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The Effect of Waste Oil-Cracking Catalyst on the Properties of MCC-Type Castable

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In this study a possibility to use the waste oil-cracking catalyst from fluidized cracking in the production of middle cement castable (MCC) was investigated. Viscosity tests of cement paste as well as dilatometric, X-ray investigations and SEM observations of structure of castable matrices (binder) were done. The effect of waste oil-cracking catalyst (the amount of which was 0; 2,5; 5,0; 7,5 %) on the rheologic characteristics of the castable‘s mixture and exothermic temperature during the hardening process was analyzed. It was established that the additive of the waste catalyst reduces the appearance time of maximum exothermic temperature. The resulted rheological and physical-mechanical characteristics show that the optimal amount of waste catalyst in the composition of the castable reaches 5 %. This amount of the additive allows to improve the strength characteristic of the castable (the compressive strength of the castable after hardening and firing at different temperature is 35 % – 20 % higher when compared to the compressive strength of the castable without the additive.

Keywords: waste oil-cracking catalyst, refractory MCC-type castable, mechanical tests.

1. INTRODUCTION

Most of waste catalyst from the plants of spent fluid catalytic cracking (FCC) in the oil industry is disposed of into special landfills. Therefore, from the ecological standpoint, it is expedient to use the waste catalyst in building materials. It is reported [1] that waste catalyst can stand heat of more than 1750 °C. Therefore, it can be used for manufacturing fire-proof materials, or can be added to clay for production of ceramic tiles, refractory bricks, or insulation bricks. It was found [2], that the hardness of asphalt concrete could be greatly improved by combining industrial fly ash, particulates from bag filter and waste catalyst in different proportion. Recent investigations [3 – 5] showed that waste catalyst could be successfully utilized in concrete mixes with Portland cement.

As the waste catalyst mainly consists of alumina and silica, it may be used in production of refractory castables.

The earlier research [6, 7] were carried out into the liquid glass-based refractory castable where the content of waste catalyst varied from 10 % to 30 %. It was established that along with the proportional increase of catalyst, the density of castable, as well as its compressive strength and thermal stability decreases.

In the later research [8] the waste catalyst, as a fine additive to aggregate, was investigated in the traditional refractory castable within the interval of temperatures from 110 °C to 1200 °C. It was established that the compressive strength of the castable with the added ground catalyst was higher by ~12 %.

The aim of this study is to investigate the possibilities how to use the FCC catalyst in the middle-cement castable.

2. EXPERIMENTAL

2.1. Raw materials

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 %. The main mineral phases are as following: CA, ferrite phase, $C_{12}A_7$, C_2AS; bulk density of 1160 kg/m^3, refractoriness, not lower than 1280 °C.

Chamotte aggregate was made crushing chamotte bricks, the density of which was 1920 kg/m^3 (the amount of Al_2O_3 in the aggregate is 33 % – 38 %, the bulk density of chamotte aggregate (fr. 0 mm – 10 mm) is 1260 kg/m^3). Dispersive chamotte was made by grinding chamotte of the same type in the laboratory ball mill. (Dispersive chamotte of 75 % is made up of <0.08 mm fraction. Bulk density is 1100 kg/m^3).

We have used microsilica (grade 983U) (**MS**) that is a product from Elkem ASA Materials (SiO_2 makes up not less then 98 % of its composition, bulk density of 410 kg/m^3).

