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AN ATTEMPT TO IMPROVE THE POZZOLANIC ACTIVITY OF WASTE ALUMINOSILICATE CATALYST

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Abstract

The so-called pozzolanic activity of waste catalysts from fluidised cracking was investigated. For this purpose a series of cement mixtures with this waste material were prepared and subsequently the pastes and mortars were produced. Waste aluminosilicate catalyst was used both in raw form and after grinding in a ball mill for 60 min. The hydrating mixtures were subjected to the calorimetric measurements in a non-isothermal/non-adiabatic calorimeter. After an appointed time of curing the hydrating materials were studied by thermal analysis methods (TG, DTG, DTA). The pozzolanic activity factors were determined, basing on the compressive strength data. The increased activity of cement – ground pozzolana systems has been thus proved. An accelerated $Ca(OH)_2$ consumption as well as higher strength were found for materials containing ground waste catalyst, as compared to those, mixed with the raw one. Thus grinding was also proved to result in mechanical activation in the case of the waste catalyst from fluidised cracking.

Keywords: cement hydration, pozzolanic activity, waste aluminosilicate catalyst

Introduction

Thermal analysis is often used to study cement hydration in the presence of active additives, for example pozzolanic materials such as silica fume [1], or in the presence of waste materials (solidification/stabilization process) [2].

Spent catalysts from fluidised bed cracking of petroleum (FBCC), mixed with cement paste, were found recently to act as a pozzolanic agent: the $Ca(OH)_2$ liberated on cement hydration is effectively consumed by this admixture. Thus the positive modification of microstructure results in a higher strength and in improvement of other properties of cementitious composite [3–9].

Two types of aluminosilicate waste catalysts can be obtained after catalytic reaction in the fluidised catalytic cracking unit: waste catalyst removed from the pro-

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cess because of reduced activity and the other type collected by an electrostatic precipitator [10, 11]. Their chemical composition is similar but the grain size distribution differs significantly. In our works these materials were described as FBCC G (coarse catalyst) and FBCC D (fine-grained one) respectively [3, 4].

In comparative studies of FBCC G and FBCC D a higher activity of finer material was found [3], as well as a higher strength of cement concretes [4]. A better effectiveness of FBCC D as a finer material suggested how to modify the activity of the admixture; the preliminary grinding was thus taken into account. This operation was also used by other authors [12], who showed that the strength development was thus improved. The effect was attributed to the increased number of active acid sites reacting with $Ca(OH)_2$. In another report [9] the pozzolanic activity was determined for waste catalyst ground for 20 min and the results thus obtained were similar to those for metakaolin (very active pozzolanic material produced by thermal decomposition of kaolin). Calcium silicate hydrates of variable chemical composition (C–S–H gel) and hydrated calcium aluminates are the main products formed in this pozzolanic reaction.

Beside the thermal and chemical activation, the additional grinding is another way to modify the pozzolanic activity. A higher fineness is connected with a higher specific surface, thus the interface for the reaction between the pozzolana and calcium hydroxide solution is higher. Elevated temperature curing of cement pastes containing a pozzolan is the thermal method for modification of activity. Chemical activation concerns the application of some additives, for example Na_2SO_4 or $CaCl_2$ [13].

This work is aimed at the modification by grinding of the coarse grained waste catalyst described as FBCC G and at the evaluation of the effects by studying the cement pastes and mortars, mixed with FBCC.

Materials and methods

Materials

Experimental work was performed using Portland cement (CEM I 32,5 R [14]), standard sand and waste catalysts of different fineness from Fluidised Bed Catalytic Cracking. Two kinds of waste materials were used:

- FBCC G, waste catalyst withdraw from the installation because of the decrease of the catalytic activity, coarser-grained material;
- FBCC G (60), catalyst FBCC G ground in a ball mill for 60 min to produce a new material, fine-grained one.

