Laboratory of Construction Materials

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Chemical Shrinkage by dilatometry

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How it works:

Cement reacts with water to produce hydrates. For instance, alite, the main phase of PC (Portland Cement) according to the following reaction:

$$C_3S + H \longrightarrow C - S - H + CH$$

As the reactions goes on water is thus consumed, in other words**: the water consumption is a measure of the hydration kinetics.**

The setup is straightforward as you can see on the figure 1.

Fig. 1 (a) a chemical shrinkage bath filled with 72 tubes, (b) a single tube + rubber cap + pipette + paraffin film of an LC3 cement.

What can we get …

❑ Comparison of the reactivity of different cements over large period of time (months / years)

By contrast with calorimetry you can still measure with accuracy hydration beyond one month. However this measure is only qualitative unless you take notice of what you cannot get from this technique. By qualitative is meant that you can order / set a hierarchy of the reactivity of different binders. By quantitative is meant that you can measure the Degree of Hydration (DoH) as it is done for example by XRD.

❑ Useful for computing the autogeneous shrinkage

As the chemical shrinkage should be removed from the total shrinkage

❑ Cheap and easy to run

Thermal bath, a glass tube, a pipette, a rubber cap, paraffin film and distilled water… that's it !

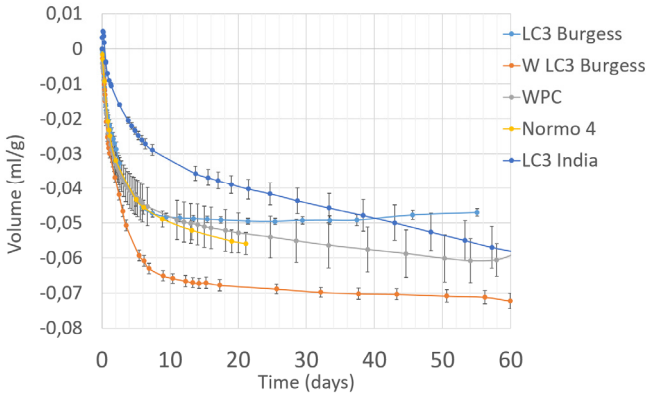

Fig. 2 Chemical shrinkage of different LC3 binders

… what we CANNOT get !

❑ You CANNOT hope to be quantitative if you work at w/c lower than 0,5

Even if numerous studies have been done at lower w/c, experiments in our lab and by Mette Geiker [1] clearly show that the permeability of the paste is a critical issue. At w/c lower than 0,5, the pore network depercolates after a few days: as a consequence the measured chemical shrinkage is dramatically impacted by the sample thickness (see figure 2). In other words: the measured signal is a combination of the actual chemical shrinkage and the permeability of the paste; there is no easy way to uncouple one from the other.

❑ You CANNOT hope to be quantitative without 4 replicates at least and a control system

Replicates are required to calculate error bars, error bars are critical to test whether two cement are statistically different (as cements DoH are always within 10% at 28d you do need short enough error bars to separate them). Also tubes have 5% of failure rates within 6 months so that there is an expected 19% probability that one out of 4 samples fails within that time; you would then be left with three replicates which is a minimum to compute a standard deviation.

Note that error bars increase dramatically at lower thicknesses (see figure 3 left): even more replicates are needed.

Control systems (just water) are required for low thickness samples as the rubber cap slowly creep with time (see figure 4). Two control systems are generally enough.

❑ You CANNOT compare to calorimetry…directly

Chemical shrinkage samples are saturated whereas calorimetry ones are not. To compare both, you need to run a calorimetry experiment with the same sample thickness and in saturated conditions.

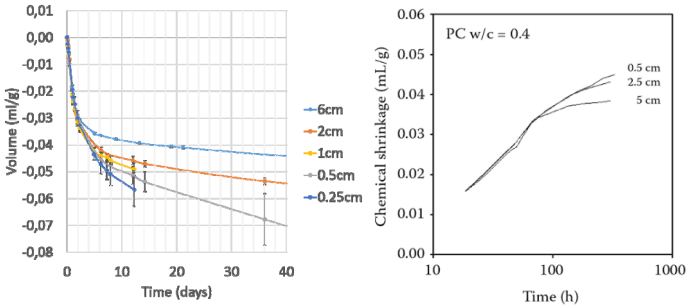

Fig. 3 Impact of the sample thickness on the measured chemical shrinkage (OPC at w/c = 0,4 left and right). Left: experiment made in our lab. It shows than even at 0,5 cm thickness there is still a permeability effect as the 0,25 cm curve separates from the 0,5 cm at 7 days. Right: Mette Geiker's experiment [1].

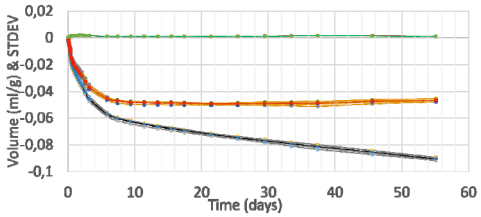

Fig. 4 Comparison of the output signal when the control system is accounted for (orange curves) or not (grey curves) for a LC3 – 50 with Burgess clay and *only 0,5 cm thick sample*. Clearly, to have no control system lead to the wrong conclusion that this binder still reacts significanly after 28 days.

Bottom line: To be quantitative, use at least w/c = 0,5 (ideally use the bleeding limit of your cement), use four replicates and two control systems. Otherwise you will only be qualitative: you will only be able to hierarchize different cement reactivities.

Notes * Room MXG230, alexandre.ouzia@epfl.ch
a: See more fundamentals in Ch.3 of "*A Practical Guide to Microstructural Analysis of Cementitious Materials*",

References
[1] Geiker, M., and T. Knudsen (1982). 'Chemical shrinkage of Portland cement pastes', *Cement and Concrete Research 12(5):603-610*