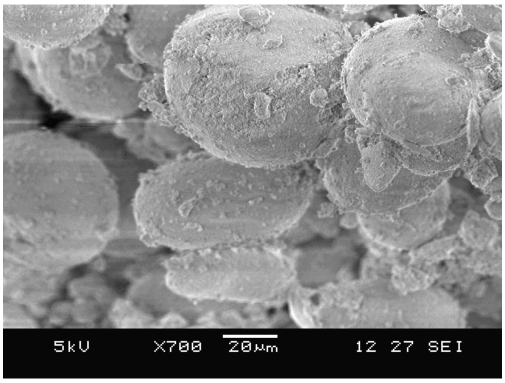

Fig. 1. Structure of the waste FCC catalyst grains

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The chemical composition of waste FCC catalyst was determined to be as follows [in mass %]: Al_2O_3 – 39.4, SiO_2 – 50.1, Fe_2O_3 – 1.3, SO_x – 2.3, CaO – 0.5, MgO – 0.49, Na_2O – 0.2, K_2O – 0.07, Mn_2O_3 – 0.06; ignition loss – 5.4 %. The powder density was 945 kg/m^3, the average particle size ~30 µm. Typical SEM photo of this waste catalyst is presented in Fig.1.

In our research we have used deflocculant Castament FS-20 (commercial product from SKW Polymers GmbH (Germany)) and, reactive alumina (**RA**) of mark CTC-20 (produced by Almatis GmbH).

2.2. Methods and equipment

The flow factor of castable was determined according ISO/DIS 13765-2 using a cone with 100 mm base diameter, 50 mm high and 70 mm top diameter. The cone was placed on a shock table and filled with castable. The cone was taken away after operating of table 25 times and the diameter (*d*) of the castable sample was measured. Flow factor (*FF*) as a percentage was calculated from the following equation:

$$FF[\%] = \frac{d[\text{mm}] - 100\,\text{mm}}{100\ \text{mm}} \times 100\,. \qquad (1)$$

The temperatures of exothermic effects during the binding and hardening of castable paste were registered according to the methodology devised by the company Alcoa [9].

The cubes of the size (70×70×70) mm were formed for all compositions of castable. After 3 days of normal curing, the samples were dried at a temperature of 105 °C ±5 °C for 48 hours in an electric furnace. Next, they were kept for three hours in each of the investigated temperatures (800, 1000 and 1200 °C) in an electronic controller furnace and cooled. Then the ultrasonic pulse velocity (LST EN 1402-7) and compressive strength (LST EN 1402-6) of castable were investigated.

Ultrasonic wave velocity (**UV**) was measured by the device UK-14P (Russia) with the frequency of 60 kHz using two standard cylindrical heads of UV device. The measuring surface on the measuring heads was pressed against the binder specimens at two exactly opposite points. The Vaseline was used to ensue good contact. The velocity of the ultrasonic wave (*V* in m/s) was found by the following formula: $V = (S/t) \times 10^6$ (where *S* is distance in metres and *t* – time in microseconds).

The dynamic viscosity of paste of binders was determined by a vibroviscosimeter SV-10 (Japan). Dilatometric analyses of the binders were performed in a Linseis apparatus L76 with a heating rate of 5 °C/min in specimens of 5 mm diameter and 50 mm length. The phase analysis of burned samples after firing at 800 °C – 1200 °C temperature was carried out by X-ray diffraction using the diffractometer DRON-7 (Russia) with a copper anticathode.

The following composition of binder (B0) was selected: 1 portion of AC, 0.5 portions of MS, 0.5 portion of RA, 1 portion of H_2O. Then the waste catalyst was added to the binder B0 in the following portions: 0.25 (composition B2), 0.5 (composition B5) and 0.75 (composition B7).

For the SEM observations JEOL equipment was used.

3. RESULTS AND DISCUSSION

At first the effect of waste catalyst on the viscosity of the binder (MCC castable matrices) consisting of AC, MS and RA was investigated.

The performed measurements of viscosity (Fig. 2) show that the additive of waste catalyst affects the rheological properties of binder as well. The investigations demonstrate that after 20 min since the mixing with water, the binder B0 singles out by the greatest viscosity.

