NEW INSIGHTS ON MECHANISMS CONTROLLING KINETICS AND IMPLICATIONS FOR PORE STRUCTURE

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1 INTRODUCTION

The study of reaction kinetics has focused mainly on the induction and acceleration period. From a practical point of view the slowdown of the reaction after about 10 hours and the continuing reaction to 28 days and beyond are also of great importance, but have received relatively little attention. The strength roughly quadruples between one and 28 days, while the degree of hydration only increases from around 50 to 80%. In this paper we present recent results from proton NMR which indicate dramatic changes in the characteristics of C-S-H formed around a few days [1]. These results indicate that some revision of the classical ideas about the types of porosity in cement paste is needed.

This revised picture of porosity highlights the difficulties in developing microstructural models to simulate cement paste microstructure.

Despite these difficulties microstructural models can be used to estimate paste permeabilities by the Lattice Boltzmann approach. These studies suggest that the diverse range of values found in the literature may be accounted for by small changed in the degree of saturation of the samples.

2 PROTON NMR MEASUREMENTS

Proton NMR is a powerful technique as it uses water, an intrinsic part of the structure of cement paste, as a probe. This means that the structure can be characterized without any particular sample preparation (e.g. drying) and that many measurements can be obtained from the same sample during the course of hydration. This technique has been used to study the evolution of pore structure for some years (as reviewed in 2), but only recently has a methodology been developed to quantify all the water present. This means that the amounts of water in different locations can be identified unambiguously and combined with mas and volume balance equations to derive the composition and density of the C-S-H phase. The details of this methodology are presented in [1, 3]. During hydration the water is partitioned into four clear locations:
1. "Crystalline" bound water in calcium hydroxide and aluminate containing phases (e.g. ettringite)
2. Water between sheets of C-S-H
3. Water in the "gel" pore of C-S-H
4. Water in capillary pores
Figure 1 from [1] shows the evolution of these different populations over time for a sealed sample of white cement paste at a water to cement ratio of 0.4.
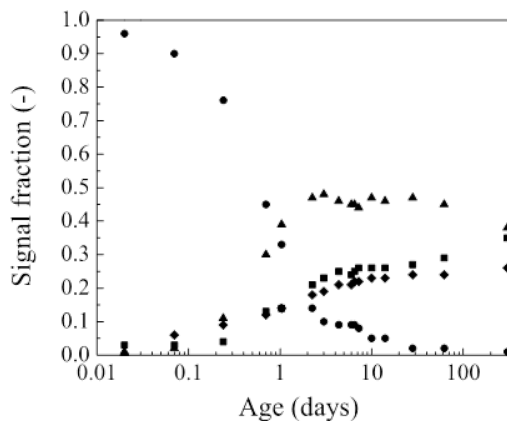

Figure 1 - Evolution of different populations of water for a paste of water to cement ratio 0.4 sealed cured. From [1]

The relaxation times, related to size in the case of the sheet and gel water, quickly stabilize to constant values values around 1 and 3 nm respectively. The amount of **water filled** capillary water quickly decreases, but so does

their size. Around 2.2 days the amount of water in capillary pores is about 10% of the original amount and their size is only 8-10 nm. From this point, we call the remaining capillary porosity "interhydrate" pores as we think is corresponds to the narrow gaps between growing "needles" of C-S-H, seen in SEM and TEM micrographs.

Up to this point the amounts of C-S-H sheet water and gel water grow in parallel, but after this point the amount of gel porosity stabilizes even though the amount of sheet water and calcium hydroxide continue to increase. This indicates that C-S-H formed from this point forms in a different way.

The inevitable consequence of this is that the average density of the "bulk" C-S-H containing gel pores increases as described and calculated in [1].

