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HYDRATION OF CEMENT SLURRY IN THE PRESENCE OF SPENT CRACKING CATALYST

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Abstract

The physicochemical properties of spent fluidized bed cracking catalyst and its influence on hydration process of cement slurry were studied. The samples were cement slurries prepared with water/solid=0.5 and additions of used catalyst amounted to 0, 5, 10, 15, 20 and 25% with resp. to the solid. After definite time they were subjected to thermogravimetric analysis (TG, DTG, DTA) and, in order to determine the progress of reaction with water, the heat of hydration was measured by means of isotherm calorimetry. The studies disclosed that the spent cracking catalyst is not merely an inactive filler in cement slurries, but it modifies the course of the hydration process. The spent catalyst is a pozzolana additive and its presence leads to a decrease of calcium hydroxide contents in the system. The spent catalyst affect on the heat of cement hydration. Small amounts additive accelerate the process of binding.

Keywords: cement slurry, hydration of cement, pozzolana additive

Introduction

Pozzolana additions to concrete improve a number of their features such as strength, water impermeability and service lifetime. The effect is due to binding of calcium hydroxide, formed in cement hydration, by pozzolana containing active silica. As a result there is an increase of hydrated calcium silicates in the system. Besides to their role of active filler pozzolana compounds act also as a microfiller that improves the homogenous distribution of cementite particles in the mixture and fills finer void spaces between mortar or concrete grains [1]. The most widely used pozzolana additions to concrete are fly ashes and silica dusts, but pozzolana properties have also been found in zeolites and other materials containing active silica. In general opinion the activity of zeolite-based pozzolana is higher than that of vitreous forms, which is due to higher porosity and ability of ion exchange. The process of binding calcium hydroxide from the liquid phase proceeds rapidly and pozzolana is transformed into an aluminum-silica gel [2].

The first part of this work was devoted to a study of physicochemical properties of spent fluidized bed cracking catalyst (FBCC) aiming at using it as an active addi-

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tion to cements. In the second part the results of studies on the effect of addition of spent cracking catalyst on cement hydration are presented.

Experimental

Used cracking catalyst was subjected to physicochemical analyses to determine its properties essential for its use as addition to concrete, namely: chemical composition, phase composition, specific surface, granulometric composition, and organic matter content. The analytical methods involved thermogravimetric analysis, infrared spectroscopy, and X-ray phase analysis. The studies of physicochemical properties of FBCC were accompanied by the studies of the effect of used catalyst on the course of hydration of cement slurries.

Table 1 Cement characteristics

Component	Content/mass%
SiO_2	19.2
Al_2O_3	5.0
Fe_2O_3	2.3
MgO	1.6
CaO	64.2
SO_3	2.9
C_3S^*	70.28
C_2S	2.09
C_3A	9.36
C_4AF	6.99
$C\overline{S}H_2$	6.24
Specific surface/$m^2\ g^{-1}$	0.25

* Symbols used in cement chemistry: C – CaO, $\overline{S}$ – SO_3, H – H_2O, A – Al_2O_3, S – SiO_2, F – Fe_2O_3

Cement slurries were prepared with water/solid=0.5 and additions of used catalyst amounted to 0, 5, 10, 15, 20 and 25% with resp. to the solid. The cement used was Portland type, produced by cement plant Małogoszcz, of chemical composition given in Table 1. Samples of slurries were packed in small plastic bags and stored at room temperature. At scheduled days samples were opened, ground without drying and subjected to thermogravimetric analysis. TG, DTG, and DTA curves were recorded in the air atmosphere at temperature range 50–1000°C using a Hungarian instrument Derivatograph C. The IR absorption spectra of used catalyst were recorded within the wave number region 4000–400 cm^{-1} by means of a Zeiss spectrophotometer Specord 75, and X-ray phase analyses involved HZG–4C diffractometer with copper cathode.

Besides, in order to determine the progress of reaction with water, the heat of hydration was measured by means of isotherm calorimetry using differential calorimeter BMR developed in the Institute of Physical Chemistry of Polish Academy of Science. Samples of cement were hydrated at 25°C. The obtained curves of heat power were used, by means of a computer program, for calculation of heat evolved in 24 and 72 h of hardening.

