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Properties of Suspension and Pastes of Different Types of Microsilica with Various Deflocculants

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Microsilica is currently being used in a wide range of refractory castables and its quality influences performance, particularly flow and set of castables. In the present work, two different types of microsilica "Elkem ASA Materials" (grade 983U) and polish "Silimic" have been investigated. It was established that the differences between the characteristics of paste and suspensions of microsilica (pH, electric conductivity, viscosity) depend on the quality of microsilica. The influence of type and amount of microsilica on the pH, electric conductivity and viscosity behavior of alumina cement Gorkal-40 and microsilica pastes has been investigated in details. Deflocculants Castament FS-20 and sodium tripolyphosphatum were used to control the characteristics of the investigated materials. The influence of their amount on the characteristics of various suspensions and pastes was estimated. It is shown that rheological characteristic of middle cement castable, which contains in its composition with microsilica of low quality, may be increased considerably if the right amount of the right deflocculant is added.

Keywords: microsilica, deflocculants, pH, electric conductivity, viscosity, rheological properties.

1. INTRODUCTION

Presently the traditional refractory castables are more and more often replaced by castables of new generation where microsilica of various types and of various content of impurities is used. For economical purposes, it is desirable to use the low-price microsilica in castables. However, the cheaper is microsilica, the greater amount of impurities it contains. On the other hand, microsilica may affect rheological properties of castables [1 – 4]. The impurities present in microsilica as well as the basic physical properties can have a marked effect on castable properties via interactions with the hydration process. It is established that carbon and other impurities, such as Na_2O, K_2O, MgO, SO_3 provoke creation of gels and flocculation, therefore reduce flow and rapid flow decay [5].

In Lithuania, for lining of thermal equipments, the refractory castables with chamotte aggregates resistant to temperature of about 1300 °C are widely used. However, there are no studies specially designed for investigation of rheology of castables containing chamotte components and microsilica of different types.

As may be seen from the references [6 – 7], addition of a deflocculant is indispensable, since its nature and properties influence the rheological properties of high temperature composition of the paste with microsilica. One of the most widespread deflocculants in the production of castables is sodium tripolyphosphatum. Lately sodium polycarboxilate – Castament FS-20 is gaining popularity.

The aim of the study is to investigate the influence of deflocculants of two types on the properties of compositions with microsilica of different quality.

2. EXPERIMENTAL

The present study deals with two different types of microsilica, namely microsilica 983U of mark (E), the Norwegian firm ELKEM ASA MATERIALS, and microsilica „Silimic" (S) produced in Poland (Huta Laziska). The chemical analysis (in mass %) and physical properties of which are presented in Table 1.

Alumina cement "Gorkal-40" (C) is manufactured in Poland. According to producer data the content of Al_2O_3 is not smaller than 40 percent. The main mineral phases are as following: CA, the ferrite phase, $C_{12}A_7$, C_2AS; bulk density of 1160 kg/m^3, specific surface of 300 m^2/kg, refractories – not lower than 1280 °C.

Chamotte aggregate is made crushing chamotte bricks, the density of which is 1920 kg/m^3. (The amount of Al_2O_3 is (30 – 33) %; water saturation (fr. 2.5 mm – 5 mm) – 16.8 %; bulk density (fr. 2.5 mm – 5 mm) – 970 kg/m^3; crushing strength in a cylinder (fr. 2.5 – 5 mm) – 4.4 MPa.

Dispersive chamotte is made grinding chamotte of the same type in a laboratory ball mill. Additionally it is sifted out using a separator the meshes of which are of 0.14 mm diameter. Dispersive chamotte of 75 % is made up of <0.08 mm fraction. A specific surface of dispersive chamotte is 400 m^2/kg, bulk density is 1100 kg/m^3. Deflocculants: sodium tripolyphosphate ($Na_5P_3O_{10}$, molecular mass 367.86, TU 2148-095-43499406-98) (NT), crystalline material dissolving in water; and Castament FS-20 (made by BASF, Germany), is belonging to polycarboxilatethers, powder well dissolving in water, dispersive polymer.