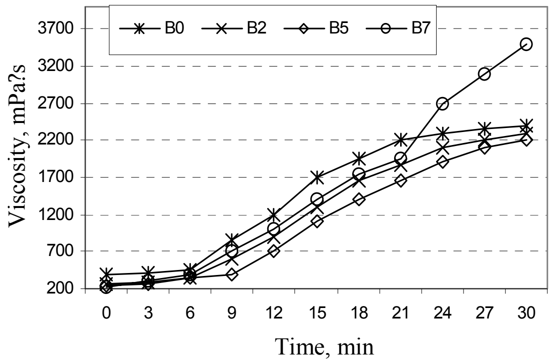


Fig. 2. Dependence of viscosity of binders B0; B2; B5; B7 on time

The viscosity of binders B2 and B5 was smaller during the entire investigation than that of binder B0 (without waste catalyst). Contrary to other binders, the viscosity of binder B7 sharply increased after the period of 21 min (from 2000 mPa·s to 3500 mPa·s). This fact shows that a small amount of waste catalyst (up to 5 %) added to the compositions of binder and refractory castable can improve the rheological properties of castable.

Fig. 3 shows the dilatometric curves of the binders during heating up to 1200 °C.

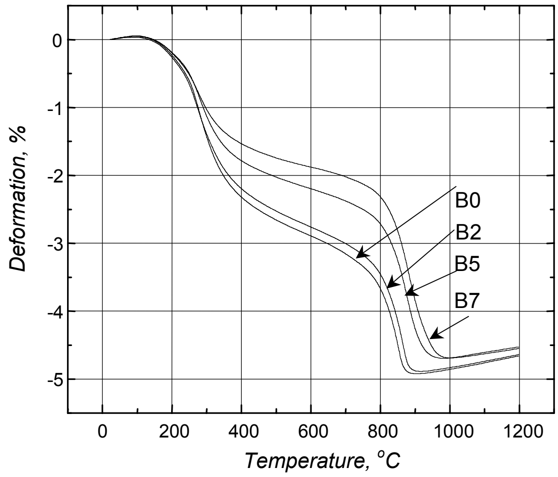


Fig. 3. Dilatometric curves of the binder during the first heating

During heating, these curves are characterised by a series of shrinkage domains: first between 150 °C and 400 °C as well as third between 800 °C and 950 °C in which high increase of shrinkage is observed. Low increase of shrinkage is observed between 400 °C and 850 °C (second domain). Dehydration and conversion of hydrates are the reason of the binders shrinkage at temperature up to 800 °C, crystallisation and sintering raise a shrinkage at 800 °C – 1000 °C.

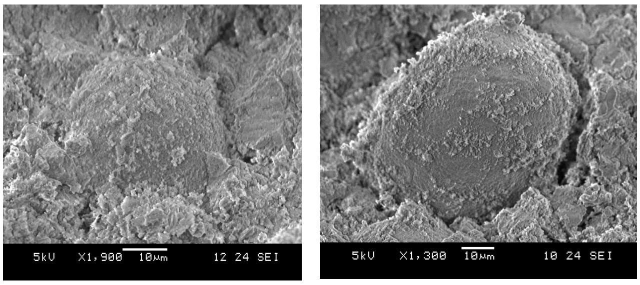
Dilatometric tests have shown that the additive of waste catalyst have substantial effect on shrinkage of the binder during heating up to 900 °C: the larger amount of waste catalyst, the smaller shrinkage in first domain and bigger shrinkage in third domain in the dilatometric curves.

The performed X-ray investigations of binder compositions show that waste catalyst induces the formation of cristobalite, anorthite and gehlenite at temperatures from 800 °C to 1200 °C.

SEM analysis of matrices after firing up to 500 °C show that the grains of catalyst firmly adhere to the matrix (Fig. 4, a).

Unfortunately after firing at 600 °C – 800 °C part of the grains break away from smooth structure (Fig. 4, b). The larger amount of catalyst was used, the larger amount of lift-off grains were observed.

Investigation of matrices of MCC castable at high temperatures show, that the additive of waste catalyst participates in the reactions with the minerals from binder components and affects the formation of binder structure.



a b

Fig. 4. Different structure of matrices of castable with waste catalyst: a – grain of catalyst accrete with binder components, b – lift-off grain

For determination of the influence of waste catalyst on the rheological, hydration and physical-mechanical properties of refractory castable, the compositions K0; K2; K5; K7 were selected (Table 1).

