3$  for aluminum.

The mass loss and the calculated corrosion rates for our set of tests are presented in Table 2. For each steel sample (galvanized or not), duplicates were analyzed in order to verify the repeatability.

Table 2. First measurements and calculations of the corrosion rate.

Sample (Solution)	$M_i$ (g)	$M_f$ (g)	Corrosion rate ( $\mu\text{m}/\text{year}$ )
Aluminum (Water)	30,489	30,501	5,2
Aluminum (NaCl 10 g/L)	30,496	30,475	-9,0
Aluminum (NaCl 300 g/L)	30,478	30,313	-70,9
Galvanized steel (Water)	267,319	267,332	2,2
Galvanized steel (NaCl 10 g/L)	265,249	265,066	-30,7
	267,803	267,737	-11,1
Galvanized steel (NaCl 300 g/L)	267,262	266,743	-87,0
	266,888	266,643	-41,1
Steel (Water)	249,447	248,071	-211,6
Steel (NaCl 10 g/L)	248,413	240,790	-1172,1
	248,164	240,440	-1187,7
Steel (NaCl 300 g/L)	250,259	248,164	-322,1
	246,894	244,701	-337,2

As expected, for aluminum, corrosion rates are very low whether it was immersed in water or brine. With a corrosion rate much lower than 0,1 mm/year, it is considered as corrosion proof. The corrosion rates of steel with no covering, on the other hand, are much higher, especially for the 10 g/L brine. Being greater than 1 mm/year, it is considered to be not usable because of its serious corrosion. Finally, galvanized steel presents rather low corrosion rates, showing the protection by the zinc layer when it comes to corrosion.

The other observation that can be made concern the repeatability of the tests. For steel, a very good repeatability is obtained. However, the galvanized steel presents important differences which could be due to a slight

difference in the zinc layer. Its thickness being around 70  $\mu\text{m}$ , very small variations can provoke rather different results in terms of corrosion protection. Even though the differences between the replicates are important, each corrosion rate is much lower than 0,1 mm/year, showing that the galvanization of steel is a good mean to prevent or diminish the corrosion risks.

#### 4. CONCLUSIONS

In this paper, we show the importance of surveillance of the corrosion appearance on infrastructure materials that are constantly exposed to corrosive products such as the de-icing salt. The maintainance of these structures against the corrosion requires technical solutions that are often expensive and nocuous for the environment. Another option is to adapt the material choice on the exposition conditions, which can permit the limitation of corrosion risks.

For that purpose, a system and a methodology for the evaluation of the corrosion risks for the infrastructure materials, inspired by standards, were developed. Tests with immersion-emersion cycles were conducted on several materials having different compositions or different coverings. Results show that the experimental system developed is able to accurately discriminate the presence of cristallisation and corrosion on the surface of metallic samples. The optical microscopy permits to identify the type of corrosion present, and the mass change during the tests permits to calculate the corrosion rate for each sample.

The aim of the tests presented here was not to study the influence of the corrosive solutions on different materials, but to validate the suitability of the system and methodology developed for the evaluation of the corrosion risks for the infrastructure materials. The first results are encouraging showing that the methodology developed for the preparation and analysis of the metal samples is suitable for the study of corrosion. Furthermore, the corrosion rates calculated show that, for homogenous samples, the results are repeatable. As these tests showed that the methodology is adequate for our study, a prototype of PORC-EPIC with optimized characteristics is under construction.

The final aim of the system and methodology developed is to study the corrosion cinetics in order to permit a preventive management of the transportation infrastructures. Further examination of other physicochemical measurements performed will permit to evaluate the corrosion processes that took place. The knowledge of these processes will permit to estimate the degradation products of the corrosion, another interest of the study being to diminish the transport of infrastructure pollutants towards the environment.

#### REFERENCES

[1] *Winter maintenance equipment and technologies. Synthesis of best practices road salt management*, Transportation association of Canada, 2003.

- [2] M. S. Switzenbum, S. Veltman, T. Shoenboerd and C. M. Durand, *Best management practices for airport deicing stormwater*, Department of Civil and Environmental Engineering, University of Massachusetts/Amherst, 1999.
- [3] *Snow and ice control: Guidelines for materials and methods*, National cooperative highway research program, Transportation Research Board, Washington, 2004.
- [4] *Impact of airport pavement deicing products on aircraft and airfield infrastructure*, Airport cooperative research program, Transportation Research Board, Washington, 2008.
- [5] *Services hivernaux sur chaussées aéronautiques*, Service technique des bases ariennes, 2002.
- [6] I. Durickovic, R. Suaire, G. Derombise and M. Marchetti, "Surveillance of road de-icers in the environment", *4<sup>th</sup> IMEKO TC19 Symposium on Environmental Instrumentation and Measurements - Protecting Environment, Climate Changes and Pollution Control*, pp. 154-157, Lecce, Italy, June 2013.
- [7] R. Suaire, I. Durickovic, M.-O. Simonnot and M. Marchetti, "Monitoring of road de-icers in a retention pond", *International Journal of Measurement Technologies and Instrumentation Engineering*, vol. 3, n<sup>o</sup>. 1, pp. 39-47, 2013.
- [8] E. L. Thunqvist, Predicting steady state concentrations of chloride in groundwater and surface water, *PIARC 11th International Winter Road Congress*, p. 8, Sapporo, Japan, Jan. 2002.
- [9] D. M. Ramakrishna and T. Viraraghavan, "Environmental impact of chemical deicers, a review", *Water, Air & Soil Pollution*, vol. 166, pp. 49-63, 2005.
- [10] R. Suaire, I. Durickovic and M.-O. Simonnot, "Use of halophytes for phytoremediation of road runoff contaminated by deicing salts", *XI<sup>th</sup> International Phytotechnologies Conference*, Heraklion, Crete, Greece, Sept. 2014.
- [11] U. S. Andersen and H. Nielsen, "Évaluation et réparation des ponts exposés aux sels de déverglaçage", *Routes-Roads*, vol. 361, pp. 82-88, 2014.
- [12] S. A. Al-Fozan and A. U. Malik, "Effect of seawater level on corrosion behavior of different alloys", *International Desalination Association World Congress*, Singapore, Japan, 2005.
- [13] EN 16811-1 standard "Winter service equipment - deicing agents. Part 1: Sodium chloride - Requirements and test methods". December 2014.