Coupling between leaching and creep of concrete

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ABSTRACT: In a radioactive waste disposal, concrete containment structures must ensure the load-bearing capacity over extended periods. During its lifetime, concrete is also degraded by calcium leaching due to on-site water. An experimental investigation is described where the effects of an accelerated calcium leaching process of concrete on creep of concrete are highlighted. The comparison with a creep test where the sample is immersed in water shows that leaching generates tertiary creep and rupture of the specimen. A Dirichlet series coupled to a mechanical damage are used to model the coupled tertiary creep. With this method we can evaluate the lifetime of concrete structures subjected to chemical and mechanical loading.

1 INTRODUCTION

The lifetime of radioactive waste storage structures must reach values of an order of magnitude one or more times greater than those of conventional civil engineering structures. This means that degradation phenomena normally only considered very rarely have to be taken into account. Leaching of calcium contained in concretes by water from the surrounding rock is one such case. This phenomenon leads to considerable change in the microstructure taking the form of increased porosity (Adenot, 92) and degradation of mechanical properties (Carde *et al*, 96), (Gérard, 96), (Torrenti *et al*, 99), (Ulm *et al*, 99), (Ulm *et al*, 2003). Leaching is also closely coupled with mechanics (Gérard, 96), (Torrenti *et al*, 99), (Ulm *et al*, 99), (Heukamp *et al*, 2003), (Kuhl *et al*, 2004), (Nguyen, 2005), (Nicolosi, 2005) and influences the delayed behavior of concrete (Lacarriere & Sellier, 2005). In the first section we will show that if leaching occurs under a sustained load, creep leads to ruin of the material. We will then propose an analysis aiming to evaluate the lifetime of structures submitted to creep and leaching.

2 EXPERIMENTAL RESULTS

2.1 *Concrete formulation*

The concrete studies is defined in Table 1. Its aggregates are siliceous and therefore resistant to leaching. Our samples are cylinders 11 cm in diameter and 33 cm high. These samples were removed from their mould the day after their manufacture and kept in water for 9 months. They were then ground to obtain good surface flatness before loading.

Table 1. Formulation of the concrete studied

components	quantity (kg/m3)
Sand siliceous	684
Gravel siliceous	1050
Cement	375
Water	225

2.2 *Leaching*

Natural leaching is a very slow process (a few centimetres per hundred years). For laboratory experiments, the use of deionised water is not an optimum choice for concrete for which we need several centimetres of degradation. Accelerated leaching is necessary to leach the samples in a reasonable time. There are three principal ways to accelerate calcium leaching: using temperature (Kamali, 2003), using an electrical field (Saito *et al*, 1992; Gérard, 1996) and by replacing deionized water with a different solution agent to increase concentration gradients between the interstitial solution and the aggressive environment. The majority of the experiments on calcium leaching of cementitious material samples are performed by using the last method. The deionized water is replaced by a strongly concentrated ammonium nitrate solution, (Goncalves, Rodrigues, 1991; Carde *et al*, 1996, 1997; Gérard, 1996; Tognazzi, 1998; Le Bellégo, 2001; Ulm *et al*, 2003; Kamali 2003). Here, we use an ammonium nitrate solution at a concentration of 6 mol/l. It has been shown that the attack of this solution is close to that of deionised water, but with kinetics roughly 200 times faster (Carde *et al*, 96), (Gérard, 96), (Tognazzi, 98), (Torrenti *et al*, 99), (Kamali *et al*, 2003).

Leaching is accompanied over time by the propagation of the degradation front corresponding to the dissolving of portlandite. The degraded depth is determined by using the phenolphthalein on sectioned samples. The pH value in the pore solution of cementitious materials is higher than 12.5, creating a very alkaline environment. Consequently, an ammonium nitrate solution with pH values below this level characterises the acid environment.

We can use the pH indicator like phenolphthalein to distinguish between the sound zone and the degraded zone. Phenolphthalein turns from colourless in acidic solutions to pink in basic solutions with the transition occurring around pH 9. But the dissolution of portlandite occurs as long as the pH values drop below 12. Therefore, phenolphthalein does not give the exact position of the dissolution front of portlandite. However, by comparison between the measurement by phenolphthalein and by SIMS microprobe analysis, (Le Bellégo, 2001) has shown that for the cement paste the total degraded depth e_t can be determined by correcting the degraded depth e_{phenol} measured by phenolphthalein.

