Molecular design and testing of organophosphonates for inhibition of crystallisation of ettringite and cement hydration

Peter V. Coveney,[*a]† **Roger J. Davey,**[b] **Jonathan L. W. Griffin**[c] **and Andrew Whiting**[c]

[a] *Schlumberger Cambridge Research, High Cross, Madingley Road, Cambridge, UK CB3 0EL*
[b] *Department of Chemical Engineering, UMIST, PO Box 88, Manchester, UK M60 1QD*
[c] *Department of Chemistry, Faraday Building, UMIST, PO Box 88, Manchester, UK M60 1QD*

We report the synthesis and testing of novel macrocyclic organophosphonate retarders which have been proposed using rational molecular design methods based on the selective inhibition of the crystallisation of ettringite, a product of the early stages of cement hydration.

Cementitious materials are among the most widely used by mankind while being among the least well understood. The detailed physicochemical processes involved in the hydration and setting of cement slurries are very complex, and a clearly defined quantitative account is still lacking; indeed, even the precise composition of the cement powder is unknown. Although numerous additives are known and used to retard the cement setting process, little is understood of the mechanism by which they act. Here, we show how it is possible to design and synthesize novel macrocyclic organophosphonate retarders by rational molecular design methods[1] based on the selective inhibition of the crystallisation of ettringite, a product of the early stages of cement hydration. This delays the setting process without altering the setting properties (development of compressive strength, *etc.*) once this process begins.

It is known that phosphonate-based organic compounds, such as **1**, **2** and **3** in Fig. 1, are able to retard the onset of setting in cement slurries under ambient conditions;[1,2] however, the mechanism by which such retarders work has hitherto not been established. Furthermore, some phosphonates (such as **1**) are such powerful cement setting retarders that they also cause the time taken for setting (that is, the compressive strength development, once setting commences) to increase substantially.[1] From the point of view of engineering applications of cement in the oil and construction industries,[3–5] it is usually desirable for cement slurries to set rapidly once the setting process is initiated, thus ensuring the development of the required mechanical properties of the resulting concrete matrix as rapidly as possible. There is, therefore, a need to devise cement setting retarders which not only accurately control the time taken for setting to take place, but also maintain the setting characteristics of neat (untreated) cement once set is initiated. To enable the development of such retarders, however, it is necessary to have an accurate understanding of the processes which control the setting of cement.

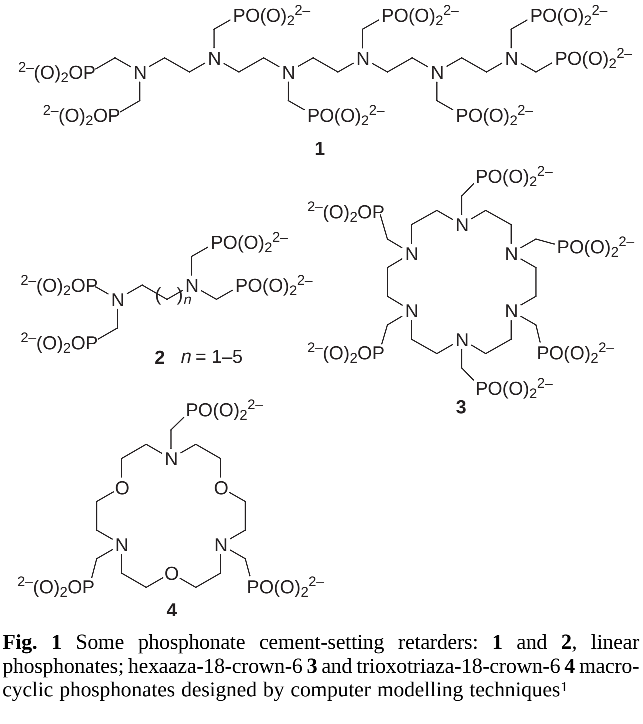

Fig. 1 Some phosphonate cement-setting retarders: **1** and **2**, linear phosphonates; hexaaza-18-crown-6 **3** and trioxotriaza-18-crown-6 **4** macrocyclic phosphonates designed by computer modelling techniques[1]

