ACTUAL VIEWS ON HIGH ALUMINA CEMENT

by

J. TALABÉR

Department of Building Materials, Technical University, Budapest

It was in 1847 that VICAT established his classic theorem stating that an eventual binder with a hydraulic index greater than unity i.e.:

$$\frac{SiO_2 + Al_2O_3}{CaO + MgO} > 1$$

would resist corrosion by seawater and other aggressive salt solutions. From molecular ratios it is evident that this binder cannot be other than high alumina cement.

In the period between 1865 and 1906, FRÉMY, MICHAELIS and SCHOTT demonstrated calcium aluminates and especially mono-calcium aluminate ($CaO \cdot Al_2O_3$) to possess excellent hydraulic properties and to develop important mechanical strength, much beyond that of Portland cement, in a rather short time.

Comprehensive study of calcium aluminates and the $H_2O - Al_2O_3$ system helped J. BIED in developing an aluminous cement, patented as "Ciment fondu" by the French Lafarge Co. in 1908.

High alumina cement has first been produced in 1913, but in terms of an agreement between the Lafarge Co. and the French government it was not marketed before 1918.

Unlike the smooth advent of Portland cement — although still decades were needed to clear essentials of setting and hardening — high alumina cement broke through with difficulties.

For the sake of clearness, the hydraulic strength of Portland cement is due to the contained calcium silicates, the most familiar being tricalcium silicate 3 $CaO \cdot SiO_2$ (C_3S), dicalcium silicate 2 $CaO \cdot SiO_2$ (C_2S), compounds called alite and belite, respectively, tricalcium aluminate 3 $CaO \cdot Al_2O_3$ (C_3A) and tetracalcium aluminate ferrite 4 $CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (C_4AF), celite in clinker chemistry. In addition, free CaO, MgO and SO_3 are always contained in Portland cement. Free CaO is characterizing the production procedure, the right

or wrong composition, and the respect of technology specifications. MgO gets from dolomitic raw materials into the clinker, while SO_3 is mixed in partly during burning, and partly as gypsum, $CaSO_4 \cdot 2 H_2O$.

Hydraulic properties of high alumina cements are, however, due to calcium aluminates of different composition, the most important being: monocalcium aluminate: $CaO \cdot Al_2O_3(CA)$, principal clinker mineral of high alumina cements. Also calcium aluminate of the formula 12 $CaO \cdot 7 Al_2O_3(C_{12}A_7)$ is present in most high alumina cements, while those rich in Al_2O_3 probably contain $CaO \cdot 2 Al_2O_3$ (CA_2).

In addition to the quoted three important calcium aluminates decisive for the hydraulic hardening character, C_2S, C_2AS (gehlenite) and C_4AF, common in Portland cement, may be contained.

Since the very beginning, the mechanism of setting and hardening presented an extreme interest for cement researchers. Differences between hydration, setting and hardening of the two cement types, responsible for the deviations between the two cements and the resulting concretes, is due to their different chemical and mineralogical composition.

Initially, one has been tempted to formulate analogies to hydration conditions of Portland cement. Soon, however, wrongness of the analogy became obvious, conditions proved to be different, hydration was of a pattern other than usual for Portland cement, while phenomena observed in strength tests vs. time and temperature did not fit into the usual pattern for Portland cement.

Portland cement exhibits a long-term — although gradually slowing — strength growth rate, while high alumina cements often show dangerous and unexplainable strength losses.

This is at the origin of the high alumina cement problem, related to a most exciting phenomenon of hydraulic binders, even now escaping perfect clearance, investigated by the leading cement researchers in factories, laboratories, research institutes.

A long time has passed until our knowledge developed sufficiently to face the problem scientifically.
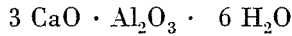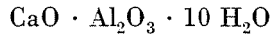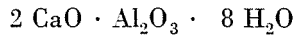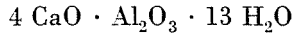
The most valuable characteristic of high alumina cements is their high early strength, responsible on one hand for the wide extension, and on the other hand for failures we have witnessed, and often suffered, for decades.

After having cleared several theoretical problems, by now, damage and destruction of high alumina cement concretes are not considered to be a mystery any more; nevertheless, the following, long-standing problems arise:

1. Are high alumina cement concrete constructions durable?

2. Are high alumina cements allowed for common construction purposes?

Before answering these questions, let us set out findings resulting from studies by eminent cement researchers during decades, fundamental for a clear view in high alumina cement problems.

