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DISCUSSION

A DISCUSSION OF THE PAPER “EFFECTS OF SOME INORGANIC ADMIXTURES ON THE FORMATION AND PROPERTIES OF CALCIUM SILICATE HYDRATES PRODUCED IN HYDROTHERMAL CONDITIONS” BY W. NOCUŃ-WCZELIK[1]

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Nocuń-Wczelik has shown that the phase composition and properties of autoclaved calcium silicate hydrates synthesised at 200°C under saturated steam pressure with and without inorganic admixtures are strongly affected by the CaO/SiO_2 ratio and the nature of the admixture utilised. Also, the xonotlite phase–which should be $Ca_6Si_6O_{17}(OH)_2$–can be synthesised as a final product at not lower than 180°C and, when the CaO/SiO_2 ratio falls below 1, the gyrolite phase $Ca_8(Si_4O_{10})_3(OH)_4\ 6H_2O$ is formed as a final product (1).

The whole area of hydrothermal calcium silicate hydrates is very complex, particularly in real cement systems where there is extensive solid solution of extraneous ions within the hydrated materials formed. Some of the interstitial C_3A and C_4AF in Portland cement systems react and become incorporated in the crystalline calcium silicate hydrate phases (2). Conditions within wells are far from ideal, and standard conditions for equilibrium transformations do not exist downhole (3,4). As a result, studies of the type performed by the author (1) are very useful for establishing base conditions, so that the real hydrothermal situations in given instances can be much better understood.

I can endorse the conclusions that xonotlite is not produced as a final product below 180°C, from work undertaken on autoclaving Class G oilwell cement blends with quartz and condensed silica fume (csf) up to 200°C for 7 days (5) and also when curing Class J (dicalcium silicate-silica based) oilwell cement for 24 h and 7 days at 20.7 Mpa and 177°C (6) under API Schedule 10S conditions (7). Tobermorite is the first crystalline phase to form preferentially when there is sufficient silica present for so doing, which is advantageous because of its high compressive strength and low permeability. In the absence of sufficient additional silica in Portland-based oilwell cements like Class G, α-dicalcium silicate hydrate $Ca_2(HSiO_4)OH$ is preferentially formed. This material has low compressive strength and high permeability, which leads to strength retrogression in hardened autoclaved cements with time. Hence, there is a need for strength retrogression inhibition to promote good well durability, which is accomplished by blending in ca. 35–40 wt.% silica sand or silica flour under normal operational conditions for such well sections.

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[1] Cem. Concr. Res. 27, 83–92 (1997).

In addition, I would agree that the presence of aluminium has a stabilising effect upon tobermorite, where it can readily substitute for silicon within the crystalline structure. In 11.3Å tobermorite $Ca_5H_2Si_6O_{17}$ $4H_2O$ there are infinite chains with some Si-O-Si bridges, giving a ^{29}Si CPMAS NMR spectrum close to that of xonotlite (8). This supports the basic idea of a double chain silicate structure for tobermorite of the type previously propounded by Wieker (9).

Undoubtedly the work undertaken by Dr. Nocuń-Wczelik is a further valuable step towards our understanding more fully how different types of calcium silicate hydrates are formed under autoclaved conditions in the presence of a number of inorganic admixtures. The critical importance of the CaO/SiO_2 ratio in these hydrothermal systems is clearly illustrated.

References

1. W. Nocuń-Wczelik, Cem. Concr. Res. 27, 83–92 (1997).
2. J. Bensted, World Cement 22, 8, 27–32 (1991).
3. C.A. Langton, E.L. White, M.W. Grutzeck, and D.M. Roy, 7th International Congress on the Chemistry of Cement, Vol. III Communications, pp. V/145–151, Editions Septima, Paris, 1980.
4. J. Bensted, P.E. Haynes, E. Henderson, A. Jones, and T.B. Smallwood, Roy. Soc. Chem. Spec. Publ. 45, 42–60 (1983).
5. G. Bell, J. Bensted and F.P. Glasser, Adv. Cem. Res. 2, 61–72 (1989).
6. G.M.M. Bell, J. Bensted, F.P. Glasser, E.E. Lachowski, D.R. Roberts, and S.A. Rodger, Adv. Cem. Res. 5, 71–79 (1993).
7. American Petroleum Institute, Specification for materials and testing for well cements, API Specification 10, 4th edition, API, Washington DC (1988).
8. G.M.M. Bell, J. Bensted, F.P. Glasser, E.E. Lachowski, D.R. Roberts, and M.J. Taylor, Adv. Cem. Res. 3, 23–37 (1990).
9. A. Winkler and W. Wieker, Z. Anorg. Allgem. Chem. 451, 45–56 (1979).