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Penetration of chlorides in hardened concrete during frost salt scaling cycles

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Abstract. Sixty samples from three concrete mixes (same components) were prepared and subjected to frost salt scaling cycles. A set of 20 samples from the same mix was tested according to the French standard XP P18-420. Another set was exposed to different chloride concentrations. Different numbers of freeze/thaw cycles were applied to the last set. The mass of scaled-off particles follows a lognormal distribution. Despite high standard deviation, this scaling test enables to separate high resistant from very low resistant concrete. A combined analysis reveals that the scaling and the chloride penetration front are independent from a phenomenological point of view and that the chloride concentration on the exposed surface directly influences the amount of scaled mass according to the typical pessimum effect. These results raise two main questions: is the amount of chloride on the surface solution a direct or indirect parameter and what happens to this pessimum effect if we take into account the scaling test dispersion?

Frost salt scaling (figure 1) refers to superficial damage that occurs to geomaterials like cement-based materials when submitted to freezing/thawing cycles, particularly in the presence of de-icing salts. The latter are usually sodium-chloride aqueous solutions used in civil engineering to prevent the formation of slippery ice layers on roads, pavements, etc.

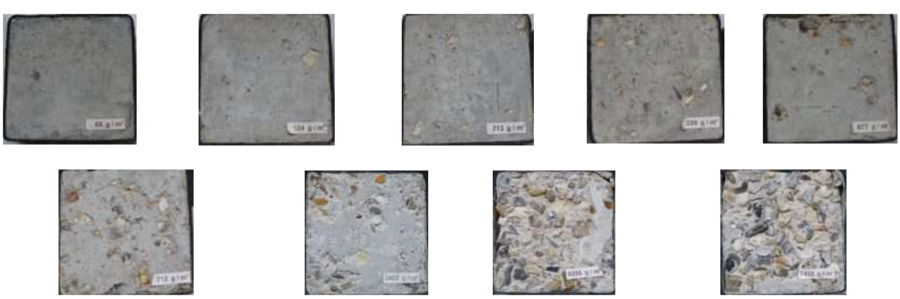

Fig. 1. Salt scaling evolution with freezing/thawing cycles: the concrete surface becomes increasingly damaged.

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Whilst adopting the French XP P18-420 standard, which enables different concretes to be rated with regards to their frost salt scaling resistance, this study investigates means of better characterizing the frost salt scaling phenomenological behaviour of a concrete, in quantitative terms. Focus is given to the experiment dispersions, the statistical correlation between spalled weight and chloride penetration (front and concentration) in hardened concrete. The overall aim is to better understand the mechanisms leading to this kind of deterioration.

1 - FRENCH XP P18-420 STANDARD

The French XP P18-420 standard presents the particularity of including specifications on manufacturing and storage before scaling tests. Samples are fabricated in 150 mm steel cube moulds and compacted on a vibrating table according to the NF P18-421 with the following caracteristics: vibrating frequency of (150 ± 3) Hz and a top acceleration of (65 ± 5) m/s².

1.1 Dry storage and pre-humidification

After (24 ± 2) h of curing, the samples are removed from the mould and stored for (13 ± 1) days in water at (20 ± 2)°C or in a wet room (relative humidity above 95%). During the last 7 days, the samples are cut parallel to the bottom side of the mould, to a height of (70±2) mm. The samples have the following dimensions: 150 x 150 x 70 (± 2) mm.

The concrete samples are stored in a climatic chamber: (20 ± 2)°C and (65 ± 5)% RH for (14 ± 1) days. During the last 3 days of this step, a rubber sheet is stuck on the lateral sides of the sample, which are first brushed to provide a correct seal. A sealant string is used to fill the corner between the concrete and the rubber sheet to prevent water penetration.

Following dry storage, the tested surface is pre-humidified with tap water for (72 ± 4) hours.

