Unifying Autogeneous and Drying Shrinkage of Cement Paste by the use of
Isothermal Sorption/Desorption Curves

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Abstract

Since the beginning of his work on cement paste, T.C. Powers used isothermal water sorption experiments as a basis for all his reflections. The main outcome of such a reasoning is of course his hydration model. Starting from cement chemistry and water/cement ratio, one can evaluate the different volumic fractions (gel, capillary pores, ...) of the cement paste as a function of the hydration rate.

Nowadays, the mechanics of porous media allow a new interpretation of these curves. As far as you are convinced that capillarity is the main driven force of the cement paste hydraulic behaviour, a key characteristic for structural applications such as shrinkage can be deduced from it. Being able to build it from simple parameters could be really interesting.

We illustrate in this paper how to combine Powers' work with the modified BET theory to achieve this goal. Then we will use this building process to compute both autogenous and drying shrinkage in a unified way, that even allows us to study a possible coupling between the two.

1. Introduction

We often find two distinct approaches when dealing with cementitious materials shrinkage in the literature. One aiming at modeling the so-called autogeneous shrinkage. And the other dealing with the drying shrinkage. Cement mineralogy and w/c ratio will be the major parameters for the former, w/c ratio the major parameter for the latter. Equations and coefficients will then be determined based on experimental data, but will of course roughly depend on it: are we working on cement paste, concrete, mortar, etc. Shortly said, we have equations that work well on the data used for fitting their parameters.

The amazing thing with that distinction is that the mechanisms of these 2 shrinkages are nearly the same: a gaz phase appears in the previously saturated porous medium. This porous medium then shrinks but in a granular skeleton, the whole process driving the hydric behavior of concrete.

This paper explains how we managed to describe both autogeneous and drying shrinkage using a common theoretical approach, i.e. a combination of porous mechanics and micromechanics. This allowed us to derive a general model that evaluates the impact of the concrete mix-design on its shrinkage.

2. Modeling concrete shrinkage

2.1. The paste content

As water leaves the material, capillary tensions are generated. The resultant is a deformation of the material: shrinkage. One speaks about drying shrinkage when the water departure is done towards the environment and of autogenous shrinkage when the water departure is caused by hydration. However in a concrete (i.e. a mix of aggregates and paste), only the paste is subjected to this water departure.

This simple observation brings out a first assumption that allows to evaluate the drying shrinkage of our materials:

$$\varepsilon_{concrete} = \varepsilon_{paste} \cdot f_{paste} \qquad \textit{(Eq. 1)}$$

Written in this form, equation 1 is in fact only the rewriting of the Reuss hypothesis, the aggregates shrinkage being neglected. Many authors published around a more complex relation [1,2,5,6,8,9,10] resulting from calculations of homogenization [11,12].

$$\varepsilon_{concrete} = \varepsilon_{paste} \cdot f_{paste}^{\alpha} \qquad \textit{(Eq. 2)}$$

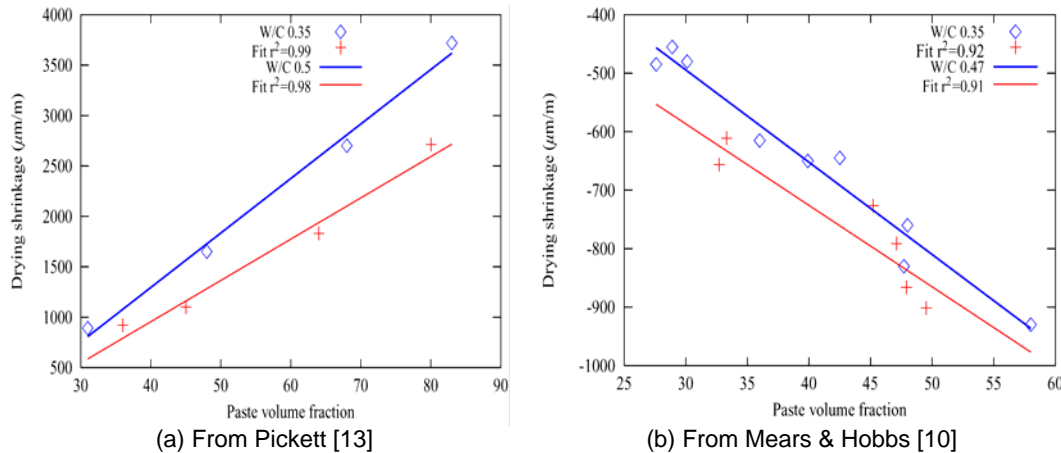(a) From Pickett [13]   (b) From Mears & Hobbs [10]

