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DEFLOCCULATED REFRACTORY CONCRETES WITH A HIGH CEMENT CONTENT

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Dependences are provided for the spreadability and mechanical characteristics of deflocculated concretes on the content of microsilica, deflocculant and water. The effect of microsilica on hydration of calcium aluminate cements is discussed.

The disadvantages of refractory concretes with a high content of calcium aluminate cement are mainly caused by the significant amount of water required for cement hydration. On heating the hydrate formed during cement hardening breaks down, and water leaves the concrete forming pores; the concrete structure is loosened and the strength is reduced. Technology free from these disadvantages for low-cement concretes, in which part of the cement is replaced by finely-dispersed corundum powder, reactive alumina and microsilica (MS) exists, and it has already been developed for several decades.

Deflocculation of low-cement and particularly ultralow-cement concretes exhibit not only a dense and stable structure, but also exceptional high-temperature properties that are due to the low CaO content. However, for concretes intended for operation at temperatures below 1300°C a reduction in cement content is not mandatory. In this case it is possible with success to use deflocculated concretes with a high cement content exhibiting good rheological properties, a dense and stable structure, as for low-cement concretes. In addition, it is possible to expect from them certain production advantages in laying, i.e. for example less sensitivity to overdosage of water [1].

Deflocculated concrete with a high cement content has been the subject of a number of publications [1 – 3], but dependence of its production properties (spreadability, setting and hardening times, rate of strength increase) and physicotechnical properties on the content of MS, deflocculant, retardant and the amount of added water requires further study. The aim of experiments described in this article was clarification of these dependences.

The starting materials for test composites were granular highly dense bauxite containing more than 90% Al_2O_3, chamotte with a Al_2O_3 content of 41%, finely ground electrically melted corundum with an Al_2O_3 content of more than 99%, calcium aluminate cements Secar-71 (70% Al_2O_3), Secar-51 (52% Al_2O_3), Ciment Fondu (40% Al_2O_3), MS with an SiO_2 content of 96%. The deflocculant used was sodium tripolyphosphate (STPP), and the retardant was citric acid. Spreadability was determined by means of a cone 50 mm high and a lower diameter of 100 mm. The cone was filled with concrete, then the cone was removed making it possible for the concrete to spread over the surface of a table fitted with a shaking mechanism. The increase in concrete diameter was determined after free spreading and subsequent 30-fold shaking.

In the first stage simple rheological properties were evaluated for the mix of cement and MS without adding deflocculant. Results shown in Fig. 1 confirm the known fact

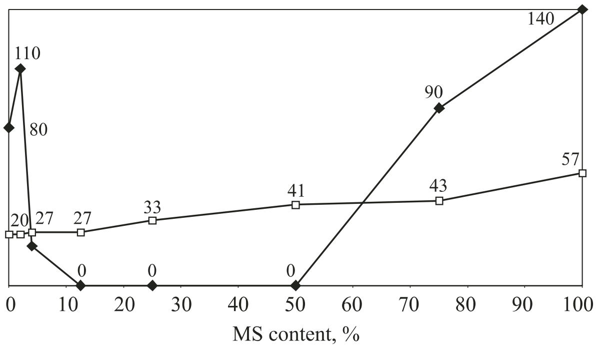

Fig. 1. Water requirement (□), %, and spreadability with shaking (◆), %, for mixes of cement Secar-71 and MS without adding deflocculant.

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that in the absence of deflocculant MS sharply reduces cement fluidity and increases the water requirement [1, 4]. Normally this is explained by coagulation of MS and cement particles having respectively negative and positive surface charges, and absorption of Ca^{2+} ions whose source is cement at the MS surface [4].

In order to reduce the amount of water added and to increase spreadability it is necessary to introduce deflocculant for which phosphates are used that create at the surface of particles finely-dispersed binding matrix positive charge and prevent absorption of calcium ions by miocrosilica. Sodium tripolyphosphate is an effective cement deflocculant. Whereas pure cement Secar-71 does not exhibit self spreadability even with addition of 30% water, on adding 0.2% STPP even with introduction of 25% of water the spreadability is more than 180% (Fig. 2). Combined introduction into the composition of the test mix of MS and STPP makes it possible to reduce even more the amount of water required for providing high fluidity. Values of spreadability for mixes of the system cement – MS – STPP are shown in Fig. 3. With an MS content of 10 – 40% and 0.2% of STPP the self spreadability of the mix may be obtained on adding 17.6% water. For mixtures containing less than 10% or more than 40% MS self spreadability is reached with a higher water content.

