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DETERMINATION OF THE EXPECTED DECREASE IN STRENGTH OF HIGH ALUMINA CEMENT CONCRETE BY DERIVATOGRAPHY

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ABSTRACT

Methods involving the use of the derivatograph in the determination of the expected decrease in strength of high alumina cement are described. In a series of steps the strength, porosity and the cement content of the concrete are determined by physico-chemical measurements. The actual phase composition of the cement component of concrete is determined by derivatography. Methods of separating the two overlapping peaks due to the dehydration of the calcium aluminate hydrates present in the cement are described.

INTRODUCTION

It is known, that during the last decades a significant decrease in strength, sometimes resulting in serious damage to constructions built in Hungary with the use of high alumina cement concrete, could be observed[1, 2]. Since many constructions were built of high alumina cement concrete the investigation of the causes of this decrease in strength is very important.

In the course of this investigation the following question had to be answered: Is it possible to determine the expected degree and rate of this decrease of strength on the basis of the present information?[3]

CHEMISTRY OF HIGH ALUMINA CEMENT CONCRETES

During the hardening of high alumina cements, the first step is the formation of unstable hexagonal calcium aluminate hydrates of the calcium aluminates of cement, which later transform into stable aluminate hydroxide, C_3AH_6. It is important to note that in this process the sum of molar volumes of stable compounds is smaller than that of the unstable ones, i.e. the transformation results in an increase in porosity (Table 1).

The formation of stable compounds is significantly accelerated at elevated temperatures, unfortunately the literature describing the relationship of transformation rate and temperature is very poor, sometimes showing contradictions[4–6].

TABLE 1

PROCESSES OF TRANSFORMATION OF CA

Chemical reaction	*Volume of solid phases*		
	Before reaction	*After reaction*	*Volume change*
$CA + 10\ H \rightarrow CAH_{10}$	52.68	198.24	+145.56
$CA + 5\frac{1}{2}\ H \rightarrow \frac{1}{2}\ C_2AH_8 + \frac{1}{2}\ AH_3$	52.68	122.90	+ 70.22
$CA + 4\ H \rightarrow \frac{1}{3}\ C_3AH_6 + \frac{2}{3}\ AH_3$	52.68	92.92	+ 40.24
$CAH_{10} \rightarrow \frac{1}{3}\ C_3AH_6 + \frac{1}{2}\ AH_3 + \frac{1}{2}\ H$	198.24	82.16	−116.08
$C_2AH_8 \rightarrow \frac{2}{3}\ C_3AH_6 + \frac{1}{3}\ AH_3 + 3\ H$	181.22	121.27	− 59.95
$C_3AH_6 + 3\ CO_2 \rightarrow 3\ CaCO_3 + AH_3 + 3\ H$	149.60	166.97	+ 17.37

These processes can be very much modified by carbonation. Several authors pointed out that due to air-borne CO_2 almost all calcium aluminate hydrates may be transformed into a carbonated form, which is unstable, later transforming into $CaCO_3$ and aluminium hydroxide. In the presence of CO_2 the C_3AH_6 is not stable but transforms into the previously mentioned compounds without forming intermediates. Due to this process compounds of larger molar volume are formed, i.e. carbonation reduces the porosity. Table 1 shows these chemical processes for the case of CA, the most important clinker mineral of high alumina cement, and indicates the volumetric changes accompanying the processes[7-9].

THEORIES ABOUT THE DECREASE IN STRENGTH OF HIGH ALUMINA CEMENT CONCRETES

The loss of strength — not regarding some rare cases — is generally explained by the transformation of unstable compounds[1, 4, 5, 7, 8, 10-13]. Considering, however, the fundamental causes, a lot of disagreement can be observed. Some research workers relate the loss of strength to the decrease in dispersity of new formations occurring due to transformation[7, 14, 15].

Other authors write about the increase in porosity accompanying the transformation[1, 4, 6, 10, 13, 16-18]. There are alternative explanations of the effect of carbonation; some authors consider it to be the cause of the loss of strength[18], while according to others the effect of carbonation is favourable[1, 2, 6, 11].