The work reported here makes use of a recently proposed theoretical model for the setting of cement involving the initial nucleation and growth of crystalline ettringite, $[Ca_3Al(OH)_6]_2$-$[SO_4]_3\cdot 26H_2O$, from a gelatinous precursor.[1,6,7] An important consequence of this model is that, if retarders can be designed which interfere solely with the process of ettringite nucleation and growth, then cement slurries should set normally once the silicate hydration process is initiated, thus ensuring mechanical integrity of the resulting cured product; a separate mechanism for the retardation of silicate hydration has also recently been proposed.[8] The structural basis for the design of such ettringite-specific retarding agents has been discussed previously[1] and is based on the strategy exemplified earlier by Davey *et al.*[9–12] in which the geometry and functionality of additive molecules are chosen such that they are capable of recognising and binding to the growing surface of nuclei or crystals, thereby accomplishing inhibition of nucleation and/or crystal growth.[1] In turn, if such specific retarding agents designed for an ettringite substrate also exhibit an ability to inhibit the setting of cement, without changing its essential setting properties, then this would be consistent with the nonlinear chemical clock-type hypothesis of Billingham and Coveney[6] in which the autocatalytic formation of crystalline ettringite is the rate determining step.

Although molecular modelling studies have proved useful for the rational design of crystal growth inhibitors for simple inorganic systems,[9–12] the design of crystal growth inhibitors for ettringite is a much more challenging prospect due to the complexity of the inorganic matrix. It was however possible to propose that compounds such as **3** and **4** should be effective agents for inhibiting the crystal growth of ettringite, since they possess the ideal structural motifs for molecular recognition with the most rapidly growing [001] face of the ettringite matrix.[1] In particular, the geometry of the phosphonate functions of **3** and **4** in Fig. 1 are such that they fit into the sulfate binding sites of ettringite ensuring enhanced molecular recognition compared to acyclic phosphonates **1** and **2**.[13] Compound **4** exhibits a greater level of conformational flexibility and is expected to be the more active of the two.[1]

Hexaphosphonate **3** was prepared as reported previously[1,14] and triphosphonate **4** was prepared using analogous methods.[14–17] These two compounds were then used as additives during the formation of ettringite and also in cement samples.

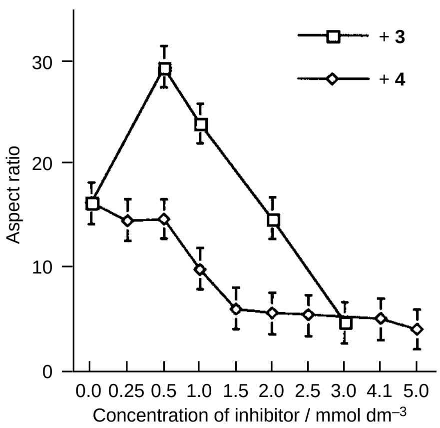

Fig. 2 The influence of additives **3** and **4** on the aspect ratio of ettringite crystals; the data were obtained from SEM images. Note that the trioxygen containing macrocycle **4** is more efficient at limiting ettringite crystal growth at lower concentrations than the macrocycle **3**.

Ettringite crystals,[18] prepared by reacting aqueous $Al_2(SO_4)_3$ with a calcium hydroxide suspension for 30 min at 70 °C, exhibit a prismatic morphology, being elongated about the *c*-axis. Additives **3** and **4** had a profound effect on ettringite crystal morphology, producing a remarkable reduction in the length of the ettringite crystals even at low concentrations: for example at concentrations of **3** and **4** of 1.00 mmol dm^{-3}, there were respectively 45 and 75% reductions in crystal lengths compared to untreated ettringite. Fig. 2 shows the data as the change in measured aspect ratios and indicates clearly the transition from needle to prism. These results are in agreement with the prediction that both compounds **3** and **4** are preorganised to recognise and bind to the growing {001} faces of ettringite, and that **4** should be a superior inhibitor to **3**.[1]

These results are supported by X-ray powder diffractograms of the solid products of ettringite crystallisations carried out in the absence of additive and in the presence of 4.0 mmol dm^{-3} of additives **3** and **4**. The diffractogram for a pure ettringite sample exhibits the preferred orientation expected for *c*-axis needles, with all {*hkl*} reflections having significantly reduced intensities. This X-ray pattern is entirely consistent with pure, well crystalline ettringite; the relative intensities of diffraction from the (100) and (114) lattice planes at 9 and 22.8° would be 2 : 1 in a powder comprising isometric crystals. The observed enhancement to 4 : 1 is consistent with a product comprising *c*-axis needle shaped crystals. In the presence of additive **3**, this relative intensity is 1 : 1, implying significantly more equant crystal habits; at the same time the pattern indicates the presence of two other crystalline phases, calcium hydroxide and gypsum, not normally seen as a product in these reactions (the relatively intense diffraction peaks at 29.3 and 47.3° are consistent with the existence of gypsum [(111) reflection] and calcium hydroxide [(102) reflection] respectively). In the presence of additive **4** the result is even more extreme, indicating significantly lower levels of ettringite, some gypsum, and calcium hydroxide, together with significant amounts of amorphous material. These data confirm the observed morphological change in the ettringite crystals and also suggest that ettringite nucleation is indeed inhibited by these additives, leading to the production of amorphous material and crystalline gypsum together with a reduction in the overall reaction rate, resulting in unreacted calcium hydroxide. Again molecule **4** is found to be the more active as originally predicted.

