20th International Conference on Structural Mechanics in Reactor Technology (SMiRT 20)
Espoo, Finland, August 9-14, 2009
SMiRT 20-Division 1, Paper 1926

A probabilistic approach for assessing concrete degradation due to leaching

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Keywords: concrete, calcium leaching, Finite Volume Method, Ammonium Nitrate Accelerated Degradation, probabilistic approach.

1 ABSTRACT

The work presented here is the first step of a project aiming at developing a predictive model for concrete structures under leaching attack based on a probabilistic approach. For this purpose, a large experimental campaign is being carried out simultaneously with the development of a numerical modelling for leaching.

The experimental campaign follows two real building sites, thus the samples for the measures have been moulded as long as the building operation lasted. It aims at first investigating a correlation between measures performed in a laboratory (being mechanical experiments such as compressive or tensile strength or Young modulus, as well as measures of durability indicators like water porosity or Ammonium Nitrate Accelerated Degradation tests) and in situ measurements (such as electrical resistivity). The second goal of the campaign is to find out a statistical variability of characteristics of the material.

The second aspect of the study concerns the modelling of calcium leaching using the Finite Volumes Method, and is based upon the results of the above mentioned experimental campaign so as to integrate the variability of the material in the calculation of the long-term behaviour of the structure.

2 INTRODUCTION

The work presented here performed within an ANR project (the French National Agency for Research) named APPLET, a part of which aims at taking into account the variability of the material in the assessment of long-term behaviour of concrete structures. The first step of this task is to quantify this variability through a large experimental campaign led in several research laboratories in France. The concrete samples required for the experiments are provided by the Vinci Company, partner of the project. The samples are coming from two different building sites and are moulded all along the duration of the building operations. The variability of the concrete can thus be investigated in terms of variability between different batches of a same mix design and also in terms of variability between two different concrete mix designs. The first building site is a tunnel near Paris, where a high-performance concrete is used and thus supposed to have a rather low variability. The second building site is a bridge close to Compiègne, where the concrete is expected to have lower performances and more variability. Many tests are performed as described below.

The first section of the present paper describes the various tests performed in our laboratory on both concrete mixes and investigates correlations between measurements, the target objective being to assess the quality of batches of concrete regarding their characteristics which influence their long-term behaviour (durability with regards to leaching) only thanks to non-destructive tests. The second section is devoted to the integration of the measured variability of the material into the modelling of the long-term behaviour of a structure with regards to leaching. For this purpose, a Finite Volume Modelling for leaching is developed, so that probabilistic calculations taking into account the variability of the parameters of calcium diffusion can be envisaged.

3 THE APPLET EXPERIMENTAL CAMPAIGN

For each building site, 40 batches are studied, and for each of those batches 3 samples are moulded for our experiments. All samples are preserved in lime solution for at least one year. The point here is to study the variability of matured concrete. No early-age measure is performed.

3.1 Non-destructive testing

Non-destructive testing is especially attractive considering the aim of developing diagnostic methods. The non destructive tests presented here do not require encumbering devices neither very expensive equipments. They are developed in collaboration with GHYMAC Laboratory which intends to use them in situ. A correlation between in situ and laboratory results is investigated so as to validate the in situ experimental protocol. For every sample of the APPLET project, it is worth mentioning that each non-destructive measurement is carried out on the very same sample. One of the non-destructive measure is based on electrical resistivity. It is deduced from the electrical resistance of the concrete sample which is measured through two steel electrodes and two wet sponges limiting the resistance of contact between concrete and steel. Before testing, the samples are saturated with lime water which electrical conductivity has been measured. The electrical resistivity is usually considered to be related to the diffusivity and porosity of the material (cf. Snyder (2001), Lataste et al. (2003)). Correlations between electrical resistivity and other indicators of the concrete quality are widely expected.

Another non-destructive test is the measurement of the propagation velocity of the longitudinal ultrasonic waves. Two piezoelectric sensors are laid out on both sides of the sample and an oscilloscope enables to visualise the ultrasonic waves on the inner and outer sides of the sample. Ultrasonic wave velocity is linked to Young modulus and should be a relevant indicator of concrete quality (cf. Voigt et al. (2005)).