A clear consequence of these disagreements is that there exists no uniform point of view concerning the change of strength and the industrial building service-ability of high alumina cements.

OBJECT OF THE INVESTIGATIONS

Considering the above-mentioned circumstances, in order to reach our basic objective the following questions had to be properly answered.

(1) What kind of relationship describes the rate of transformation for reactions of unstable compounds and how does this rate depend on temperature?

(2) How is the texture of the formed products influenced by the rate of transformation?

(3) How is the strength influenced by the porosity and texture of the cement stone?

The actual problems were studied on synthetic, pure compounds, CA,CAH_{10}, C_2AH_8, C_3AH_6.

RATE OF TRANSFORMATION OF UNSTABLE CALCIUM ALUMINATE HYDRATES

In order to determine the rate of transformation after the hydrothermal treatment (carried out at different temperatures and for different times) of the two unstable compounds (calcium monoaluminate hydrate, C_2AH_8) playing the most important role in the hydration of high alumina cement, the degree of transformation was determined by derivatography.

From the derivatogram of calcium aluminate the amount of water lost calculated on the basis of the TG curve — with some neglection — is as follows:

at 100–110°C: 0.5 mole;
at 160–170°C: 1.5 mole;
at 270–280°C: 5.0 mole.

Slightly different is the derivatogram of C_2AH_8, for which the structural water losses are as follows:

at 100–110°C: 1.25 mole;
at 160–170°C: 1.25 mole;
at 260–270°C: 5.5 mole.

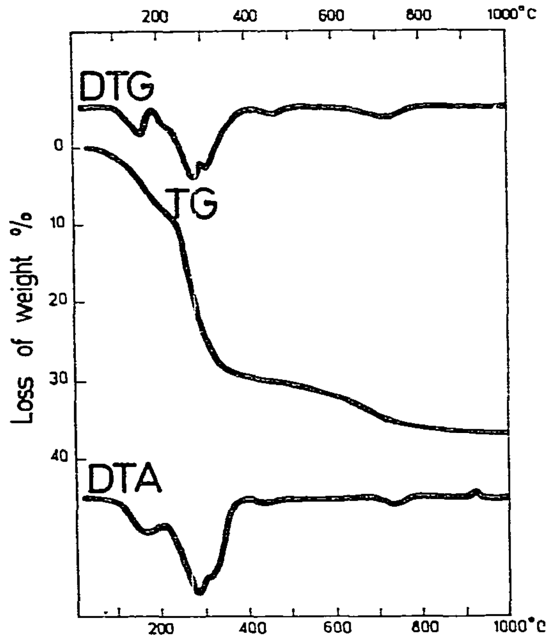
Exothermal peaks at 910°C on the DTA curve of calcium monoaluminate hydrate and at 620°C on that of the C_2AH_8 are caused by the formation of calcium aluminates (CA and $C_{12}A_7$, respectively).

Considerably different from the above is the derivatogram of C_3AH_6, which showed the following structural water loss values:

at 145°C: 0.25 mole;
at 325°C: 4.25 mole;
at 490°C: 1.50 mole.

The exothermal peak at 620°C here again shows the formation of $C_{12}A_7$. On the basis of the fundamental derivatograms there was no trouble in evaluating those recorded on samples subjected to hydrothermal treatment. As an example, the derivatogram of the calcium monoaluminate hydrate sample treated hydrothermally at 90°C for 2 and 72 h, respectively, is shown here (Figs. 1 and 2).