FBCC G is a porous, aluminosilicate material of $SiO_2 + Al_2O_3 + Fe_2O_3$ exceeding 90% and specific surface of about 100 $m^2 g^{-1}$. Some properties of FBCC G were described in our papers [3, 4]. In this research grain size distribution and SEM observations of FBCC G and FBCC G (60) were made.

Preparation of pastes and mortars

Pastes and mortars were produced using cementitious material prepared from standard cement type CEM I 32.5 R mixed with waste catalysts FBCC G or FBCC G (60). Cement pastes were prepared at water to solid ratio *w/s* = 0.5 (solid = cement + admixture). Either FBCC G or FBCC G (60) was introduced as 0, 10, 20 or 30% by mass of binder. The pastes were thoroughly homogenised with water and then sealed in polyethylene bags. After an appointed time the pastes were crushed and washed with acetone to remove free water and thus stop the hydration reactions. The dried, powdered samples were subsequently analysed by TG/DTA.

Cement mortars were prepared from Portland cement, FBCC G or FBCC G (60) and standard sand. The cement mortars containing 25% replacement of cement with FBCC G or FBCC G (60) were produced. The mortar without admixture was also produced as a reference. Some amount of additional water was used to attain the standard consistency of mortars with admixtures.

Investigation methods

For the SEM observations of FBCC G and FBCC G (60) JEOL equipment with LINK-ISIS microanalyser was used.

For thermoanalytical studies of cement pastes the SDT 2960 TA Instruments Thermoanalyser was used, working in the temperature range up to 1000°C in air, at the heating rate 10°C min^{-1}, the sample mass was 9–13 mg. The TG, DTG and DTA curves were registered.

For the calorimetric measurements a differential BMR calorimeter was used, built in the Institute of Physical Chemistry in Warsaw. The hydrating pastes were studied as prepared at *w/s* = 0.5 (5 g solid substance + 2.5 mL water) at the starting temperature 25°C. The heat evolution curves were registered, and the heat that evolved after 24 and 72 h from the beginning of the reaction with water were computed.

The compressive strength of mortars was tested after 28 and 90 days storage in water (standard procedure). The pozzolanic activity index was calculated following the rules recommended by Building Research Institute (Instructions no. 328). This is determined as a ratio of compressive strength for mortar with 25% cement replacement to the strength of reference mortar [15].

Results and discussion

Waste catalyst

Grain size distribution and SEM observations of FBCC G and FBCC G (60) results are presented in Figs 1–3. These results show difference between original material FBCC G and ground catalyst – FBCC G (60). FBCC G composed mainly of spherical grains, while the FBCC G (60) grains were much smaller and irregular (Figs 1, 2) These results proved the aluminosilicate character of FBCC G material (Fig. 3).