1. In high alumina cement hydration the following important hydrate compounds develop:

$$4 \ CaO \cdot Al_2O_3 \cdot 13 \ H_2O$$
$$2 \ CaO \cdot Al_2O_3 \cdot \ 8 \ H_2O$$
$$CaO \cdot Al_2O_3 \cdot 10 \ H_2O$$
$$3 \ CaO \cdot Al_2O_3 \cdot \ 6 \ H_2O$$

The number of water molecules may vary in wide ranges depending on various conditions (water content, temperature, pressure, atmospheric CO_2, etc.) much increasing the number of aluminate hydrate varieties classified in four basic types. These are, however, strictly related both structurally and as concerns their properties. Composition of the aluminate hydrates in the first three groups is not constant — mainly because of the varying water content. Hexahydrate $3 \ CaO \cdot Al_2O_3 \cdot 6 \ H_2O$ belonging to the regular system as against the other hydrate components in the hexagonal system, and thus, one of the most stable hydrates in the ternary system $CaO-Al_2O_3-H_2O$ is, however, quite different, changes in this system tending to $3 \ CaO \cdot Al_2O_3 \cdot 6 \ H_2O$.

These changes are due partly to the change of water content and partly to the temperature rise, but there are also other decisive effects causing stable crystal phases to develop.

2. The above statements lead to the conclusion that hydration conditions of high alumina cements are governed by the changes of the $CaO-Al_2O_3-H_2O$ system. Changes can be attributed in simple cases to the variation of some factors of the system (temperature, pressure, concentration etc.) and to that of thermodynamical conditions in more complex cases.

3. The scheme of high alumina cement hydration may be outlined as:

Simplified reaction equations of the hydration of $CaO \cdot Al_2O_3$, the most familiar calcium aluminate:

Below 20 °C or for a low w/c ratio, solution

$$CA + 10 \ H \rightarrow CAH_{10} \ (hex) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad 1$$
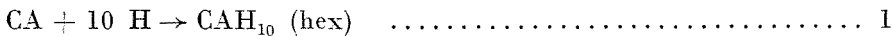
at 20 to 35 °C, or for a high w/c ratio, solution

$$2 \ CA + 11 \ H \rightarrow C_2A \ H_8 \ (hex) + AH_3 \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad 2$$

over 35 °C, solution

$$3 \ CA + 12 \ H \rightarrow C_3AH_6 \ (reg) + 2 \ AH_3 \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad 3$$

produces C_4AH_{13} (hex).

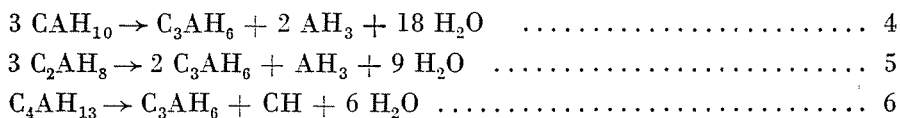Hydration of $C_{12}A_7$ proceeds in a similar way. Over 30 °C exclusively C_3AH_6 and AH_3 are produced.

CA_2 is hydrated more slowly.

4. In the $CaO - Al_2O_3 - H_2O$ system, any change after the initial hydration period can be of a single direction: to pass from unstable to stable system. The hardening pattern resulting from the hydration of high alumina cements is determined by the stable compounds arising in the system.

5. Stable compounds in the system are:

Hydrargillite (gibbsite) $Al(OH)_3$, $3\ CaO \cdot Al_2O_3 \cdot 6\ H_2O$, $CaCO_3$. From the viewpoint of geologic stability, even $3\ CaO \cdot Al_2O_3 \cdot 6\ H_2O$ may be assumed not to be stable. In this case, the final, stable condition is represented by $CaCO_3$ and $Al(OH)_3$.

6. Transformation of unstable, hexagonal calcium aluminate hydrates follows the pattern:

$$3\ CAH_{10} \rightarrow C_3AH_6 + 2\ AH_3 + 18\ H_2O \quad \dots\dots\dots\dots\dots\dots \quad 4$$

$$3\ C_2AH_8 \rightarrow 2\ C_3AH_6 + AH_3 + 9\ H_2O \quad \dots\dots\dots\dots\dots\dots \quad 5$$

$$C_4AH_{13} \rightarrow C_3AH_6 + CH + 6\ H_2O \quad \dots\dots\dots\dots\dots\dots \quad 6$$

7. At 20 °C, the stability range of C_3AH_6 is extremely narrow, hence at normal temperature, it cannot be considered as the dominant compound of the $CaO - Al_2O_3 - H_2O$ system. At a rising temperature, the stability range of regular C_3AH_6 increases and at 30 °C or over, it is the determinant compound of the system. This explains for the accelerated transformation of aluminate hydrates at higher temperatures.