On the basis of this, knowing the chemical transformation reactions and the loss of weight at 325°C characteristic of C_3AH_6, the amount of the original (CAH_7 and C_2AH_8, respectively) compounds as well as that of the newly formed compounds can be calculated. The "degree of transformation", which means the ratio of the



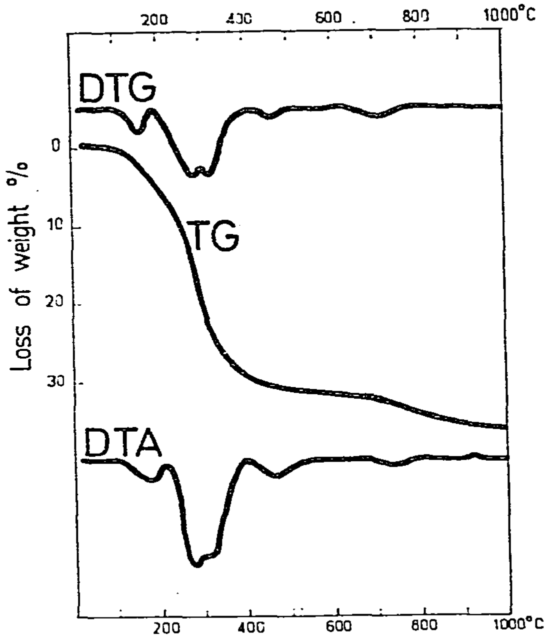


Fig. 1. Derivatogram of hydrothermally treated CAH_7 (temperature: 90°C; time: 2 h).

Fig. 2. Derivatogram of hydrothermally treated CAH_7 (temperature: 90°C; time: 72 h).

amount of CaO bond in the C_3AH_6 and of the total amount of CaO, can also be calculated.

By further calculation it is found that the transformation reaction is approximately kinetically third order.

The logarithm of the rate constant of reaction shows plotted linear changes with the reciprocal of absolute temperature subjected to the Arrhenius law.

According to the calculations made on the basis of the above relationships, the necessary time for atransformation to 75% of calcium monoaluminate hydrate is 76 years at 10°C, but it is only 10 min at 90°C. These transformation times are in good agreement with those observed in practice.

EFFECT OF POROSITY AND TEXTURE OF CEMENT STONE ON THE STRENGTH

For studying the relationships existing between strength and porosity and texture, respectively, prepared samples of CA were used. The different values of porosity and textural characteristics were secured by changing the water/cement ratio, the hardening temperature and time. The different characteristics of the samples were studied as follows: phase composition by X-ray diffractometry and derivatograph; the porosity by Hg-pycnometer; the textural characteristics by scanning electron microscope, Hg-pressure porosimeter and BET-surface measurement. The determination of the quantitative changes in the phase composition of cement stone was again carried out by derivatography. The reliability of this latter method is proved by the very good coincidence of porosity values measured by the experimental method

TABLE 2

CALCULATED AND MEASURED POROSITY OF SOME HYDRATED CA SAMPLES

Denomination	*Measured by*		*Calculated*
	mercury picnometry	*mercury pressure porosimeter*	*on the base of derivatograms*
v/c = 0.2; 14 days; 5°C	13.54%	14.55%	13.05%
v/c = 0.2; 14 days; 70°C	7.35%	7.93%	8.12%
v/c = 0.6; 14 days; 5°C	26.44%	25.32%	25.88%
v/c = 0.6; 14 days; 70°C	39.44%	38.89%	40.25%

and of those calculated on the basis of the amount and density of phases determined by derivatograph (Table 2).

We do not present further details of our investigations but wish to make known our final conclusions.

Our experiments confirmed those views, according to which the strength of high alumina cement is first of all determined by its porosity. Similarly to Cottin and Reif[6], the following relationship was found to exist between porosity (P) and strength

$$R = R_0 e^{-bP}$$

where R is the strength (kp cm^{-2}); R_0 and b are constants. The constants of the equation however, depend very much on the storage circumstances of the samples, first of all on temperature. This shows that the strength is influenced by factors other than porosity. Specific surface measurements explained this phenomenon. It was proved that in the course of the transformation of calcium aluminate hydrates the porosity remains unchanged, the strength decreases with the increase in specific surface, i.e. with the increase in the number of pores.

This can be explained by the fact that a pore forms discontinuity in cement stone, i.e. the increase in their number which, supposing otherwise unchanged circumstances, results in the decrease in strength.

