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The Influence of Hybrid Deflocculant on Hardening Process of Refractory MCC-type Castable

INA PUNDIENĖ*, VALENTIN ANTONOVIČ, RIMVYDAS STONYS

Institute of Thermal Insulation of Vilnius Gediminas Technical University, Lithuania
* e-mail: futer@centras.lt

Abstract

The influence of different types of deflocculants and their combinations upon structural formation during hardening of MCC-type refractory castable with mulite aggregates was analyzed using an ultrasonic method.

It was established that the structure of castable formed in two stages when the sodium tripolyphosphate deflocculant was used. In the first stage the speed of ultrasound reached approximately 2500 m/s, while in the second one it was approximately 5000 m/s. With polycarboxylate ether (Castament FS 20), as many as three stages were detected in formation of castable. The speed of ultrasound in every stage was as follows: 1000 m/s, ~2500 m/s and ~5000 m/s. In case of a hybrid deflocculant, three stages of structural formation remained, however, in the second stage the speed of ultrasound impulse exceeded 3000 m/s.

When the hybrid deflocculant was used, the cold compressive strength (CCS) of castable after the hardening process ranged within 58-65 MPa. It did not differ much from CCS of castable with the additives of sodium tripolyphosphate or polycarboxylate ether (about 55 MPa). Nonetheless, after drying of castable at 110°C and its firing at temperature of 800-1000°C, CCS of castable with the hybrid deflocculant was twice higher than that of CCS of castable, where only the sodium tripolyphosphate or polycarboxylate ether deflocculant was used.
Keywords: Castable refractory, Ultrasonic method, Deflocculant, Structure, Mechanical properties

WPŁYW DEFLOKULANTA HYBRYDOWEGO NA PROCES TWARDNIENIA ODLEWANEGO WYROBU OGNIOTRWAŁEGO TYPU MCC

Za pomocą metody ultradźwiękowej zanalizowano wpływ różnych rodzajów deflokulantów i ich kombinacji na powstawanie podczas twardnienia struktury odlewanego wyrobu ogniotrwałego typu MCC zawierającego agregaty mulitu.

Ustalono, że struktura wyrobu odlewanego powstawała w dwóch etapach wtedy, gdy użyto trójpolifosforan sodu jako deflokulant. W pierwszym etapie prędkość ultradźwięku osiągnęła w przybliżeniu 2500 m/s, podczas gdy w drugim wynosiła w przybliżeniu 5000 m/s. Po zastosowaniu eteru polikarboksylowego (Castament FS 20), stwierdzono aż trzy etapy podczas tworzenia wyrobu odlewanego. Prędkości ultradźwięków w kolejnych etapach były następujące: 1000, ~2500 i ~5000 m/s. W przypadku hybrydowego deflokulanta pozostały trzy etapy tworzenia się struktury wyrobu, jednak w drugim etapie prędkość impulsu ultradźwiękowego przekroczyła 3000 m/s.

Wtedy gdy użyto deflokulanta hybrydowego wytrzymałość na ściskania na zimno (CCS) wyrobu odlewanego po procesie twardnienia mieściła sie w przedziale 58-65 MPa. Nie różniła się ona znacznie od wytrzymałości CCS wyrobu odlewanego z dodatkami trójpolifosforanu sodu czy eteru polikarboksylowego (około 55 MPa). Pomimo tego, po wysuszeniu wyrobu odlewanego w 110°C i jego wypaleniu w temperaturach z przedziału 800-1000°C, CCS wyrobu z deflokulantem hybrydowym była dwukrotnie większa od CCS wyrobów, w przypadku których zastosowano trójpolifosforan sodu lub eter polikarboksylowy jako deflokulant.
Słowa kluczowe: wyrób ogniotrwały odlewany, metoda ultradźwiękowa, deflokulant, struktura, właściwości mechaniczne

1. Introduction

In production of alumina cement-based refractory castables with ultra-dispersive additives, various deflocculants are used and these deflocculants exert different influence not only on rheological properties of castable paste, but also on processes of hydration [1, 2]. Knowledge of mechanical behavior of deflocculated castables at a young age becomes essential to forecast their performance in service. For this purpose, the ultrasonic techniques are used to reveal the development of structure in the material from the placing moment to hardened state [3-5].