Fig. 1 Relation between drying shrinkage and paste content

Nevertheless, Hansen [7] showed that it could, in practice, be brought back to equation 1, exponent α being justified only for very high paste contents. Thus, considering Pickett's data [13], for a paste volume ranging between 30% and 80%, the granular skeleton and the composition of the paste remaining identical, the drying shrinkage of the mortar or concrete is actually proportional to the paste volume (cf. Fig. 1(a)). Mears and Hobbs [10] took again the same type of tests but wanted to maintain a constant workability whatever the proportioning in paste. They were thus brought, while preserving a constant D_{max}, to adjust the grading curve. According to Figure 1(b), this small modification already degrades the results quality: on the basis of Pickett's data, the correlation coefficient is almost 1, whereas with those of Mears and Hobbs, it is only 0.9.

Earlier, Carlson [4] had emphasized the limits of this approach: in the particular case of a mortar formulated with a restricted granular grading (4.75-9.5mm), the ratio between the paste shrinkage and that of the mortar are two times higher than the ratio of the paste volumes (cf. Table 1).

Aggregates volumic fraction	Shrinkage measured at 2 years (µm/m)	Shrinkage calculated using Eq. 1 (µm/m)
0	3500	
56 %	725	1540

Table 1 – Shrinkage of mortars using single sized aggregates (w/c = 0.4)

At this point, an immediate conclusion can be drawn: the granular phase plays a considerable role in the expression of shrinkage. A simple volume ratio does not translate this role. It is therefore essential to better describe what a granular skeleton is.

2.2. The granular skeleton

The first value which characterizes the aggregates is of course their size and in particular the maximum size D_{max}. Carlson [4] produced on this subject an interesting work. In order to focus on the effect of the aggregates size, he tested mortars using tightened granulometries that follow the progression of the ASTM sieves. Such mixtures thus approach the ideal monogranular case (cf. Fig. 2).
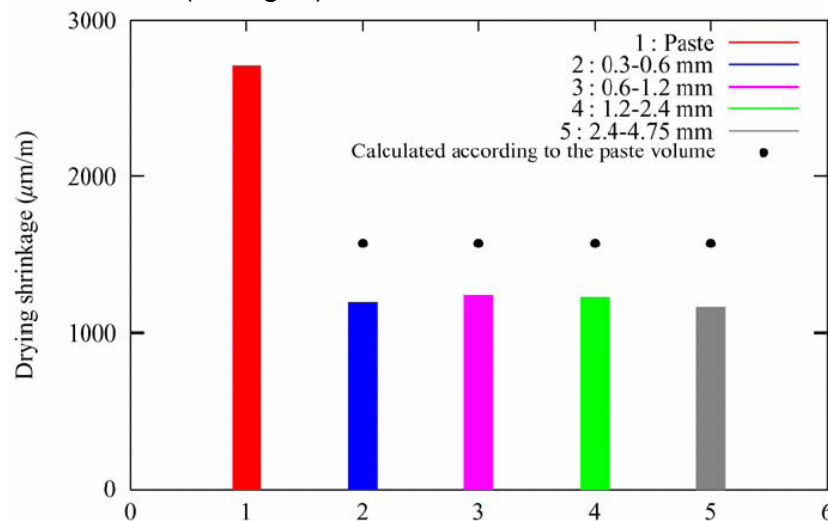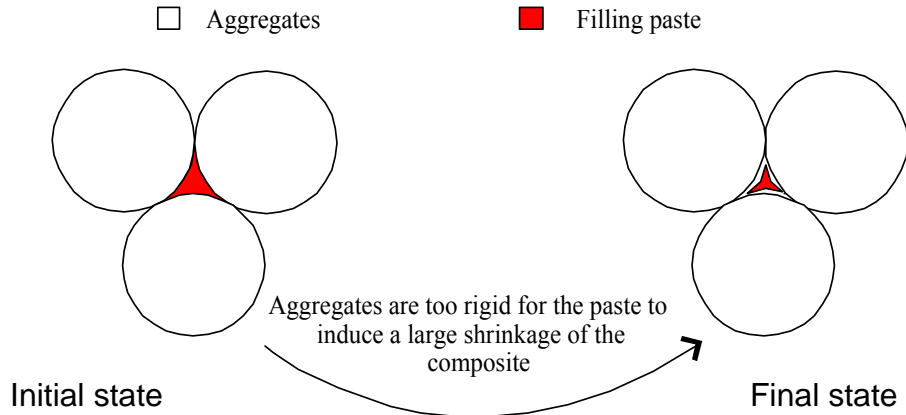