Our further investigations again proved that for phase transformations resulting in identical increases in porosity, with the increase in the rate of transformation, the average size of pores is decreasing and their number is increasing.

This latter phenomenon can be explained by the consideration that with increasing temperature the rate of the formation of crystal centres is more rapidly increasing than the rate of crystal growth; thus at higher temperatures (in the case of the higher transformation rate) crystals of smaller size are formed. As for the size of pores, they are determined by the size of the crystals (solid parts) in such a way that between the bigger crystals are pores of larger diameter and between smaller crystals pores of smaller diameter are positioned.

Finally it can be stated that as a result of changes taking place near to the phase-equilibrium the porosity is not changing but the average size of pores is increasing and their number is decreasing.

An explanation of this phenomenon is that materials of larger specific surface and thus of higher superficial energy are less stable thermodynamically than those of smaller dispersity. Consequently, near to the phase-equilibrium processes accompanied by specific surface, can only decrease take place.

In the investigation of the influence of the effect of carbonation, the determination of the influence of the change of porosity and dispersity on the strength was carried out with special care. The phase-composition investigations showed that by the effect of CO_2 the $CaCO_3$ and aluminium hydroxide content of the cement stone increases while the amount of C_3AH_6 decreases, as expected. Since the molar volume of phases formed due to carbonation is larger than that of the starting phases, the process is accompanied by a decrease in porosity. This, however, does not cause an increase in strength at the beginning since the specific surface, i.e. the number of pores, is increasing due to the high dispersity of aluminium hydroxide formed at the decomposition of C_3AH_6, thus counteracting the positive effect of the decreasing porosity. Later on, however, the dispersity of aluminium hydroxide decreases due to causes mentioned above, resulting in the decrease in the number of pores and the increase in strength.

CONCLUSIONS ON THE CHANGES OF STRENGTH OF HIGH ALUMINA CEMENT CONCRETES

On the basis of the problems discussed above and Fig. 3, we present our point of view concerning the changes in strength of high alumina cement concretes[6].

In Fig. 3 the calculated porosity values which belong to the different transformation stages of pure CA are plotted as a function of the water/cement ratio. These are as follows:

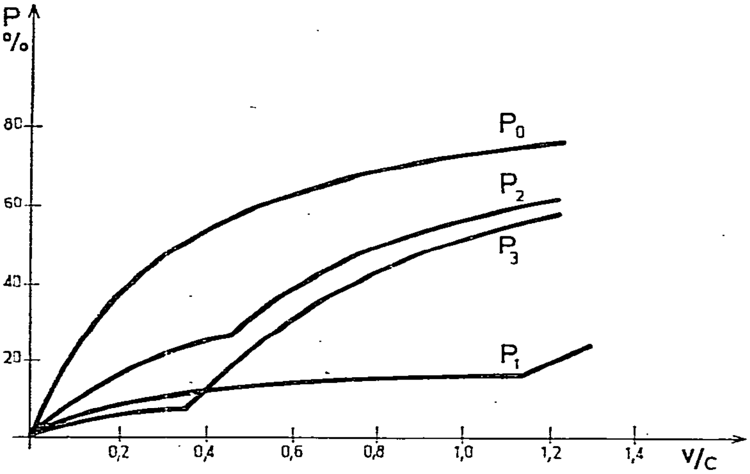


Fig. 3. Change of porosity, as function of water/cement ratio.

nominal porosity before hydratation (P_0);

porosity after full hydratation (in the case of the formation of calcium monoaluminate hydrate) (P_1);

porosity after the full transformation of unstable phases (C_3AH_6 and AH_3) (P_2);

porosity after full carbonation ($CaCO_3$ and AH_3) (P_3).

For all water/cement ratios, the strength of concrete increases to the point where porosity — effected by hydration — reaches its possible minimum (P_1).

