ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 10, No. 1. 2004

Some Aspects of Influence of Microsilica and Admixtures on Hydration Kinetics of the Alumina Cement "Gorkal-40"

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Received 30 September 2003; accepted 26 October 2003

The effect of microsilica (in the amount from 7 to 35 % by the mass) and deflocculation admixture on setting and flowability of pastes with the cement "Gorkal-40", when W/C + S = 0.3 is constant, was investigated. When the amount of microsilica is increased (from 7 to 35 %) the flowability of the paste is decreased, while the addition of deflocculation admixture results in the increased flowability. The setting time is the lowest when the amount of microsilica in the paste is the highest. For the continuous registration of kinetics of hydration process of cement "Gorkal-40" the EXO (exothermic) method was used. The influence of microsilica and deflocculation admixture on the initial EXO effect as well as on the duration of the induction period and the main EXO effect was also established.

1. INTRODUCTION

Most of the authors [1, 2] state that the initial time of the EXO (exothermic) effect in alumina cement matches the end of the paste flow, while the maximum time of the effect duration correlates with the stage of paste setting allowing for the samples to be demoulded.

In [3], we can find a description of two EXO effects: the beginning of the first effect matches the end of paste setting though demoulding of samples is not yet possible. Only at the beginning of the second effect the cement is hydrating, resulting in the hardening of the material. However, the above data were obtained in testing refractory concrete with alumina cement CA-14M (70 % of Al_2O_3) and the disperse Al_2O_3 admixture. It has been found that the addition of microsilica increased the induction period many times, while decreasing the EXO effect.

Microsilica is a typical pozzolana, not possessing any binding properties. However, it can react with lime at normal temperature with water. In [4] it is shown that during the reaction with pozzolana a certain amount of heat is released. The rate of the reaction depends on the dispersity of pozzolana. It has been stated that the reaction may yield 0.8 – 1.5 $CaO \cdot SiO_2 \cdot aq$ or $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot aq$, depending on other materials present.

Unfortunately the hydration process of cement "Gorkal-40" is less investigated than of other alumina cements and compositions with different admixtures. In [5], the suspension (W/C + S = 2), consisting of the cement "Gorkal–40" with microsilica and deflocculation admixtures, are described. It has been found that the admixture of SiO_2 can accelerate the hydration of the cement "Gorkal-40", thereby accelerating the setting of the suspension. In testing the suspension with a deflocculation admixture, an intermediate EXO effect, with less heat released, has been obtained. The deflocculation material increases the time of gel formation.

As can be seen from mentioned above of literature, the authors place the emphasis on various problems associated with the kinetics of alumina cement hydration. However, the data on the effect of admixtures on the hydration kinetics of the cement "Gorkal-40" is scarce. Therefore, the main objectives of the present investigation are as follows:

– to test the flowability and setting properties of the alumina cement "Gorkal-40" paste containing various amounts of microsilica, with or without the deflocculation admixture;

– to test the effect of microsilica and deflocculation agent on the cement hydration by applying an EXO approach.

2. EXPERIMENTAL

Alumina cement "Gorkal–40" (*C*) used in the experiment was manufactured in Poland. The content of Al_2O_3 in cement is not smaller than 40 per cent. The main mineral phases are: CA, the ferrite phase, $C_{12}A_7$, C_2AS; bulk density is 1160 kg/m^3, specific surface 300 m^2/kg, fire resistance – not lower than 1280 °C.

Microsilica (*S*) (manufactured in Poland) had a chemical composition, % by mass: SiO_2 less than 93 %, with inclusion of Al_2O_3, Fe_2O_3, K_2O, Na_2O, C. Specific surface $15 \cdot 10^3$ m^2/kg, bulk density – 330 kg/m^3.

As a *deflocculation agent* (*D*) water-free sodium polyphosphate (technical) $(NaPO_3)_n$ was used.

To make paste, dry components of paste cement and microsilica, were mixed in a Hobart mixer when same amount of water or water solution of a deflocculation agent was poured into the mix. Setting time of the paste were determined on the basis of LST EN 196 – 3: 1996, while the consistency was found according to paste flowability, using the shaking table (LST 1413.1:1995).

EXO temperature during the setting of paste was found by the technique developed by the "Alcoa" company [6]. The tests were performed at the ambient temperature (20 ±1) °C, with the temperature of the components (water, cement, microsilica, etc.) being (20 ±1) °C. A paste specimen of 1.5 kg was made of the size (10×10×10) cm in textolite form. During the formation of a specimen, an XA type thermocouple was inserted into it in a glass tube.