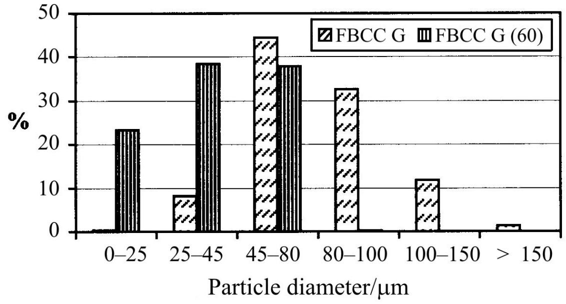

Fig. 1 Grain size distribution of FBCC G and FBCC G (60) samples

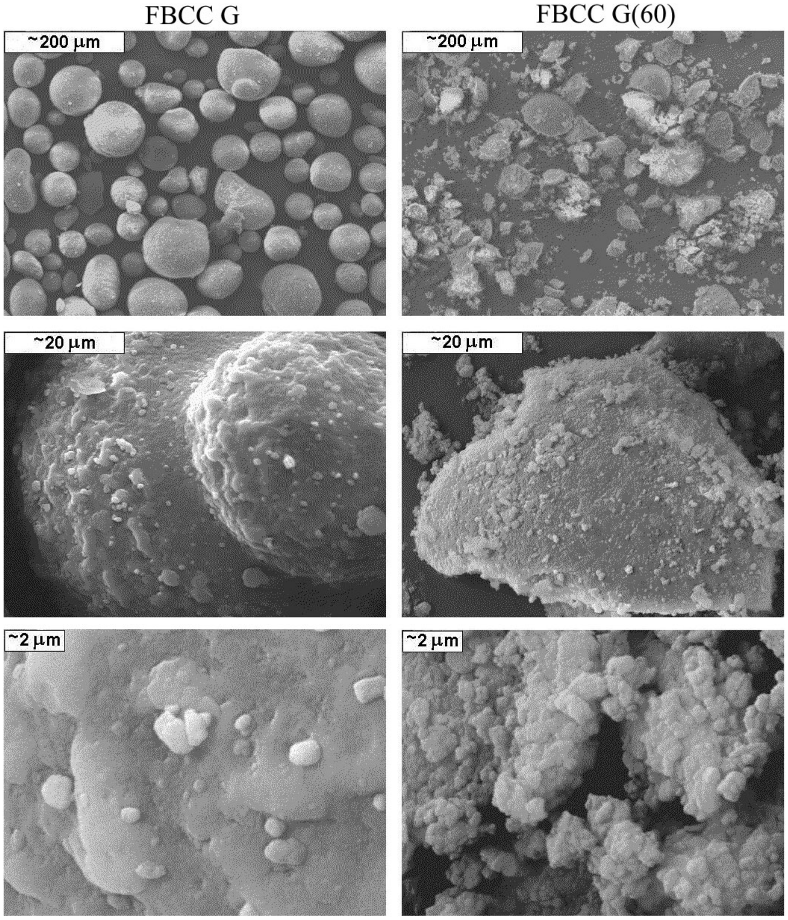

Fig. 2 FBCC G and FBCC G (60) grains at different magnification

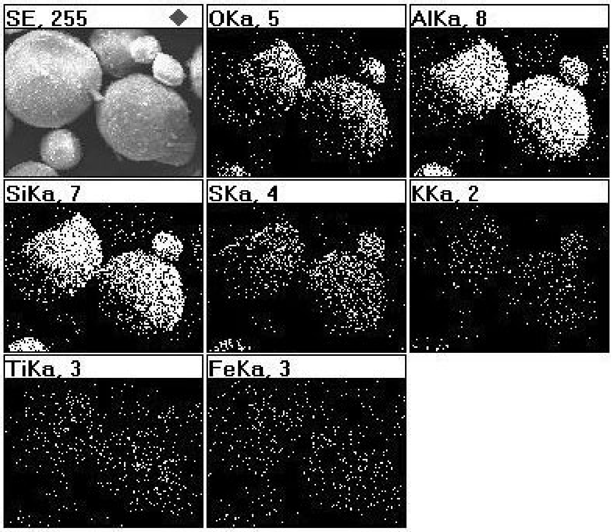

Fig. 3 EDS distribution maps of particular elements in FBCC G grains

Thermal studies of cement pastes

The examples of results of thermal studies are presented in Fig. 4 (TG, DTG and DTA curves).

They are typical for cement pastes: TG curves show three 'thresholds', which can be attributed to the following decomposition reactions:

- up to the temperature about 420°C – dehydration of C–S–H products, as well as hydrated calcium aluminates/sulphoaluminates
- from about 420 to 480°C – decomposition of $Ca(OH)_2$
- above 500°C – decarbonation

The DTG curves for samples with admixture differ, in the range up to 300°C, from those obtained for reference samples. The mixtures with waste catalyst show some additional peaks, apart from the one peak at about 85°C, occurring at temperatures 100–200°C. They can be attributed to the presence of different aluminate phases. The earlier observations [3] have been thus confirmed. In the previous paper the occurrence of additional peaks about 200°C on DTG curve for pastes mixed with FBCC material was reported; these peaks were stronger for higher percentage of admixture and longer time of hydration [3].

