SYNTHETIC CRISTOBALITE AS A REFERENCE REACTIVE AGGREGATE

J S Lumley
Blue Circle Industries PLC
Product R&D Department
305 London Road
Greenhithe
Kent
England
DA9 9JQ

ABSTRACT

The requirements of a reference reactive aggregate for asr studies are outlined. The preparation of cristobalite from flint is detailed, and the asr characteristics of the cristobalite are compared with other reactive aggregates.

1. INTRODUCTION

Several UK organisations are conducting tests on hydraulic binders to assess the effectiveness of secondary binders such as ground granulated blastfurnace slag (ggbs) and pulverised fuel ash (pfa) to alleviate asr expansion in concrete. No standard method for such tests exists in the UK, but the long term expansion of laboratory made concrete prisms is coming to be accepted as more likely to relate to field experience than other published methods. In order that laboratories may readily compare their test results it is necessary for them to use the same reactive aggregate.

There are four main requirements for a reference reactive aggregate as follows:-

[1] Its particle size, or its particle size grading (psg), should be similar to that of the reactive component usually occurring in field aggregates.

[2] The reactivity of the silica of the aggregate should be such that at the particle size in use, reaction in the concrete occurs at a reasonable rate at 20°C without requiring excessively high alkali metal ion concentrations in the concrete.

[3] The aggregate should be homogenous in its properties and reproducible between batches.

[4] It should not be too expensive.

For general research work two or more reactive aggregates of different reactivities, and perhaps other characteristics, would be required for fully testing the asr performance of a hydraulic binder combination. This paper is concerned only with the production and characterisation of calcined flint cristobalite (cfc) used as a reference reactive aggregate.

2. SPECIFYING A REFERENCE REACTIVE AGGREGATE

2.1 Particle Size Grading and Reactivity of the Substance

Since the rate of dissolution of silica varies with the psg the first two parameters should be considered together. During the mid 1980's verbal reports from workers investigating asr affected structures in the UK indicated that the particle size range of reactive materials which appeared to give the most trouble was about 1 mm to 5 mm, so it was decided to adopt a nominal particle size

range of 1 to 2 mm to obtain a little acceleration whilst remaining within the field range. A narrow particle size range was chosen partly to simplify production of the aggregate in bulk, and partly to improve reproducibility. Also, it might simplify calculations should any modelling of the reaction and its effects be attempted.

At ordinary temperatures moist Portland cement continues to hydrate for several months, and to a minor extent, for some years, yet previous work has shown that the concentrations of the various ions in the pore fluid do not change appreciably after a few weeks age [1]. However, should the cement contain ggbs or pfa, the pore fluid chemistry may continue to change for several months after mixing the concrete.

Most UK reactive aggregates are slow in their reaction. Although dissolution of silica starts almost as soon as water is added to the mix, the rate of gel formation is such that several months or a few years may pass before significant expansion becomes apparent. Thus most of the reaction appears to take place after the hydration of the cement and of slag or pfa (if present) has reached an advanced stage. In order to reproduce this condition in laboratory work, an aggregate of moderate reactivity is required. That is, one which does not dissolve to too great an extent in the first two or three months, but which at the same time yields comparisons between cements within a year or so.

2.2 Reproducibility of the Aggregate

Successive batches of a reference reactive aggregate need to possess identical character-istics within narrow limits. This condition might need to apply for many years particularly if the material is used by several laboratories.

3. THE CASE FOR CALCINED FLINT CRISTOBALITE

Several materials were considered for use as a reactive aggregate. Beltane opal and fused silica react much too quickly in comparison with known UK reactive aggregates [2,3]. The reactive component in Schleswig-Holstein aggregate is an opaline sandstone [4], and it again is considered too reactive for normal testing of UK cements. Other naturally occurring aggregates were found to react too slowly to provide test results in a reasonable time. These included Malmesbury horn-fels from South Africa [5], a gravel dredged from the English Channel, and Kentish flint.