The results from proton NMR can be used to draw a modified version of the Powers-Brownyard model of the evolution of the different phases with hydration, Figure 2. At high degrees of hydration the volume repartition agrees well with that proposed by Powers-Brownyard. However it is seen that the evolution of gel porosity with degree of hydration is not linear. It increases more rapidly at low degrees of hydration.
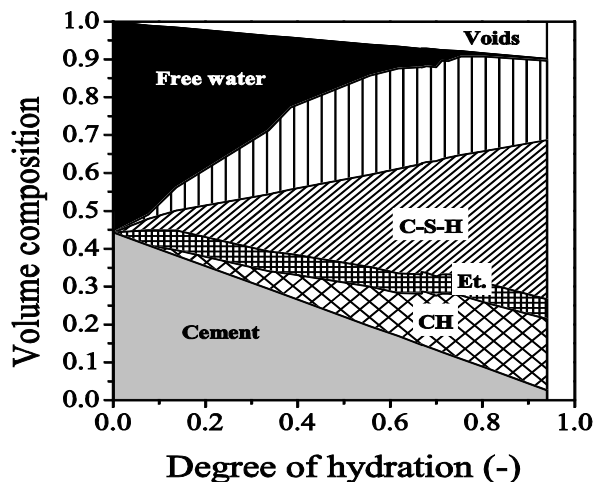

Figure 2 - Evolution of volume fractions for a paste of water to cement ratio 0.4 sealed cured. From [1]

3 MICROSTRUCTURAL SIMULATION

Several groups have tried to develop models to simulate the microstructure of cementitious systems as a basis for understanding structure property relations. In our group we have worked on a vector representation of the particles in the microstructure (**µic**), which allows a realistic size distribution of cement to be modeled (<1 µm to 60 µm, around 3 million particles in a 100 x 100 x100 µm^3 box in a few hours on a desk top computer). Despite the ability to represent all the cement particles there is still a problem to characterize pores down to a small enough size after hydration. Progress in computational methods now allows us to describe pores down to 5 nm in size in the **µic** model. Despite the possibility to capture very small pores and to simulate the distribution of pore entry diameters – such as produced in a Mercury intrusion experiment, the pore structure from the simulation is quite different from the experimental MIP results. As described in [4] this discrepancy can best we explained by a "roughening" of the surface of the C-S-H which is entirely consistent with the results from proton NMR as described above.

4 SIMULATING WATER TRANSPORT

It is well known that water transport underlies most degradation phenomena in cementitious materials. For this reason there is great interest to be able to model water transport from the cement paste microstructure. This is a great challenge as the dimension of a representative volume element for the paste microstructure is of the order of 100 µm, while we now see that the water filled capillary porosity is dominated by pores around 8-10 nm in size. Even if such a complex microstructure can be represented the flow of water through it then poses new questions.

To look at this process we have started to use the lattice Boltzmann approach for solving problems of fluid dynamics in the context of cement model microstructure [5]. The LB method can be regarded as a microscopic approach from which the macro-dynamics emerge. Previous application of lattice Boltzmann approaches to cement overestimated the water permeability by several orders of magnitude [5,6,7]. One of the main causes of this over overestimation is that the conventional LB method can handle only two types of nodes: (1) pores with free fluid flow and (2) solids where the no-slip boundary condition is usually applied.

This is inconvenient for multi-scale heterogeneous porous media because resolving the flow requires an excessive amount of computational resources. Consequently, previous applications were limited to a percolated capillary pore network and failed to capture the complexity of the flow. Recently we developed a 3D LB model based on the effective media approach to calculate the permeability of cement model microstructures determined using the model µIC. The model comprises capillary pores, C-S-H gel pores and solid phases. Critical input, such as the C-S-H density and water-filled capillary porosity, are taken from the proton magnetic resonance relaxation analysis emerging results [1,3]. The bulk C-S-H is assigned a very low permeability that connects the depercolated water-filled capillary pores and air voids [8,9].

The results from this approach suggest that the strong variation in permeabilities found in the literature almost certainly results from quite small differences in the degree of saturation of the materials studied. After setting the chemical shrinkage associated with the hydration reaction will cause the formation of voids. Most materials designated as water cured are only immersed in water after demoulding at 18 to 48 hours when the material may already contain significant voids. Even samples which are put under water before setting must be thin enough for the water fully access the porosity.

5 ACKNOWLEDGEMENTS

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