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3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. The effect of microsilica and deflocculation agent on cement paste flowability and setting time

Three paste compositions (Table 1) containing various quantities of microsilica were prepared, with the constant water/dry solids ratio W/C + S = 0.3. Deflocculation admixture made 0.35 % or 0.70 % of the amount of dry solids.

The flowability tests of the paste (Fig. 1) have shown that the flowability of paste without deflocculation admixture is the lowest when the amount of microsilica in a composition is the highest. This may be accounted for very high microsilica surface adsorption of water.

The addition of a deflocculation agent considerably increases the paste flowability (especially, that of the paste K-1D) by forming double layers of the electric charges around the particles of cement and microsilica. With a higher content of microsilica (21 and 35 %), the flowability of the paste is largely decreased due to the adsorption effect of microsilica. By increasing the amount of the deflocculation admixture twice, the flowability is decreased correspondingly.

Table 1. Cement paste compositions

Grade		Components, %		
without D	with D	water (W)	C	S
K-1	K-1D	23	70	7
K-3	K-3D	23	56	21
K-5	K-5D	23	42	35

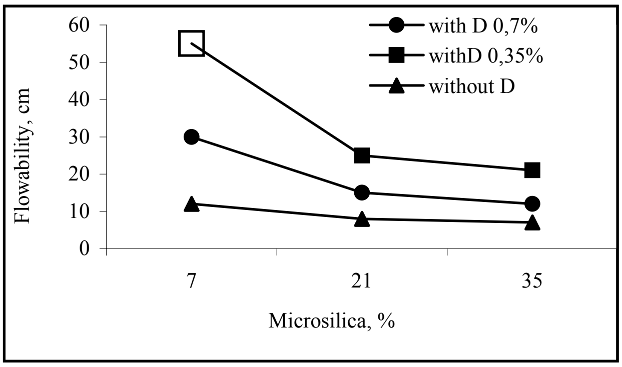

Fig. 1. The dependence of the amount of microsilica on flowability of pastes with and without deflocculiation (D) admixture; □ – flowability is more than 30 cm

The initial and final setting time of the paste (Fig. 2) largely depends on the amount of microsilica in the composition. The increase of its content considerably accelerates the initial and final setting time of the paste. The investigation made by the company "Lafarge" [7] has shown that the initial and final setting time of the cement "Fondu", which chemical composition is near to that of "Gorkal-40", are 200 min and 230 min, respectively. However, W/C ratio of the cement paste has not been given. The present tests have shown higher values for the initial and final setting time of purity cement "Gorcal-40" paste (230 and 300 min) accordingly, which, probably, may be accounted for different chemical and mineralogical composition of the above cements. X-ray difraction analysis of the "Gorkal-40" has shown that it contains free lime ((0.3 – 0.5) %) and more gelenite than the cement "Fondu". In [8] it is noted that some alumina cements fired at relatively low temperatures contain free lime, which hydrates intensevely.

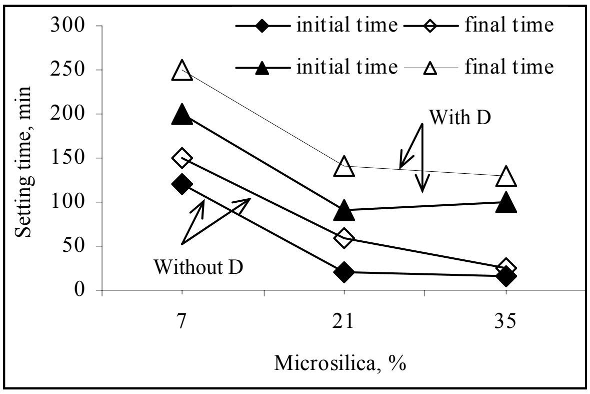

Fig. 2. The initial and final setting times of pastes with and without deflocculation (D) admixture

It has been found that the deflocculation admixture retards the setting. Some authors [9] note that deflocculation agents known for their retarding ability are adsorbed by the surface of cement particles, thereby increasing zeta potential and, because of the repulsion of positively charged particles, increase the dispersity of the material. The retarders of setting reduce the rate of solution, thereby improving the flow, retarding crystallization and increasing the setting time.

3.2. The study of exothermic effects (EXO) in the paste

Testing of the paste EXO was made with (0.35 %) or without deflocculation admixtures. It has been found that during the preparation of paste and compacting it in the mould – the period A (about 6 min.), the temperature of all the pastes (Fig. 3a and 4a) increase (by (2 – 3) ºC), except for the paste K-5, the temperature of which reached 26.5 ºC at the same time. It may, probably, be accounted for the EXO effect associated with wetting the surface of the particles of the paste with water.

