Recent Developments with High Alumina Cement

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1. Hydration of High Alumina Cement

- The basic chemistry of hydration of the dark grey/black variety of HAC can be summarised thus:

- $CA + 10\ H$ (mainly below ca. 15ºC) → CAH_{10}
- $2CA + 11\ H$ (mainly above 25ºC) → $C_2AH_8 + AH_3$
- $3\ CA + 12\ H$ (mainly above 60ºC) → $C_3AH_6 + 2AH_3$
- $C_{12}A_7 + 51\ H \rightarrow 6\ C_3AH_6 + AH_3$
- $CA_2 + 13\ H \rightarrow CAH_{10} + AH_3$
- $C_4AF + 16\ H \rightarrow 2\ C_2A_{0.5}F_{0.5}H_8$
- $C_2AH_8 + 2$ ‘CH’ $+ 3\ H \rightarrow C_4AH_{13}$
- $C_2AS + 8\ H \rightarrow C_2ASH_8$

- CONVERSION (OR TRANSFORMATION):

- $3\ CAH_{10} \rightarrow C_3AH_6 + 2\ AH_3 + 18\ H$
- $3\ C_2AH_8 \rightarrow 2\ C_3AH_6 + AH_3 + 9\ H$
- $C_4AH_{13} \rightarrow C_3AH_6 + CH + 6\ H$

- Bold print indicates where more recent information is available:

- CA_2 can be present in dark grey/black HAC in quantities 0–2% mass and (like $C_{12}A_7$) can have a catalytic effect on CA hydration.

- C_4AF is actually a main phase along with CA (with C_4AF usually present in ca. 15–30% mass in different cement plants), but has not been universally recognised (as also happened previously with C_4AF in Portland cements), because the main hydration and conversion products of ferrite phase hydration are similar to and in solid solution with those of CA, which increases sulphate resistance.

- C_4AH_{13} (present in small amounts) can also convert to C_3AH_6.

2. White HAC (WHAC)

- CA_2 (grossite) is a main phase in WHAC as also commonly is the less hydraulic phase CA_6 (hibonite).

- In the past WHAC was used almost exclusively for refractory purposes (still its main current usage), due to resistance against fluctuating temperatures, as in industrial chimney stacks.

- Garden furniture (often pigmented) is increasingly being made from WHAC because of its rapid-hardening which increases mould turn-around time during manufacture, with dark grey/black HAC sometimes being used for the darker shades.

- Specialist well cementations for the oil and natural gas industry, where the properties of relatively slow setting, rapid hardening and good resistance to fluctuating temperatures are beneficial has meant that increased usage of HAC in well cementing formulations is increasingly taking place. Under hydrothermal conditions at very high temperatures (above ca. 1000^{o}C) WHACs are sometimes being utilised because of their greater durability under these circumstances.

- WHAC used in the UK normally contains ca. 70% mass Al_2O_3 and is manufactured to the French Standards NF P15-315 (*Hydraulic binders- melted aluminous cement*) and NF P15-316 (*Hydraulic binders- use of melted aluminous cement in concrete structures*), because there are neither current British/European Standards nor any apparent desire to create such standards for WHACs.

3. Where HAC is NOT recommended for use

- AT TOTAL WATER/CEMENT RATIOS ABOVE 0.40: A precautionary measure for obtaining a satisfactory long-term compressive strength in concrete/mortar.

- IN PRESTRESSED CONCRETE: Another precautionary measure, as overdosing with water can be harmful.

- IN LINING PIPES FOR CONVEYANCE OF DRINKING WATER: A further precautionary measure since, in some situations, leaching of aluminium can be one hundredfold that of Portland cement.

- IN ALKALINE ENVIRONMENTS: Due to the likelihood of alkaline hydrolysis.

- USE WITH ALKALI- RELEASABLE AGGREGATES: Again, due to the likelihood of destructive hydrolysis.

- IN ENCAPSULATION OF TOXIC WASTE: Insufficient experimental data are as yet available for making clear technical recommendations; various laboratory studies have shown promising results in fixing heavy metals; however, the long-term ramifications of the effects of conversion remain to be reliably ascertained.