In the next stage a study was made of actual granular concretes with a different MS content. Apart from STPP the mix contained other modifying additions for a different purpose. In order to determine the sensitivity of concretes to overdosing with water for each composition the amount of added water was measured. Results obtained (Fig. 4) point to exceptional mechanical properties for deflocculated concretes. The ultimate strength in compression after firing at 800°C for some concrete compositions exceeds 200 MPa. Whereas normal concretes do not exhibit self-spreadability even with addition of 11% water, deflocculated concretes spread well without application of an external action on introducing 6% water. With shaking for spreadability of concretes of optimum composition 5% of water is sufficient and with application of vibration it is 4.5%

Compared with low cement concretes deflocculated concretes with a high cement content exhibit less sensitivity to overdosing with water. Addition of 2% water above the required amount leads to a reduction by 25 – 30% in the strength of concretes containing 20% cement, by 30 – 50% for concretes containing 10% cement, and 50 – 70% for concretes containing 5% (cement was replaced by finely ground corundum).

The well-known fact is also confirmed of a slowdown of cement setting by microsilicon. For a further slowdown in setting it is possible to use citric acid. Here there is also a slowdown in hardening, the rate of increase in strength falls, and early strength is reduced, but citric acid has almost no effect on the properties of concretes after firing at 800°C (i.e. on operating properties) (Fig. 5).

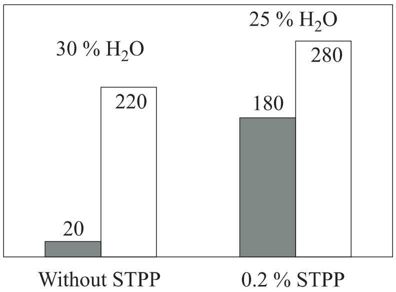

Fig. 2. Effect of STPP on spreadability, %, of cement Secar-71 without shaking (■) and with shaking (□).

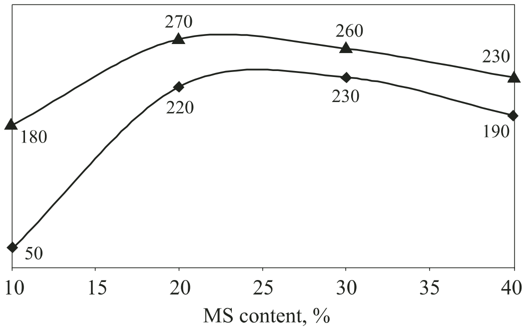

Fig. 3. Spreadability with shaking (▲), %, and without shaking (◆), %, of a mix cement Secar-71 with MS and addition of 0.2%

The mechanism of setting and hardening of refractory concretes based on calcium aluminate cement containing microsilica is very complex, it has been studied from different directions, but so far it is not clear [4 – 9]. It is apparent that the mechanism of hardening and formation of the binding skeleton in deflocculated compositions is different from that in normal concretes. The fact of a two-fold reduction in water requirement points to a radical change in the chemical nature of cement hydration on adding MS and STPP. In order to form hydrates C_3AH_6, C_2AH_8, CAH_{10}, 31 – 53% of water is required, whereas the water-cement ratio in the concretes used is about 25%. A study of the effect of MS on hydration of calcium aluminate, that exhibits a very high specific surface of MS, is connected with a considerable amount of added water, the hydration reduction period is prolonged, and conversion of hydrates into stable cubic form C_3AH_6 and the level of crystallization AH_3 are reduced [7]. At the surface of cement particles there is formation of a screening layer of colloidal silica, and setting of the concrete may be considered as a sol-gel process whose rate is determined by diffusion of calcium ions through the surface layer [8].