1.2 Freeze-thaw testing

After this 31-day conservation period, a 3 % NaCl salt solution replaces the pre-humidification water and covers the exposed surface for 56 freeze-thaw cycles. The sample is insulated and protected from evaporation (figure n°2).

A freeze-thaw cycle lasts 24 hours (figure n°3) with a period of 4 hours at -20°C and another period of 5 hours at +20°C.

Fig. 2 Cross section of a concrete sample and thermal insulation.

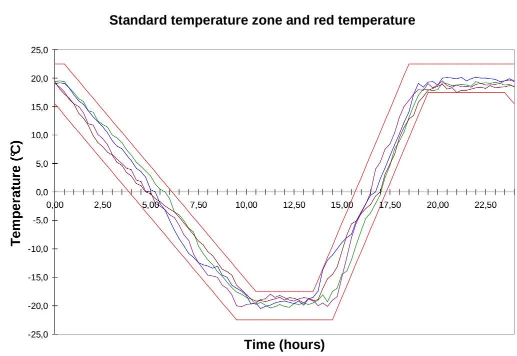

Fig. 3 Freezing/thawing cycles.

1.3 Scaling assessment

The amount of scaled-off particles is assessed every 7 cycles. In order to remove loose scales, the test surface is swilled under a filter. The 3% NaCl solution is renewed and the samples are replaced in the climatic chamber.

The filter and the scaled material are dried at 110°C until the difference between two weighings is lower than 0.1%.

The mass of scaled material related to the test surface is:

$$M = (Mm / Sm) \ (g/m^2)$$

Mm (g) is the full mass of scaled material at each 7-day measuring interval

Sm (m^2) is the area of the test surface determined with an accuracy of $\pm$ 10 cm^2.

The scaling result is the median of the 4 samples' results. The extreme values are eliminated and the average of the two mid ones is calculated.

2 - MIX CHARACTERISTICS AND SAMPLE PREPARATION

The concrete mix comes from prefabricated concrete for bridge cornices. By varying the entrained air content, we are able to obtain a mass of scaled-off particles per exposed area sample surface ranging from 150 g/m² to 5000 g/m². The rate of occluded air is fixed at 2.5%, which should lead to a result ranging from 2500 to 3000 g/m².

Table 1. Mix composition (1m^3 of concrete).

Cement	Aggregates			Additive (% of cement)			Water
CEM I 52,5 N PMES Lafarge, Le Teil	0/4	4/12.5	11.2 /22.4	Super plasticizer	Accelerator agent	Air entraining agent	
350 kg/m^3	655 kg/m^3	280 kg/m^3	920 kg/m^3	0.743%	0.763%	0.100%	135 l/m^3

The experiment was performed on a total of 60 samples. For repeatability purposes, we produced 3 batches of 20 samples with the same mix composition (Table n°1):

- 5 sets of 4 samples were exposed to a 3% NaCl concentrated solution for 56 cycles, one of which has an exposed surface reduced by 2 (150 x 75 mm).
- 4 sets of 4 samples were exposed to 0, 1.5, 3 and 6% NaCl concentrated solution for 56 cycles, and 1 set of 4 reduced–size samples (150 x 75 mm) was exposed to a 3% NaCl concentrated solution.
- 4 sets of 4 samples were exposed to a 3% NaCl concentrated solution for 14, 28, 42 and 56 cycles, and 1 set of 4 reduced-size samples (75 x 75 mm) was exposed to 56 cycles with a 3% concentrated solution.

Both mass of scaled-off particles and chloride penetration front are available on the 60 samples.

3 – STATISTICAL-BASED ANALYSIS

If we examine the scaling values through the median, the average of 4 samples results or the individual sample's results they are all in accordance with previous results obtained with the same concrete mix. However, although the average result of the 24 samples (3% NaCl concentrated solution for 56 cycles) is equal to 3090 g/m², the standard deviation (59%) is very high (figure 4).

Median or average results of 4 samples are very close and the analysis with these results produces a substantial reduction of the standard deviation, which remains at 41% respectively for the median analysis (figure 5).

