Pergamon

Cement and Concrete Research, Vol. 25, No. 8, pp. 1811-1813, 1995
Copyright © 1995 Elsevier Sciences Ltd
Printed in the USA. All rights reserved
0008-8846/95 $9.50+.00

# A Discussion of the Paper "MICROSTRUCTURAL AND MICROANALYTICAL STUDIES OF SULFATE ATTACK. II. SULFATE-RESISTING PORTLAND CEMENT: FERRITE COMPOSITION AND HYDRATION CHEMISTRY" by R.S. Gollop and H.F.W. Taylor*

**Jasbir S. Lota,[1] (the late) Peter L. Pratt[2] and John Bensted[3]**

**[1]Concrete Technology Unit, Department of Civil Engineering**
**University of Dundee, Dundee DD1 4HN, UK**

**[2]Formerly Emeritus Professor of Crystal Physics, Department of Materials**
**Imperial College of Science, Technology and Medicine**
**University of London, Prince Consort Road, London SW7 2BP, UK**

**[3]Industrials Materials Group, Department of Crystallography**
**Birbeck College, University of London, Malet Street, London WC1E 7HX, UK**

We welcome the work reported by Roger Gollop and Professor Hal Taylor concerning the hydration chemistry and ferrite phase composition of sulphate-resisting Portland cement (SRPC) [1]. We are surprised that the authors are apparently unaware of the existence of a substantial body of work on Class G oilwell cement which is a coarsely ground high sulphate-resisting Portland cement detailing its unhydrated characteristics, hydration chemistry and development of microstructure at 20°C and 5°C with and without the presence of accelerating admixtures [2]. This information may be helpful in preventing any inadvertent duplication of work and is in the process of being prepared for publication [3-7].

We found that the hydration of Class G oilwell cement shows some interesting differences in behaviour when hydrated at 20°C and 5°C as would have been expected in a typical construction Portland cement (OPC). The hydration of the ferrite phase played a substantial part in the overall hydration of the oilwell cement as compared to the other cement phases (mainly the alite phase) at 5°C than at 20°C. The hydration of the aluminium bearing phases (mainly the ferrite phase) was found to be less affected by temperature decrease from 20°C to 5°C than the calcium silicate phases. More AFt phase (impure ettringite) was formed at early times (15 minutes) with the cement paste hydrated at 5°C than at 20°C, despite the overall lower rate of chemical reactivity. The apparent accelerated development of AFt phase at 5°C compared with the situation at 20°C seems to be due to greater availability of space for the $SO_4^{2-}$ ions to react with the ferrite (and aluminate) phases under these conditions, because of the much slower development of C-S-H gel from alite phase in particular.

The paste hydrated at 5°C showed the presence of ettringite at all ages up to 1 year as evidenced by DTA curves, IR spectroscopy and XRD traces. In contrast the paste hydrated at 20°C showed no significant presence of ettringite in the paste until 28 days which persisted in the paste at 1 year. In agreement with Gollop and Taylor's SRPC results, the oilwell cement paste showed some evidence of AFm phase (impure

---

*CCR 24 (7), 1347-1358 (1994)

monosulphate). The paste hydrated at 5°C showed some evidence of monosulphate at 1 year in IR spectra and XRD traces. At 20°C, IR spectra showed the presence of monosulphate at all ages from 15 minutes to 1 year hydration.

At 20°C, as hydration of the paste continues, the reactions of the calcium silicate phases decline relatively, whilst at the same time the comparatively slow hydration of the ferrite phase becomes more significant at later times, thus resulting in some consumption of calcium hydroxide.

For the Class G oilwell cement the hydration of the ferrite phase cannot be considered to be negligible with respect to the other cement phases. At early ages, the ferrite phase contributes a more important part in the overall hydration process at 5°C, while the reactivity of the calcium silicate phases is relatively suppressed. At 20°C the reverse situation applies.

In our XRD studies we may have evidenced hydrogarnet phase as shown by very small, broad peaks centred at about 17.2 and 19.9°2-theta. However, we were not able to confirm these observations by SEM studies. Did Gollop and Taylor find evidence of a hydrogarnet phase in their SEM studies?

A discussion of the hydration observations and mechanism of Class G oilwell cement which gives an explanation of the development of cement microstructure is detailed in references [2,3,4] which may be able to assist the authors in explaining their results.

We agree with the authors that not much X-ray spot analysis data is available in the literature for the composition of the ferrite phase as found in SRPCs. Bergstrom et al [8] reported X-ray spot analyses of a Portland cement (PC) and for some oilwell clinkers. They did not state what Class of oilwell cement clinker was used and it appears that they used a mixture of high and moderate sulphate-resisting oilwell clinkers. Furthermore, Bergstrom et al confused one oilwell cement (clinker C4 in their notation) as a clinker. Actually, clinker C4 was in fact a high sulphate-resisting Class G oilwell cement which was extensively used for hydration studies in reference [2]. Table 1 below shows the variation in the chemical composition of the ferrite phase as determined from different Portland cement types.

