Discussion on paper published in
Advances in Cement Research
1989, 2, No. 7, July, 99–106

An investigation of the carbonation of cement paste using trimethylsilylation

A. M. Dunster

Contribution by E. E. Lachowski* and D. E. Macphee†

In this study of the carbonation of cement pastes by trimethylsilylation, Dr Dunster reported that he did not observe any ageing effects of the type that we reported in this journal.¹ We would agree that the small effect apparent in Fig. 3 may not be significant, in the light of the very poor reproducibility of the trimethylsilylation method. In any case we would not expect to see much change in the polymers MW for the reasons given in our paper. On the basis of work done on C–S–H made by precipitation from solution, we suggested that the gel is most susceptible to polymerization at early ages, and that water loss is the principal driving agent in the absence of carbonation. In alite or C₃S the unhydrated core of a grain could dehydrate the freshly formed C–S–H, so the ageing process occurs almost immediately. This situation would occur in Dr Dunster's work, so our findings are not incompatible with his. Unfortunately, he did not give data for the nitrogen-stored samples at the earliest ages, which might have shown such an effect. We would also suggest that the state of polymerization of the silicates in C–S–H is particularly sensitive to sample handling, especially where samples may experience drying brought about by, for example, washing with volatile solvents or direct or indirect (grinding) temperature effects.

We also feel that certain aspects of the trimethylsilylation procedure require clarification. Trimethylsilylated silicate derivatives are readily soluble in chloroform, so one would expect some loss of product during the washing procedure. Additionally, the monomer derivative in particular is quite volatile. Drying cement paste derivatives at 115°C removes all

monomer and dimer,² while drying at 110°C removes amounts of monomer derivative which depend on the MW and connectivity of the bulk of the derivatives.³ It is therefore not impossible that the more or less constant monomer yield reflects an equilibrium concentration at 105°C. Furthermore, while it is true that for C₃S pastes no monomer is found in the hydration products within the rather broad limits of experimental error,⁴ this is not the case for real cements,² where about 10% of the silica is found as monomer in fully hydrated pastes. This monomer is probably present in the aluminate phases. We would therefore urge considerable caution in the interpretation of the monomer data, although we do not dispute the conclusion that the anhydrous silicates are unaffected by carbonation.

References

1. MACPHEE D. E. *et al.* Polymerization effects in C–S–H: implications for Portland cement hydration. *Adv. Cem. Res.*, 1988, 1, No. 3, 131–137.
2. LACHOWSKI E. E. Trimethylsilylation as a tool for the study of cement pastes. 2: Quantitative analysis of the silicate fraction of Portland cement pastes. *Cem. Concr. Res.*, 1979, 9, 337–342.
3. DENT GLASSER L. S. *et al.* Studies on sodium silicate solutions by the method of trimethylsilylation. *J. Appl. Chem. Biotechnol.*, 1977, 27, 39–47.
4. DENT GLASSER L. S. *et al.* A multi-method study of C₃S hydration. *Cem. Concr. Res.*, 1978, 8, 733–740.

Reply by the author

I would like to thank Drs Lachowski and Macphee for their discussion, which raises some interesting points. The materials for the carbonation experiments (both carbonated and control regimes) were subsamples taken from the powdered cement paste following grinding at 28 days age. The earliest exposure duration (0 days) included in Fig. 3 of my paper therefore

---

*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, UK.

†CSIRO, Division of Building, Construction and Engineering, P.O. Box 56, Highett, Victoria 3190, Australia.

represents the composition of the bulk sample and hence the initial composition in both exposure regimes.

The control subsample was then subdivided and sealed in plastic bags under nitrogen to prevent carbonation and to minimize atmospheric dehydration of the C-S-H. As indicated in my paper, examination of the control specimens at ages greater than 40 days did not provide evidence of any silicate polymerization. I agree that drying of C-S-H at very early ages might show such an effect, but such an investigation of very immature pastes is beyond the scope of this work.

I am happy to clarify aspects of the trimethylsilylation (TMS) procedure. Direct and indirect temperature effects during treatment of the cement paste were kept to a minimum. Although I accept the possibility that some changes occurred in the C-S-H during grinding, any differences between the control and exposed samples must be due to subsequent exposure.

The cement paste samples were stored and subsequently dried at ambient temperature before TMS without the use of solvents. The insoluble residue was washed with chloroform to ensure removal of any traces of soluble products before determination of chemically combined carbon in the residue following a period of drying at 105°C. Evaporation to dryness of the chloroform extract showed that a negligible quantity of soluble TMS products was extracted during the washing procedure.

The HMD layer was evaporated in air to constant weight at ambient temperature. It is thought unlikely that an appreciable loss of the monomer derivative (boiling point 184°C) could occur at such a low temperature.

I would agree that some results have indicated the presence of a proportion of the silicate as monomer in fully hydrated cement pastes,¹ although the cement paste used in the present work was not fully hydrated so the results may not be directly comparable. I have always found a fairly good reproducibility of the TMS method ($\pm 5\%$ or better). However, results of a study in which cement paste, C_3S and beta C_2S were compared² suggest that the differences between C_3S and cement pastes are probably within the experimental error. Another study³ showed no significant differences between the relative proportions of monomer, dimer and polymer which could not be accounted for by experimental error.

I would suggest on the basis of data given by Taylor⁴ that insufficient aluminate phase is present to accommodate the amount of monomer, although in a study of C_3S pastes some monomeric SiO_2 has been detected in the C-S-H.⁵

References

1. SARKAR A. K. and ROY D. M. A new characterisation technique for trimethylsilylated products of old cement pastes. *Cem. Concr. Res.*, 1979, **9**, No. 3, 343-352.
2. MASSAZZA F. and TASTOLIN M. Trimethylsilylation in the study of pozzolana containing pastes. *Cemento*, 1983, **80**, 49-62.
3. MOHAN K. and TAYLOR H. F. W. A trimethylsilylation study of tricalcium silicate pastes. *Cem. Concr. Res.*, 1982, **12**, No. 1, 25-31.
4. TAYLOR H. F. W. *Cement chemistry*. Academic Press, London, 1990, 218.
5. CLAYDEN N. J. *et al.* The application of solid state NMR techniques to the study of hydration of tricalcium silicate. *8th Congress on the Chemistry of Cement*, 1986, Rio de Janeiro, Vol. 2.