In the period B (about one hour) the paste temperature varies, depending on the addition of microsilica and deflocculiation admixtures. In deflocculation admixture free pastes (Fig. 3a) the temperature has raised sharply once again by (3 – 4) ºC (in 10 min for paste K-1 and in 20 min for K-3). This may be explained by the pozzolana reaction between SiO_2 and CaO. For a larger amount of microsilica (K-3) the pozzolana reaction takes place later than that for paste K-1. It may be assumed that, in paste K-5, the above reaction took place when the paste was being prepared, since the same initial EXO effect (25 – 26.5) ºC was finally obtained for all three types of paste. The temperature during the time period B has not

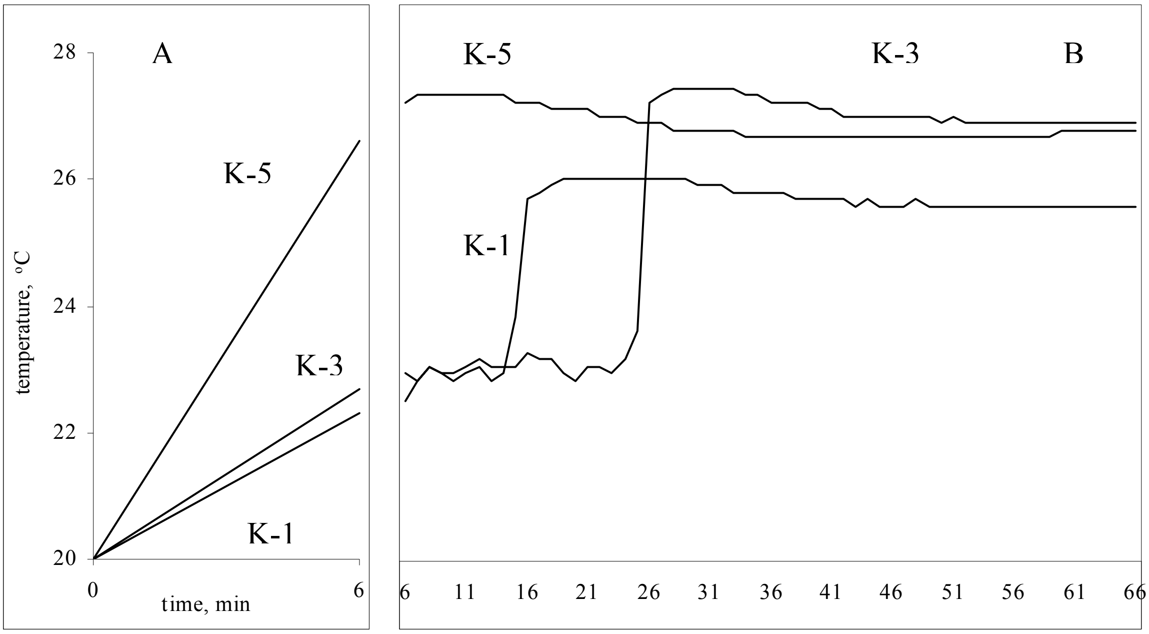

Fig. 3 a. Temperature variation in pastes without deflocculation (D) admixture and with different amounts of microsilica during hydration: period A – where time 0 min – temperature of materials before mixing; time 6 min – temperature of paste after mixing and compacting, period B – temperature of the compacted paste

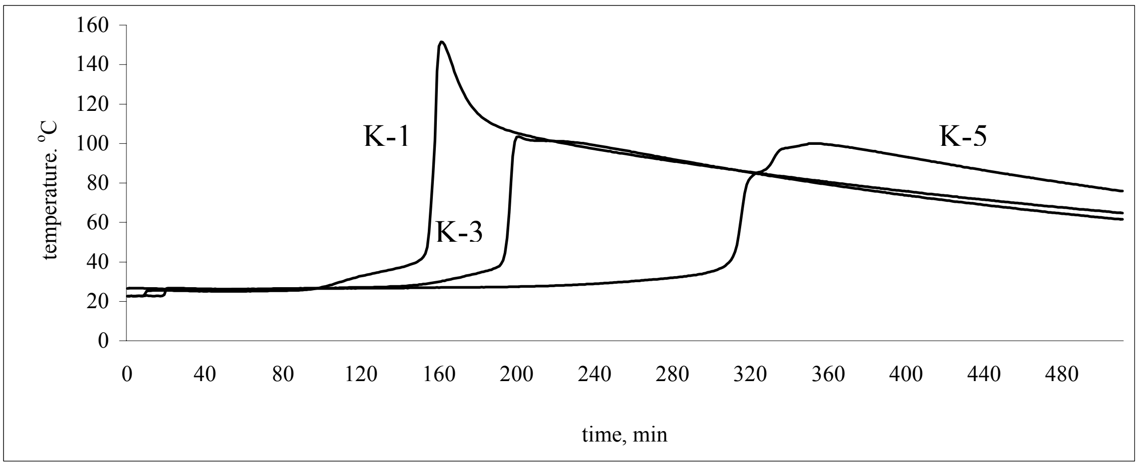

Fig. 3 b. Variation of EXO temperature in pastes without deflocculiation (D) admixture and with different amounts of microsilica