Silica exists in many phases at the atomic level and since cristobalite and tridymite possess structures which are more open than quartz, but less open than lechatelierite, they should have reactivities lying between those of quartz and fused silica. Experimental work has shown that cristobalite can readily be produced from flint and that it has a reactivity between that of fused silica and raw flint. Prism tests with the cristobalite of particle size 1 to 2 mm produced expansions starting at ages ranging from $2\frac{1}{2}$ months to 18 months in concrete of realistic cement contents. Although the aggregate is artificial it is virtually wholly silica and dissolves in alkaline solution to produce similar substances to those derived from quartz or lechatelierite.

Several commercially produced batches of cfc have exhibited a high degree of reproducibility as indicated by XRD spectra and the material thus closely satisfies the criteria proposed in Section 2.

4. THE OCCURRENCE AND NATURE OF FLINT

Flint, occurs as nodules in chalk beds and the individual flints vary in size from about one cubic millimetre to several cubic decimetres. Deposits have been found in all the inhabited continents but the processes of its origin are unknown. Several theories have been discussed by Shepherd [6] and it is quite likely that flints were formed by more than one process. Further, individual flints may have been partly produced by one process, and completed by a second, as conditions in the chalk changed.

Flint is a member of the chalcedonic group of silica minerals. The group includes chert which occurs in limestone. Flint and chert vary in their lithologies but their characteristics seem to overlap considerably. Thus there is little tendency nowadays to distinguish between the two though some authorities regard flint as a variety within a sub-group of chert.

The remainder of this section relates only to those flints found in the South-East of England.

Kentish quarry flints are embedded in chalk having a permanent water content of 22% by weight. Some possess a white cortex integral with the stone. An uncorticated or completely decorticated flint consists essentially of quartz crystals cemented together by amorphous silica. The degree of crystallinity of the flint is remarkably high at around 95% as determined by XRD, and peak broadening indicates a mean crystallite size of 60 nm. Its relative density is 2.55, that of quartz being 2.65. The Vickers microhardness is typically around 1300 Kg/mm^2 - a value in the range of massive quartz. Minor regions within a flint where porosity or hydration are higher than typical can show hardness values a few hundred Kg/mm^2 lower.

Flint is a fairly pure form of silica. The main impurities are water and perhaps a little organic matter. After removal of these substances by ignition, the remaining solid is generally over 99% SiO_2. The chief inorganic impurities are then calcium - about 0.4% as $CaCO_3$ and about 0.1% iron as Fe_2O_3.

5. THE PREPARATION OF CALCINED FLINT CRISTOBALITE

5.1 Preliminary Laboratory Studies

12 gram lots of crushed flint granules were calcined in a tube furnace under the regimes given in Table 1. The temperature was raised at 250 C° per hour to the calcining level which was maintained for the stated time. The furnace was then switched off and allowed to cool naturally to around 300°C before removing the charge, to obviate thermal shock. Each firing was ground to -90 um and subjected to XRD analysis to provide the semi-quantitative results shown in Table 1.

Table 1 - Laboratory Experimental Calcinings

Calcining Temp	Calcining Time	Phases Detected by XRD
1250°C	4 hours	Some cristobalite, but mostly quartz.
1300	6 hours	Roughly 50/50 quartz/cristobalite.
1350	6 hours	Mainly cristobalite, about 3% quartz.
1350	8 hours	Very slightly less quartz.
1375	6 hours	About 1% quartz.

It is clear that a temperature in excess of 1350°C is required to secure a substantial conversion of quartz to cristobalite in a reasonable time. Six to eight hours at 1375°C is adequate to effect the conversion provided that the flint granules are not too deeply layered.