8. Densities of CAH_{10}, C_3AH_6 and AH_3 differ considerably. Therefore water will occupy the greatest part (over 50 per cent) of the space originally filled out by hydro compounds. By its great volume and space need as well as high mobility (evaporation), water entrains further important changes.

In course of the hydration process, the strength development is affected by two basic factors:

a) The forming hydrate is of greater volume than the anhydrous basic material.

b) The forming hydrate is of lesser volume than the total volume of the anhydrous basic material and the water.

These aspects affect the concrete porosity. Its increase loosens the originally dense, strong structure. This fact is already responsible for a great strength loss. What is worse, with the decomposition of the dense texture, the concrete permeability to gases is increased, giving way for the corrosion by the atmospheric CO_2.

CO_2 corrosion is initiated and facilitated by alkalis, always present in the cement or aggregates.

**9.** Theoretical reactions demonstrating the action of CO_2 and alkalis:

$$2\ K_2CO_3 + 2\ CaOAl_2O_3 + aq \rightarrow 2\ CaCO_3 + K_2OAl_2O_3 + KOH + aq \dots\dots 7$$

upon increase of the alkali concentration in the solution, the solubility of Al_2O_3

is abruptly increased. This reaction is itself a sign of unstability of hexagonal hydrates and of the appearance of $CaCO_3$, a new stable compound.

$K_2O \cdot Al_2O_3$ in solution reacts with CO_2, always present in the pores, as follows:

$$CO_2 + K_2O \cdot Al_2O_3 + aq \rightarrow K_2CO_3 + Al_2O_3 \cdot 3 H_2O + aq \quad \ldots\ldots\ldots\ldots \; 8$$
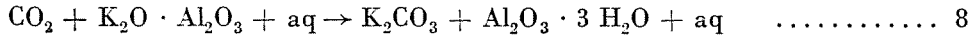
overall equation of the eight reactions above:

$$CO_2 + 2 CaOAl_2O_3 + aq \rightarrow 2 CaCO_3 + Al_2O_3 \cdot 3 HO + aq \quad \ldots\ldots\ldots\ldots \; 9$$
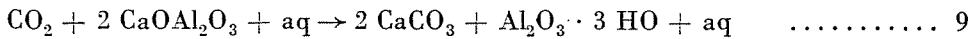
Thus, alkali carbonate is totally regenerated and induces the total decomposition of high alumina cement. In this process, the alkali carbonate acts about as a catalyst.

This is why researchers and concrete technologists point out the importance of alkali-free aggregates.

Of course, fast progress of the variations depends on the simultaneity of several effects such as:

— presence of water;
— high porosity of high alumina cement concrete;
— presence of CO_2;
— presence of alkalis;
— warm, moist ambiance.

Their coincidence may entrain reactions likely to decompose high alumina cements in the worst case.

There are, however, means to prevent high alumina cements from damaging. First of all, cement dosage must be so that the desired consistence is obtained at 0.4 or lower w/c ratio either by

— increasing the cement dosage. Though a bit late, we have also concluded — together with French colleagues — that a high-quality high alumina cement concrete requires a 400 kg/cu·m or higher cement dosage. Beside technical aspects, also economy problems arise, that cannot be irregarded in view of the high cost of high alumina cement; or by

— reducing the water content, the w/c ratio.

Without examining particulars, it can be stated that in the hydration process, strength is strictly correlated to porosity. Green concrete exhibits a relatively low porosity, hence freshly set concrete is of rather high strength. Logarithmic strength and porosity values are known to be linearly related. Hence, the strength of (little porous) neat cement paste fully depends on the strength of developed hydrates. The single factor that may alter the strength is that altering the porosity, i.e., the w/c ratio, to be applied as low as possible, but anyhow below 0,4.

In case of identical porosity, strength of the hardened paste depends on the basic mechanical properties of hydrates. The higher the strength of the

aluminate hydrate, the less its structural water, and the lower its density, the stronger the resulting cement paste.

