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Use of spent catalyst from catalytic cracking in fluidized bed as a new concrete additive

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Abstract

The hydration of cement paste was studied as a function of addition of spent catalyst for catalytic cracking in fluidized bed, as compared with similar use of microsilica and fly ashes. The course of the hydration process was studied by TG and DTA, X-ray diffraction, and infrared absorption methods. The time of setting of freshly prepared pastes and the compressive and bending strengths of sample beams after the 7th and 28th days of setting were determined. The contents of $Ca(OH)_2$ in the pastes at different times of hydration were determined from the results of the thermogravimetric studies.

The studies disclosed the pozzolana nature of the additives. The ability of combining with $Ca(OH)_2$ was similar in the spent catalyst and microsilica. In the presence of the spent catalyst, the hydration process was strongly exothermic which promoted rapid setting of the cement paste. Calcium carbonate–aluminates formed in the system affect favorably the strength of the concretes formed. © 1998 Elsevier Science B.V.

Keywords: Cement paste; Fly ash; Hydration; Silica dusts; Synthetic zeolite

1. Introduction

Use of industrial wastes as additives for cement materials reduces the consumption of energy in the manufacture of building materials by partial substitution of cement, but it contributes also to the environment protection. Hydrated calcium silicates (the so-called C–S–H phase) that constitute almost 80% by volume of hydrated cement can stabilize various kinds of waste materials, also those including heavy metals [1]. In many cases, the use of industrial wastes as cement additives promotes also the development of building industry. An ideal example is the utilization of silica dusts, which is a side product of metallurgical industry, for manufacture of high strength concretes but the influence of microsilica on the hydration process and properties of concrete is still studied [2–5].

The Faculty of Construction Engineering, Mechanics, and Petrochemistry of the Warsaw University of Technology has been involved for many years in research works on use of spent catalyst from catalytic cracking in fluidized bed (further referred to as KFKK) as a concrete additive [6–8]. The catalyst is a synthetic zeolite, thus, it may be expected to have pozzolana properties, just like naturally occurring

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zeolites as well as silica dusts and fly ashes containing active silica [9].

The aim of this work was to compare the effect of spent catalyst, microsilica, and fly ashes on the course of hydration of cement pastes.

2. Experimental

The object of the studies were cement pastes featured by water : cement ratio 0.5, content of additive 25% with respect to the mass of cement (0% in control paste). The cement used was CP 35 from Małogoszcz cement plant, and the additives studied were: KFKK and, for comparison, microsilica from Huta Łaziska and fly ashes from heat and power generating plant Ostrołęka. For freshly prepared pastes the time of binding was determined with the use of Vicat app. [10], and temperature during the initial period of hydration was measured with a mercury thermometer. The pastes were formed into small beams having dimensions 4×4×16 cm^3. The molds were removed in 24 h, and the samples were kept for 28 days in water at room temperature. In definite time intervals some samples were taken for physicochemical and structural studies.

Thermogravimetric studies (TG, DTG, and DTA) were performed at temperature range 50–1000°C in air with the use of Derivatograph C, Hungary. The X-ray diffraction studies used a HZG-4C diffractometer with a Cu cathode. IR spectra were recorded within 4000–400 cm^{-1} using a spectrophotometer Specord 75 IR (Germany), and samples in KBr tablets. In order to determine the effect of the additives on mechanical properties of the obtained paste beams, bending and compressive strengths [10] were measured with the aid of Michaelis device (Poland) and P-50 press (Russia), respectively. The contents of calcium hydroxide in the pastes after various times of hydration were determined from thermogravimetric studies.