Although tridymite is the thermodynamically stable phase of slightly impure silica between 867 and 1470°C [7], quartz changes first to cristobalite at temperatures in this range, and only after further weeks or months of heating would the conversion of cristobalite to tridymite take place. On cooling the cristobalite, it passes through an inversion temperature at 272°C. At ambient temperature cristobalite is tetragonal and although only metastable, it would take geoligical time to convert to the stable quartz, if the conversion takes place at all.

5.2 Large Scale Production of Cristobalite

Crushed Kentish flint in a range of particle size fractions is commercially available in England and extensively used by the pottery industry. Flints from the wash mill are scanned by an optical sorter which rejects chalk coated stones, and the flint is sieved into size fractions after crushing. The following states the procedure adopted for producing the reference reactive aggregate. The process may be scaled for quantities other than 100 Kg.

Sieve 100 Kg of crushed flint to -2.00 mm + 1.00, wash to remove dust, and dry at 110°C. Spread the flint evenly over three decks about 70 cm square made from silicon carbide vats placed in kiln having a cubic firing chamber of about one metre side length. The decks are spaced about 15 cm apart vertically and the flint beds are no more than 5 cm deep. The kiln is gas fired and has high degree of temperature uniformity. Set the gas and air controls to yield a minimum oxygen content of 5% in the flue gas. Charge the kiln at ambient temperature and then heat at a rate of 225 ± 25 C° per hour to 1380 ± 15°C. Maintain at this temperature for 8 ± ½ hours, then shut off the gas and air supplies. Allow the kiln chamber to cool naturally to 250 ± 20°C whilst its door and ports remain closed. Discharge the kiln and sieve the product through a 2.00 mm screen to remove agglomerates of granules cemented together by small particles of impurities which are thinly scattered through the raw flint.

The calcining conditions were specified to secure the maximum possible homogeneity within the finished product. Ideally, each granule should have the same constitution and texture throughout its bulk. The maximum depth of the flint beds and the slow rate of heating were both chosen to ensure no great difference betweeen the temperature/time regimes of the granules on top of the layers, and those closer to the decks. The slow cooling regime is intended to ensure that all calcined flint granules receive much the same treatment. If the red hot cristobalite were raked out straight onto a cold surface, some particles would be subjected to thermal shock.
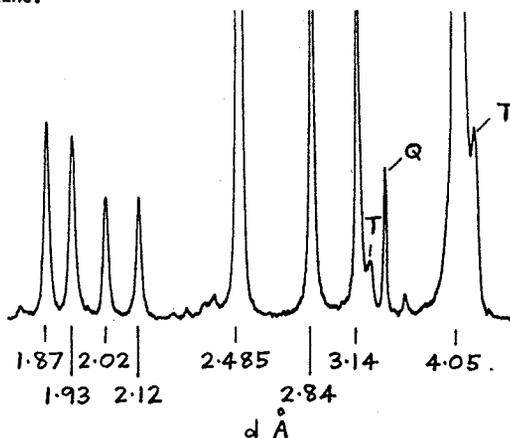

Fig 1. Cfc XRD Spectrum showing Quartz (Q) and Tridymite (T) Peaks

6. THE NATURE OF CALCINED FLINT CRISTOBALITE

Flint calcined to the Section 6 specification consists of about 96% tetragonal cristobalite and up to 2% each of quartz and tridymite as can be seen in the XRD spectrum, Fig 1. Peak broadening indicates a mean crystallite size of approximately 60 nm. This is much the same size as the quartz crystals in the flint, so possibly each quartz crystal converts to a cristobalite crystal independently with no general re-crystallisation.