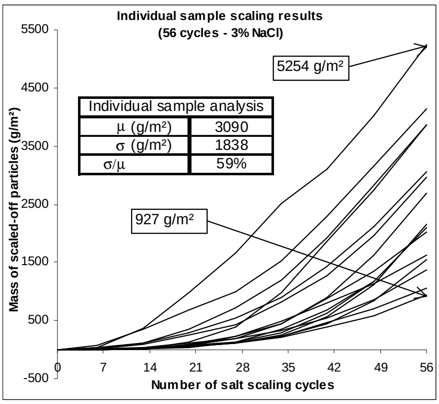

Fig. 4 24 individual samples scaling results.

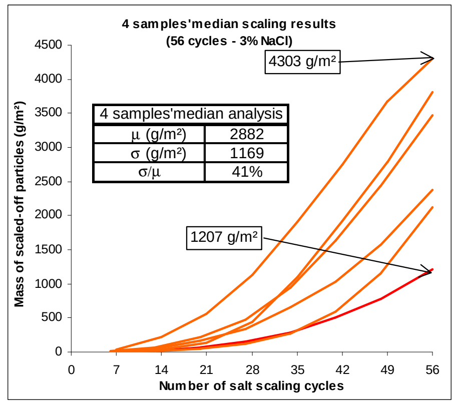

Fig. 5 Median of 4 samples scaling results.

A quantitative statistical-based analysis allows us to establish that these results follow a lognormal distribution.

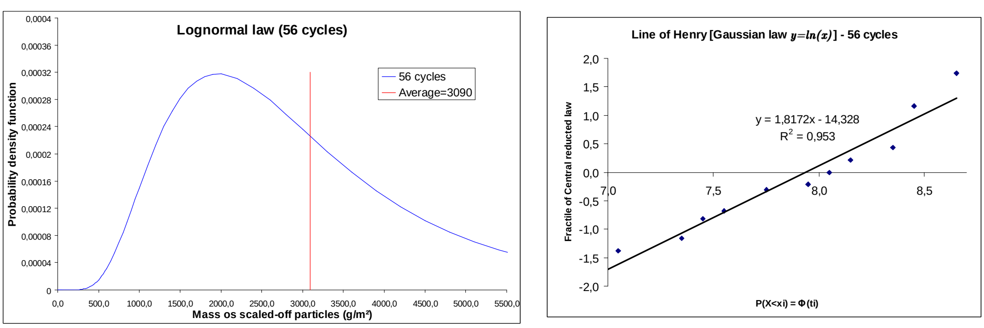

Fig. 6 Lognormal distribution law.

This distribution law correctly translates the asymmetry and the observed dispersion. In particular we can note a high number of low values and a low number of high values. The threshold value of 600 g/m² given in [6] is reached around the 27th cycle with an arithmetic mean of 616 g/m². But in the case of a lognormal distribution, the median value is the geometric mean, which is equal to 347 g/m². In this case, we can also note the 25% fractile is reached at a mass of scaled-off particles of 203 g/m² (figure n°7). If we consider that the critical value of 600 g/m² corresponds to the geometric mean, which is almost reached at 34 cycles, in this case the arithmetic mean is equal to 1132 g/m² and the 75% fractile to 1357 g/m².