- IN ENCAPSULATION OF RADIOACTIVE WASTE: Not recommended because of uncertainties about very long-term structural integrity where safety is needed for hundreds/thousands/millions of years (depending on the half-lives of the radioactive isotopes in the waste materials) as a result of conversion causing increases in permeability and porosity.

4. Applications of HAC

- ACID RESISTANCE: Better than Portland cements in acidic environments, including sewer pipes where bacterial corrosion is present.
- CHEMICAL RESISTANCE: High resistance to chemical attack (including sulphates) largely due to lack of discrete calcium hydroxide forming; greater resistance than Portland cement concrete against aggressive agents like pure waters, water and ground-containing sulphates, seawater, diluted organic or mineral acids, plus solutions of organic products like sugars, oils, beers, wines and hydrocarbons.
- CHLORIDE RESISTANCE: Often better than that given by Portland cement.
- COLD WEATHER CONCRETING: Early rapid heat evolution enables concreting to take place in temperatures as low as -10ºC, provided that warm water is used for gauging, frozen aggregates are not employed and the concrete is protected from freezing until it begins to harden and the temperature starts to rise.

- CORROSION RESISTANCE: Reinforcement is protected by the alkaline pH of 11 of the interstitial solution, plus the very low solubility of AH_3 in the pH range 4-11, provided that the total water/cement ratio does not exceed 0.40.

- EFFLORESCENCE INHIBITION: Very effective inhibition is given on external surfaces of HAC concrete or mortar, due to absence of residual CH in the hardened cement.

- FREEZE- THAW CYCLES: Good resistance is given like Portland cement concretes where porosity is low (below ca. 13%).

- GARDEN FURNITURE: This application is now increasing, since the slow setting and rapid-hardening properties are beneficial and economic due to quicker turn-around of moulds during manufacture; WHACs neat or pigmented are periodically utilised here.

- GROUTS, TILE ADHESIVES AND FLOORING COMPOUNDS: As well as dark grey/black HAC usage, white HACs (often pigmented) are now increasingly being employed where aesthetic considerations are becoming increasingly important.

- HOT WEATHER CONCRETING: For success by not exposing concrete constituents to the sun, use chilled gauging water, and carefully cure with water as cold as possible during hardening.
- MINING AND TUNNELLING: HAC provides support where rapid setting and rapid hardening, *but not very high strength*, are required.
- RAPID REPAIR MIXES: These are usually sold as proprietorial formulations that may contain a variety of components, including lime and/or Portland cement and/or gypsum and/or various admixtures.
- REFRACTORY APPLICATIONS: Higher temperatures require WHACs with greater Al_2O_3 contents than dark grey/black HACs; the advantages include resistance to temperature fluctuations as lack of CH is beneficial for overcoming spalling; good sulphate resistance militates against gases like SO_2 produced.
- RESISTANCE TO TEMPERATURE, THERMAL SHOCKS AND ABRASION: Good resistance is given with appropriate aggregates, and better than Portland cements with fire resistance and fluctuating temperatures.

- SEAWATER RESISTANCE: Good resistance to seawater is demonstrated with HAC.

- SELF-LEVELLING GROUTS: These are commonly based upon ternary systems of HAC, Portland cement and calcium sulphate (bassanite $CaSO_4 0.5H_2O$ or anhydrite $CaSO_4$) to form ettringite, involving controlled shrinkage and expansion to achieve excellent flatness of floor surfaces that should be maintained to meet super-high-strength concretes applied to pillars and beams so as to realise large spans and section reductions in buildings; currently ca. 10-40 mm thickness is very common for self-levelling works; these cementing compositions often involve *in situ* formation of sulphoaluminate and/or sulphoferrite cements.

- WELL CEMENTING: This application is steadily increasing in critical well cementations, particularly at high, low and fluctuating temperature regimes downhole, in deepwater well cementing, and in special cementing formulations that include (for example) phosphates for resisting CO_2 corrosion in critical geothermal well applications; the relatively slow setting, rapid hardening and resistance to temperature fluctuations are beneficial here.