The cfc granules have a particle density of 2.21 $g.cm^{-3}$ and comparison with the cristobalite single crystal density of 2.32 $g.cm^{-3}$ gives a mean porosity of the granules of some 4.75%. Part of this porosity arises from fissures in the granules as apparent in Fig 2.
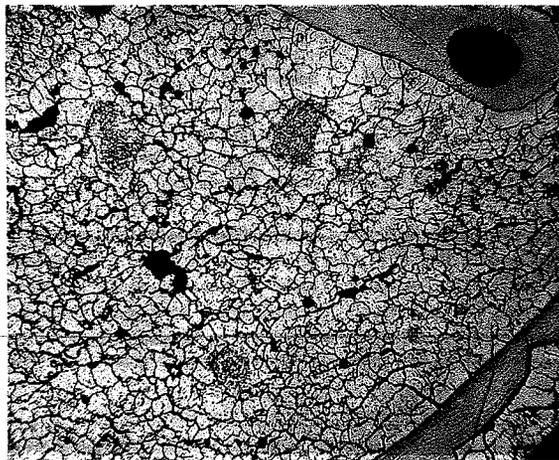

Fig 2. Polished Section of a CFC Granule

$100 \mu m$

These fissures render the cfc a little friable and some attrition of the granules will take place in forced action concrete mixers. Trowel mixing of concrete for individually made test prisms causes negligible breakage of the cfc. Examination of cfc under a low power microscope shows the granules to be angular, and most are equant with some tending to elongated. The Vickers microhardness of the cristobalite substance is about 600 Kg/mm^2.

7. EXPANSION TEST RESULTS

The initial assessment of calcined flint cristobalite as a reference reactive aggregate was done with 25 x 25 x 280 mm mortar prisms of 1:2.25 : 0.50 mix proportions and all prepared from the same opc of eq Na$_2$0 0.92%. The principal aggregate of the mortars was a good quality quartz sand and this was replaced by five different reactive aggregates in various proportions by mass. The eq Na$_2$0 of each mix was around 5.4 Kg/m^3, varying a little between prisms according to the proportions of the reactive aggregates, each of which had a different particle density from that of the sand. Prisms were demoulded at 24 hours age, wrapped in plastics foil, weighed, measured, and then stored in fog at 20°C. The foil permitted slow ingress of water and prisms gained 6 to 8 grams of water during the first year.

Linear expansions of six prisms containing different quantities of cfc are shown in Fig 3. Cfc contents varied from 5% to 35% of the total aggregate and it can be seen that the pessimum for this particular mix is close to the low end of the range. It should also be noted that the pessimum value is not revealed until expansion is complete at all levels of sand replacement. Eg, at 40 weeks age the pessimum appears to be about 20%, but at 100 weeks it is clearly seen to be less than 14%.
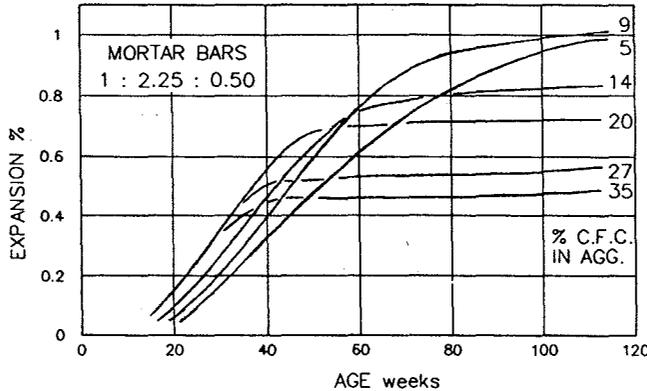