Monitoring of this front over time shows evolution in proportion to the square root of time until it reaches the center of the sample (Figure 1). This result is characteristic of diffusive phenomena and has been observed by many authors (Adenot, 92), (Carde *et al*, 96), (Gérard, 96), (Tognazzi, 98), (Torrenti *et al*, 99), (Kamali *et al*, 2003) and corroborated by theoretical considerations (Mainguy *et al*, 2000).

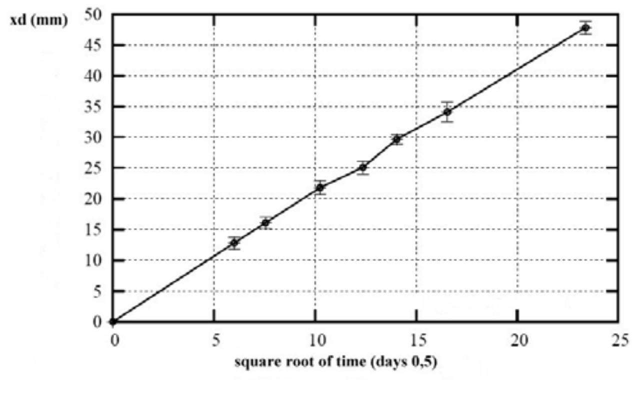

Figure 1. Evolution of degraded depth over time : $x_d = k\ t^{0.5}$ where x_d is the degraded depth expressed in mm and t is time in days. This relation was established through testing without mechanical load (Nguyen, 2005).

2.3 *Leaching under load*

2.3.1 *Description of tests*

Two creep test frames were used. Each has a particular function:

- one frame is used for a control basic creep test in water,

- the other is used for the creep test with leaching by ammonium nitrate at 6 mol/l and allows combined chemical and mechanical effects to be observed.

An experiment setup was specially designed for these tests. Firstly the test pieces were surrounded by plastic cylindrical recipients containing liquids (water or the ammonium nitrate solution). Impermeable seals were fitted to prevent any leakage. Secondly, the parts outside the recipients were covered with a silicon resin and plastic film to prevent extraneous diffusion into the test pieces or drying. Figure 2 shows the ammonium nitrate test bench.

The test principle consists in compressing the concrete test piece between the plates of the creep frame at a constant force over a long duration.

The force applied is kept constant using a nitrogen-oil oleopneumatic accumulator (see Figure 2). The load is applied by a flat jack fed with oil by a hand pump. The force aimed for is 25% of the resistance of the test piece, i.e. roughly 10 MPa. First the oleopneumatic accumulators are inflated using a nitrogen cylinder at a pressure equal to 80% of the required oil pressure. The test pieces are then installed on the creep test frames, and the recipient is filled with ammonium nitrate. Another large recipient is used to renew the ammonium nitrate (see Figure 2) so that the pH remains sufficient for leaching. Whenever the pH reaches 8.2, the solution is renewed. An electrode and thermal probe are installed to monitor the pH and temperature of the solution. Movement between the plates is measured by an LVDT movement sensor. All the systems are connected to a computer for data acquisition. Finally, the load is applied to the test piece by increasing the flat jack pressure with the hand pump. The oil pressure is monitored by a pressure sensor. The oil in the oleopneumatic tank is then connected to the oil in the flat jack and the nitrogen tank compensates to a large extent the effect on the oil pressure caused by deformation.

The force applied to the test piece is verified by lifting off the upper load cell. This is done at set times to check the constancy of the force applied. If there are losses, oil is added to compensate for them. In our test, the lift-off force F is 105 kN, corresponding to mean stress of 10.5 MPa.