**Table 1. Comparison of ferrite phase compositions from different sources**

| Ferrite Phase Source | Element Relative to 2 Calcium Atoms | | | | | | | % Wt Ferrite in Cement (Bogue) | A/F |
|---|---|---|---|---|---|---|---|---|---|
| | Ca | Al | Fe | Mg | Si | Ti | O | | |
| **Bogue** | 2 | 1 | 1 | - | - | - | 5 | 100 | 1 |
| **OPC** [9] | 2 | 1 | 0.6 | 0.2 | 0.15 | 0.05 | 5 | nd | nd |
| **OPC (low Al)** [9] | 2 | 0.7 | 0.9 | 0.2 | 0.1 | 0.05 | 5 | nd | nd |
| **PC** [8] | 2 | 0.94 | 0.54 | 0.24 | 0.19 | nd | 4.84 | 7.7 | 2.12 |
| **SRPC** [1] | 2 | 0.75 | 0.75 | 0.22 | 0.20 | nd | 4.87 | 14.3 | 0.81 |
| **Class G Oilwell Cement** [8] | 2 | 0.81 | 0.83 | 0.12 | 0.13 | nd | 4.83 | 15.9 | 0.74 |

nd not determined/determinable

Before considering the data in Table 1, it is assumed that the various experimenters have conducted their X-ray spot analyses in the same manner such that there is no variation in experimental technique, sample selection and preparation and number of analyses conducted *i.e.* the errors in their results are of the same order of magnitude.

Consider just the PC, SRPC and oilwell cement ferrites. As the quantity of the ferrite phase (estimated by applying the Bogue calculation) in these cement increases, the ferrite phase contains more iron at the expense of magnesium and silicon in its structure. In the SRPCs the ferrite phase composition containing low quantities of magnesium and silica may make it favourable for AFt and AFm phase hydration products to form, where these hydration products contain both iron and aluminium ions in their structures, and these products undergo further change to give hydrogarnet products [10].

In hydrating SRPC the absence of monosulphate (AFm) phase at comparable conditions and times to an OPC could be explained by (i) the AFt phase derived from ferrite phase hydration being more resilient in converting to AFm phase as compared with the AFt phase derived from the hydration of the aluminate phase, and (ii) differences in cement phase composition between SRPC and an OPC, in particular the aluminate phase content and the lower hydration reactivity of the ferrite phase (as compared with the aluminate phase) that would result in relatively more availability of $SO_4^{2-}$ ions amongst the hydrating cement grains for a greater time duration in an SRPC than in an OPC, thus preventing the AFt phase in converting to AFm phase. If there is variation in the phase composition of the ferrite phase from one cement type to another, then it is likely that there is also compositional variation in the other cement phases. If this is so, then could one make a direct comparison of the cement phase compositions between different types of cement?

Detailed knowledge of the compositional variations of the major cement phases found in different types of cement may be valuable to the cement scientist and civil engineer such that the cement hydration processes may be favourably manipulated in the presence of admixtures and additives to obtain a cementitious product sought for a particular intended function.

## References

1. R.S. Gollop and H.F.W. Taylor, "Microstructural and microanalytical studies of sulfate attack. II Sulfate-resisting Portland cement: Ferrite composition and hydration chemistry", Cem. Concr. Res., 24, No. 7, pp 1347-1358, 1994.
2. J.S. Lota, "The hydration of Class G oilwell cement", Ph.D. Thesis, Imperial College, University of London, 1994.
3. J.S. Lota, P.L. Pratt and J. Bensted, "Characterisation of unhydrated Class G oilwell cement", (In Preparation).
4. J.S. Lota, P.L. Pratt and J. Bensted, "Hydration of Class G oilwell Cement at 20°C and 5°C", (In Preparation).
5. J.S. Lota, P.L. Pratt and J. Bensted, "The hydration of Class G oilwell cement with the addition of calcium chloride at 20°C and 5°C", (In Preparation).
6. J.S. Lota, P.L. Pratt and J. Bensted, "The hydration of Class G oilwell cement with the addition of calcium formate at 20°C and 5°C", (In Preparation).
7. J.S. Lota, P.L. Pratt and J. Bensted, "The hydration of Class G oilwell cement with the addition of sodium aluminate at 20°C and 5°C", (In Preparation).
8. T.B. Bergstrom, C. Hall, and K.L. Scrivener, "Interstitial materials in oilwell cements: Evidence from X-ray microanalysis", Adv. Cem. Res., 4, 141-147, 1991/1992.
9. H.F.W. Taylor, "Cement Chemistry", Academic Press, London, pp 10-11, 1990.
10. *ibid.*, pp 196.