Discussion of results

Studies of spent cracking catalyst

Spent cracking catalyst of chemical composition presented in Table 2 is a fine-grained material of particle size not exceeding 150 μm. Studies of granulometric composition of FBCC used in this work for preparation of slurries (Fig. 1) showed that most particles fell in the range 0–20 μm, and average particle diameter was 21 μm.

Table 2 Characteristics of spent catalyst

Property	Content
Chemical composition	
SiO_2	55.89%
Al_2O_3	37.60%
RE_2O_3	1.58%
P_2O_5	0.22%
TiO_2	1.35%
SO_3	1.73%
Other metal oxides*	0.69%
V	1446 ppm
Ni	615 ppm
Other (Cu, Sb, PbO)	80 ppm
Specific surface	105 m^2 g^{-1}

* CaO, BaO, each in amount <0.3%; MgO, K_2O, ZnO, SrO, each in amount <0.05%

The specific surface of the catalyst, as determined from N_2 adsorption isotherm, was 105 m^2/g.

Thermogravimetric studies (Fig. 2) exhibited rather high thermal stability of the spent catalyst used. A small loss in mass of about 3% by mass was mainly due to the loss of water at temperatures below 300°C. A further loss in mass (less than 1% by mass) observed on heating above 500°C, may be due to the combustion of small amounts of organic compounds remained on the surface of the catalyst particles.

The X-ray diffraction pattern of the spent catalyst (Fig. 3) may correspond to a zeolite structure with a probable chemical formula of $Na_9(AlO_2)_9(SiO_2)_{15}27H_2O$. Some discrepancies in diffraction patterns between the sample studied and the accepted standard may be due to the fact that the catalyst is not a chemically homogenous substance, but presents a mixture of zeolite-type compounds. One cannot exclude the presence of amorphous phases formed in repeated regeneration processes, too.

The infrared spectrum of spent catalyst, shown in Fig. 4, is characteristic with a high intensity band in the region 1300–950 with a maximum at about 1055 cm^{-1}. It is probably due to valency vibrations of O–Si(Al)–O bonds [3]. Less intensive bands are observed within 850–700 cm^{-1} (probably due to symmetric valency vibrations of

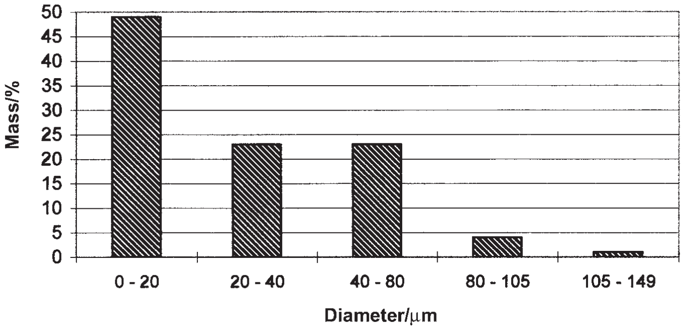

Fig. 1 Granulometric composition of spent catalyst

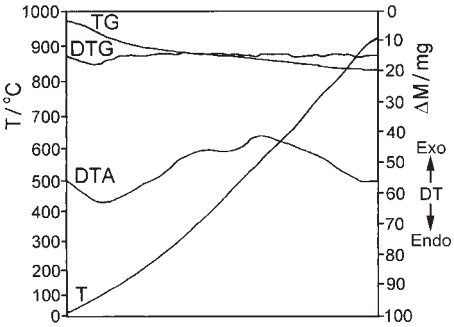

Fig. 2 TG, DTG and DTA curves of spent catalyst (sample mass 650 mg)