For investigations of electric conductivity and pH of suspensions, a device MPC 227 of the firm METTLER TOLEDO (electrode InLab 410, measurement precision of 0.01 pH and electrode InLab 730, measurement range of 0 μS/cm – 1000 μS/cm) was used. The first measurements of pH and electrical conductivity in suspensions were performed after 3 min. since their mixing with water. All suspensions were made with distilled water, solids-water ratio being constant as 1:10. The content of deflocculant in suspensions was calculated in per cent of solids content. The microsilica-cement ratio in suspensions was 1:1, while

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Table 1. Chemical analysis and physical properties of microsilica of two types

Type	SiO_2, %	Al_2O_3, %	Fe_2O_3, %	C, %	CaO, %	MgO, %	K_2O, %	Na_2O, %	SO_3, %	pH	LOI, %	Bulk density, kg/m^3
E	98.6	0.26	0.02	0.2	0.15	0.07	0.12	0.06	0.08	5.5	0.44	410
S	90.6	1.2	1.5	2.83	0.5	1.5	0.63	0.68			2.0	330

the content of deflocculant was also calculated in per cent of solids content.

For investigations of viscosity of pastes, the vibroviscosimeter SV-10 was used. The solid-water ratio in pastes with microsilica was 0.9, while that in compositions of cement and microsilica paste 0.7. For estimation of rheological properties of the paste of refractory castable, the flow factor (ISO/DIS 13765-2) in % was determined.

3. RESULTS AND DISCUSSION

3.1. Experiments with suspensions and pastes

The two-hour investigations of electrical conductivity in the suspensions of two-type pure microsilica E and S (Fig. 1) showed that the electrical conductivity in the suspension S increased by 2.4 times, due to much greater amount of impurities dissolved in the course of the investigation period, meanwhile in the suspension E the electric conductivity hardly changed. Respectively, pH shows that in the suspension with microsilica S the alkaline medium formed, while in that with microsilica E the neutral one.

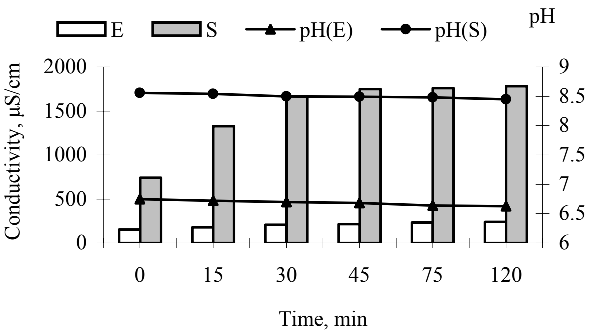


Fig. 1. Changes of pH and electrical conductivity in the suspensions with microsilica E and S within two-hour period

It is important to determine the influence of deflocculants addition in solution. The solutions of deflocculants were made by dissolving 0.1 g of deflocculant in 100 g of water. The indices of pH and electrical conductivity of pure solutions of deflocculants are presented in Table 2.

Table 2. Electrical conductivity and pH of solutions of deflocculants

Name of deflocculant	pH	Electrical conductivity, µS/cm
NT	8.54	900
FS-20	4.35	250

The influence of content of deflocculant on pH and electrical conductivity in the suspensions E and S was investigated (Figs. 2 and 3).

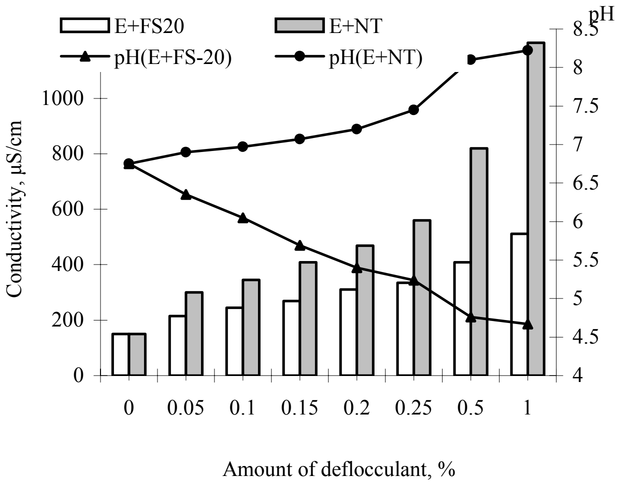


Fig. 2. Changes of pH and electrical conductivity in the microsilica suspension E subject to the amount of added deflocculant NT and FS-20