Fig. 2 - Influence of the aggregates size on the drying shrinkage (measurement at 1 year, W/C=0.4)

These measurements lead to two major remarks. Firstly, once again, the shrinkage does not evolve proportionally to the paste volume fraction: if such were the case, the measured value on mortar should be close to 1600µm/m, which is 30% higher than those obtained in the experiments. Secondly, the aggregate size does not seem to influence the free drying shrinkage of the material.
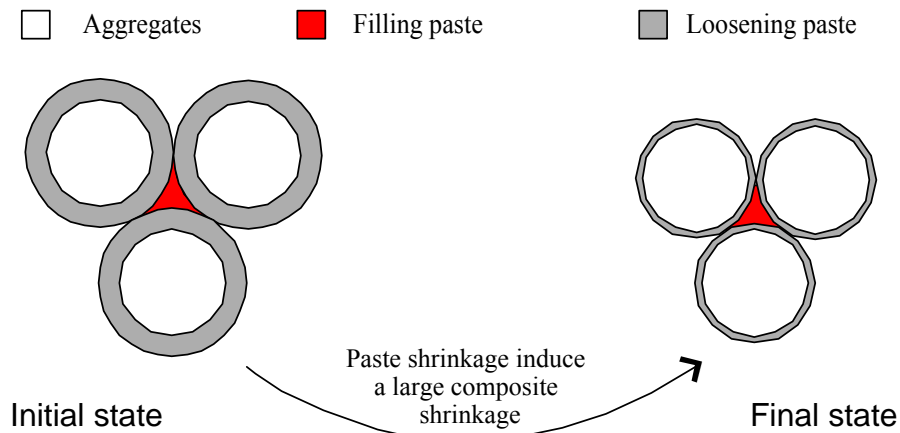
To better understand what occurs, we start again from a simple remark: a mixture of sand and gravel constitute a porous "solid". One can then speak about porosity of the granular skeleton (and its complement, compacity), concept which becomes essential when this solid is mixed with paste. Indeed, if the paste volume introduced is lower than the porosity of the granular skeleton, the grains will remain in contact with one another (cf. Fig. 3).

☐ Aggregates   ■ Filling paste

Aggregates are too rigid for the paste to induce a large shrinkage of the composite

Initial state   Final state

Fig. 3 – Compact granular skeleton

Since their rigidity is four times higher than that of the paste, one can easily understand that such an arrangement will exhibit a quasi negligible shrinkage. A limiting volume below which the paste does not affect the composite behavior then exists.

Now, if the paste volume introduced is higher than the porosity of the skeleton, the surplus of paste *will loosen* the grains, giving them a degree of freedom between each other (cf. Fig. 4).

☐ Aggregates   ■ Filling paste   ▨ Loosening paste

Paste shrinkage induce a large composite shrinkage

Initial state   Final state

Fig. 4 – Loosen granular skeleton

As a result, the composite shrinkage will rapidly increase with the loosening paste volume (the surplus of paste compared to the porosity of the granular skeleton). However this porosity depends on D_{max}, but also on d_{min}, i.e. actually on the granular distribution of the sand/gravel mixture. For

an optimal mixture, we can, using the Caquot's equation [3], calculate this porosity according to the d_{min} and the D_{max}:

$$p = 0.47 \times \frac{d_{min}}{D_{max}} \text{ with } \begin{array}{l} d_{min} = d_{10\% \text{ passing}} \\ D_{max} = D_{90\% \text{passing}} \end{array} \qquad \text{(Eq. 3)}$$

R. Leroy first described this distinction in volume [15]. He took into account the granular skeleton and its grading by using a 3 phases micromechanical model. He obtained better agreement between calculated and measured properties than with the Reuss hypothesis. Besides, he could then account for aggregates variations, what was impossible without distinguishing the 2 paste volumes.