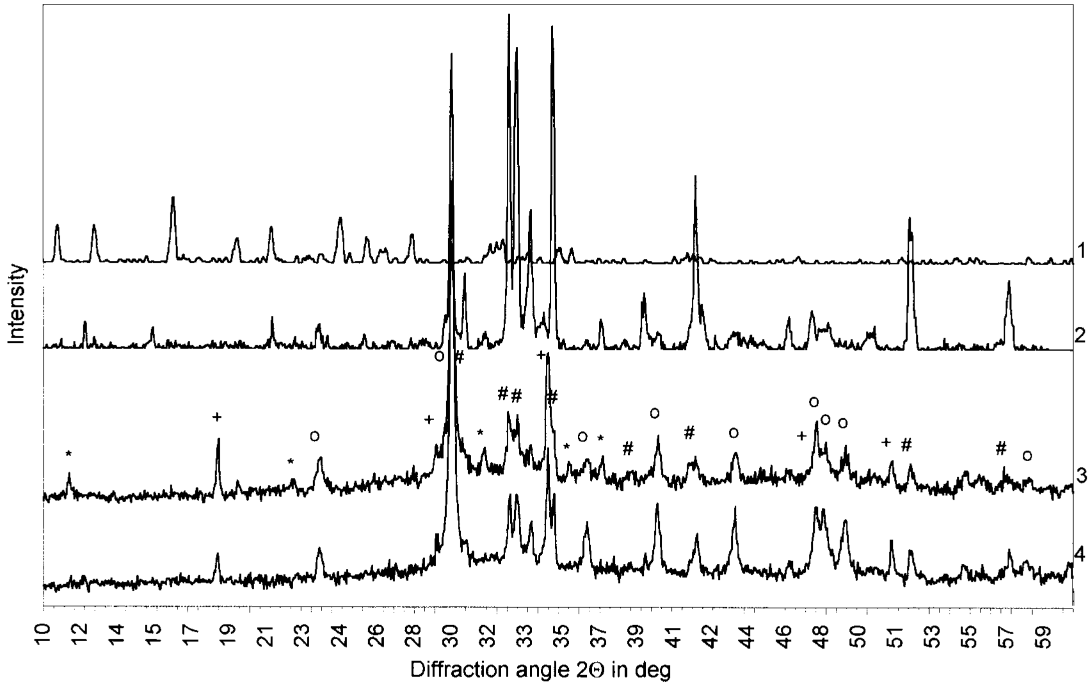

Fig. 1. Comparison of X-ray diffraction patterns of cement paste containing KFKK and of its components. 1 – KFKK, 2 – portland cement, 3 – 28th day of hydration of cement paste, 4 – 7th day of hydration of cement paste; components of cement pastes: * – calcium carbonate–aluminates, + – calcium hydroxide, ○ – calcium carbonate, # – calcium silicates.

3. Discussion of results

3.1. Components of cement pastes

DTA and thermogravimetric studies revealed the presence of thermal effects and mass losses that enable to evaluate the chemical composition of the materials. Except for the ashes the heights of the observed peaks and the losses in mass are small. In the case of cement an endothermic peak observed at ca. 150°C may be due to water evaporation or dehydration of gypsum, and another one at ca. 750°C may be accounted for the presence of carbonates. The used KFKK exhibited two endothermic peaks below 200°C corresponding to the loss of water, a small loss in mass at ca. 700°C with no noticeable thermal effect, and an exothermic effect at 950°C probably due to rearrangement of the zeolite structure. The microsilica was stable within the whole temperature region studied. In the case of ashes, the loss in mass observed within 500–900°C was due to the presence of carbon in the samples. The combustion of carbon was accompanied by an exothermic effect.

The IR spectrum of cement exhibited absorption bands at 1110, 930, and 890 cm^{-1} due to silicates. The band observed at 890 cm^{-1} may also be due to carbonates, the presence of which is confirmed by a characteristic band at 1440 cm^{-1}. The spectra of KFKK, fly ashes, and microsilica are similar to one another. In all cases the IR spectra exhibited absorption bands at 1100 and 800 cm^{-1}, characteristic for silica. These bands were the most intensive for the samples of silica dust.

The X-ray diffractograms enabled the identification of crystalline components of the samples. The X-ray diffraction patterns showed that:

– the highest degree of crystallinity was observed in cement, for which the diffraction lines were the most intensive; the identified species were calcium silicates (Ca_2SiO_4, Ca_3SiO_5), calcium carbonate and gypsum;

– fly ashes contained crystalline silica (quartz) and mullite ($3Al_2O_3{*}2SiO_2$);

– X-ray diffraction pattern of KFKK was composed of a number of lines mostly in the 2θ-range of 10 to 36°, corresponding to zeolite structure of probable chemical composition $Na_9(AlO_2)_9$-$(SiO_2)_{15}{*}27H_2O$.

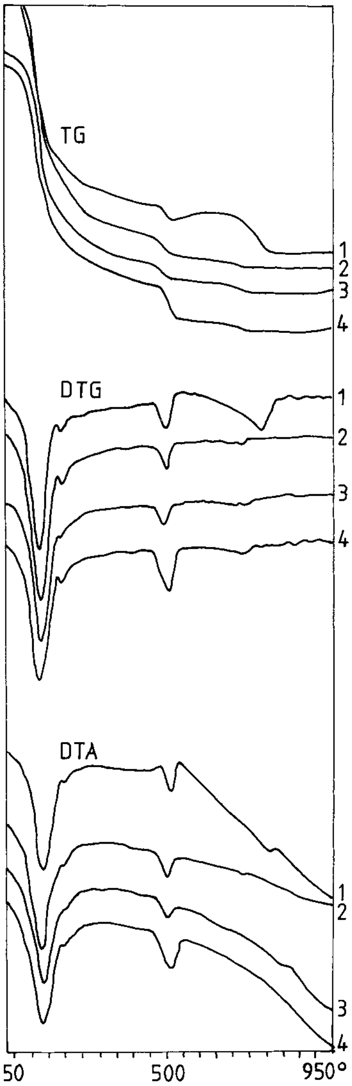

Fig. 2. Comparison of TG, DTG and DTA of cement pastes on the 28th day of hydration. Cement pastes: 1 – 25% of ashes, 2 – 25% of KFKK, 3 – 25% of microsilica, 4 – no additions.