The added deflocculant NT, in comparison to that of FS-20, increases considerably the indices of pH and electrical conductivity of suspension of microsilica E. The deflocculant FS-20 increases the values of electrical conductivity much slower, but it highly reduces the pH values.

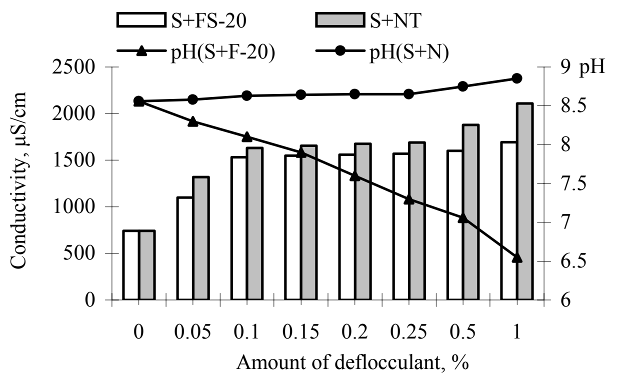


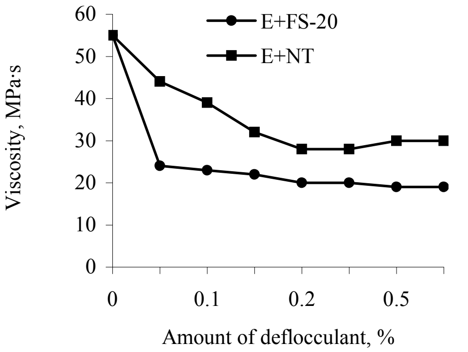
Fig. 3. Changes of pH and electrical conductivity in the suspension of microsilica S subject to the amount of added deflocculant NT and FS-20

In the suspension S the effect of deflocculants shows up in the similar way as in the suspension E, however, in the former case the indices of electrical conductivity and pH are much higher, since the impurities contained in microsilica dissolve in water. When the amount of deflocculant FS-20 added to the suspension of microsilica E reaches 1 %, then pH decreases down to 4.5, while pH of suspension of microsilica S is 6.5. The effect of deflocculant NT on pH changes in both suspensions is much poorer than that of deflocculant FS-20. It is obvious that regardless of the nature of deflocculant, it is easier to control the values of pH and electric conductivity in the suspension E.

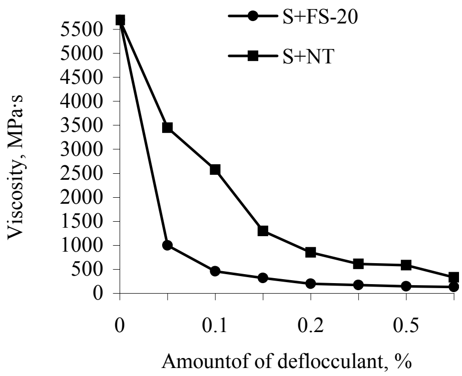
The rheological properties of pastes of both microsilica (Fig. 4, a and b) demonstrate the influence of deflocculants. Namely, in the pastes without any deflocculant the indices of viscosity differ between each other by 100 times. The minimal amount of deflocculant FS-20 decreases the viscosity approximately twice in the suspension of microsilica E. The further addition of deflocculant hardly affects the values of viscosity of paste. To achieve similar values of viscosity with deflocculant NT, its amount should be not less than 0.2 %.

In the paste of microsilica S the differences in the impact of deflocculants are more noticeable. It is obvious that only the maximal amount of NT can reduce the viscosity to same value as can be achieved with FS-20 of 0.15 %.