Following this the strength — due to the transformation of unstable compounds — decreases up to the point of possible maximal porosity (P_2). The value of maximal porosity depends on the mineralogical composition of cement, the cement-content of concrete and on the water/cement ratio. The value of minimal strength corresponding to maximal porosity, however, also depends on the ambient temperature. If the temperature is higher, the strength will decrease since the size of the formed pores will be larger. After reaching the maximal porosity the number of pores will, however, decrease, which may result in a minimal increase in strength. This general scheme cannot substantially be changed even by carbonation.

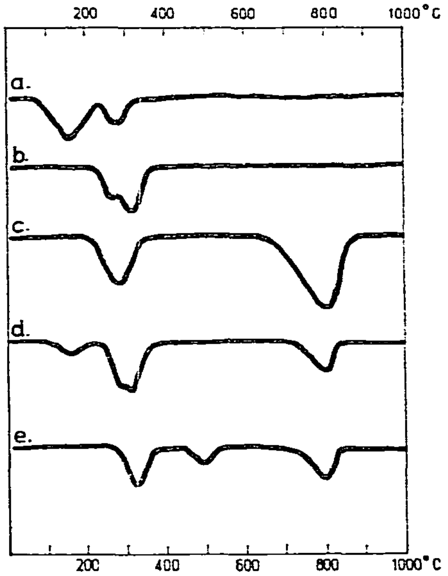
Our theoretical conclusions are also supported by practice: the continuous control of the strength of Hungarian buildings built of high alumina cement concrete shows that the rate of the loss of strength decreases with time. Some buildings were found in which a further loss of strength could not be observed, moreover, a certain increase in strength could be detected.

As a consequence of these considerations it can be stated what the loss of strength of high alumina cement concrete is regular but the final damage is not. The fate of the individual buildings or of a part of them depends on the question as to whether the minimal strength is bigger or smaller than the load.

DERIVATOGRAPHIC METHOD FOR THE DETERMINATION OF THE CHEMICAL STATE AND EXPECTED CHANGES OF STRENGTH OF HIGH ALUMINA CEMENT CONCRETES

It can be seen that the strength of high alumina cement concretes is first of all determined by the changes in porosity accompanying the transformation processes of calcium aluminates. This enables us to establish a method of investigation by which the expected loss of strength of high alumina cement concretes can be determined. The theoretical basis of this method is as follows. The present strength and porosity of concrete and the amount of unstable calcium aluminates in it is measured. Knowing the transformation reactions of the latter compounds and the molar volumes of the phases taking part in the process, the possible changes in porosity — and thus the possible maximal porosity — is determined by stoiciometric calculations. At the end, knowing the relationship existing between the porosity and strength of concrete, the expected changes in strength and thus the value of minimal strength can be determined.

For the determination of strength, porosity and cement content, methods



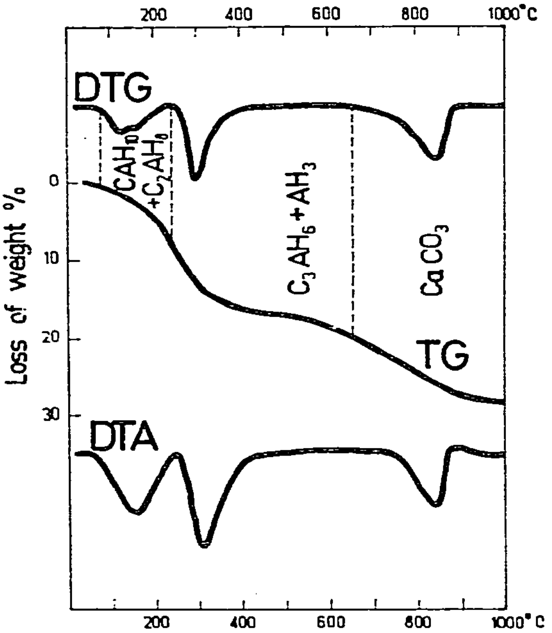
a./ CAH_{10}
b./ 1/3 C_3AH_6 + 2/3 AH_3
c./ $CaCO_3$ + AH_3
d./ average high alumina cement concrete
e./ autoclaved high alumina cement concrete