3.2. Cement pastes

The studies have shown the three kinds of additives used take part in chemical reactions with the paste components and exert a bearing on the hydration process.

Studies of cement pastes with additions of microsilica and fly ashes have confirmed their pozzolana properties. In the case of the KFKK, the studies have shown its accelerating effect on the process of hydration. The hydration was strongly exothermic, and the increased temperature accelerated the process of setting. Under the actual experimental conditions (proportions of ingredients and uncontrolled consistency), the KFKK-containing samples were set as early as in 4.5 h after mixing the dry components with water. In pastes modified with silica dusts or with fly ashes the setting was complete in 7 h, whereas in pure cement paste the setting just started at such a time.

X-ray diffraction studies have shown that even after 28 days of hydration the crystallinity of the samples was still poor. The X-ray diffraction patterns exhibit peaks characteristic for crystalline $CaCO_3$ and $Ca(OH)_2$. In a sample with KFKK-containing paste the X-ray diffraction pattern recorded on the 28th day of hydration process exhibits a line due to calcium carbonate–aluminate. The presence of this compound is favorable for the system. In the opinion of some authors [9], calcium carbonate–aluminates formed at the boundary zone increase the surface roughness of aggregate and grains contribute to binding strength between aggregate and paste.

Comparison of X-ray diffraction patterns of KFKK and KFKK-containing paste (Fig. 1) shows that in the latter case the reflexes due to zeolite structure disappear. This suggests, that the hydration process may proceed in a similar way as in the case of natural pozzolana compounds, where the mechanism of the process is reduced to dissolving of crystalline zeolite.

DTA and thermogravimetric analysis of cement paste samples have given a possibility of evaluating the composition of the materials based on mass losses and thermal effects recorded [11,12]. Fig. 2 gives a comparison of TG, DTG and DTA curves of cement pastes on the 28th day of hydration.

In all the pastes, the progress in hydration is accompanied by changes in the shape of the TG curve. A distinct loss of mass at 100°C corresponds to evaporation of free water and partial dehydration of hydrated forms (C–S–H phase, ettringite). A peak on DTG observed at ca. 200°C, probably due to evaporation of water from aluminate hydration products, occurs in samples after two days of hydration. The loss of mass at 450°C corresponds to decomposition of $Ca(OH)_2$ to CaO and H_2O. Untypical shape of TG curve observed for a sample of paste containing fly ashes results from the presence of carbon which is oxidized to CO_2 at ca. 500°C. The effect of mass increase is due to reaction of CO_2 with CaO, confirmed by increasing height of a peak due to carbonates.

The mass losses observed on TG and DTG curves are accompanied by thermal effects on DTA curve. Distinct endothermic effects are observed at ca. 100°C, and 450°C, and for ash-containing samples

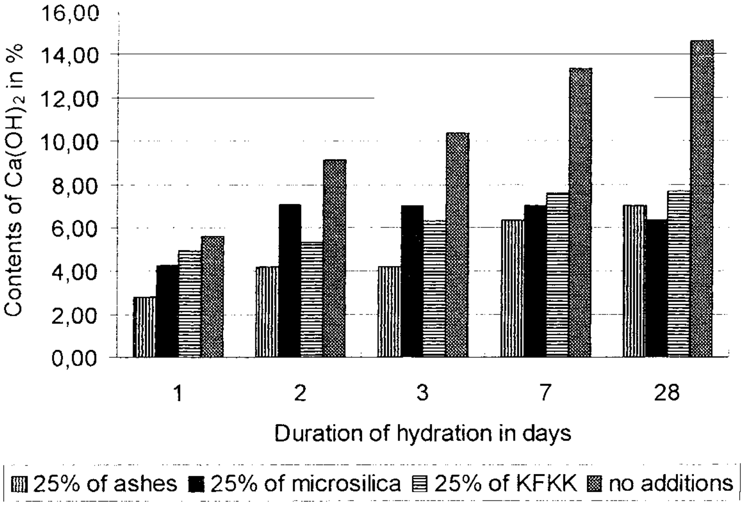

Fig. 3. Contents of $Ca(OH)_2$ in cement pastes as a function of hydration time.

also at ca. 750°C. For other cement pastes the effect due to decomposition of carbonates above 700°C is rather small. In the case of KFKK- and ash-containing pastes, the endothermic effect at ca. 200°C becomes visible from the 7th day of hydration. For microsilica-containing pastes an exothermic effect is observed at ca. 900°C. It is supposed to be due to mullite formation at elevated temperatures, but a formation of wollastonite (CaO*SiO_2) from the C–S–H phase with C/S<1.5 is also probable.