We thus choose to use a similar morphological description. The micromechanical model is the generalized n-layer phase model from Hervé and Zaoui [14]. Its outputs are the elastic modulus of the homogenized medium, and its deformation due to cement paste shrinkages. We made the assumption that aggregates are surrounded by a constant thickness of paste.
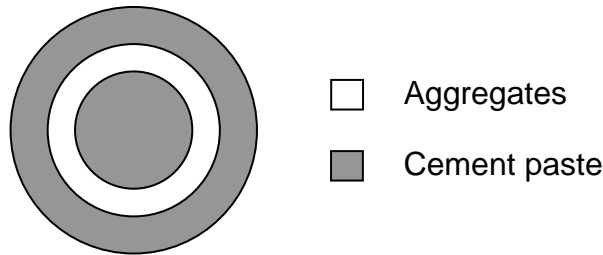

□ Aggregates

▪ Cement paste

Fig. 5 – The n-layered spherical inclusion embedded in an infinite matrix

Going back to experimental results, we tried to use this micromechanical model to derive concrete drying shrinkage from its equivalent mortar drying shrinkage (same w/c ratio, cured for 7 days at 20°C/100% RH). Fig. 6 confirms that Eq. 1 is not adapted when the particule size distribution of aggregates changes.
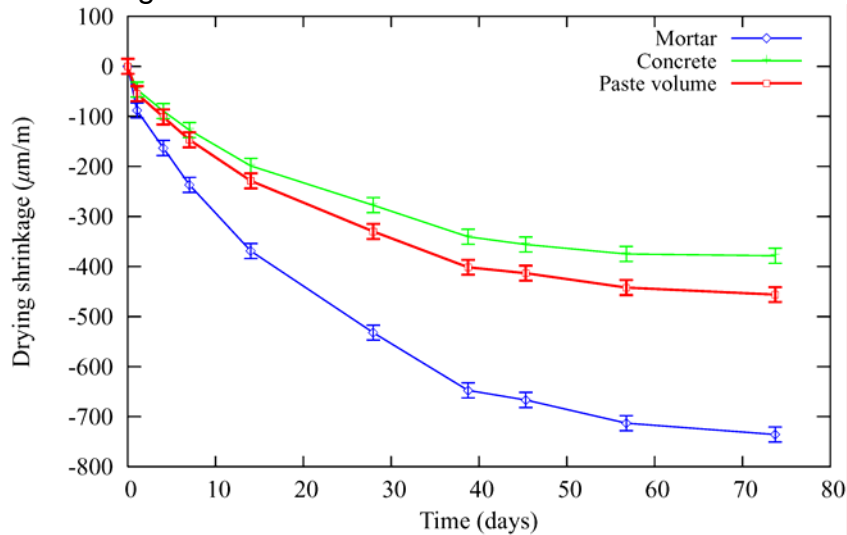

Fig. 6 - Going from mortar to concrete using Eq. 1

But using our 3 phases model gives a perfect agreement between measured and calculated values (cf. Fig. 7). The only input are the gradings of the different aggregates.
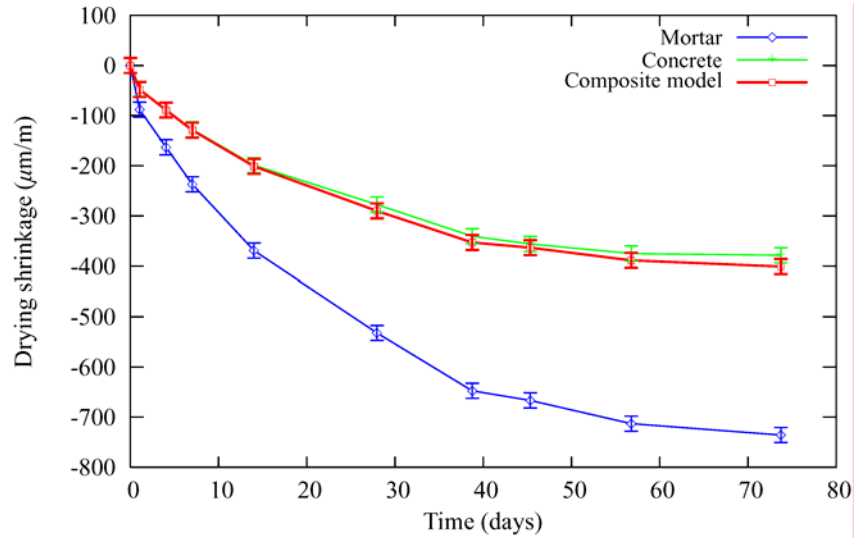