Observing such big differences between the microsilica of two types and the impact of deflocculants on them, the suspensions and pastes of cement and microsilica were further investigated. The changes in electrical conductivity and pH of suspensions of microsilica E and S with cement, subject to the amount of deflocculant, showed that they resulted because of the nature of microsilica (including also the suspensions with microsilica only) (Figs. 2, 3). Table 3 presents the data how the values of electrical conductivity and pH change in the suspension of cement and microsilica without deflocculant and with the maximal amount of it. It was established that in the suspension of cement and microsilica S without deflocculant, the values of electrical conductivity are four times greater than those of the suspension of cement and microsilica E.



a



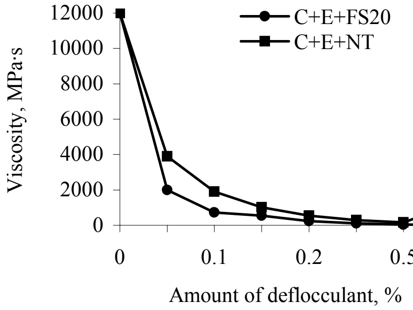
b

Fig. 4. Dependence of viscosity on added amount of deflocculants NT and FS-20 in: a – paste E, b – paste S

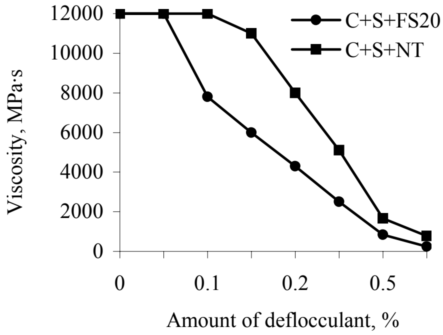
Table 3. Changes in pH and electrical conductivity in the suspensions E + cement and S + cement

Suspension	FS-20		NT	
	pH changes from to	Changes in electrical conductivity (μS/cm) from to	pH changes from to	Changes in electrical conductivity (μS/cm) from to
E + Cement	9.25 – 6.7	717 – 1980	9.25 – 10	717 – 3990
S + Cement	9.5 – 8.1	2700 – 5000	9.5 – 10,8	2700 – 5400

The investigations of viscosity in the paste of cement with microsilica (Fig. 5) showed the great difference between the microsilica of both types. If the paste of cement and microsilica E can be influenced by the minimal amount of added deflocculant (though the deflocculant FS-20 is more effective than NT), then the paste with microsilica S needs the quadruple amount of deflocculant FS-20 and the tenfold amount of NT. This fact proves the enormous effect of microsilica's quality on the rheological properties of pastes and the undoubted superiority of deflocculant FS-20 to NT.



a



b

Fig. 5. Effect of amount of deflocculant on viscosity of cement paste: a– with microsilica E, b – with microsilica S

The analysis of provided results shows that due to big quantity of impurities contained in microsilica S, the indices of electrical conductivity and pH are much higher than these of suspension with microsilica E. In contrast to NT, the deflocculant FS-20, thank to its peculiar properties (low pH and low electrical conductivity) reduces the electrical conductivity and pH of suspensions and pastes of microsilica, as well as those of suspensions and pastes of cement with microsilica. That is confirmed by the investigations of viscosity, which obviously prove that the deflocculant FS-20 is superior to the deflocculant NT. The

Table 4. Compositions of MCC refractory castables

Reference mark of castable	Composition of castable in mass %							
	Gorkal-40	Microsilica		Dispersive chamotte	Chamotte fr. up to 5 mm	FS-20	NT	Water above 100 % of dry matter
		E	S					
E1	12	5		15	68	0.05	0.05	11
S1	12		5	15	68	0.05	0.05	11
S2	12		5	15	68	0.1	0.1	11
S3	12		5	15	68	0.125	0.125	11
S4	12		5	15	68	0.15	0.15	11

minimal amount of deflocculant FS-20 succeeds in reducing effectively the viscosity of the paste of cement with microsilica S.