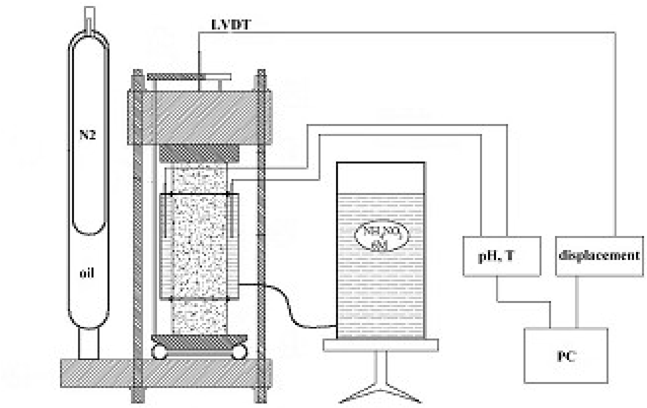

Figure 2: Diagram of the test bench for creep combined with leaching.

2.3.2 *Test results*

Figure 3 shows the evolution of deformation for both tests Initially there is very little difference between the two tests. Then deformation in the combined test accelerates to reach a tertiary creep phase leading to ruin. This demonstrates the effect of creep combined with leaching. Similar results have been obtained with concrete containing calcareous aggregates (Lacarriere *et* Sellier, 2005).

The test was interrupted after 435 days and a cross-section of the leached test piece was made. The leached area could then be revealed using the colored indicator phenolphtalein. As this indicator does not reveal the exact position of the degradation front a correction factor must be applied (Le Bellego *et al*, 2001). The mean degraded depth determined by experiment is therefore 29 mm.

This corresponds to k=1,4 mm $d^{-0,5}$ and can be compared with the degraded front one obtains without mechanical loading for t = 435 days: 44 mm. We have a difference that can be explained by two ways:

- there is a coupling between diffusivity and the stress state of the leached material. Nicolosi (2006) has shown that a coupling between the chemical process and the mechanical behavior is possible through the effect of the interstitial pressure. But his results indicate a small influence;
- in spite of the pH control, the boundary conditions for leaching in the creep test are not exactly the same compared to the leaching test without mechanical load. A lower renewal of the solution around the sample may explain a lower degradation.

We think the second possibility is the more likely because the degraded depth was variable around the sample but another test would certainly be useful.

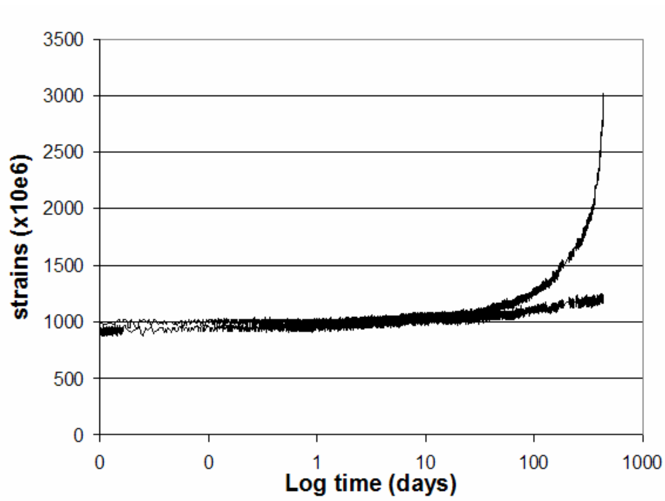

Figure 3: Creep strain under water and in the ammonium nitrate solution.

3 MODELING

3.1 *Modeling creep - Dirichlet series development*

We use a description in the form of a Dirichlet series to model the concrete creep (Bazant and Chern, 85), (Granger, 95):

$$\varepsilon_{fl}(t)=\sum_{s=1}^{n}\int_{\tau=0}^{t} J_s\left[1-\exp(-t/\tau_s)\right]\dot{\sigma}(\tau)d\tau \qquad (1)$$

Breaking down the creep strain ε^{fl} on the basis of $\{1, \exp(-t/\tau_i)_{i=1,n}\}$ produces (Granger, 95):

$$\varepsilon_{fl}(t_i)=A_0^i+\sum_{s=1}^{n} A_s^i \qquad (2)$$

Knowing the creep strain ε^{fl} (t_i) at time t_i makes it possible through recurrence to construct the response to time t_{i+1}, ε^{fl} (t_{i+1}):

$$A_0^{i+1}=A_0^i+\Delta\sigma(t_{i+1})\sum_{s=1}^{n} J_s(t_{i+1}) \qquad (3)$$

$$A_s^{i+1}=A_s^i\exp\left(-\frac{t_{i+1}-t_i}{\tau_s}\right)-\Delta\sigma(t_{i+1})\,J_s(t_{i+1})\exp\left(-\frac{t_{i+1}-t_i}{\tau_s}\right) \qquad (4)$$

All that is required therefore is to store the n+1 A_j at each time step. The functions $J_s(t_i)$ should enable the various effects to be taken into account, particularly the ageing of concrete or, in the problem concerning us, the effect of leaching. The effect of ageing will not be taken into account in what follows. Figure 4 presents the adjustment to the Dirichlet series for the creep itself (Figure 3).