An interesting effect was noted in studying the stability of pastes that are a mix of cement with microsilica and STPP. With a constant STPP content (0.2%), a quite high MS content (20 – 40%) and addition of the minimum amount of water (17.6%) fluidity in a stirred mix occurs suddenly, i.e. the dry mixture becomes fluid during several seconds after prior prolonged mixing. The prior mixing time required for

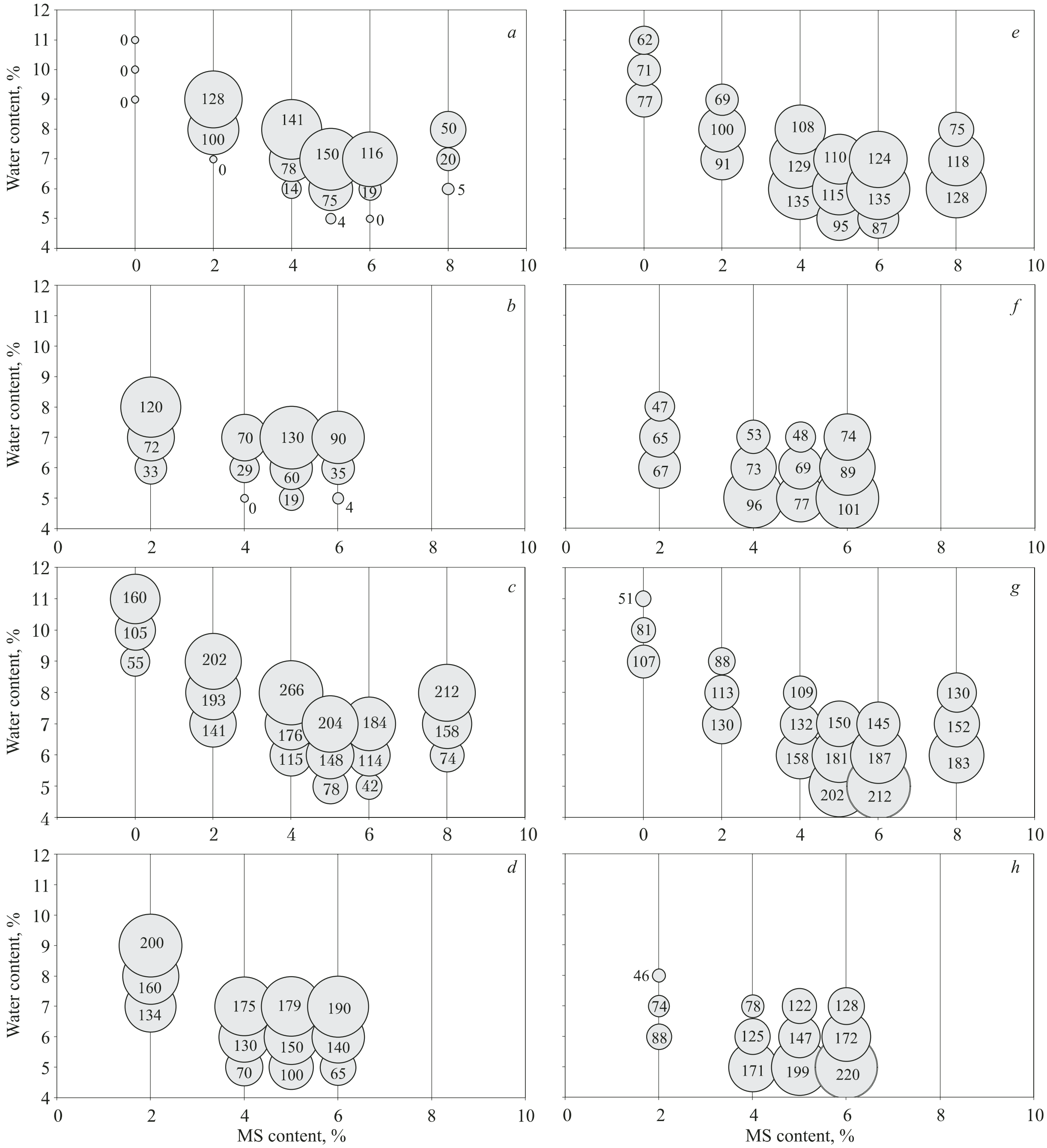

Fig. 4. Spreadability (*a* – *d*), %, and ultimate strength in compression (*e* – *h*), MPa, of deflocculated concretes based on granular bauxite and finely ground electrocorundum with addition of 20% (*a*, *c*, *e*, *g*) and 10% cement Secar-71 (*b*, *d*, *f*, *h*): *a*, *b*) spreadability without shaking; *c*, *d*) the same with shaking; *e*, *f*) strength seven days after formation; *g*, *h*) same after firing at 800°C.

liquifying the mix, during which STPP is distributed in the system, exhibiting a very high specific surface, increases markedly with an increase in MS content.