The investigations of suspensions and pastes of two-type microsilica with different content of impurities showed that the deflocculant FS-20 is much more effective in control of indices of pH, electrical conductivity of suspensions and viscosity of paste.

3.2. Investigations of rheological properties of MCC (middle cement castable) type castable

For investigations, two series of castable compositions with microsilica S were prepared. In the first series the deflocculant NT was used, while in the second one FS-20. The amount of deflocculant added to the compositions was changed from 1.05 mass % to 1.15 mass %. For comparison of rheological results of paste, the castables with microsilica E and minimal amount of both deflocculants were prepared (Table 4).

The rheological characteristics of MCC castable with microsilica S (flow factor and viability) and with different amount of deflocculants NT and FS-20 are shown in Figs. 6 and 7.

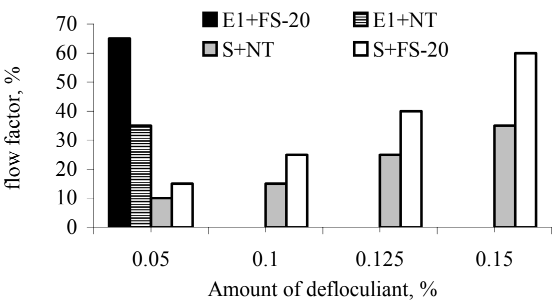


Fig. 6. Flow factor of castable E1 and S (1 – 4) subject to the amount of deflocculant FS-20 and NT

It was established that with microsilica S of lower quality used in the composition of castable, the flow factor was much lower than that in the castable with microsilica E of high quality and with the minimal amount of deflocculant of 0.05 %. In all cases the added deflocculant FS-20 more effectively increases the flow factor of castable versus the deflocculant NT. To reach the optimal flow factor for the castable with microsilica S, the amount of added deflocculant FS-20 should be increased up to 0.15 %. In this case the workability of castable with microsilica S will be practically the same as of the castable with microsilica E and FS-20 of 0.05 %.

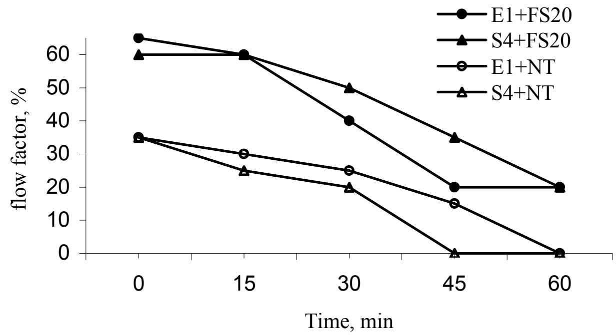


Fig.7. Workability of castable E1 and S4 with deflocculant FS-20 and NT

The investigations of flow factor (Fig. 7) prove that after a certain period of time the deflocculant FS-20 better retains the deflocculating properties than NT.

4. CONCLUSIONS

1. The values of pH and electrical conductivity of microsilica suspensions depend on type of microsilica, due to the different amount of impurities contained in microsilica. The greater content of impurities is in microsilica, the higher values of pH and electrical conductivity are observed. The values of pH and electrical conductivity of microsilica of higher quality may be easier controlled by means of deflocculant than those of microsilica of lower quality.

2. The quality of microsilica influences the viscosity of microsilica paste. With microsilica of higher quality (and lower content of impurities), the viscosity of paste is about 100 times lower than that with microsilica containing a great amount of impurities. The viscosity of microsilica of higher quality hardly depends on the nature of deflocculant (the microsilica disperses well with both deflocculants). For dispersion of microsilica of low quality, a right deflocculant should be selected carefully.

3. The greater content of impurities in microsilica (the poorer quality), the greater viscosity of cement pastes with microsilica and the lower flow factor of MCC castables.

4. The different deflocculants influence differently the values of pH and electrical conductivity of suspensions with microsilica and suspensions with cement and

microsilica, as well as the viscosity of their pastes. Provided a good deflocculant (FS-20) and its optimal amount are selected, the flow factor and workability of MCC castable with microsilica of low quality may be controlled.

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