Fig. 4. DTG courves of the different stages of CA transformation.

elaborated earlier were used. The determination of the amount of unstable calcium aluminate hydrates of the cement was, however, problematic. X-ray diffractometry of the available methods is not satisfactory since the cement stone contains a lot of gel-like, poorly crystallized phases, and, on the other hand, there are a lot of aggregate particles in the cement-rich fraction of the concrete, the crystal constituents of which disturb the evaluation. More suitable is derivatography, but its evaluation is made more difficult because the water loss from unstable compounds C_3AH_6 and CH_3 at 280–350 °C takes place simultaneously, so their separate determination is impossible.

This problem is illustrated in Fig. 4, in which DTG curves of high alumina cement concrete samples of different stages of transformation as well as those of an average high alumina cement concrete sample can be seen. This problem could be solved by making derivatograms on samples taken from the concrete not only in the original state, but also after autoclave treatment under 20 atm pressure. Thus, due to autoclaving the C_3AH_6 remains unchanged, and AH_3 transforms into boehmite containing 1 mole of water, which is eliminated at 500 °C (see Fig. 6). This peak can be well differentiated from that showing the water loss of C_3AH_6. The unstable calcium aluminate hydrates are also transformed by autoclaving, thus the autoclaved sample contains more C_3AH_6 and aluminium hydroxide than the original one. On the basis of this — also taking into account the AH_3–AH transformation — the following equation can be written

$$S_{300A} + 3\, S_{500A} - S_{300N} = \Delta S_{300} \geqq 0$$



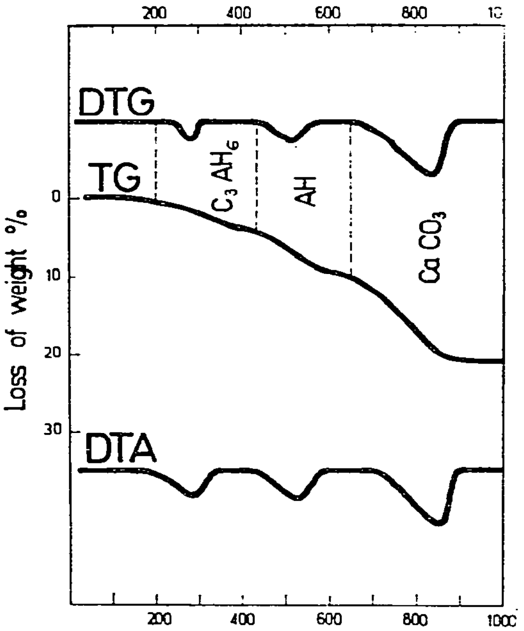


Fig. 5. Derivatogram of the fine fraction of high-alumina cement concrete.

Fig. 6. Derivatogram of the fine fraction of high-alumina cement concrete after autoclave treatment.

where S_{300A}, S_{500A} and S_{300N} are the weight losses that belong to the corresponding DTG peaks (300 and 500°C) of derivatograms made on autoclaved (A) and normal state (N) samples, calculated for 1 g of material free of loss on ignitions. ΔS is proportional to the amount of unstable calcium aluminate hydrates (and incidental unhydrated calcium aluminates). Derivatograms of an original state and of an autoclaved sample are shown in Figs. 5 and 6.

On the basis of this data the amount of the most important constituents of the cement component of high alumina cement concrete, such as unhydrated calcium aluminates, unstable and stable calcium aluminate hydrates, aluminium hydroxide and calcium carbonate, can be determined by stoichiometric calculations. Using this data the degree of hydration, transformation and carbonation can also be determined. Knowing the amount of unstable calcium aluminate hydrates the expected changes in strength of high alumina cement concretes can be estimated in the following way.