Table 1. Compositions of refractory castable

Components	Compositions of castable in mass %			
	K0	K2	K5	K7
Waste catalyst	0	2.5	5.0	7.5
AC	12	12	12	12
MS	5	5	5	5
RA	5	5	5	5
Dispersed chamotte	15.0	12.5	10.0	7.5
Chamotte aggregates	63	63	63	63
Castament FS-20	0.1*	0.1*	0.1*	0.1*
H_2O	11*	11*	11*	11*

* over 100 % of dry components.

For compositions of refractory castable mixtures, the equal amounts of AC, MS, RA, chamotte aggregate, plasticizer and water were selected and the amount of waste catalyst was increased at the expense of ground chamotte. In the compositions of dry mixtures the waste catalyst was increased proportionally up to 2.5 %; 5.0 % and 7.5 % (the compositions K2; K5 and K7).

The results of investigations were compared to those of the refractory castable without waste catalyst (the composition K0).

The performed investigations of flow of paste of refractory castables K0, K2, K5 and K7 (Fig. 5) demonstrated that the paste of castable K0, though of good workability (hand-ball), is not notable for the excellent flow (flow factor ~14 %) after mixing. Nevertheless, upon introduction of waste catalyst in amounts of 2.5 % and 5.0 % into the mixture of refractory castable, the flow factor of pastes K2 and K5 increased up to 90 %. With introduced 7.5 % of waste catalyst (the composition K7), the flow factor was ~45 % only. After 20 min the flow factor of all castable pastes decreased down to 15 %. After 35 min the flow factor of castable pastes K0; K2 and K5 was about 9 %, and that of K7 was the least, 4 %.

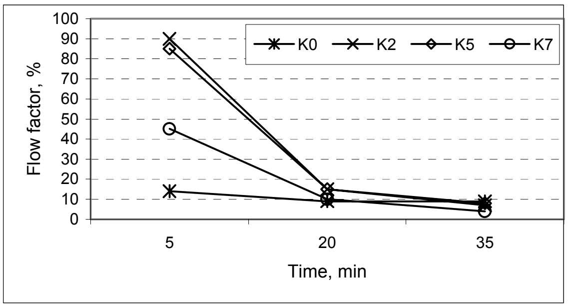


Fig. 5. Flow of paste of castables K0, K2, K5 and K7 subject to duration

These results of flow of refractory castables correlate with those of viscosity of binder presented in Fig. 2 and prove that even a small content (up to 5.0 %) of waste catalyst in the composition of refractory castable improves the flow of the paste of castable.

The effect of waste catalyst on the proceeding hydration of alumina cement was estimated by measurements of exothermic temperature (Fig. 6).

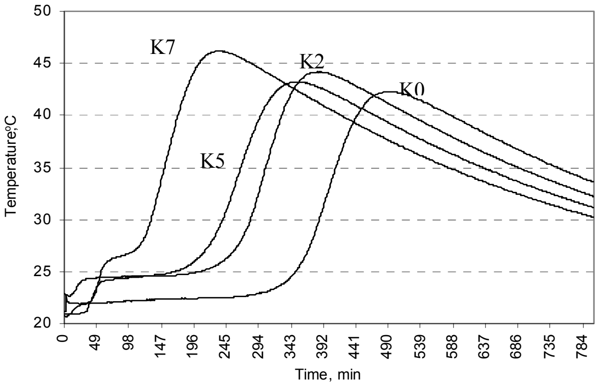


Fig. 6. Changes in temperature during hydration in the castables

We can see (Fig. 6) that in the refractory castable K0 the heat release starts after 360 min and the maximum temperature is recorded approximately after 460 min. The more waste catalyst is contained in the compositions, the earlier appears the maximum temperature of exothermic effect, namely, after 360 min in the composition K2, after

300 min in K5 and after 220 min in K7. These experimental curves of exothermic temperatures indicate that while increasing the content of waste catalyst in the composition of refractory castable, the processes of hydration of alumina cement pick up speed considerably.