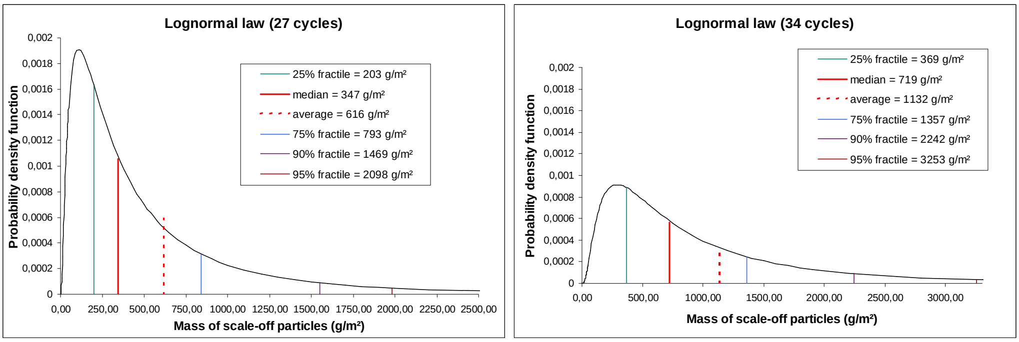

Fig. 7 Lognormal distribution laws at 27 and 34 cycles.

The XP P18-420 standard analyses the results with a median of 4 samples and with such a low number of samples, the average and the median are not notably different. Added to the dispersion of the results, it is difficult to reach a conclusion with a scaling result of 4 samples between 350 and 800 g/m².

The log-normal laws allow to evaluate the fractile above the threshold value of 600 g/m² wich is 3.6% at 13 cycles (average = 100 g/m²) and 12.8% at 20 cycles (average = 285 g/m²). Assuming for calculation a linear evolution between the 13^{th} and the 20^{th} cycle, this means that the test discriminates high resistant concrete with individual scaling values under a result of 228 g/m² (90% fractile = threshold value of 600 g/m²) or 128 g/m² (95% fractile = 600g/m²).

This threshold of 600 g/m² has been established for 4 samples median scaling result correspondingly to the XP P18-420 standard, witch can discriminate with certainty resistant concrete below 200 to 300 g/m².

4 – CHLORIDE PENETRATION

The chloride penetration front is assessed by a colorimetric procedure on the 60 samples [6] as described in figure n°8.

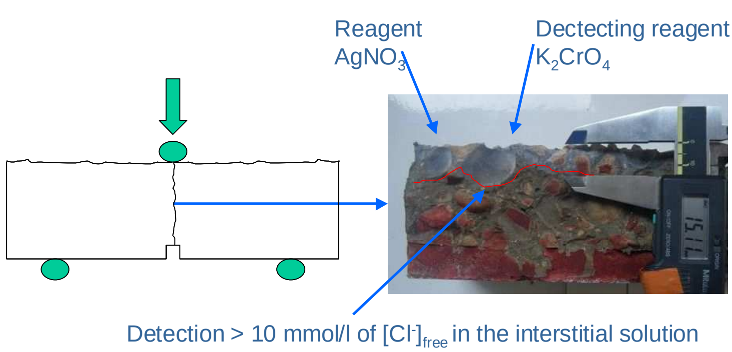

Fig. 8 Colorimetric detection of the chloride penetration front.

Some reduced surface samples were so damaged that it was not possible to obtain a threshold by the colorimetric detection of the chloride penetration front. The reduced surface samples and the samples exposed to water (0% NaCl concentration) are therefore not taken into account in this part of the study.

Time is a direct parameter for the depth of chloride penetration and the number of freeze-thaw cycles is a parameter for scaling. As the standard requires one freeze-thaw cycle per day, both the chloride penetration front and the scaling progress over time.

The NaCl dosage variation in the solution leads to relatively homogeneous chloride penetration depths.

The chloride penetration depths range from 4.3 to 15.1 mm. The average depth is 11.5 mm and the standard deviation is 27%. This high standard deviation can be due to the colorimetric procedure (weak accuracy of the reagent $AgNO_3$ and measurement method) and to the natural heterogeneity of concrete. The results are focussed on the average that shows that the depth follows a Gaussian law (analysed with the 24 samples exposed to 3% NaCl concentrated solution for 56 cycles, figure n°9).

The results are analysed by a data disjunction study (figure n°10). A weak statistical correlation exists between the chloride penetration front and the mass of scaled-off particles. Another indirect parameter can be the porosity near the sample surface.