changed further, remaining the same as it had been at the beginning.

In pastes with deflocculation admixture (Fig. 4a), the temperature during the period B sharply falls (by (1.5 – 2.5) ºC) after (20 – 35) min, depending on the amount of microsilica: the higher it is, the later the temperature falls. The fall of temperature may be accounted for the some peculiarity of microsilica inclusion solubility. It has been noted that the heat releases much slower in pastes with the deflocculation admixture than in pastes not containing it. In the paste of the pure cement "Gorkal-40", the temperature of the released wetting heat remains constant for an hour. This shows that, at that period, gel structures are being formed in the paste with admixtures, releasing not much heat. In Fig. 3b and 4b, further hydration development is shown, at first with the temperature in the paste being stable (induction period). At this stage, a high concentration of ions is reached, with more cement minerals being solved [10]. In pastes with and without the deflocculation agent the dependence of the process on the amount of microsilica added may be observed: the higher the content of SiO_2, the longer the induction period. It may be assumed that the amount of water, which is adsorbed by microsilica, is not sufficient for the intense cement hydration, while the deflocculation admixture some more retards this process.

When the induction stage is complete, the temperature of the samples begins to rise sharply, reaching about 60 – 150 ºC. This is caused by the processes of alumina cement hydration. The highest temperature is recorded in the paste K-1, while in other pastes, main EXO effect is smaller when the amount of microsilica in a composition is larger, since the cement amount in the paste is respectively lower.

It has already been noted, that, according to some authors, the temperature of the beginning EXO effect corresponds to the initial setting of the alumina cement, while at the maximum EXO temperature the setting of the paste has already been over. The present tests have revealed some differences in the above processes with

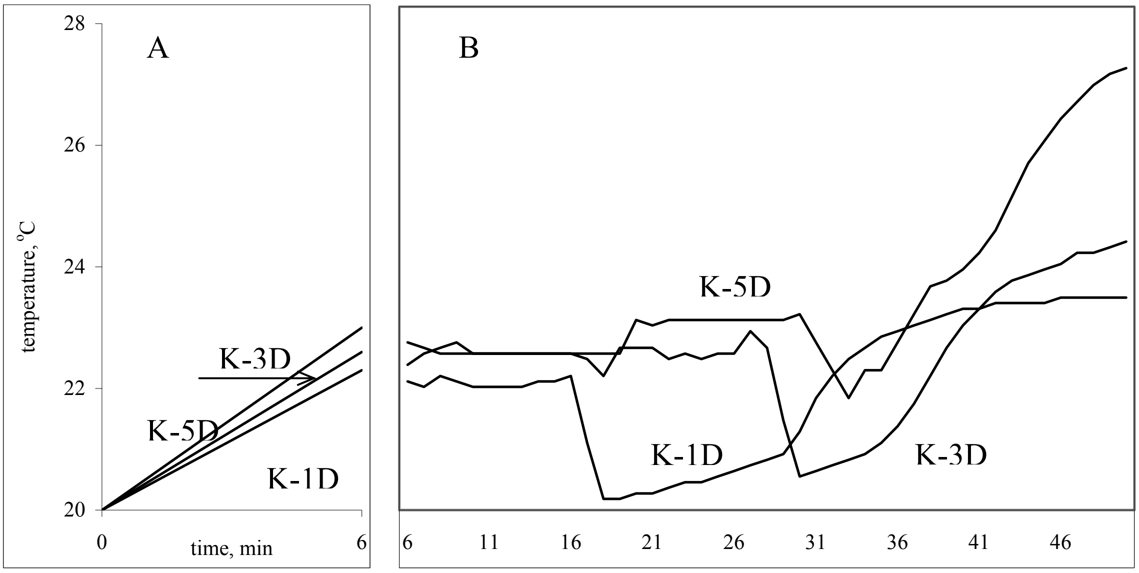

Fig. 4 a. Temperature variation in pastes with deflocculation (D) admixture and different amounts of microsilica during hydration: period A – where time 0 min – temperature of materials before mixing; time 6 min – temperature of paste after mixing and compacting, period B – temperature of the compacted paste