3.2 Mechanical tests

For every batch of concrete, Young modulus, compressive and splitting tensile strengths are measured. One of the three samples of the batch is dedicated to a compressive test. First, a device made of three displacement sensors is settled on the sample in order to measure the Young modulus during the elastic phase of the test. This device is then removed before the sample is loaded till failure to measure its compressive strength. The tensile strength is measured through a splitting (Brazilian) test: a cylindrical piece of material is cut into the second sample of the batch and laid out on one generatrix; the cylinder is pressed till failure and the tensile strength is calculated knowing the maximum force applied before failure and the geometry of the sample.

3.3 Porosity and degradation depth

One major parameter for durability concerns with regards to diffusion issues is the porosity of the material. A 5 cm slice of concrete is cut into the remaining part of the sample used for the splitting (Brazilian) test. The porosity is calculated on the basis of three mass measurements: two performed on the saturated slice (full atmospheric and hydrostatic weight) and one performed on the dried slice (105°C in a furnace till constant mass).

The third and last sample of each batch is devoted to a leaching test. Leaching is a degradation process that may occur when concrete is exposed to waters which are not in chemical equilibrium with concrete pore water. It induces dissolution of the solid phase and thus, increases the porosity of the material. Consequently, the diffusion within the material is faster. Leaching usually presents a very slow kinetic and one of the most common way to accelerate it is to use ammonium nitrate solution (cf. Lea (1965), Goncalves et al. (1991), Carde (1996), Tognazzi (1998), Le Bellego (2001), Perlot (2005)). Solubility of portlandite increases significantly (from 21 mmol/L to 2,7 mol/L for a concentration of 6 mol/L of ammonium nitrate), which accelerates the degradation kinetic at least by a factor 100.

The concrete samples are exposed to leaching in a 6 mol/L solution of ammonium nitrate. At fixed dates, samples are taken out from the vat, sawn, and phenolphthalein is used to reveal the degradation depth. The rest of the sample is brought back to the leaching bath. Phenolphthalein is a pH-indicator which becomes pink on the sound area of the sample, where the ammonium nitrate did not turn the initial basic pH of the concrete into values lower than 9. The so-coloured face is then scanned and the degradation depth is digitally measured.

3.4 Results

Table 1 summarises all the results acquired until now for the concrete mix design of the first building operation studied in the APPLET project: electrical resistivity $_{elec}$, velocity of ultrasonic waves C_{long}, apparent density mass $_{dry}$, porosity , degradation depth after 28 days of leaching d_{28}, 56 days d_{56}, 98 days d_{98}, compressive strength F_c, tensile strength F_t and Young modulus E. For each result, Table 1 indicates the number of samples tested, the mean value, the standard deviation and the associated coefficient of variation. Table 2 presents the same results for the second building site, for which the concrete is expected to have rather lower characteristics.

Up to now, only few samples were tested because of the long curing time in lime water. However, it may be underlined that concerning electrical resistivity, our results (mean value, standard deviation and coefficient of variation) are absolutely identical to the ones obtained by GHYMAC Laboratory in Bordeaux, associated with the APPLET project.

Table 1. Variability of the measures acquired until now for the first concrete mix (A1).

Measurement	Number of tests	Mean value	Standard deviation	Coefficient of Variation [%]
$_{elec}$ [.m]	119	352,28	53,39	15,16
C_{long} [m/s]	31	5462,3	226,97	4,16
$_{dry}$ [g/cm^3]	40	2,25	0,08	3,51
[%]	40	12,87	1,02	7,92
d_{28} [mm]	32	3,83	0,58	15,02
d_{56} [mm]	16	5,26	0,5	9,53
d_{98} [mm]	40	8,83	1,48	16,78
F_c [MPa]	16	85,7	8,1	9,51
F_t [MPa]	15	4,5	0,47	10,45
E [GPa]	16	45,3	2,5	5,44

Table 2. Variability of the measures acquired until now for the second concrete mix (A2).

Measurement	Number of tests	Mean value	Standard deviation	Coefficient of Variation [%]
$_{elec}$ [.m]	72	519,01	151,46	29,18
C_{long} [m/s]	16	5163,2	178,69	3,46
$_{dry}$ [g/cm^3]	16	2,26	0,03	1,31
[%]	16	14,63	1,31	8,93
d_{28} [mm]	16	4,61	0,41	8,86
d_{56} [mm]	16	7,02	0,52	7,38
d_{98} [mm]	8	9,74	0,93	9,56

As expected, the concrete from the second building site has a higher porosity and a lower velocity of ultrasonic waves (its stiffness is also expected to reach lower values but could not have been measured yet). One can observe too that the degradation depth after leaching in ammonium nitrate solution is more significant (which can be related to the higher porosity). Indeed, porosity and degradation depth are obviously correlated when comparing the materials, but the values are too close to one another between the batches of a same concrete mix design. The standard deviations for the test of accelerated leaching are to be considered with caution due to the fact that, because of the experimental set up, all samples do not have the same temperature history and the very same conditions of chemical aggression (pH of the ammonium nitrate solution for instance).