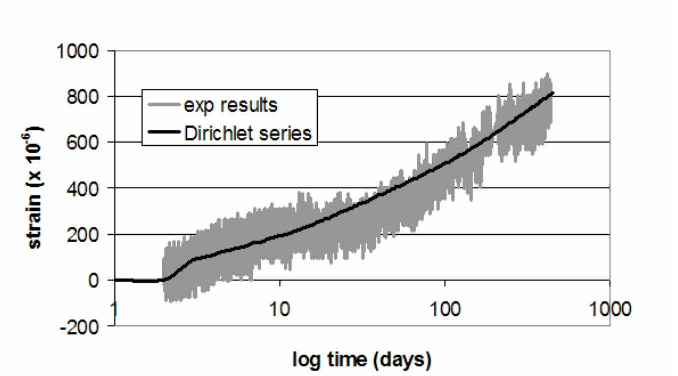

Figure 4 : adjustment of the Dirichlet series to the basic creep of concrete - n=7; t1=0,002 d; t2=0,02 d; t3=0,2 d; t4=2 d; t5=20 d; t6=200 d; t7=2000 d; J_0=1/36.2 GPa^{-1}; J_1=1/800 GPa^{-1}; J_2=1/800 GPa^{-1}; J_3=1/400 GPa^{-1}; J_4=1/200 GPa^{-1}; J_5=1/50 GPa^{-1}; J_6=1/25 GPa^{-1}; J_7=1/17 GPa^{-1}.

3.2 *Tertiary creep*

When a concrete specimen is subjected to a creep test and the stress applied exceeds approximately 80% of the material strength, we know since (Rüsch *et al*, 58) that ultimately the material ruptures. This phenomenon is called tertiary creep and relates to strong interaction between the creep and the damage to the materials (Bazant *et a*l, 97).
This coupling can be taken into account by means of a visco-elasto-plastic (Bertholler *et al*, 2004). Here, following an idea suggested by various authors but applied to Maxwell chain models (Omar et al, 2004), (Cervera *et al*., 99), the coupling with the damage is taken into account by assuming that all the terms of the Dirichlet series are affected by scalar damage d(t). Relationships 3 and 4 are maintained with:

$$J_0(t_i)=J_0/(1-d(t_i)) \text{ and } J_s(t_i)=J_s/(1-d(t_i)) \qquad (5)$$

Changes in the damage are as proposed by (Mazars, 84). The threshold function is as follows:

$$f(\tilde{\varepsilon},d)=\tilde{\varepsilon}-K(d) \qquad (6)$$

with K a damage parameter, equal to the maximum value reached by the equivalent strain $\tilde{\varepsilon}$ during the loading history, with an initial value equal to K_0. The equivalent strain is defined by:

$$\tilde{\varepsilon}=\sqrt{\sum\langle\varepsilon_i\rangle_+^2} \qquad (7)$$

where $\langle\varepsilon_i\rangle_+=0$ if $\varepsilon_i < 0$ and $\langle\varepsilon_i\rangle_+=\varepsilon_i$ if $\varepsilon_i > 0$. Following an idea suggested by (Omar *et al*, 2004) and (Mazotti *et* Savoia, 2003) we define ε_i as being the sum of the instantaneous extensions and a fraction of the delayed extensions:

$$\varepsilon_i = \varepsilon_{i\_inst} + \beta\, \varepsilon_{i\_fl} \qquad (8)$$

β being an adjustment coefficient. Figure 5 presents the creep deformation simulations obtained with the model adjusted to Figure 4 coupled with the damage, the additional hypotheses being: the creep Poisson coefficient is assumed equal to 0.2, value of the instantaneous Poisson coefficient and β=0.05. Note that the delayed strain ε_{del} includes also the variable part of the instantaneous strain (because it is so in the experimental measurement):

$$\varepsilon_{del}(t)=\varepsilon_{fl}(t)+J_0(t)\sigma(t)-J_0(t=t_0)\sigma(t=t_0) \qquad (9)$$

where t_0 is the time when loading is applied.