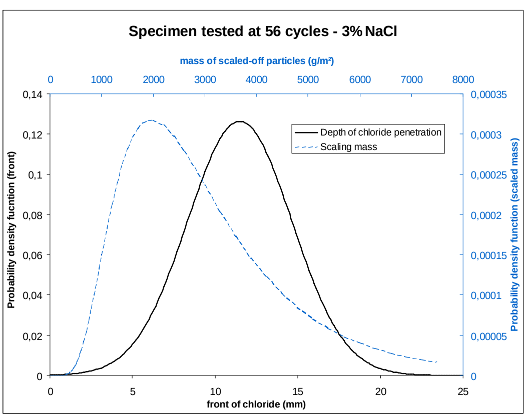

Fig. 9 Distribution laws of scaling and chloride penetration front.

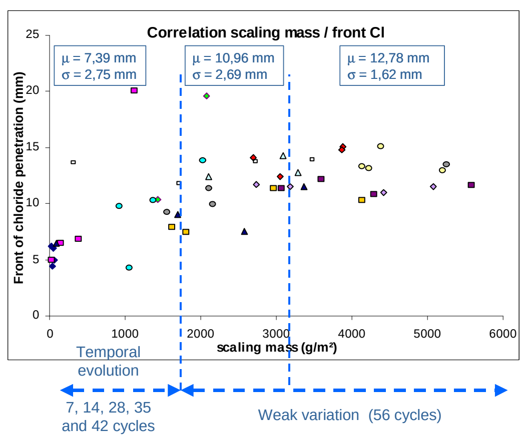

Fig. 10 Data disjunction analysis between chloride penetration front and mass of scaled-off particles.

The Gaussian law, confronted to a lognormal law, adds to the previous weak statistical correlation, and leads to the following conclusion: the scaling and the chloride penetration front are independent from a phenomenological point of view.

5 – CONCENTRATION OF THE SOLUTION

The NaCl concentration in the solution laid on the surface of the concrete sample is also a parameter in this problem [1,2]. When expressed in terms of averaged mass of scaled-off particles, our results recover the pessimum effect often described in literature as the prominent feature of scaling (figure n°11).

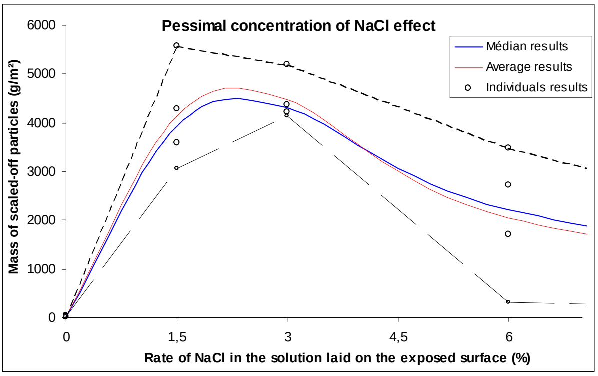

Fig. 11 Pessimum effect of NaCl concentration in the solution on mass of scaled-off particles.

6 – CONCLUSION

This experimental study provides both scaling and chloride penetration results on 60 samples of concrete with the same mix. The depth of chloride penetration has a distribution at 56 freeze-thaw cycles which follows a normal law. The scaling results are distributed according to a lognormal law with a standard deviation higher than 50%. However, with a set of 4 samples, the XP P18-420 standard remains discriminant, considering a threshold of 600 g/m². A concrete mixture that leads to a scaling median lower than 350 g/m², for 4 sample results, can be considered resistant, and above 800 g/m² it can be considered low resistant concrete.

A combined analysis reveals that scaling and the chloride penetration front are independent from a phenomenological point of view and the NaCl concentration of the solution on the exposed surface directly influences the amount of scaled mass.

But our current study raises two major questions about the pessimal chloride concentration in the outer solution: what happens to this pessimum effect if we take into account the scaling test dispersion? And is this a direct parameter or an indirect one by the chloride concentration underneath the surface of the concrete?

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