2. Experimental

The present study deals with two different types of deflocculants - sodium tripolyphosphate (TP) and Castament FS-20 (made by BASF, Germany) (FS). We used microsilica (RW-Füller) that is a product from RW Silicium GmbH (SiO_2 content of 96 ± 1.5 %, bulk density of 330–360 kg/m^3). In our research alumina cement „Gorkal 40“(AC) manufactured in Poland was used. The content of Al_2O_3 in it is not less than 40 %. Mulite aggregate was made by crushing of mulite bricks (Al_2O_3 content not less than 65 %), density of which was 2340 kg/m^3, bulk density of mulite aggregate (fr. 0–10 mm) is 1490 kg/m^3. Dispersive mulite was made by grinding of mulite of same type in the laboratory ball mill. The bulk density of powder is 920 kg/m^3.

For investigation of ultrasonic wave velocity in castable samples, the Schleibinger Geräte GmbH datalogger [7] with the Pundit 7 ultrasonic pulse indicator was used. Fresh concrete was set between two ultrasonic transducers operating at 10 pulses per second and frequency of 54 kHz.

The cubes sized 70 x 70 x 70 mm were formed for 9 compositions of castable. After 3 days of normal curing, the samples were dried at temperature of 105 ± 5°C for 48 hours in the electric furnace. Afterwards they were kept for 5 hours at each of investigated temperatures (800°C, 1000°C) in the electronically controlled furnace and finally cooled. Then the cold compressive strength (LST EN 1402-6) of castable was measured.

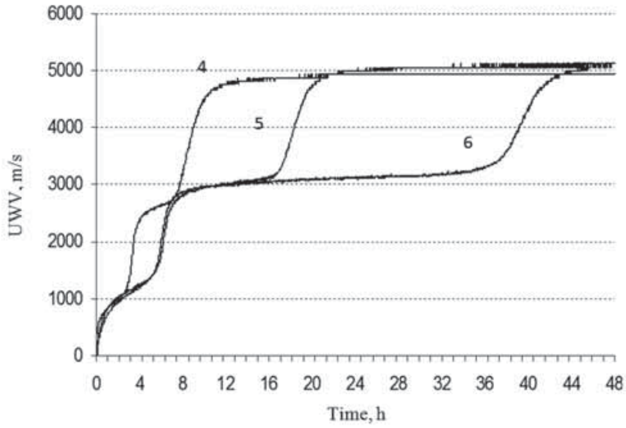

Fig. 2. Change in UWV during hardening for castables with FS deflocculant; 4, 5, and 6 – numbers of castable compositions.

3. Result and discussions

Upon investigation of the influence of the deflocculants of different type (TP and FS) and their combinations (hybrid deflocculant) on formation of castable structure during the hardening process, the compositions of MCC castable with mulite aggregate shown in Table 1 were prepared.

Along with increase of content of deflocculant TP in castable (Fig. 1), UWV increases the faster, the greater TP content in castable. In the curves we can see two well expressed steps, which show the slowdown of ultrasonic impulse speed. Considering the TP content, the first step appears with UWV values of from 2400 to 3100 m/s, while the second one within 4600–4800 m/s. In approximately 12 h since the start of mixing, the maximal UWV values are reached in the samples.

Observing the influence of deflocculant FS on formation of castable structure (Fig. 2), we can see that unlike TP, three steps of UWV slowdown show up. The first step was observed at 600–1400 m/s, the second one in the interval of 2300 and 3200 m/s, while the third step within 4850–5100 m/s (the second and third steps are analogical to TP case). The greater FS content, the longer is the second step. After 48 h from the beginning of test, UWV of all three compositions stabilizes at 5000 m/s.