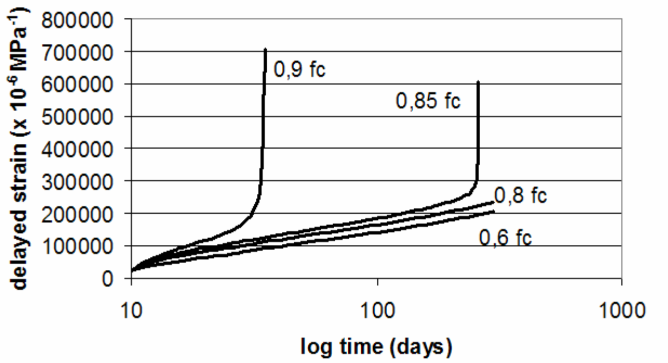

Figure 5 : evolution of the delayed strains divided by the applied stress when this stress is varying from 0.2 fc to 0.9 fc. The parameters of the Dirichlet series are those of figure 4. For the damage model Ac=1.5, Bc=1500, K_0=120 10^{-6} (Mazars, 84).

3.3 *Creep coupled with leaching*

For the instantaneous part of the model we have the classical relation:

$$\sigma_{ij} = (1-d)\, \Lambda_{ijkl}\, \varepsilon_{kl} \qquad (10)$$

with $(1-d)=(1-d_{ch})\,(1-d_m)$ (11)

as proposed by (Gérard, 96) and where d_{ch} is the chemical damage and d_m is the mechanical damage.

In our case, stress taken up by the degraded area is ignored. This is a realistic hypothesis as the degraded area can only take up a limited fraction of the initial resistance and it can be assumed that the creep of the degraded area is faster than that of the sound area. The consequence is d_{ch} does not influence the results and that J_s are constant.

Assuming the degraded depth is the experimental mean degraded depth (k=1,4 mm $d^{-0,5}$); it is possible to calculate at each time step the stress $\sigma(t_i)$ which is applied to the sound part of the concrete:

$$\sigma(t_i) = \sigma(t_0)\frac{\pi R}{\pi\,(R-k\sqrt{t_i})} \qquad (12)$$

Using the model developed in paragraph 2.2, it is possible to calculate the delayed strains of the specimen which is leached (equation 9). The calculation is halted when damage d reaches 1. Figure 6 shows the result. The estimation of the service life is correct. We therefore have a simplified method of forecasting compressive loaded structures subject to leaching over long periods

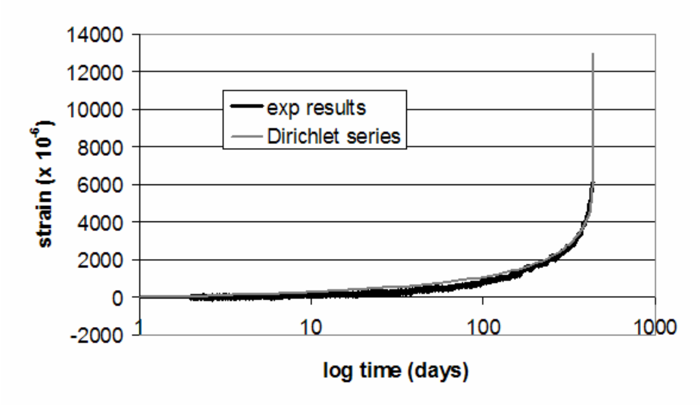

Figure 6 : creep test under leaching - comparison between experimental results and modeling. The parameters of the Dirichlet series are those of figure 4 and the parameters of the damage model are those of figure 5.

4 CONCLUSIONS

Experimental results show there is a coupling between creep and leaching. The deformation in the combined test accelerates to reach a tertiary creep phase leading to the ruin of concrete. Using a Dirichlet series for creep coupled with a scalar damage we are able to reproduce this phenomenon and to predict the service life of concrete structures subjected to a sustained compressive loading and to leaching.

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