A surprising result at this stage of the study is that no obvious correlation can be pointed out between porosity and electrical resistivity or between Young modulus and ultrasonic waves velocity while shown in previous studies (Snyder (2001), Lataste et al. (2003), Voigt et al. (2005)). This absence of obvious correlation is also observed in the other laboratories associated with the APPLET project.

However, electrical resitivity seems to provide, for a given concrete mix, a reliable information with regards to the resistance to a leaching attack, but the values are not to be compared for different materials (in other words: for different concrete mixes). This can be explained by the high dependency of the electrical resistivity on the chemical constitution of the porous solution, which itself depends on the formulation of the concrete and on the material that were used (cement, aggregrates, admixtures, mineral additives).

It may be expected that more results shall induce some correlations. At least, one can infer that the variability of results that will be observed on the second building site will allow to define, for each concrete and every quantity studied here, an acceptable interval of values so that any odd value measured, for instance, by a continuous electrical resistivity survey of the batches, would immediately be noticed.

4 MODELLING LEACHING WITH A FINITE VOLUME SCHEME

4.1 The Finite Volume Scheme applied to the non-linear equations of leaching

A review of the literature (Adenot (1992), Tognazzi (1998)) shows that the different calcium-based minerals in cement pastes dissolve successively beginning with portlandite, followed by C-S-H and ettringite. The degraded depth in the leached cement paste is defined as the zone where portlandite is dissolved (the dissolution front is very sharp). The porosity increases a lot within this zone due to this dissolution phenomenon. Moreover, the dissolution kinetic of solid calcium phases is much faster than the diffusion process. Considering that the dissolution is immediate and that only calcium species are to be taken into account, the leaching of a cement paste can be described, as proposed in Buil at al. (1992), with the mass balance equation of calcium (1), where C_{Ca} is the calcium concentration in the porous solution, ϕ is the porosity, D_{Ca} is the apparent diffusivity of calcium through the porous medium, S_{Ca} is the solid calcium concentration and $\mu^{Ca}{}_{S\ \ L}$ is the exchange rate between the liquid and solid phases of calcium.

$$\frac{\partial(C_{Ca}\phi)}{\partial t} = -div(-D_{Ca}(\phi)grad(C_{Ca})) + \mu^{Ca}_{S\to L} \qquad (1)$$

$$\frac{\partial S_{Ca}}{\partial t} = -\mu^{Ca}_{S\to L}$$

The non-linearity of the former equation is due to the diffusivity which depends on the porosity, itself depending on the solid calcium concentration. The numerical solution of this equation has already been attempted through Finite Difference Method (Moskowicz et al. (1996)) and Finite Element Method (Celia et al. (1990)), but the Finite Volume Method seems to be more suitable for such a non-linear problem (Eymard et al. (1998)). A Finite Volume scheme has thus been chosen to pursue our study as proposed in (Mainguy et al. (2000)). Figure 1 shows an acceptable mesh for a Finite Volume scheme adapted for a one-dimensional axisymmetric simulation. The center of the sample is in x_0 where the flux of calcium is set to 0 (because of symmetry). On the opposite face of the mesh, the liquid calcium concentration is set constant and equal to 0. At the beginning of the simulation, the material is considered to be completely sound and the liquid calcium concentration in the pore solution is set to 21 mmol/L for a simulation of water leaching, while it is set to 2730 mmol/L in case of accelerated degradation with ammonium nitrate solution (which stands for the increased solubility of the portlandite).

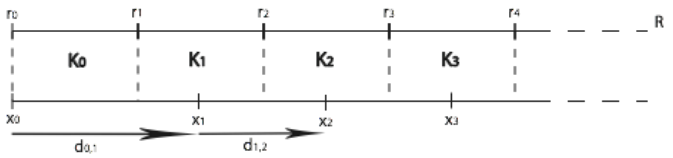


Figure 1. The Finite Volume mesh from the center of the sample to its external face.