Microsilica markedly increases the time for the start of exothermic reactions, corresponding to the initial formation of calcium aluminates, and this provides more prolonged spreadability and viability [5]. It is well known that depending on the amount of MS (mainly the soluble impurity content) dissolution of cement particles may slow down from 30 to 240 min, and in the presence of STPP during an even longer time. Spreadability for compositions with a different amount of MS may also differ by 30 – 50% [6].

Thus, processes that occur in deflocculated concretes containing MS cannot only be considered from the point of view cement hydration, if the cement content is high, then in the presence of MS a significant part of calcium aluminate is not hydrated and remains in an unchanged form [9], i.e. it enters into the role of rather a finely dispersed filler more

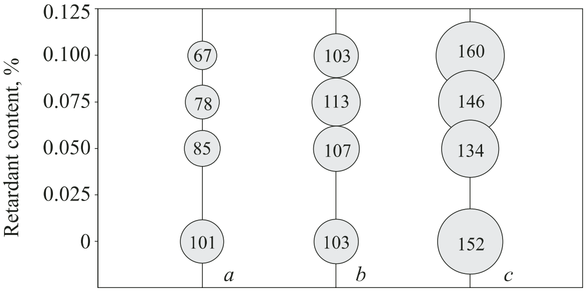

Fig. 5. Effect of retardant content on the ultimate strength in compression (shown in circles, MPa) for deflocculated concrete: *a*) 3 days are forming; *b*) 7 days after forming; *c*) after firing at 800°C.

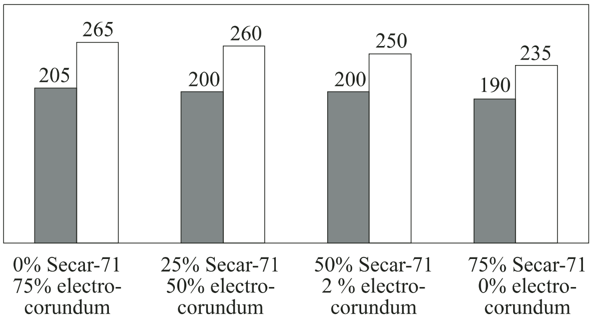

Fig. 6. Spreadability, %, of a mix of the system Secar-71 – 25% MS – 0.2% STPP – 17.6% water; ■) spreadability without shaking; □) same with shaking.

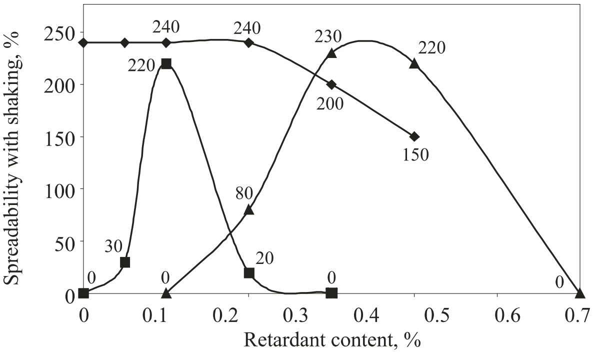

Fig. 7. Spreadability of a mix of different calcium aluminate cements with 20% MS and 0.2% STPP; ♦) Secar-71 (water content 17.6%); ■) Secar-71 (water content 18.6%); ▲) Ciment Fondu (water content 18.6%).

