

# Observing Microstructural Evolution During Plaster Hydration

Kyung-Min Song, Jonathan Mitchell, Lynn F. Gladden\*

Department of Chemical Engineering and Biotechnology, University of Cambridge,  
Pembroke Street, Cambridge CB2 3RA, U.K.

\*Corresponding author e-mail: [gladden@cheng.cam.ac.uk](mailto:gladden@cheng.cam.ac.uk) (L.F. Gladden)

(received 9 July 2008, accepted 08 March 2009)

## Abstract

Calcium sulphate hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ), commonly known as plaster of Paris, is used extensively in the construction, ceramics, and medical industries. There are two varieties of plaster referred to as  $\alpha$  and  $\beta$ , produced by “wet” or “dry” methods respectively. Plaster hydrates to form crystalline gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , dihydrate). We present a comparative *in situ* study of the microstructural changes that occur during the hydration of the two forms of plaster at a water-to-plaster ratio of  $w/p = 0.8$  using NMR relaxometry and electron microscopy. In the  $\alpha$ -plaster, pores evolve gradually to form a uniform, interconnected structure. In contrast, the  $\beta$ -plaster hydrates faster, leading to a less homogeneous product with micro-cracks resulting from rapid chemical shrinkage.

## Keywords

NMR relaxometry; Electron microscopy; Hydration; Gypsum; Plaster

## 1. Introduction

Dry plaster powder is produced commercially by the partial dehydration of gypsum. This is achieved by removing three-quarters of the combined water from the raw material. Depending on the process of industrial manufacture – the so-called “wet” and “dry” methods – the plaster powder is categorised into one of two forms,  $\alpha$  or  $\beta$ , respectively [1]. When the plaster powder is exposed to water, the paste hardens as the water combines with the hemihydrate to reproduce the original gypsum dihydrate; the result is a high porosity material. The microstructural changes that occur during hydration define the mechanical properties (durability, strength) of the set plaster. Many studies have been carried out on both types of plaster including the determination of the mechanisms and factors governing the hydration reaction [2, 3]. However, the pore structures of the plasters are not well characterised and understood. To improve the reproducibility and the quality of the mechanical properties of the hydrated plaster, it is important that the evolution of the pore structure during hydration is fully characterised.

The pore structure of plaster has been monitored previously using NMR relaxometry [4] and the results combined with acoustic measurements of the mechanical properties of the material [5]. It has also been shown that the hydration of plaster can be followed using  $T_2$  relaxometry on low-field, portable NMR devices [6].

In this work the evolution of the pore structures during the hydration of  $\alpha$ - and  $\beta$ -plasters are monitored *in situ* using  $T_2$  relaxation measurements of the mobile  $^1\text{H}$  protons in the samples. NMR relaxation times ( $T_1$  and  $T_2$ ) of liquids confined in small pores are proportional to the pore size [7]. The relaxation measurements are acquired on a time scale that is short ( $\sim 1$  min) compared to the hydration time of the plasters ( $\sim 50$  min) allowing the structural changes to be probed without perturbing the system. The NMR results are supported by a study of the morphology of the set plaster using Scanning Electron Microscope (SEM) images.

## 2. Methods and Materials

The  $\alpha$  and  $\beta$  plasters were commercial powders with a purity  $> 98$  wt %. The samples were prepared by manual mixing of the powder and deionised water at  $w/p = 0.8$  by mass. The plaster pastes were poured into  $25 \text{ mm} \times 100 \text{ mm}$  glass tubes and sealed to limit evaporation.

The NMR measurements were performed on a Bruker AV spectrometer with a 2 T horizontal bore imaging magnet giving a  $^1\text{H}$  resonance frequency of 85 MHz.  $T_2$  decays of the water confined within the sample were measured using the Carr-Purcell-Meiboom-Gill (CPMG) sequence [8] with an echo time of  $2\tau = 800 \mu\text{s}$  and 1024 echoes. Each data set was recorded every 1 minute during hydration and two scans were acquired for each data set. The  $T_2$  decays were fitted with double or triple-component exponential decays, as required.

## 3. Results and Discussion

The variations of  $T_2$  with hydration time for the two different forms of plaster are shown in Fig. 1. For the  $\alpha$ -plaster, two water populations are present throughout the hydration process. The  $T_2$  of both water populations decreases gradually over the entire hydration period as the water in the sample becomes confined in the steadily evolving pore structure.