The performed investigations of the strength characteristics of refractory castable (Fig. 7) show that after hardening of 3 days at temperature of 20 °C and after drying at temperature of 110 °C, the compressive strength of specimens of castable increases subject to the amount of waste catalyst.

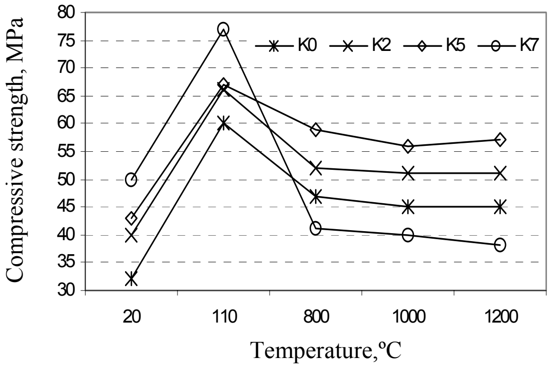


Fig. 7. Dependence of compressive strength of specimens of castable on firing temperature

The strength of specimens K7 is higher by 25 % – 20 % than that of specimens K0 after hardening and drying. After firing at temperatures of 800 °C, 1000 °C and 1200 °C, the compressive strength of specimens K7 is practically the same (~39 MPa) and is lower by 15 % versus K0. However, after firing at temperatures of 800 °C, 1000 °C and 1200 °C the compressive strength of specimensK2 and K5 increases up to 25 % versus the specimens K0.

The investigations of strength properties of refractory castable show that the additive of waste catalyst (up to 5.0 %) can improve the strength characteristics of castable from 1.3 to 1.5 times.

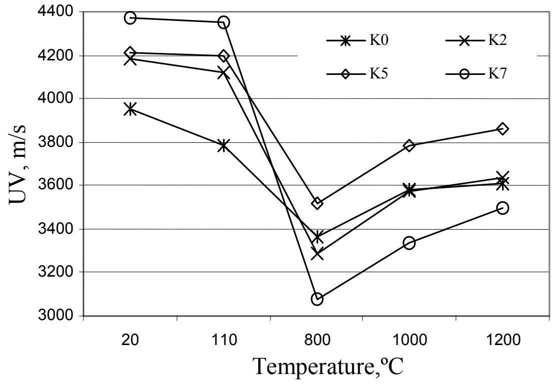


Fig. 8. Dependence of UV in specimens of castables on firing temperature

These results are confirmed by ultrasound velocity (UV) measurements in the specimens (Fig. 8). After hardening of 3 days at temperature of 20 °C and after drying at temperature of 110 °C, UV was higher in those castables, which contained more waste catalyst, namely, UV of specimens K7 was higher by 10 % – 15 % than that of K0. After firing at temperatures of 800 °C, 1000 °C and 1200 °C, UV was lower by 5 % in the specimens of castable K7, and higher by 5 % in specimens K5 versus K0.

The results of compressive strength and UV investigations of castable composition K7 after processing at temperature of 800 °C may be explained by the SEM tests of matrices structure (Fig. 4). It seems that large content of waste catalyst does not ensure any good adhesion between the matrix and grains of waste catalyst. Beside these, microcracs are formed.

4. CONCLUSIONS

It was established that in the castables of type MCC the best flow of paste is found out with 5 % of waste catalyst. The higher content of waste catalyst decreases the flow of castable paste.

The additive of waste catalyst also affects the course of hydration in the mixture of castable. Along with the increase of content of waste catalyst in the composition of mixture of castable MCC, the appearance time of exothermic temperature shortens considerably.

In comparison with the castable without waste catalyst, the castables with waste catalyst added in amounts of 2 % and 5 % have the strength characteristics increased up to 25 %. The content of waste catalyst above 5 % affects negatively the strength characteristics of castable.

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