- WITH SUPERPLASTICISERS: Previously HAC only revealed plasticising rather than superplasticising properties with superplasticisers like sulphonated melamine formaldehyde condensate (SMFC) and sulphonated naphthalene formaldehyde condensate (SNFC) that dispersed satisfactorily with Portland cements; the introduction of ‘new generation’ superplasticisers such as the polycarboxylate types has allowed superplasticising properties to be shown by HAC, which has facilitated concrete and mortar workability.

5. Accelerated Testing

- Compressive strength testing after conversion can be easily predicted by laboratory testing, where conversion from the metastable hexagonal phases CAH_{10}, C_2AH_8 and C_4AH_{13} initially formed, to the stable, dense cubic hydrogarnet phase C_3AH_6 is accelerated by curing HAC concrete under hot water, for example during 5 days at 38^0C as given in the British and European Standard BS EN 14647:2005.

- Previously it was thought that the metastable hydrates should be 'preserved' if at all possible, whereas nowadays it is found that conversion at low water/cement ratios not exceeding 0.40, especially during early hydration before hardening takes place, aids long term durability in HAC concretes and mortars by lowering the permeability and porosity of the concrete/mortar being produced.

6.The Concrete Society Technical Report

- Following the well-publicised collapses of three HAC containing concrete structures during 1973-4 in the UK, HAC was banned from use in structures. By the 1990s there had been no further collapses involving HAC-containing structures, nor any noteworthy problems reported within the UK for HAC in use. As a consequence the Concrete Society set up a working party to take a fresh look at HAC and re-assess its position in construction. Their Technical Report was published in 1997:

- R. Cather (Chair), J. Bensted (Secretary), A. Croft, C.M. George, P.C. Hewlett, A.J. Majumdar, P.J. Nixon, G.J. Osbourne and M.J. Walker: *Concrete Society Technical Report No. 46, Calcium aluminate cements in construction- a re-assessment.* The Concrete Society, Slough (now based at Camberley), 1997.

- The main recommendations were:
- (1) Specifiers, users and clients should be encouraged to consider applications where HACs would have technical and commercial benefits, either in conventional concrete form or as specialist proprietary products.
- (2) A change of emphasis should be considered for the *Approved Documents to the Building Regulations* to reflect more fully selection on the basis of the demonstration of suitability contained in the regulation itself.
- (3) To underpin 1 and 2 above, further coherent detailed and independent guidance should be developed as a safe basis for determining *in situ* strength of HAC concrete for particular structures.
- (4) Further to 3, research should be undertaken and guidance developed, which is devoted to understanding more fully the nature and behaviour of HAC concrete in aggressive service conditions. In particular, the role of the various cement hydrates and microstructure in influencing performance should be examined further. The studies should include examples of both good and bad performance.

- The Concrete Society Report was well received within the construction industry and the recommendations made have been or are being implemented. Key to this was the change in the Building Regulations in 1999 to report:

- *...calcium aluminates (HAC)...can be used in works where these changes do not adversely affect their performance. They will meet the requirements of the Regulations provided that their final residual properties, including their structural properties, can be estimated at the time of their incorporation in the work. It should also be shown that these residual properties will be adequate for the building to perform the function for which it is intended for the expected life of the building.*

- Surprisingly, there has been no mention of the Concrete Society Report in the informative bibliography section of the standard BS EN 14647:2005, when the contents of this Report have aroused considerable international interest!

7. Conclusions

- In recent years there have been many investigations of the scientific and engineering properties of HAC in the aftermath of the unexpected collapses in three UK buildings in the 1970s.

- This activity has resulted in much more knowledge being made available about the nature of HAC, particularly in the conversion of its metastable binding hydrates into the stable hydrogarnet and the concomitant changes in the engineering properties as a result of the conversion reactions, which has given new confidence in the usage of this material.

- The areas of interesting HAC cementing activity that have been highlighted here are important at the present time from the user viewpoint.

- It should be emphasised that HAC is a speciality cement and not a direct substitute for Portland cement. Users should be aware of where HAC can be employed and importantly where it cannot be utilised.