For comparison between the activity of FBCC G and FBCC G (60), the mass loss up to the temperature of 420°C was analysed, as corresponding to the progress of hydration. Also the $Ca(OH)_2$ content in pastes was calculated basing on the mass loss in the range of 420–480°C.

From the data presented in Fig. 5 and relating to the mass loss up to 420°C one it can be seen that for the pastes mixed with FBCC G and hydrated for 3 days these mass loss values are lower than for reference sample. It means that the amount of

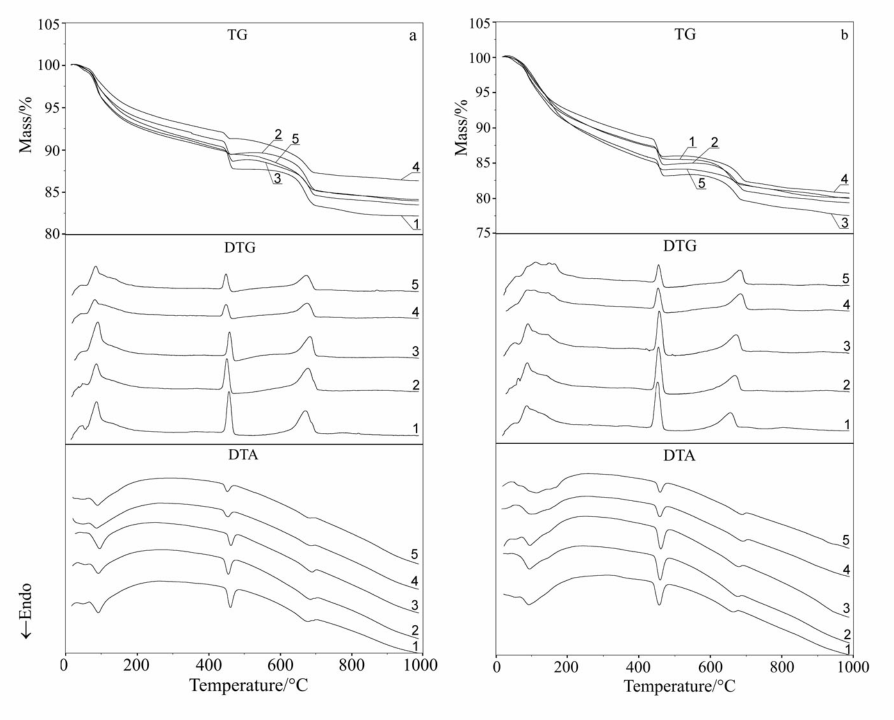

Fig. 4 Comparison of TG, DTG and DTA data for cement pastes with the lowest (10%) and the highest (30%) admixture content, a – 3-day hydration, b – 28-day hydration 1 – 0%, reference, 2 – 10% FBCC G, 3 – 10% FBCC G (60), 4 – 30% FBCC G, 5 – 30% FBCC G (60)

bound water is lower. In the samples mixed with FBCC G (60) the percentage of water after the same hydration time, is similar as that of the reference one. After 7 days hydration the bound water content of samples mixed with FBCC G is similar as that of the reference and after 28 days it is higher. The samples mixed with FBCC G (60) show a higher bound water content after 7 days hydration as compared to the reference and these values become higher at a longer hydration time.

The results thus obtained can be explained by relatively low activity of FBCC G. The increase in bound water content after a longer hydration, can be attributed to the pozzolanic reaction in which the C–S–H and calcium aluminate hydrates are formed. At an early hydration, the porous structure of the admixture should be taken into account. Higher water demand of FBCC G (60) may also result from higher, active specific surface produced on grinding.