Fig. 7 - Going from mortar to concrete using our 3 phases model

At this point, we have a valid concrete shrinkage model, but you still have to measure cement paste shrinkage for using it. If this can be considered as feasible for the drying shrinkage, dealing with autogeneous shrinkage would be far more complicated: the restraint of aggregates is influence by the cement paste elastic properties. We thus need more than an autogeneous shrinkage curve.

3. Modeling paste shrinkage

We first have to better describe what we call "paste". First we have an heterogeneous medium made of anhydrous cement, hydrates, water, etc. If we consider a well matured paste, we will have to quantify the different volumic fractions. But if we want to include autogeneous shrinkage in our modeling process, we will also have to quantify both the volumic fractions of the different phases and their evolution due to chemical reactions. Shortly said, we need an *hydration model*. Then we have to consider that cement paste is a porous medium. To evaluate its deformation behavior, we need a stress-strain relation for that medium.

What first comes to mind to address the second point is the Laplace-Kelvin equation.

$$p_c = \frac{-RT\rho_{sl}}{M}.\ln(h) = \frac{2\gamma\cos\theta}{r} \quad \text{with } r\text{: pore radius, } \rho_{sl}\text{: water specific mass} \qquad (Eq.\ 4)$$

The main drawback of this relation is that we model the pore scale. Generalizing Eq. 4 at the paste scale implies that we are able to measure precisely the pore size distribution of the cement paste. Given that this point is still subject to strong debates in the literature, we chose to use exactly

the opposite way [21]. Why not describing the phenomenas using macro-scopic tools?

[16,17] first illustrated how to bypass this difficulty using porous mechanics and isothermal sorption/desorption curves. The isothermal sorp-tion/desorption curve is a direct macroscopic translation of the microscopic behavior. It gives you the relation between saturation degree and the rela-tive humidity. Once you have it, the porous mechanics allow you to estab-lish a stress-strain relation:

$$d\sigma = K_0.d\varepsilon + S_l dp_c - dp_g \qquad \text{(Eq. 5)}$$

with p_c: capillary pressure,
        S_l: saturation degree,
        p_g: gaz pressure,
        K_0 : compressibility modulus of the solid

In our particular case, we can assume that:
        $p_g = p_{atm}$,
        $d\sigma = 0$ (no external stress applied),
        cement paste is an isotropic material.

This leads to a relation between free deformation, i.e. shrinkage, and satu-ration degree / relative humidity which can be integrated using the sorp-tion/desorption curve:

$$d\varepsilon_{lin} = \frac{d\varepsilon}{3} = \frac{\rho_l.R.T}{3K_0 M_v}.\frac{S_l}{h}dh \qquad \text{(Eq. 6)}$$

So all we have to know are the sorption/desorption curve and the elastic properties of the cement paste (K_0 in Eq. 6). For drying shrinkage, there is no particular issue (apart from the time needed to generate these data). But for the autogeneous shrinkage, a massive quantity of data is required to capture the impact of chemical reactions.

We decided to bypass this problem by modeling these characteristics. First, the sorption curve can be described using a BET equation [18]:

$$W = \frac{C.k.V_m.h}{(1 - k.h)(1 + (C - 1).k.h)} \qquad \text{(Eq. 7)}$$

with $C = \exp\left(\dfrac{C_0}{T}\right)$ constant relative to adsorption heat $(C_0 = 855$ et $T(K))$

        h: relative humidity.