Starting from the volume losses occurring during the transformation of unit weight compound (for 1 kg of CAH_{10}: 296 cm^3; for 1 kg of C_2AH_8: 173 cm^3) we calculate the expected increase in porosity and the possible maximal porosity. To make the calculation more accurate we assume that unstable compounds present are in the form of CAH_{10}. On the same basis the maximal decrease in porosity due to carbonation of concrete can also be calculated.

The strength data corresponding to these porosity values are derived by the relationships elaborated in a Hungarian research institute by applying mathematical statistics on the basis of the investigation of some thousand high alumina cement concrete samples[26].

TABLE 3

CHARACTERISTICS OF HIGH-ALUMINA CEMENT CONCRETE SAMPLES

	1	*2*	*3*	*4*
Cement content (kg/m^3)	269	234	263	185
Degree of hydration (%)	97.12	97.04	94.92	97.13
Degree of transformation (%)	97.12	75.38	86.07	79.72
Degree of carbonation (%)	49.54	54.96	30.68	78.07
Porosity (%)	14.02	17.80	10.98	14.02
Possible maximum porosity (%)	14.65	22.92	12.54	16.52
Expectable final porosity (%)	12.90	22.44	11.57	16.50
Comressive strength (kp/cm^2)	94	96	148	106
Possible minimum strength (kp/cm^2)	90	64	122	87
Expectable final strength (kp/cm^2)	103	67	141	87

As a consequence of the tendency-character of the statistical relationship the strength cannot be directly determined from porosity. The expected changes in strength can, however, be estimated, if the quotients of strengths calculated from porosities corresponding to the different states of concrete are multiplied by the value of the present strength (Table 3). Finally, as an example, we present the results of some calculations made on high alumina cement concrete samples.

It must be noted that we are conscious of the limited accuracy of the described method caused by the problematic selection of representative samples, the problems of sampling, inaccuracies in the determination of strength, porosity and cement-content, as well as some simplifications, etc. experience shows, however, that this method is suitable for improving the correctness of responsible decisions made concerning the fate of some individual high alumina cement concrete constructions.

REFERENCES

1 J. Talabér, *Epitoanyag*, 8, (1956) 161, 202, 295.
2 J. Talabér, *VI. Mezdunarodny Kongress po Himii Cementa*, Stroizdat, Moscow, 1976.
3 M. Révay, *VI. Mezdunarodny Kongress po Himii Cementa*, Stroizdat, Moscow, 1976.
4 H. G. Midgley, *Trans. Br. Ceram. Soc.*, 67 (1967) 1.
5 A. M. Neville, *Proc. Inst. Civ. Eng.*, 1963.
6 B. Cottin and P. Reif, *Rev. des Mater. Constr. Trav. Publics*, 661 (1970) 293.
7 I. V. Kravtshenko, *Glinosemisty Cement*, Gosstroyizdat, Moscow, 1961.
8 N. F. W. Taylor, *The Chemistry of Cement*, Academic Press, London, New York, 1964.
9 H. Lehmann and K. J. Leers, *Tonind. Ztg.*, 2 (1963) 29.
10 H. Lafuma, *Assoc. Fr. pour l'Essaides Mater.*, 14 (1934) 11.
11 H. Lafuma, *Epitoanyag*, 21 (1969) 162.
12 P. Lhopitalier, *4th Int. Symp. Chem. Cement*, Washington, 1960.
13 H. E. Schwiete, V. Ludwig and P. Müller, *Epitoanyag*, 17 (1965) 157.
14 P. K. Mehta, G. Lesnikoff, *J. Am. Ceram. Soc.*, 54 (1971) 210.
15 L. S. Wells, E. T. Carlson, *J. Res. Natl. Bur. Stand.*, 57 (1956) 335.
16 P. Stiglitz, *Rev. Mater. Constr. Trav. Publics*, 671–672 (1971) 219.
17 P. Stiglitz, *Epitoanyag*, 24 (1972) 45.
18 M. R. Fourie and R. Rabot, *Epitoanyag*, 25 (1973) 129.
19 K. Szepesi, *EAKI Report*, 1962.
20 I. Szilágyi, *10th SILICONF*, Budapest, 1970.