Considering the chemical laws of local equilibrium between the concentrations of liquid and solid calcium, every quantity can be derived from the concentration of solid calcium, which reduces the problem to a single variable. Figure 2 shows experimental data of this equilibrium for water without ammonium nitrate and the calculation results obtained with the adopted model to fit it.

A similar approach has been adopted concerning the calcium diffusivity through the porous medium of the cement paste, which has been related to the porosity with the use of an empirical law (cf. equation 2). This law introduces two parameters identified from experimental data (cf. Tognazzi (1998)): D_0 is a kind of an initial diffusivity chosen equal to $2{,}355.10^{-13}$ m^2/s and k is a dimensionless parameter to account for the influence of porosity and set to 9,95. Figure 3 shows that the adopted model fits very well with Tognazzi's data (cf. Tognazzi (1998)).

$$D = D_0 \, e^{k\phi} \tag{2}$$

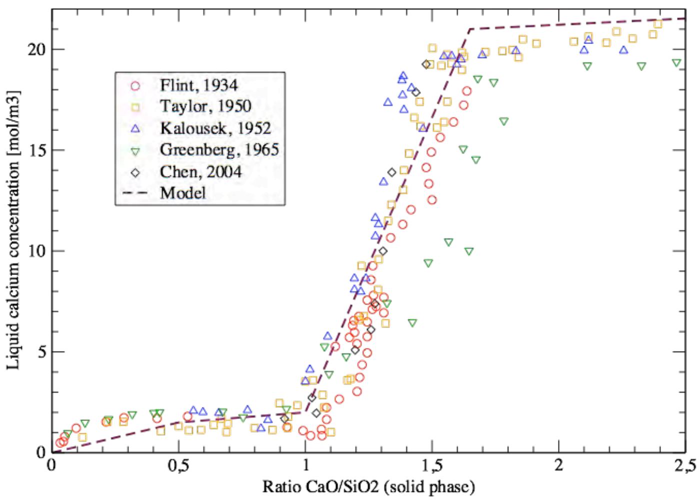


Figure 2. Equilibrium between the calcium in solid phase and the ionic calcium in the pore solution: comparison between experimental data and chosen model results (after Berner (1990)).

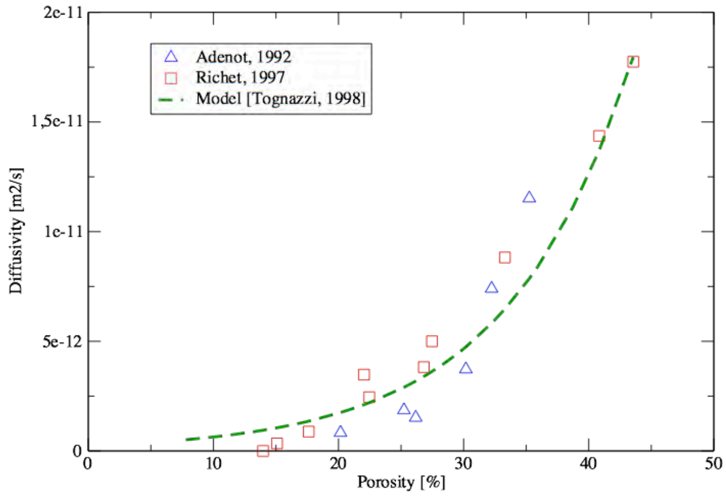


Figure 3. Relation between the apparent diffusivity and porosity. Comparison of the chosen model with experimental data on sound pastes (after Tognazzi (1998)).

4.2 Numerical simulations of the leaching of cement paste, mortar and concrete

In a first step, we have compared our modelling with experimental data relative to leaching of cement paste from the literature: Adenot (1992) for leaching in pure water and Tognazzi (1998) and Nguyen et al. (2007) for accelerated leaching in a 6-mol ammonium nitrate solution. In both cases, the numerical simulations are in good accordance with experimental data. The proportionality of the degradation depth to the square root of time is also retrieved.

Figure 4 shows the results sensibility to a refinement of the mesh, in terms of solid calcium concentration profile in a sample exposed to ammonium nitrate solution. In our tests, only the position of the degradation front is measured and thus, a 40 volumes mesh appears accurate enough for our concern. More refined meshes improve the shape of the calcium profile but require longer computational times, 25 times longer for a 100 volumes mesh and 125 times longer for a 200 volumes mesh. Simulations have then been performed on mortar samples and compared to the experimental data from Tognazzi (1998) and Nguyen et al. (2007) with the same consistent fit.