We have 2 constants to determine in Eq. 7: V_m and k. We thus need to identify 2 specific points on the sorption curve to solve the underlying equations. The use is to distinguish 2 domains in these curves. The low relative humidity domain, typically less than 30-40%, where water is only adsorbed on hydrates surface, and the high relative humidity domain

where condensed capillary water is added to the previous one [20]. We then decide to identify 3 specific points on the sorption/desorption curve (cf. Fig. 8):
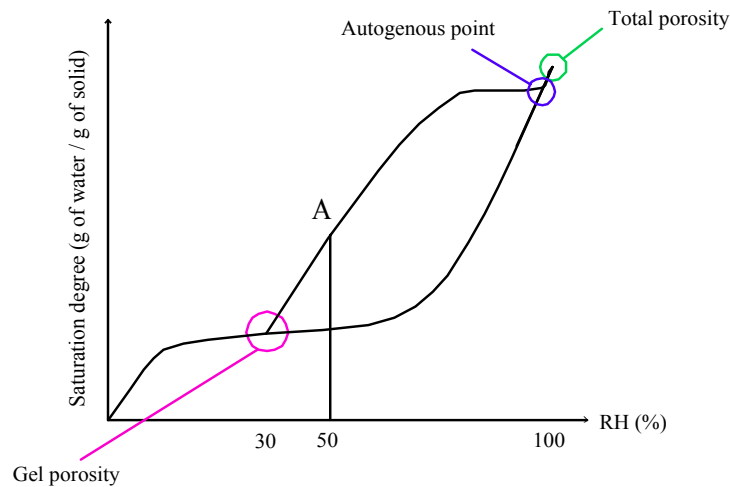

Fig. 8 - Schematic description of a sorption/desorption curve

- *Fully saturated point* (RH=1): this characterize the total porosity,
- Gel point (RH=30%): characterize the low relative humidity domain and is directly related to the surface area developed by hydrates.
- *Autogeneous point*: Hydrates occupy less space than the initial products (Le Chatelier contraction). As the cement paste hydrates, a new pore space is created, in which water will be adsorbed. This will cause a "chemical" desaturation.

Powers built a complete hydration model using this type of curves. It gives simple relations between hydration and volumic fractions of the different phases [19]. The following equations are the commonly used ones. But one can find more specific relations in Powers work, especially coefficients taking cement mineralogy into account [19].

- Hydrates gel:
$$\frac{0.68\,m}{(w/c)+0.32}$$ *(Eq. 8)*

- Anhydrous cement:
$$\frac{(1-m)\,0.32}{(w/c)+0.32}$$ *(Eq. 9)*

- Gel pores:
$$\frac{0.19\,m}{(w/c)+0.32}$$ *(Eq. 10)*

- Capillary pores:
$$\frac{(w/c)-0.36\,m}{(w/c)+0.32}$$ *(Eq. 11)*

- Empty capillary pores:
$$\frac{0.0575\,m}{(w/c)+0.32}$$ *(Eq. 12)*

Summing equations 10 and 11 gives us the fully saturated point.

$$w_{sat} = Eq.10 + Eq.11 \qquad\qquad (Eq.\ 13)$$

Now we have to convert Eq. 8 which gives the gel volumic fraction in a quantity of water adsorbed on the gel to get the gel point. We thus need two more characteristics: the surface area developed by the hydrates, and the thickness of the water film adsorbed on it, i.e. a t-plot curve. Eq. 14 is the generally accepted relation giving access to this thickness:

$$t(RH) = 3.95 - 1.89\ln(-\ln(RH)) \quad \text{with RH in \% and t(RH) in Å} \qquad (Eq.\ 14)$$

V. Baroghel-Bouny [18] and H. Jennings [22] made several estimations of the gel surface area using different techniques. What comes out of their results is that we have to distinguish 2 kinds of hydrates (inner/outer CSH, or high density/low density CSH). They differ both in density and specific surface area. As a first approach we used Jennings' relation to evaluate the proportion of each kind of hydrates (Eq. 15) [22].