Fig 3. Expansion of Mortar Bars Containing CFC

Expansions of mortar prisms containing five different reactive aggregates are given in Fig 4. The curve for fused silica is the pessimum line for granules - 1.18 mm + 0.60 mm. The particle size for the other four aggregates was -2.00 + 1.00 mm. No pessimum was found for the Pyrex which was tested at the replacement levels of 9, 14, 20, and 30%. Expansion increased with Pyrex content and the curve relates to the 30% level.
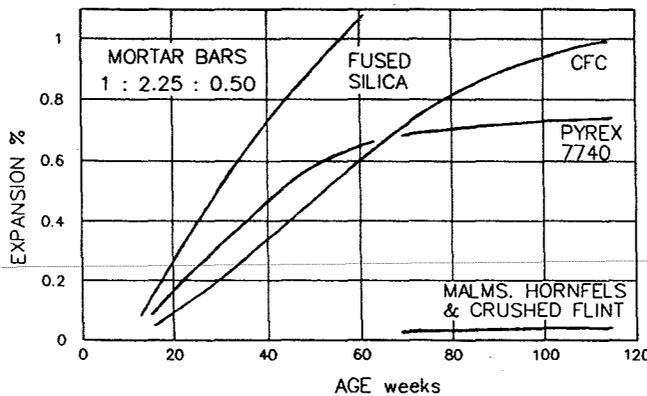

Fig 4. Comparison of Reactive Aggregate Performances

Having established by mortar tests that cfc generated asr expansions over a satisfactory time scale, cfc was then used as the reference reactive aggregate in a more realistic test programme involving concrete prisms of

size 75 x 75 x 270 mm. Some results from this programme are the subject of another paper at this Conference [8].

The coarse aggregate of these prisms was a dense grano-diorite of 0.5% water absorption. Some additional prisms were prepared in which the granite was replaced by the same volume of a river gravel of 2.8% water absorption. As seen in Fig 5 the expansions of these latter prisms were far less than those of the granite concretes indicating that the porosity of the aggregate alleviates asr expansion by providing space for gel to expand into, a theme suggested by Vivian [9] and recently developed by Collins and Bareham [10].
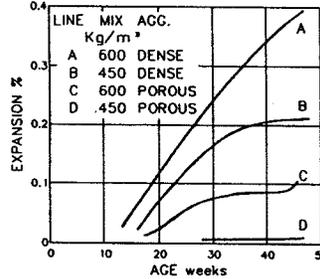

Fig 5. Effect of Agg Porosity

9. CONCLUSION

An artificial aggregate exhibiting asr has been identified. At a particle size relating to field cases of asr it reacts at a generally suitable rate for laboratory work at 20°C. Commercially produced batches have shown a high degree of reproducibility.

ACKNOWLEDGEMENTS

REFERENCES

1. Kollek J.J., Varma S.P., and Zaris C.G., Measurement of OH⁻ ion concentration of pore fluids and expansion due to alkali-silica reaction in composite cement mortars. Proc. 8th ICCC, Rio de Janeiro, Theme 3, IV, 183, 1986.

2. Hobbs D.W., Influence of mix proportions and cement alkali content upon expansion due to the alkali-silica reaction, C&CA Technical Report 534, 1980.

3. Swamy R.N., and Al-Asali M.M., Expansion of Concrete due to Alkali-Silica Reaction, ACI Materials Journal, 85, 1, 33, 1988.

4. Ludwig U., Theoretical and Practical Research on the Alkali-Silica Reaction, 5th ICAAR, Cape Town, Paper S252/24, 1981.

5. Oberholster R.E., Brandt M.P., and Weston A.C., The Evaluation of Greywacke, Hornfels, and Granite Aggregates for Potential Alkali Reactivity, 4th ICAAR, Purdue Univ., 141, 1978.

6. Shepherd W., Flint, Its Origin, Properties, and Uses, Chapter 3, Faber and Faber, London, 1972.

7. Floerke O.W., A Discussion of the Tridymite – Cristobalite Problem, Silicate Industriels, 26, 415, 1961.

8. Moir G.K. and Lumley J.S., Influence of Partial Cement Replacement by Ground Granulated Slag on the Expansion of Concrete Prisms Containing Reactive Silica, 8th ICAAR, Kyoto, Japan, 1989.

9. Vivian H.E., The Effect of Void Space on Mortar Expansion, CSIR Bulletin, 229, 55, 1947.

10. Collins R.J. and Bareham P.D., ASR : Suppression of Expansion using Porous Aggregate, Cement and Concrete Research, 17, 1, 89, 1987.