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FACTORS ACCELERATING TRANSFORMATION OF HIGH ALUMINA CEMENTS

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Abstract

During hydration of alumina cements, the initially forming unstable hexagonal hydrates (CAH_{10}, CAH_8, C_4AH_{13}) are transformed sooner or later into stable C_3AH_6 belonging to the regular system. Factors accelerating transformation are:

- temperature
- water content (high w/c ratio)
- CO_2 content in the system
- presence of alkalines.

Transformation has a significant strength loss as concomitant. This results directly from the fact that unstable compounds of higher mole volume change into stable products of less mole volume. Strength loss is due to porosity decrease in transformation.

Presence of alkalines is a special risk, since — in final account — alkaline reactions may be accompanied by decomposition of aluminate hydrates.

By chance, extreme effects are seldom to coincide. Such a careful technology may help to utilize to a certain degree valuable properties of alumina cements (high strength, corrosion resistance, fire resistance). Under normal conditions, no further strength loss of constructions already transformed, subject to strength loss, needs to be reckoned with.

Keywords: alumina cement, transformation, strength loss, stability.

1. Introduction

Hexagonal hydrates (CAH_{10}, CAH_8, C_4AH_{13}) — primarily forming in the hydration of alumina cements — are unstable, and are transformed to stable products in a shorter or longer time, depending on

- temperature
- moisture content (w/c ratio)
- CO_2 content in the system
- alkali content in the system.

Because of porosity conditions due to the transformation stoichiometry (the role of water) an important strength loss occurs.

Typical products of the transformation process, most typical compounds of the transformation of alumina cements are C_3AH_6 belonging to a regular system, as well as initially amorphous, then partly crystallizing colloidal compounds such as AH_3 and FeH_3.

Strength loss is directly due to the transformation of unstable compounds of less molar volume to stable products of less volume, with the concomitant porosity increase.

2. The Reactions

Essential reactions of transformation have been compiled in *Table 1*.

Table 1
Reactions of transformation

Reaction	Volume of solid phases before reaction cu·cm/mol	after	Change cu·cm/mol	% by vol.
1 $CA + 10H \rightarrow CAH_{10}$	52.68	198.24	+145.56	+276.8
2 $CA + 5\frac{1}{2}H \rightarrow \frac{1}{2}C_2AH_8 + \frac{1}{2}AH_3$	52.68	122.90	+70.22	+133.3
3 $CA + 4H \rightarrow \frac{1}{3}C_3AH_6 + \frac{2}{3}AH_3$	52.68	92.92	+40.24	+76.4
4 $CAH_{10} \rightarrow \frac{1}{3}C_3AH_6 + \frac{2}{3}AH_3 + 6H$	198.24	92.0	−106.0	−54.5
5 $C_2AH_8 \rightarrow \frac{2}{3}C_3AH_6 + \frac{1}{3}AH_3 + 3H$	181.22	121.27	−59.95	−33.45
6 $C_3AH_6 + 3CO_2 \rightarrow 3CaCO_3 + AH_3 + 3H$	149.60	175.16	+25.56	+17.1
7 $CAH_{10} + CO_2 \xrightarrow{alk} CaCO_3 + AH_3 + 7H$	198.24	101.36	−66.88	−48.8

Density of solid phases:
$CA = 2.98\,g/cu{\cdot}cm$
$C_2A = 2.40\,g/cu{\cdot}cm$
$C_3AH_6 = 2.52 - 2.53\,g/cu{\cdot}cm$
$CAH_{10} = 1.72 - 1.78\,g/cu{\cdot}cm$
$C_2AH_8 = 1.95\,g/cu{\cdot}cm$
$CaCO_3 = 2.50 - 2.70\,g/cu{\cdot}cm$

The table shows that hexagonal hydrates forming in the first stage of hardening (CAH_{10}, C_2AH_8), the volume of solid phases significantly increases in proportions of 276.8% and of 133.3%, respectively (*Eqs.* (1) and (2)), responsible for the high early strength of alumina cements (with CA as the most important clinker mineral).