The explanation presented above is based upon the assumption that the chemically bound water (in silicates and aluminate hydrates) is liberated mainly at temperatures below the $Ca(OH)_2$ decomposition. The water content results may be considered as a rough estimation of hydration progress, because the new pozzolanic component gives the other hydration products of different water content than in case of neat

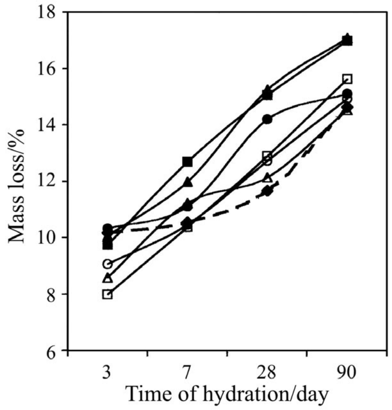

Fig. 5 Mass loss on heating up to about 420°C, ◆ – 0% control paste; ○ – 10% FBCC G; △ – 20% FBCC G; □ – 30% FBCC G; ● – 10% FBCC G(60); ▲ – 20% FBCC G(60) ■ – 30% FBCC G(60)

cement (different CaO/SiO_2 and H_2O/SiO_2 ratios). The variability in composition of the hydration products does not allow to determine exactly the degree of hydration. However, the studies on hydrated systems with and without admixtures reveal the differences in the hydration mechanism [16].

The pozzolanic activity of FBCC G and FBCC G (60) was evaluated by comparison of calculated $Ca(OH)_2$ content in cement pastes. This method based upon the mass loss in the range of $Ca(OH)_2$ decomposition is one of the best among various methods of pozzolanic activity characterization [17]. The results are given in Fig. 6. Lower calcium hydroxide contents were found for pastes mixed with FBCC G and FBCC G (60) than for reference. At 10% of FBCC G the content of $Ca(OH)_2$ increased within 28 days hydration and then it was reduced. For pastes with higher con-

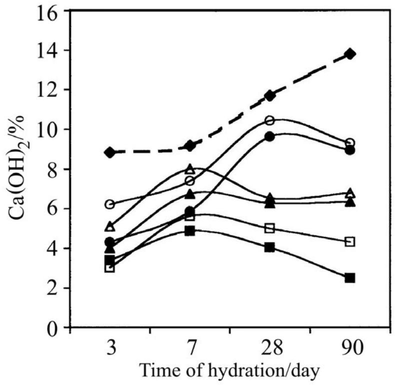

Fig. 6 $Ca(OH)_2$ content in cement pastes, ◆ – 0% control paste; ○ – 10% FBCC G; △ – 20% FBCC G; □ – 30% FBCC G; ● – 10% FBCC G(60); ▲ – 20% FBCC G(60) ■ – 30% FBCC G(60)

tent of admixture, the lowering in calcium hydroxide content is observed between 7 days and 28 days. The pastes produced using FBCC G (60) show a lower calcium hydroxide contents than corresponding samples with FBCC G; this would indicate a better pozzolanic activity of ground catalyst. However, after 90 days the differences between the 10 and 20% FBCC G or FBCC G (60) doped samples are not significant. They are clearly visible for higher content of admixture (30%).

Calorimetric studies of cement pastes

In Figs 7 and 8 the results of calorimetric measurements are shown as the rate of heat evolution curves and as the heat released after 24 and 72 h hydration (Figs 7 and 8, respectively). The results for pastes with FBCC G (60) were compared with those for FBCC G, shown earlier [3].

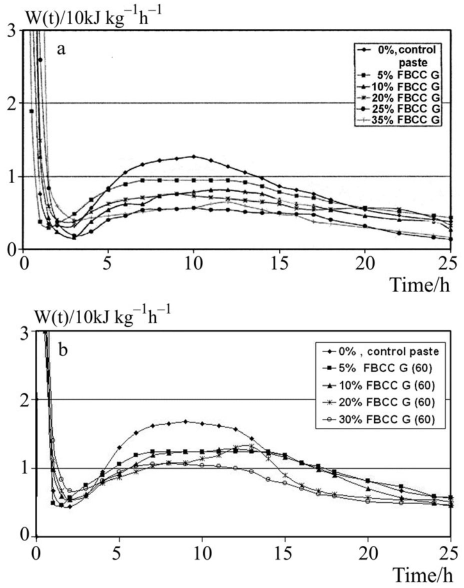

Fig. 7 Heat evolution curves for cements hydrating with a – FBCC G [3] and b – FBCC G (60)

In both cases the rates of heat evolution in the presence of admixture are reduced. The curves for the pastes with admixture are more flat than for reference. At a higher admixture content the third peak appears; it can be attributed to the hydration of aluminate component with the formation of aluminate product. It is particularly clear for the pastes with 20% FBCC G (60).