Thus, chemical variations and porosity variations have to be co-evaluated, and for a favourable coincidence of the factors, a high alumina cement concrete may be produced that is little affected by harmful transformations likely to destroy it.

Damages may largely be prevented by:
— achieving careful placing, hence high compacity;
— applying well graded aggregate;
— applying aggregates exempt of free or releasable alkalis;
— preventing the concrete from overheating, e. g. by water cooling the surface, with the double aim of inhibiting temperature conditions facilitating critical transformation of high alumina cements, and minimizing evaporation of mixing water from the concrete. Namely, rapid hydration accelerates heat release, excessively drying out the concrete surface and damaging the concrete.

Also risk of reinforcement corrosion must not be overlooked.

Freshly mixed Portland cement concretes have pH-values of 12.5 to 13.0. There is no risk of corrosion, namely in occurrence of these pH-values, reinforcement is soon coated by a thin oxide layer inhibiting further oxidation.

Green high alumina cement concretes have pH values of 11.5 to 11.7, at a basicity irrelevant to corrosion. In case of a high porosity, however, atmospheric CO_2 may carbonize the concrete reducing pH values that are still tolerable at 11.0 to 10.0. Still lower values, below about 9.0, especially in the presence of humidity, entrain rapid oxidation of steel surfaces. This phenomenon still contributes to the known harmful effect of CO_2. Still a thick concrete cover provides a certain safety by counteracting CO_2 penetration. The risk of corrosion is imminent in case of a thin concrete cover, and in the presence of chlorides and other electrolytes, likely, in addition to reduce pH values, to remove neutralizing coats of the reinforcement.

Without claim to completeness, some rather schematic statements and theoretical considerations on high alumina cements and their hydration have been outlined, noting as an apology that each publication rests on decades of research work by Hungarian and foreign (mostly French) scientists.

The introductory question:
are high alumina cement concrete constructions durable?
cannot be unambiguously answered, especially as concerns preexisting concretes.

Durability of high alumina concrete constructions made under other conditions than those providing soundness is more than doubtful. These conditions are: maximum concrete compacity (w/c as low as possible, anyhow below 0.4), high cement dosage, little porosity, exclusion of high temperatures, possibly exclusion of alkalis.

Unfortunately, Hungarian building practice often despised these conditions, resulting, of course, in disasters, deficiencies in high alumina cement concrete structures. In most cases, construction conditions are irreproducible, nevertheless it is most likely that severe damages had occurred already at the time of concreting the structures exhibiting actually the most serious destructions.

This statement would logically lead to the conclusion that once the specifications are observed, the high alumina cement concrete will be sound and durable.

In France, most of the earlier, strict prohibitions have been cancelled. Nevertheless we are of the view that strict cautiousness, reservation are imperative still for long, our very long-term standard strength tests demonstrate often important strength losses, in spite of specimens made with an about critical w/c ratio, high cement dosage, and stored at about 20 °C for years. Though, strength losses were less than for high w/c concretes, nevertheless they hint to caution. Besides physical factors, also chemical changes, crystallographic conditions, colloid chemistry processes and thermodynamic changes may largely be responsible for alterations of aluminate hydrates that cannot thus be considered as stable.

As concerns the second question, cement researchers of different countries are unanimous in that universal constructional use of high alumina cements is not to be spoken of. High alumina cement is an expensive hydraulic binder. For a high quality it depends on high-grade bauxite. Thus, it is no substitute for Portland cement.

Now, where is high alumina cement of use? For urgent works, rapid accessibility, important constructions of temporary or limited use, winter concreting, heat resistant or refractory concretes, grouting, expansive cement, repairs where — provided due cautiousness and strict respect of specifications prevail — high alumina cements may keep their appreciated but confined field of applicability.

Summary

Setting mechanisms of Portland cement and high alumina cement differ, and so does stability of hydrate products giving rise to the high alumina cement problem, i.e., whether high alumina cement constructions are durable, and whether high alumina cements are admissible for general constructional use.

Hydration of high alumina cement is affected by several factors likely to impair the high alumina cement concrete. Soundness may be improved, although not perfectly, by reducing porosity, w/c, overheating, excluding alkalis; all these, together with the high cost of high alumina cement prevent a general constructional use.

Prof. Dr. József TALABÉR, 1111 Budapest, Műegyetem rkp. 3. Hungary