This reaction is rapid, also the high early strength develops rapidly.

Even in course of the hydration of CA directly to C_3AH_6 (hence, at a higher temperature), volumes of solid phases increase by 76.4% (*Eq.* (3)).

During transformation, however, in case of transformation of hexagonal hydrates to C_3AH_6, the volume of solid phases decreases, namely for CAH_{10} by 54.5% and for C_2AH_8 by 33.45% (*Eqs.* (4) and (5)).

This reduction of molecular volume has a porosity increase of similar order as concomitant. It is common knowledge that porosity reduces the strength responsible for the strength loss of alumina cements in transformation.

3. Factors Accelerating Transformation

3.1 The Role of Temperature

Transformation of alumina cements primarily depends on temperature, but it is rather strictly related to the moisture content in the system, hence, to the w/c ratio. According to X-ray tests, in the temperature range of 25 °C to 30 °C, transformation goes regularly along, and reaction results in stable C_3AH_6 and AH_3. Temperature has a decisive effect. In the $CaO - Al_2O_3 - H_2O$ system, C_3AH_6 has a very narrow range of primary segregation below 25 °C. Beyond 30 °C, however, determinant compounds of the system are C_3AH_6 and AH_3 (gibbsite). This is why the transformation of aluminate hydrates accelerates with temperature increase to a degree that e.g transformation of CAH_{10} at 90 °C is nearly complete in 10 minutes.

Of course, it is perfectly irrelevant for the thermal effect on concrete whether it is affected by outer temperature inducing transformation, or it is warmed by the heat of hydration. Heat released inside large concrete masses in one day is about equal to the hydration heat released by portland cement in 90 days.

In the strength development of aluminates, this is an essential factor, its various risks may arise for alumina cement concretes (e.g. cracking).

The effect of temperature has been recognized since long. Let me simply refer to experiments by Prof. Mihailich in the '30 s, but similar tests were made also in the laboratory of MÁK Felsőgalla, Hungary. Temperature values inside large ($2000\times1500\times1200$ mm) concrete masses with the concomitant strength losses caused doubts for specialists. But they did not know the cause of the strength loss.

3.2 The Role of Water

It is useless here to discuss the w/c ratio. Nevertheless, in the use application of alumina cements, the greatest mistake was that concerning the w/c ratio. Users, and even producers and cement specialists were mislead by favourable concrete strengths in the early period of utilization achieved with a relatively low cement dosage, and a high w/c ratio (0.50 to 0.60) easing casting.

Although, the well-known data how the w/c ratio alters the concrete strength, in particular, in coaction with temperature, should have been taken as a hint.

Unfortunately, in the first decades of producing and utilizing alumina cements in Hungary, problems related to the transformation of crystal structure, risks of w/c ratio, porosity, temperature were not yet known.

3.3 Carbonation of Alumina Cements

Essential factors affecting concrete carbonation are: environmental CO_2 and alkalinity, atmospheric humidity, temperature, cement quality (type) and dosage, w/c ratio, curing conditions, and for alumina cements, even the rate of transformation.

Although these parameters are inseparable (since e.g. porosity change occurs also in transformation), this time only role and effect of CO_2 will be examined.

In the $CaO - Al_2O_3 - H_2O$ system above 25 °C to 70 °C — depending on the temperature — relatively stable condition develops. This stability persists, however, only in an atmosphere exempt form CO_2, never occurring in practice.

CO_2 may react with the most of calcium-aluminate-hydrates to form calcium-aluminate-carbonate-hydrate, with a composition of $C_3A \cdot CaCO_3 \cdot H_{12}$. This compound, similar in composition to C_4AH_{13}, has been detected by X-ray diffraction testing.

Carbonate hydrate formation is, however, only an intermediate station of the carbonation process. After completion of the process, only some modified form of $CaCO_3$ will be present in form of aluminium hydroxide (hydrargillite, maybe gibbsite).