$$f_{outer} = 0.706\frac{w}{c} + 0.131 \ ; \ f_{inner} = 1 - f_{outer} \qquad\qquad (Eq.\ 15)$$

with the following physical properties:
- outer C-S-H : $\qquad\qquad$ $SS_{outer} = 250 \ m^2/g$ $\qquad$ $\rho_{outer} = 2.1 \ g/cm^3$
- inner C-S-H : $\qquad\qquad$ $SS_{inner} = 450 \ m^2/g$ $\qquad$ $\rho_{inner} = 2.5 \ g/cm^3$

Finally, the gel point can be defined as:

$$w_{gel} = t(HR).f_{gel}.(\ f_{outer}.SS_{outer} + f_{inner}.SS_{inner}\ ) \qquad\qquad (Eq.\ 16)$$

and the autogeneous point as:

$$w_{endo} = w_{sat} - Eq.12 \qquad\qquad (Eq.\ 17)$$

At this point we can use Eq. 13 and Eq. 16 to determine V_m and k, and consequently the sorption curve as a function of the cement paste composition and its maturity. The autogeneous shrinkage can then be calculated using Eq. 18.

$$d\varepsilon(_j) = \int_{HR(t_{j-1})}^{HR(t_j)} K \times \frac{w}{h}dh \quad \text{for } \alpha(t_j) \qquad\qquad (Eq.\ 18)$$

with $\quad$ t_j:time,
$\qquad$ α: maturity.

Unfortunately, we could not find a lot of information in the literature concerning desorption, which is interesting for modeling drying shrinkage [19]. We thus chose to use a very rough estimation of this curve using a polynomial interpolation based on the previously defined points. Shortly said, we managed to get a correct shape out of an interpolation. Desorption is then a function of the paste mix-design and hydration state, even if its modeling is not perfect.

4. The complete model

Being confident in our composite model, we can combine it with the modeling of the paste shrinkage described in previous section. This combination gives us a concrete shrinkage model that only needs the initial composition as input parameter. We compared the E-modulus as well as the autogeneous shrinkage of 5 concrete mixes:

- C40 : 400 kg cement, 215 l water
- C60 : 400 kg cement, 50 kg filler, 176 l water
- C80 : 450 kg cement, 50 kg filler, 158 l water

The results are shown in tables 2 & 3.

Concrete	E-modulus exp. (MPa)	E-modulus calc. (MPa)	Error (%)
C40	32	33	5.6
C60	41	40	-2.4
C80	44	43	-2.3

Table 2- Modeling the concrete E-modulus

Concrete	Exp. autogeneous shrinkage (μm/m)	Calc. autogeneous shrinkage (μm/m)	Error (%)	Exp. Error (%)
C40	83	67	-19	± 18
C60	110	95	-13	± 13
C80	142	144	1.4	± 10

Table 3 - Modeling the autogeneous shrinkage at 28 days

We also ran some drying shrinkage tests on mortars containing different paste volumes, and with a varying w/b ratio. These tests were performed at 20°C/50% RH. The only input was the mix-design of the different mortars. Table 4 shows the comparison between measured values and calculated ones.

W/B	Paste volume (l)	Exp. Drying shrinkage (μm/m)	Calc. Drying shrinkage (μm/m)	Error (%)	Exp. Error (%)
0.46	475	749	723	+3.5	± 5.5
0.375	475	601	698	+16	± 10
0.55	475	862	908	-5	± 5
0.419	445	633	583	+8	± 4.5
0.506	445	763	723	+5	± 5
0.419	505	727	854	-17	± 7
0.55	505	850	950	-12	± 15

Table 4 - Drying shrinkage tests on various mortars. Comparison with our modeling

In all these examples, the agreement between calculated values and measured ones is good, and pretty close to experimental precision (sometimes better).

5. Conclusion

We derived a generic model to simulate the impact of the mix-design on both autogeneous and drying shrinkage of concrete. These 2 shrinkages are modeled using a unique theoretical approach that is a composite model and porous mechanics. The only input parameters are those related to the mix-design: cement, water and aggregates content, aggregates particules size distribution, cement mineralogy. This leads to a very powerfull tool applicable to all kind of mix without fitting parameters. Simulating coupling between hydration processes and drying becomes straightforward.

Of course, there is still some work left. What is presented here is based on linear poro-elasticity. We know that creep is important especially at early ages if we want to derive stresses. Aggregates are modeled as spheres. Maybe a more generic shape such as ellipsoids could be added.

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