The effect of these same additives on the setting of cement slurries was then examined. Rates and extent of setting of samples taken from one batch of class G oilfield cement were measured at additive concentrations of 1.0 mmol dm^{-3} by heat flow calorimetry[1] in which the magnitude and time evolution of the heat of reaction were recorded. It was found that hexaphosphonate **3** doubles the induction time for the onset of setting of cement while triphosphonate **4** extends this period threefold. In addition, however, it is evident that in both cases the setting characteristics, as judged by the profile of the heat flow curves, remain unchanged compared with the case of neat cement, suggesting that these compounds act to inhibit nucleation of ettringite and do not interfere with compressive strength development once that nucleation process has occurred. This is in marked contrast with the general behaviour of acyclic phosphonate cement setting retarders which both delay the onset of setting and inhibit the setting process once it has begun.[1] It is important to note that aged cements, which have been exposed to atmospheric humidity for extended periods, show no delay in the onset of setting and display calorimetric profiles identical to neat cement when treated with these additives. This result is consistent both with the specificity of these additives towards ettringite, which has presumably already formed in these aged materials, and their inability to influence other hydration products such as calcium silicate or hydroxide.

Our results show that additives designed as selective inhibitors for the crystallisation of ettringite can be used to delay the onset of setting of cement slurries without interfering with the eventual setting process itself. This behaviour was discovered on the basis of two central concepts: firstly, that the formation of crystalline ettringite from an amorphous precursor plays a rate determining role in cement setting, and secondly, that it is possible to rationally design compounds which are preorganised for molecular recognition at the surfaces of complex inorganic matrices, such as ettringite, and thus act as powerful crystallisation inhibitors. In the case of cement slurries, the use of such phase-selective retarders should result in the production of cured concrete with very similar mechanical properties to that from the untreated cement.

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Notes and References

† E-mail: coveney@cambridge.scr.slb.com

1 P. V. Coveney and W. Humphries, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 831.
2 H. Taylor, *Cement Chemistry*, Academic Press, London, 1989.
3 *Schlumberger Oilfield Rev.*, 1991, **3**: Special Issue on Cementing.
4 P. V. Coveney, T. L. Hughes and P. Fletcher, *Proceedings of the 1996 Annual Conference of the American Association for Artificial Intelligence*, Portland, Oregon, USA, vol. 2, p. 1471.
5 P. V. Coveney, T. L. Hughes and P. Fletcher, *AI Mag.*, 1996, **17**, 41; *Well Cementing*, ed. E. Nelson, Schlumberger Educational Services, Houston, 1990.
6 J. Billingham and P. V. Coveney, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3021.
7 J. A. D. Wattis and P. V. Coveney, *J. Chem. Phys.*, 1997, **106**, 9122.
8 I. S. Bell and P. V. Coveney, *Mol. Sim.*, 1998, **20**, 331.
9 R. J. Davey, S. N. Black, L. A. Bromley, D. Cottier, B. Dobbs and J. E. Rout, *Nature*, 1991, **353**, 549.
10 S. N. Black, L. A. Bromley, D. Cottier, R. J. Davey, B. Dobbs and J. E. Rout, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3409.
11 L. A. Bromley, D. Cottier, R. J. Davey, B. Dobbs, S. Smith and B. R. Heywood, *Langmuir*, 1993, **9**, 3594.
12 A. L. Rohl, D. H. Gay, R. J. Davey and C. R. A. Catlow, *J. Am. Chem. Soc.*, 1996, **118**, 6042.
13 V. S. Ramachandran, M. S. Lowery, T. Wise and G. M. Polomark, *Mater. Struct.*, 1993, **26**, 425.
14 G. W. Morris, N. D. Feasey, P. A. Ferguson, D. Van Hemelrijk and M. Charlot, *UK Pat.*, GB 88-17185 880719, 1988.
15 E. Graf and J. M. Lehn, *Helv. Chim. Acta*, 1981, **64**, 1040.
16 D. Chen, P. J. Squattrito, A. E. Martell and A. Clearfield, *Inorg. Chem.*, 1990, **29**, 4368.
17 K. Moedritzer and R. Irani, *J. Org. Chem.*, 1966, **31**, 1603.
18 M. Atkins, F. P. Glasser and A. Kindness, *Cement Concr. Res.*, 1992, **22**, 241.

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