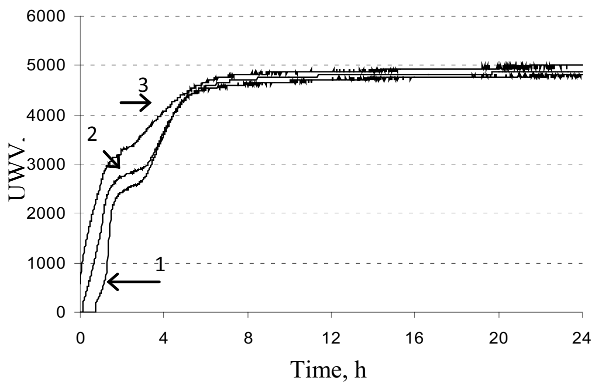

Fig 1. Change in UWV during hardening for castables with TP defloculant; 1, 2, and 3 – numbers of castable compositions.

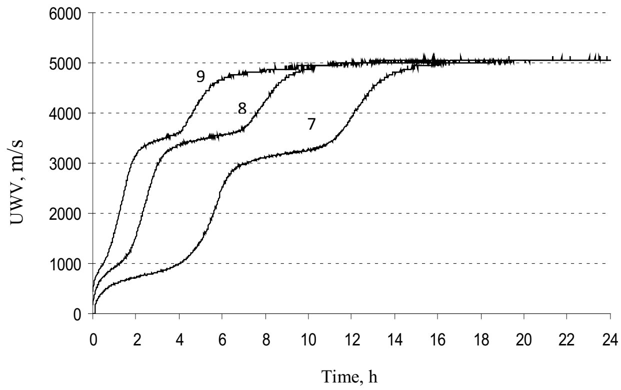

Fig. 3. Change in UWV during hardening for castables with hybrid deflocculant; 7, 8, and 9 – numbers of castable compositions.

Table 1. Composition of refractory concrete in [%].

Composition number	Alumina cement	Microsilica	Mulite aggregate	TP*	FS*	Water
1	10	5	85	0.1		7
2	10	5	85	0.2		7
3	10	5	85	0.3		7
4	10	5	85		0.1	7
5	10	5	85		0.2	7
6	10	5	85		0.3	7
7	10	5	85	0.1	0.1	7
8	10	5	85	0.2	0.1	7
9	10	5	85	0.3	0.1	7

* *over 100 % of dry components*

Comparing the influence of deflocculants TP and FS on development of castable structure at a younger period of hardening, one may notice that the main difference between them lies in gradual formation of castable structure. Using TP, the structure is forming faster (two steps), while using FS-20, the process is slower (three steps).

Using the hybrid deflocculant (with stabe FS content and NT content increasing from 0.1 to 0.3 %, Table 1), three steps persist in UWV curves. With increase of TP content, the first step of UWV slowdown draws in and shows up earlier (Fig. 3).

The time of showing up and duration of the second step also decreases along with increase in TP content, nevertheless, the UWV values at the beginning and end of the step are higher (from 2800 to 3300 m/s at the beginning and up to 3200–3700 m/s at the end). During formation of steps, the structure of samples changes the faster, the greater is TP content in castable. The shorter first and second step, the faster is formation of sample structure. After 20 h since the beginning of test, the ultrasonic impulse speed of all compositions reaches 5000 m/s.

Summarizing the results of abovementioned investigations, we can notice that due to the deflocculant FS, in the structure of castable, during the hardening process, a certain change in the hydration process (crystallization) is going on (additional sharp second step) and that change is related to the slowdown effect of hydration of this deflocculant. In TP case the duration of the second step is very short. With TP, in the course of the first step, the ultrasound impulse speed reaches 2400–3400 m/s, while with FS, during the second step, it is somewhat lower and reaches 2500–3000 m/s. In castables with the hybrid deflocculant, these values are obviously higher and count 2840–3840 m/s. That means that the hybrid deflocculant exerts more influence on formation of structures in this period of hydration.