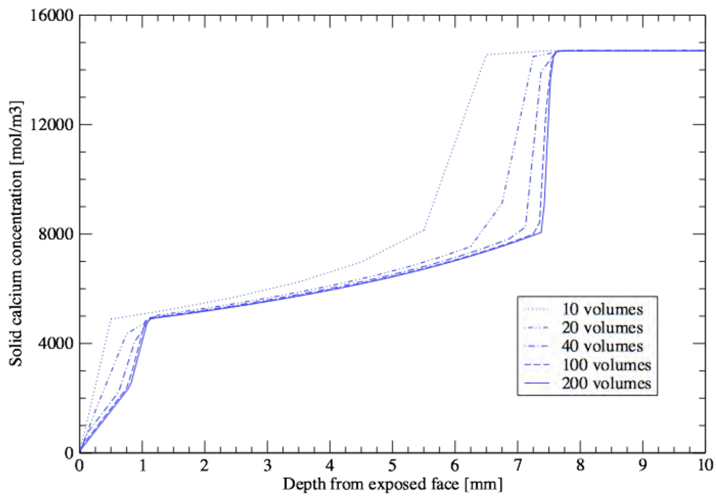
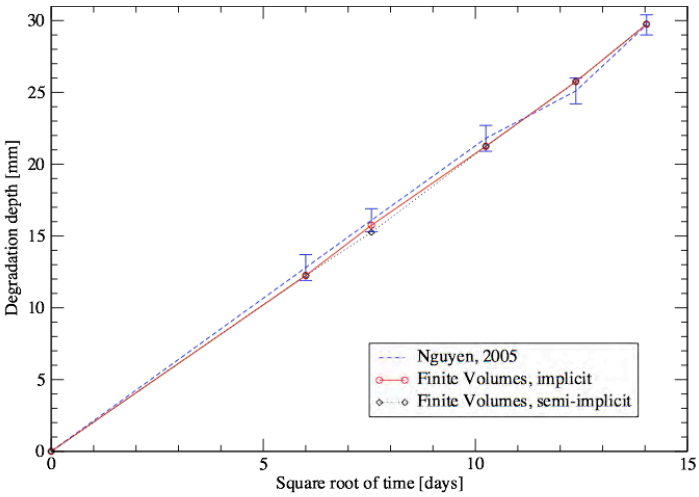


Figure 4. Influence of the mesh refinement over the calcium profile after 18 days of leaching on a cement paste sample (profile plotted from the exposed face of the sample to its center).

The next step concerns the simulations of concrete sample in ammonium nitrate 6M solution tests. When considering concrete instead of bulk cement paste, one assumes that only the cement paste participates to the leaching process and gives place to diffusion through its porosity. Moreover, on the one hand aggregates leads to a tortuosity which reduces the global kinetic of diffusion but on the other hand, they create around them Interfacial Transition Zones of higher porosity which have exactly the opposite effect. In order to take these additional phenomena into account, the empirical law linking diffusivity to porosity (cf. equation 2) has to be improved (cf. equation 3). Two new parameters are introduced: $f_{p/m}$ is the voluminal proportion of cement paste with reference to mortar, and   is the tortuosity (cf. Nguyen et al. (2006)) which accounts for the two antagonist phenomena related to aggregates mentioned above. The voluminal proportion of mortar with reference to concrete is also used to express the global porosity in relation with the solid calcium concentration.

$$D = \tau f_{p/m} D_0 e^{k\phi} \tag{3}$$

Figure 5 shows a comparison between experimental data from Nguyen et al. (2007) and simulations for a leaching test performed on a concrete sample. Two numerical schemes were tested. A completely implicit scheme was tested first and the results were very satisfactory. A semi-implicit scheme was tested then, in which only the diffusivity was explicitly expressed (meaning that at the time step t_n, the diffusivity $D(t_n)$ was used instead of $D(t_{n+1})$ in the totally implicit scheme). The profit in computing time was so little that it was



decided to keep the fully implicit scheme, which is more accurate.

Figure 5. Leaching of a concrete sample: comparison of experimental data from Nguyen (2005) with the results of numerical simulation with a complete implicit scheme and a semi-implicit scheme.