TABLE 1. Technical Properties of Chamotte Deflocculated Concretes of Compositions 1 – 3

Index	1	2	3
Content, %:			
chamotte (41% Al_2O_3)	74	74	74
Secar-71	20	–	–
Secar-51	–	20	–
Ciment Fondu	–	–	20
microsilica	6	6	6
water	5.8	6.2	6.5
addition	+	+	+
Ultimate strength in compression, MPa:			
3 days after forming	90	74	82
after firing at 800°C	110	90	73

than a hydraulically active binder. In comparing concretes containing 20% Seacar-71 cement and 10% of this cement (i.e. with replacement of 10% of cement by corundum fraction,0.063 mm) no marked change in properties is observed with the exception of some reduction in the original strength (see Fig. 4*e*, *f*). In the presence of a marked amount of MS the water requirement and paste spreadability in the system Secar-7 – finely ground electrocorundum – 25% MS is also independent of the ratio of cement and corundum (Fig. 6).

Such a situation is only retained when high purity cements are used, such as Secar-71. Less pure cements have a marked effect on spreadability and the water requirement for compositions containing MS. Secondary impurity phases, within the composition of cements with a reduced Al_2O_3 content, react actively with MS, and this leads to rapid setting of concrete (conversely, combined with Seacar-71 cement microsilica exhibits a clearly defined retarding effect). “Matrix” pastes, containing Secar-71 cement or Ciment Fondu and STPP, have a plastic consistency. Spreadability of these compositions may only be obtained with addition of a certain amount of retardant and an increase in water content (Fig. 7). In real concretes deflocculation of MS is facilitated as a result of mechanical action of a granular filler, and economic deflocculated concretes exhibiting high strength may be prepared using cements with a reduced Al_2O_3 content. The water requirement of these concretes is somewhat higher, and fluidity is lower, than in the case of using Secar-71, but the mechanical properties are quite high (see Table 1) The ratio of the content of deflocculant and retardant in these concretes may be optimized in relation to the mineral composition of the cement and MS properties.

Phase and structural changes of MS-containing concretes with a high cement content at high temperature have not been studied within the framework of the present work. Marked shrinkage has been observed on firing starting from 1400°C.

Thus, the effect of adding MS in concrete properties with a high cement content involves the following:

- in the absence of deflocculant MS sharply reduces concrete fluidity. This may be useful in preparing mixes for torcreting and ramming;
- introduction of MS in an amount up to 6% combined with STPP markedly increases fluidity and reduces the water requirement. For concretes a property develops of self-spreadability with half the water content, and there is a sharp increase in strength and density.

Defloculated concretes with a high cement content may be recommended primarily for use at moderate temperatures (up to 1300°C) under conditions of the action of strong mechanical and abrasive loads. Due to the dense structure high resistance of these concretes to the action of molten nonferrous metals should be expected.

REFERENCES

1. C. Wörkmeyer, C. Parr, and B. Myhre, Optimization of deflocculated high cement castables (HCC)," *49th Internat. Colloquium on Refractories*, Aachen (2006).
2. V. Antonovich, S. Goberis, I. Pundene, et al., "Effect of a new generation of deflocculant and the amount of microsilica on the properties of traditional heat-resistant concrete with a chamotte filler," *Novye Ogneupory*, No. 5, 44 – 48 (2006).
3. L. Krictz and R. Fisher, "Field performance and fracture behavior of low cement, conventional high cement low moisture castables," *UNITECR*, 1116 – 1126 (1989).
4. B. Myhre and B. Strudlberg, "The use of microsilica in refractory castables," *Internat. Seminar on Refractory Materials*, Teheran (1997).
5. H. Fryda. K. Scrivener, and T. Bier, "Relation between setting properties of LLC and interaction within the binder system," *UNITECR*, 1315 – 1323 (1997).
6. C. Wörkmeyer, F. Simonin, and C. Parr, "The control and optimization of LLC," *UNITECR* (2005).
7. D. A, Fumo and A. M. Segadaes, "The effect of silica fume additions on the hydration behavior of calcium aluminates," *UNITECR*, 1325 – 1333 (1997).
8. E. Maeda and S. Kanatani, "Setting mechanisms of low-cement castables and its application for setting time control," *UNITECR*, (2005).
9. S. Bentsen, A. Selveit, and B. Sandberg, "Effect of Elkem Microsilica on conservation of HAC," *Midgeley Symp on CAC*, London (1990).