Of course, carbonation process starts at the concrete surface, later — because of concrete porosity — penetrating the concrete. This is one of the risks of porosity increase due to alumina cement transformation (in addition to pH change).

C_3AH_6 carbonation consist of the reaction:

$$C_3AH_6 + 3CO_2 \rightarrow 2Al(OH)_3 + 3H_2O\,.$$

Resulting volume increase of solid phases in case of full carbonation equals: 25.56 cu·cm/mol or 17.1% according to *Eq.* (6).

Thus, carbonation is a process reducing porosity, entraining also some strength increase.

Strength-increasing effect of carbonation for concrete structures results, however, not only from a surface process but also from spatial reactions controlled by diffusion processes. This process penetrates the concrete mass at a decreasing rapidity because of the volume increase of solid phases.

Carbonation depth may be deduced from Fick's laws of diffusion:

$$y = \sqrt{2D\frac{C_1}{C_2}t},$$

where: y = carbonation depth (mm)/;
D = diffusion factor;
C_1 = CO_2 concentration in air (0.6 – 0.8 g/cu·m);
C_2 = CO_2 required for carbonation of 1 cu·m of air (10 000 to 50 000 g/cu·m);
t = carbonation time.

Considering the D, C_1, C_2 factors as constant, carbonation depth

$$y = C\sqrt{t}\,\mathrm{mm}\,.$$

C has a dimension of m/m. Its value ranges from 1 to 4 m/m and depends on the porosity of hardened cement. All in all, the rate of carbonation depends on the specific permeability of hardened cement, on atmospheric CO_2 content and humidity, resp.

In occurrence of thermodynamical equilibrium according to *Eq.* (6), a condition of disintegration (maybe after years or decades) is exceptional. A high porosity is, however, dangerous, just as for high-porosity portland cement concretes.

3.4 The Role of Alkalis

Alkalis present in, or penetrating porous hardened cements, mortars or concretes are extremely destructive in occurrence of CO_2. Alkaline compounds in alumina cements, concrete aggregates, or mixing water rise across the concrete pores due to capillarity on the concrete surface, to react there with atmospheric CO_2. In final account, these reactions result in the complete destruction of alumina cements and concretes (*Eq.* (7)).

Reactions result in the formation of also geologically stable hydration products ($CaCO_3 \cdot 3H_2O$).

Because of the regeneration of alkalis, relatively slight quantities of alkali can make the reactions continuous and complete.

Hence, in its final development, the alkali effect is the same as the CO_2 effect, only much more emphasized.

Both factors have the same role also for effect mechanism.

Of course, the rapid evolution of changes is conditioned, here too, by simultaneity of several effects:

- presence of water;
- porosity of alumina cement or concrete;
- presence of soluble or solubilizable alkalis;
- warm, humid environment.

Practically, effects based on alkali hydrolysis become serious only if porosity, that is, permeability of concrete is elevated.

Therefore the permitted maximum w/c ratio is 0.4.

4. Conclusion

Ultimate states of the $CaO - Al_2O_3 - H_2O$ system are $Al(OH)_3$ and $CaCO_3$.

Between them, calcium-aluminate hydrates of different moisture contents and crystal structures depending on different factors (CaO/Al_2O_3 concentration, w/c factor, temperature, etc.) are formed, the most stable of them is $3CaO \cdot Al_2O_3 \cdot 6H_2O$ of regular system depending on $CaO/Al_2O_3 \cdot 6H_2O$ of regular system. Depending on CaO/Al_2O_3 concentration and on temperature, however, all compounds in the system may attain ultimate states, and there is also a possibility for aluminate cements to completely decompose. The outlined effects of CO_2 and alkalis incredibly accelerate these transformation processes.

Fortunately, these ultimate states are exceptional, and under ordinary conditions further deterioration, strength decrease of preexisting but reconstructed building structures need not be reckoned with.

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