The moderating effect of FBCC G and FBCC G (60) admixture is seen also when the values of heat evolved after 24 and 72 h hydration are considered. In both cases the lowering of the evolved heat with the increase in the admixture content can be noticed. For better presentation of the results, the relative heat values for FBCC G and FBCC G

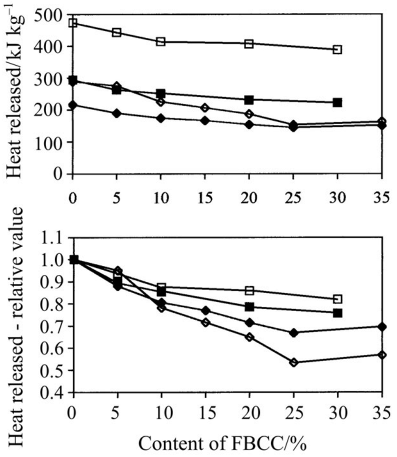

Fig. 8 Heat released within 24 h and 72 h hydration and relative values calculated basing on reference data, ◆ – FBCC G, 24 h; ■ – FBCC G(60), 24 h; ◇ – FBCC G, 72 h; □ – FBCC G(60) 72 h

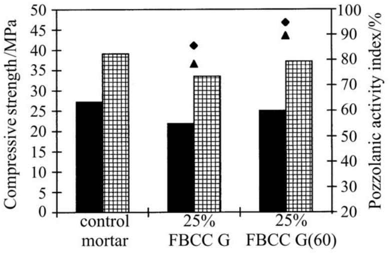

Fig. 9 Compressive strength of mortars and pozzolanic activity indexes according to [15], ■ – compressive strength, 28 days; ▲ – pozzolanic activity index, 28 days; ▦ – compressive strength, 90 days; ◆ – pozzolanic activity index, 90 days

(60) admixtures are presented in Fig. 8, as calculated using the reference values. It can be easily seen that the coarse grained FBCC G admixture causes a more evident heat lowering. In case of pastes containing FBCC G (60), the reduction of heat released is less marked. The changes are not proportional – the differences after 72 h are relatively smaller and this may result from the pozzolanic reaction initiated in hydrating system. The higher activity of ground admixture is thus proved again.

Pozzolanic activity determined basing on strength measurements

The strength results was measured for cement mortars and the values of pozzolanic activity index calculated therefrom, are shown in Fig. 9. The catalyst admixture added as 25 wt.% cement replacement causes a decrease in the compressive strength more evident in case of coarse grain FBCC G application than in case of the finer one. In both cases [FBCC G and FBCC G (60)] the pozzolanic activity indexes are higher than the limit value recommended by the Polish Building Research Institute [15], that is 75% after 28 days and 85% after 90 days hydration. Higher index for FBCC G (60) proves better pozzolanic activity of this ground material as cement admixture.

Conclusions

The ground fine-grained waste catalyst exhibits good pozzolanic activity better than the unground material. It results from the higher bound water content, more evident reduction of $Ca(OH)_2$ content in hydrating pastes and relatively lower heat evolved decrease. The compressive strength of mortars is higher as compared to those containing unground FBCC G. Thus the additional grinding is a good method of activation of waste catalyst as cement admixture.

As a further step the parameters of grinding process should be optimised or the ground material should be separated into particular grain size fractions to produce the admixture of fairly high specific surface and proper grain size distribution.

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