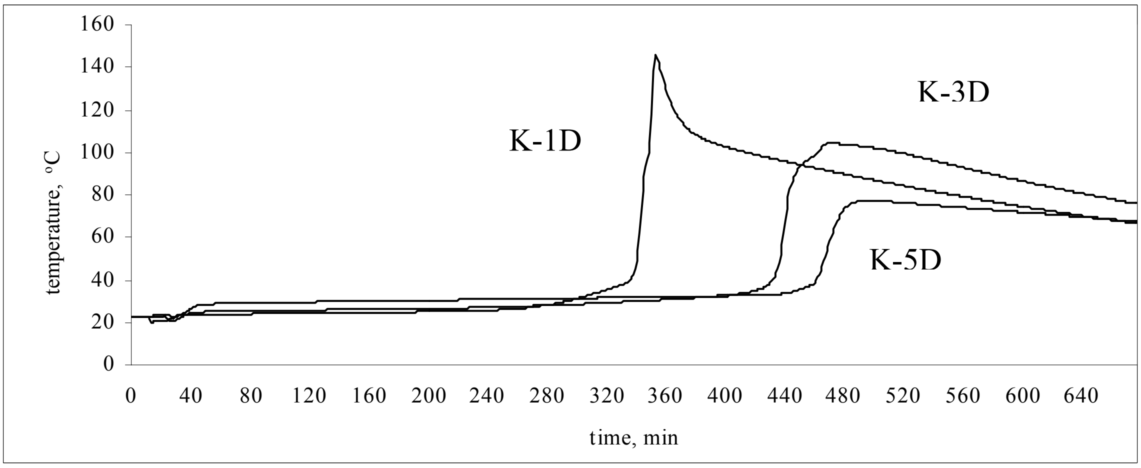

Fig. 4 b. EXO temperature variation in pastes with deflocculation (D) admixture and different amounts of microsilica

microsilica and deflocculation admixture added into "Gorkal-40" cement paste. The comparative analysis of exothermic effect and the paste setting time (Table 2) allows us to conclude that the initial and final setting time of the paste K-1 practically corresponds to main EXO effect. However, for the pastes K-3 and K-5, as well as for all pastes with deflocculation admixture, the setting of the paste occurs much earlier than the main EXO effect develops. The latter is found several hours later, when the samples have already hardened. This phenomenon may be described in terms of the hydration mechanism hypothesis.

A paste with a large amount of microsilica is setting due to the pozzolana reaction with SiO_2, when, as shown in Fig. 3a and 4a, a small amount of heat is released. Free water is adsorbed by the surface of the remaining particles of microsilica and being stored in the gel. When the gel is getting denser, the molecules of water detach and diffuse into the hardened structure to the cement particles. Their contact in the hardened paste causes the hydration.

The curves referring to the pastes with deflocculation admixture (Fig. 4a and 4b) differ from those given in Fig. 3a and 3b, because the D admixture considerably increases the induction period in the pastes.

Table 2. Comparative data on EXO effect and setting time of pastes

Paste grade	Final setting time, min	Time of reaching the main EXO maximum, min.	Maximum temperature, °C
K-1	150	150	155
K-1D	250	330	145
K-3	60	200	115
K-3D	140	425	105
K-5	30	310	115
K-5D	130	460	75

The more cement is found in the paste, the more abrupt heat release is observed during the exothermic reaction, while the smaller amount of cement in the paste is accompanied by a weaker main EXO effect, shown by a more flat – top peaked curve in the diagram.

4. CONCLUSIONS

Rheological and setting properties of cement "Gorkal-40" paste largely depend on the amount of microsilica in the composition. By increasing the amount of microsilica from 7 to 35 % by mass, the flowability of the paste is decreased while the setting is accelerated. The deflocculation admixture increases the flowability of the paste as well as decreasing the setting time.

In the first hydration period (about 1 hour after mixing) microsilica admixture increases the release of heat in the paste. The addition of the deflocculation agent causes the retarding of hydration for a short time.

In the second period (from 1 hour to 10 hours) in pastes with a larger amount of microsilica less heat is released, while the addition of the deflocculation admixture results in even lower temperature of the main EXO effect.

It has been found that, in fact, the initial and final setting time coincides with the duration of main EXO effects only for the paste with small amount (7 %) of microsilica in its composition. However, the setting time of the pastes K-3 and K-5 with big amount of microsilica is about 20 – 30 min, while main EXO effect develops several hours later in already hardened paste.

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