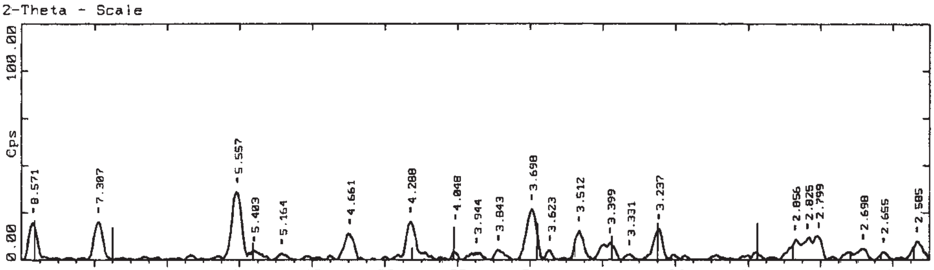

Fig. 3 X-ray diffraction pattern of spent catalyst

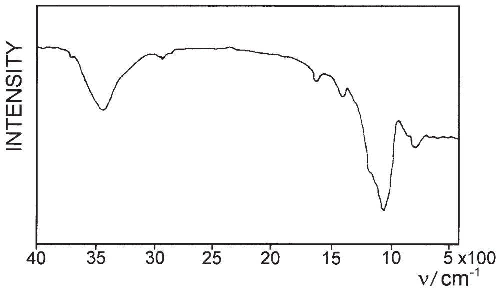

Fig. 4 Infrared absorption spectrum of spent catalyst

Si–O), at 1700–1550 with a maximum at about 1610 cm^{-1} (deformation vibrations of water molecules), and at 1500–1350 with a sharp maximum at about 1410 cm^{-1}. An intensive band within 3700–3100 with a maximum about 3440 cm^{-1} may be accounted for the presence of water. An unidentified, weak band is also observed at about 3700 cm^{-1}. No distinct band was observed in the region of 700–400 cm^{-1}, characteristic for zeolites, where one might expect absorption bands due to skeletal deformation vibrations.

Studies of cement slurries

The performed studies have shown, that a spent cracking catalyst used as additive for cement slurry modifies actively the hydration process.

Figure 5 shows a comparison of heat evolution curves obtained for slurries containing different amounts of the additive, recorded during 24 h after 72 h of hydration. The results of calorimetric studies are tightly bound with chemical composition of the binders. The course of heat evolution shown by the calorimetric curves is typical for cements. The initial hydration peak is followed by the so-called induction period, almost athermic, after which the rate of heat evolution rises markedly. The heat evolution during the first two h of the process is mainly due to wetting, dissolving of the components, liberation of

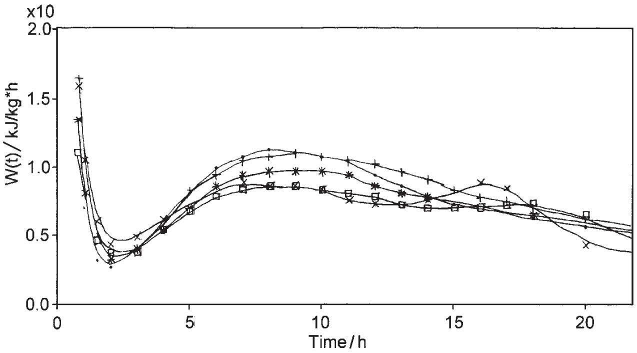

Fig. 5 Heat evolution rates of cement slurries (• – control slurry; + – 5% of FBCC; * – 10% of FBCC; □ – 20% of FBCC; × – 25% of FBCC)

lime and beginning of hydration. The second heat effect is due to hydration of silicate phases, mainly of alite. A third group of thermal effects appears after complete use-up of gypsum and is connected with hydration of tricalcium aluminate.

The heat evolution curves (Fig. 5) show that in slurries prepared with addition of spent cracking catalyst the heat effects increase considerably within the initial two h of hydration. Samples of slurries containing the highest amounts of the catalyst added (20 or 25%) are characteristic with a presence of a third peak, appearing in 18-th and 16-th h of hydration, respectively, associated with hydration of aluminates after gypsum had been used up. One can conclude, therefore, that the presence of spent catalyst accelerates the formation of ettringite and use up gypsum in the system, and thus it leads to prompter and more intense hydration of the remaining aluminates introduced with increasing amounts of the catalyst added. The shape of calorimetric curve of a slurry containing 5% additive of FBCC is similar to that of the control slurry, with much broader thermal effect due to the hydration of silicates. A small addition of the catalyst ranging 5–10% by mass acts as a cement substitute and a binding accelerator. At higher contents of the additive, more than 10%, the heat evolved after 72 h of hydration decreases probably because of the smaller amounts of C–S–H phase formed.