4.3 Parametric study on the Finite Volume Model

A parametric study was achieved so as to determine which parameters of the model should focus the attention and be the object of the identification process. Among these parameters, three of them are devoted only to the expression of the diffusivity (cf. equations (2) and (3)): D_0, k and   (named "Tau" in Figure 6). Two other parameters are related to the formulation of the concrete: the voluminal proportion of paste with regard to mortar $f_{p/m}$ and the voluminal proportion of mortar with regard to concrete $f_{m/c}$. The two last parameters are multiplier factors applied to the models adopted for the equilibrium of the phases of calcium in the porous medium (cf. figure 2) and for the porosity with regard to solid calcium concentration: X_{SCa} and X_{phi}, as they appear in figure 6. These two parameters are to be related to the quality of the cement paste and the nature of the cement used in the concrete mix.

Figure 6 represents the Pearson product-moment correlation coefficient calculated for all the 7 parameters mentioned above, with regard to the degradation depth at the experimental terms for the accelerated leaching test (28, 56, 98 and 210 days). The Pearson correlation coefficient is a well-known indicator of the linear correlation between two parameters. To achieve this study, more than 200 parameters set were generated thanks to a simulated annealing algorithm to complete a Latin Hypercube sampling. The interval for each parameter was determined after the values found in literature for materials equivalent to the concrete mixes tested in the APPLET project.

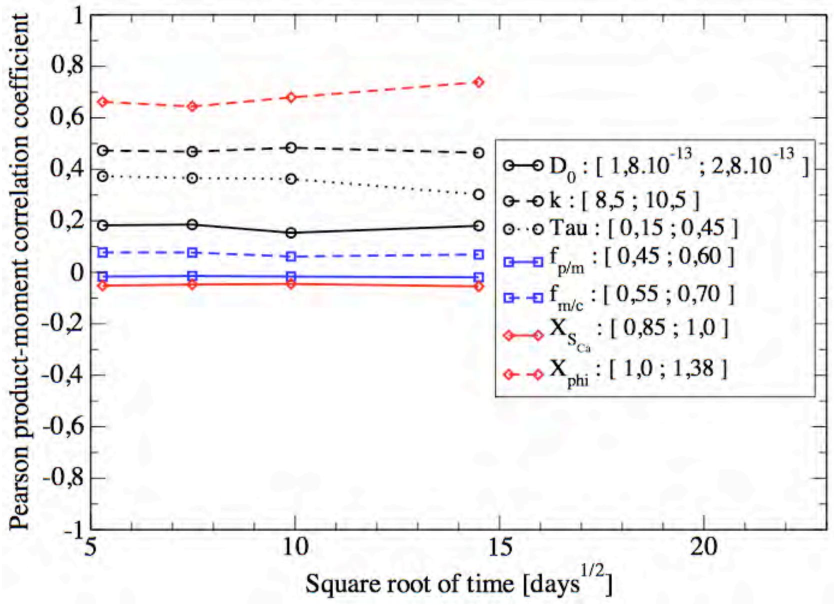


Figure 6. Sensitivity evolution for a test of accelerated leaching in ammonium nitrate solution (the intervals of variation for each parameter appear between brackets).

Figure 6 shows that the most influential parameter is the porosity deduced from the solid calcium concentration. Then come the parameters of the diffusivity: k and the tortuosity . One should keep in mind that porosity appears not only in the mass balance equation of calcium but also in the expression of the calcium diffusivity (cf. equation(3)), which explains why the Pearson coefficient for X_{phi} is so important. The large influence of the parameters of diffusion on the degradation depth is related to the hypothesis of the local chemical equilibrium and the fact that the kinetics of the leaching process is mainly conditioned by the diffusion phenomenon. It can also be noticed that the influence of the parameters remains approximatively constant during the duration of the test.

5 CONCLUSIONS AND PERSPECTIVES

A large experimental campaign is in progress in order to quantify the variability of some characteristic of concrete expected to be representative of both its mechanical behaviour and abilities in terms of durability. The durability issue is addressed through ammonium nitrate accelerated degradation tests. On the same time, an original modelling for leaching has been developed with a particular attention paid on limiting the computing times. Based on a Finite Volume Scheme, it provides satisfactory results and is now validated on experimental data. This modelling will be used for an inverse analysis approach aiming at identifying the parameters of non-linear diffusion. Later, Monte-Carlo simulations will be carried out to quantify the influence of the variability of those parameters and other values on the long-term behaviour of a concrete structure.

Acknowledgements. *The authors would like to thank IRSN and ANR for their financial support.*

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