The CCS results of investigations of mechanical properties for castables are presented in Fig. 4. The results of castables with deflocculants TP (N1) or FS (N4) show that the strength values after hardening or treatment at various temperatures are similar and vary within 45–85 MPa.

When the hybrid deflocculant (N7, N8, N9) is used in castable, the compressive strength values after hardening vary within 55–60 MPa subject to TP content and practically differ but little from castables containing only TP (N1)

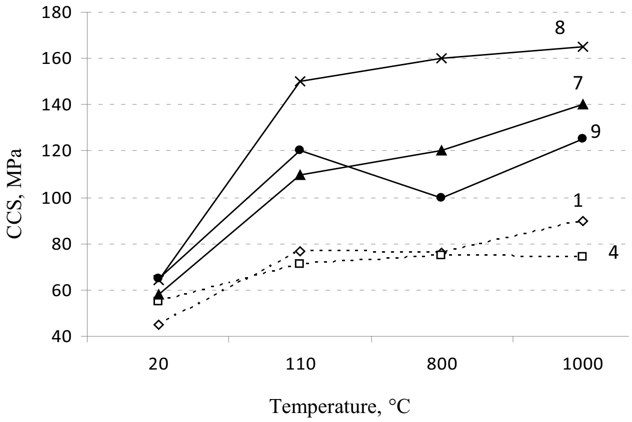

Fig. 4. CCS of investigated castable samples subject to temperature; 1, 4, 7, 8, and 9 – numbers of castable compositions.

or only FS (N4). The influence of separate deflocculants or the hybrid deflocculant on compressive strength of castable after hardening may be explained by the fact that it takes a different period of time to form a similar skeleton of crystal hydrates during the hardening process in the structure of castable and for UWV to reach a uniform index of approximately 5000 m/s (Figs. 1–3).

However, the compressive strength of dried and fired at 800 and 1000°C castable with the hybrid deflocculant, subject to TP content, may be even twice higher than that of castable with one deflocculant only. So far no explanations may be found for such a result. May be, the reason lies in structures formed at the second step of UWV change. In this period, in castable with microsilica alumina cement, the amorphic and crystallized phases (most likely nanostructures) are forming during hydration. The hybrid deflocculant stimulates their formation (maximal UWV values). The formed nanostructure of dried and fired castable gets compacted and the skeleton of large crystal hydrates undergoes transformation and disintegrates at temperatures of up to 400°C. Therefore, the skeleton formed by nanostructures has a decisive influence on compressive strength of castable.

4. Conclusion

The deflocculants of different type exert a different influence on formation of structure of MCC-type refractory castable with mulite aggregate during the process of hardening. When the deflocculant of sodium polyphosphate is used, two steps in formation of structure are observable: the first step when UWV reaches approximately 2400–3300 m/s and the second one at 4600–5000 m/s. In case of polycarboxylate ether, already three such steps may be observed: the first step when UWV is ~1000 m/s, the second one at 2500–3000 m/s and the third at ~5000 m/s. Using the hybrid deflocculant, three steps in formation of structure persist, nevertheless, during the second step, UWV values exceed 3500 m/s. We think that at the second stage of formation, the nanostructures are forming and their maximal amount is reached with the hybrid deflocculant.

The compressive strength of castable with hybrid deflocculant after hardening is 58–65 MPa and differs slightly from that of castable with sodium polyphosphate or polycarboxylate ether additive (about 55 MPa). After drying at 110°C and firing at 800–1000°C, the compressive strength of castable with hybrid deflocculant is higher up to two times (110–165 MPa) than that of castable with only polyphosphate or only polycarboxylate ether (70–90 MPa).

Acknowledgments

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