Thermogravimetric analyses have enabled to find the composition of the materials basing on the mass losses and size of associated thermal effects. Figure 6 shows a comparison of TG and DTG curves of slurries containing 0, 5 and 20% additions of FBCC taken in 1st and 28th day of hydration. In all cases the progress in hydration was accompanied by changes in the shape of the TG curve. The changes proceeding at 50–450°C where a complex effect of dehydration of silicate hydrates, aluminates, and aluminosulfates, as well as gypsum decomposition is observed, are manifested by rounding-off shapes of the TG curve, and are due to the increase of the amounts of the hydrated forms. A distinct loss in mass at about 100°C is connected with evaporation of free water and partial dehydration of the hydrous forms (the C–S–H phase,

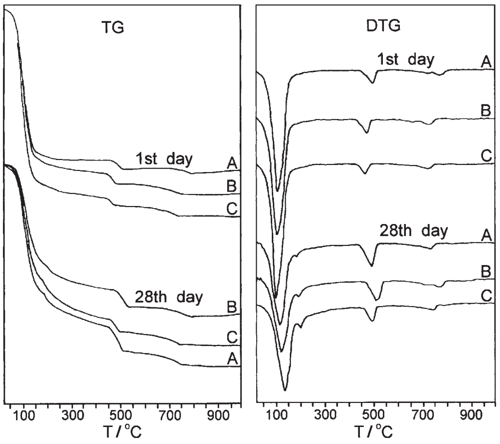

Fig. 6 Comparison of TG and DTG curves of cement slurries on 1st and 28th days of hydration (A – control; B – 5% of FBCC; C – 20% of FBCC)

ettringite) [4]. A peak at about 200°C, observed on the DTG curve, is due to the evaporation of water resulting from dehydration of aluminates (probably of calcium sulfate-aluminate). The peak becomes visible since the third day of hydration and during the following days of reaction its presence is featured by a clear inflexion on the TG curve. At about 450°C there is an endothermic peak due to the $Ca(OH)_2$ decomposition – the only peak connected with a well-defined chemical process. The decomposition of carbonates proceeds at about 750°C.

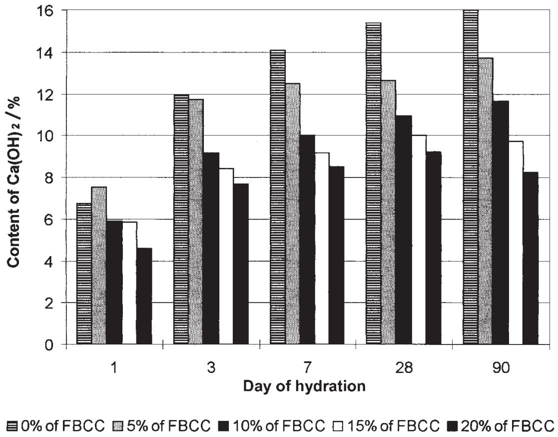

Fig. 7 Calcium hydroxide contents in cement slurries as a function of hydration time

The thermogravimetric studies enabled to determine the content of calcium hydroxide in the system. The comparison of the amounts of $Ca(OH)_2$ present in the slurries studied, as shown in Fig. 7 indicates, that formation of calcium hydroxide is intimately bound with the contents of FBCC involved. In the first day of hydration the slurry with the smallest addition of FBCC contains more $Ca(OH)_2$ than the control sample. During the following days of hydration the content of calcium hydroxide in the control slurry increases markedly with respect to the amounts found in slurries with addition of FBCC. The content of $Ca(OH)_2$ decreases also with increasing amount of the additive. The fact may be accounted to the pozzolana properties of FBCC. Most probably the mechanism of the process consists in dissolving the crystalline zeolite. In strongly alkaline medium the pozzolana components are hydrolyzed with transition of aluminum and silicon ions to the liquid phase, where they react with calcium ions to form the C–S–H phase and hydrated calcium aluminates and, in the presence of gypsum, also ettringite [2].

Conclusions

1. Spent fluidized bed cracking catalyst is not merely an inactive filler in cement slurries, but it modifies the course of hydration process.

2. Addition of FBCC in amounts exceeding 10% by mass reduces the heat of hydration of cement slurries.

3. Small amounts of FBCC (<10% by mass) accelerate the process of binding, which is manifested by increased amount of heat evolved and more rapid formation of calcium hydroxide.

4. An additional effect on calorimetric curve, due to the hydration of aluminates, is observed for slurries containing 20% or more FBCC.

5. The presence of FBCC leads to a decrease of calcium hydroxide contents in the system. The decrease is more noticeable the higher the content of FBCC and the longer is the time of hydration. The fact is accounted for pozzolana properties of the fluidized bed cracking catalyst.

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