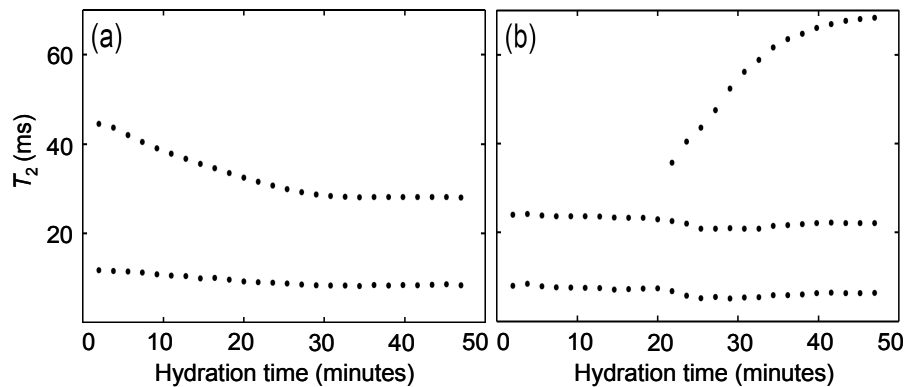
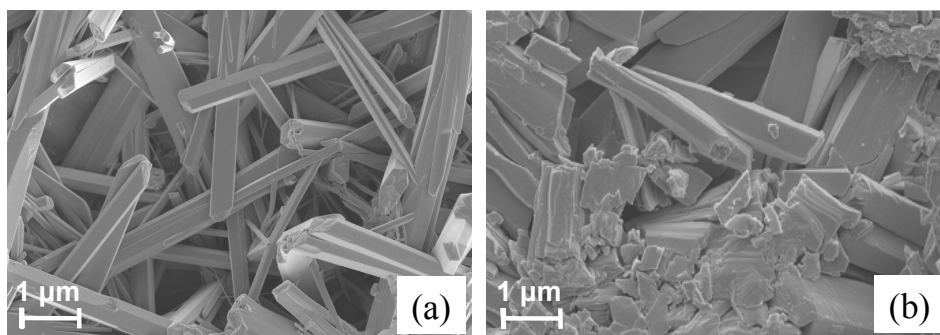


Fig. 1:  $T_2$  relaxation time components observed during hydration of (a)  $\alpha$ - and (b)  $\beta$ -plasters at  $w/p = 0.8$ .

However, for the  $\beta$ -plaster, two water populations are observed up to 18 min, without any significant change in  $T_2$ . This is the initiation period of the  $\beta$ -plaster hydration, during which no evidence of pore structure evolution occurs. After 18 min, the  $T_2$  values of both water populations decrease slightly. The shorter  $T_2$  times (compared to the  $\alpha$ -plaster) suggest a denser structure with smaller pores. A third water population with a long  $T_2$  relaxation time appears at the same time. This indicates the formation of large pores in the  $\beta$  hemihydrate.

To confirm the variations in pore structure implied by the NMR results, the hydrated plasters were examined by SEM. Exemplar images are shown in Fig. 2. The gypsum crystals in the  $\alpha$ -plaster are well formed with a high degree of entanglement resulting from the gradual evolution of the microstructure. In the  $\beta$ -plaster, the gypsum crystals are shorter and stacked rather than entangled. The morphological differences between  $\alpha$  and  $\beta$  crystals have been reviewed elsewhere [1]. These morphological differences are believed to result from different

hydration mechanisms, causing the  $\alpha$  crystals to be more regular in structure than the  $\beta$  crystals. The  $T_2$  measurements are clearly sensitive to the differences in the pore space arising from these differences in crystal structure.



**Fig. 2:** SEM images of set plasters. (a)  $\alpha$ -plaster shows well-defined, needle-like crystals with a high degree of entanglement; (b)  $\beta$ -plaster exhibits shorter crystals that are less entangled.

#### 4. Conclusions

We have used NMR relaxometry to compare the evolution of the pore structure during the hydration of two different forms of plaster. The pore structure of the  $\alpha$ -plaster evolves gradually to form a homogeneous structure consisting of interlocking gypsum crystals whereas that of the  $\beta$ -plaster evolves more rapidly after an initiation period to form shorter, fractured needles, giving rise to a less homogeneous structure. This study reveals clearly the difference in the evolution of pore structure and morphology in the hydrating plasters.

In future work we will analyse the pore structure further using rapid  $T_1$  measurements [9] and  $T_1$ - $T_2$  correlations [10], all performed on a time scale short compared to the hydration period of the plaster. Correlations between the pore structure and macroscopic mechanical properties will also be investigated.

#### 5. Acknowledgements

K.M.S. thanks Dr J. Sohn (Nanoscience Centre, Cambridge) for assistance with the SEM. J.M. thanks Schlumberger Cambridge Research for financial support.

#### References

- [1] N. B. Singh, B. Middendorf, *Prog. Cryst. Growth Character. Mater.* 53 (2007) 57-77.
- [2] U. Ludwig, N. B. Singh, *Cement Concrete Res.* 8 (1978) 291-300.
- [3] A. J. Lewry, J. Williamson, *J. Mater. Sci.* 29 (1994) 5279-5284.
- [4] H. Jaffel, J.-P. Korb, J.-P. Ndobu-Epoy, V. Morin, J.-P. Guicquero, *J. Phys. Chem. B.* 110 (2006) 7385-7391.
- [5] H. Jaffel, J.-P. Korb, J.-P. Ndobu-Epoy, J.-P. Guicquero, V. Morin, *J. Phys. Chem. B.* 110 (2006) 18401-18407.
- [6] J. Boguszynska, M. C. A. Brown, P. J. McDonald, J. Mitchell, M. Mulheron, J. Tritt-Goc, D. A. Verganelakis, *Cement Concrete Res.* 35 (2005) 2033-2040.
- [7] K. R. Brownstein, C.E. Tarr, *Phys. Rev.* 19 (1979) 2446-2453.
- [8] S. Meiboom and D. Gill, *Rev. Sci. Instrum.* 29 (1958) 688-691.
- [9] T. C. Chandrasekera, J. Mitchell, E. J. Fordham, L. F. Gladden, M. L. Johns, *J. Magn. Reson.* 194 (2008) 156-161.
- [10] Y. Q. Song, L. Venkataramanan, M. D. Hürlimann, M. Flaum, P. Frulla, C. Straley, *J. Magn. Reson.* 154 (2002) 261-268.