Thermogravimetric studies have given a possibility to evaluate the contents of calcium hydroxide as a function of hydration time (Fig. 3). Results obtained for pastes containing KFKK or silica dusts indicate that the ability of binding calcium hydroxide is similar in the two additives. On the 28th day of hydration the content of $Ca(OH)_2$ is similar in pastes containing either of these additives, but it is about half that of the control sample.

The infrared absorption studies showed distinct differences in the course of hydration process of cement pastes. The spectra of cement pastes show the presence of bands due to antisymmetrical and symmetrical valency vibrations of OH groups in water molecules (broad band at ca. 3430 cm^{-1}) and bands due to deformation vibrations (1630 cm^{-1}). A band due to the presence of $Ca(OH)_2$ in the system is observed at ca. 3650 cm^{-1}. A band featuring the presence of carbonates is seen at 1450 cm^{-1}, and distinct bands due to hydrated silicates are observed at 1100–880 cm^{-1}. A band at 875 cm^{-1} and a weak band at ca. 750 cm^{-1} may be due to CaO and/or $CaCO_3$ [12–14].

Fig. 4 shows infrared spectra of pastes on the 1st and 28th days of hydration. During the first days of hydration of cement pastes considerable differences in the shape of the infrared spectrum due to silicates are observed within 1100–880 cm^{-1}. In the case of paste containing microsilica a distinct band characteristic for silica is observed at ca. 1100 cm^{-1}. The progress in hydration is manifested by distinct reduction of intensity of absorption bands at 1100 and 880 cm^{-1}, and an increase of intensity of the 1000 cm^{-1} band. On the 28th day of hydration a distinct band due to SiO_2, evidence of the presence of free silica, is observed only in samples containing silica dust additive. The silicate bands observed for other cement pastes are similar in shape.

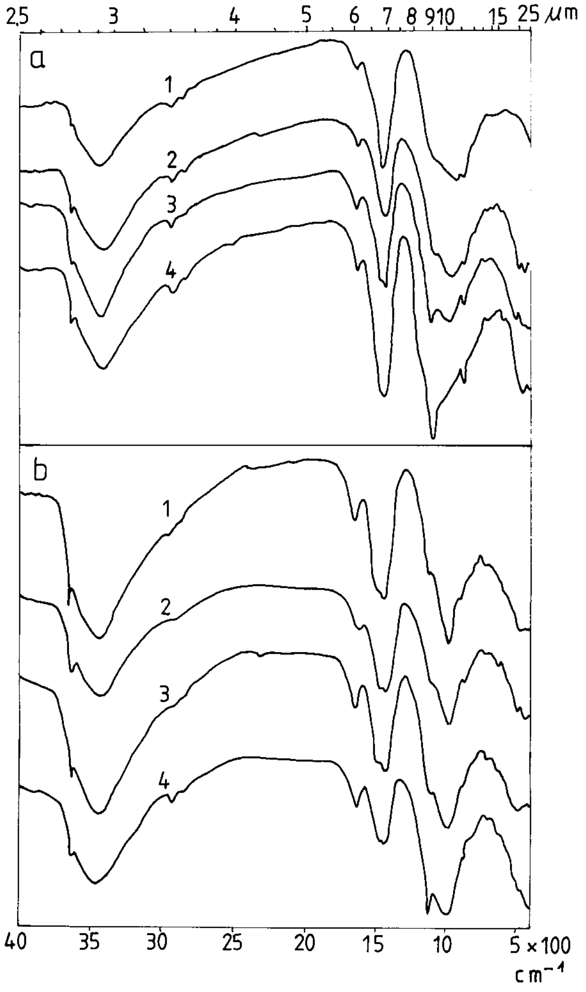

Fig. 4. Infrared absorption spectra of cement pastes on the 1st and 28th days of hydration. a – 1st day of hydration, b – 28th day of hydration, cement pastes: 1 – no additions, 2 – 25% of ashes, 3 – 25% of KFKK, 4 – 25% of microsilica.

The appearance and the increase of intensity of absorption band due to $Ca(OH)_2$ (3650 cm^{-1}) may be accounted for increasing contents of calcium hydroxide in the pastes. The highest intensities of OH vibrations in $Ca(OH)_2$ were observed in cement paste without additives.

Comparison of strength of the cement pastes (Fig. 5) shows a favorable effect of the additions on the mechanical properties. In the case of KFKK, the effect became visible from the 7th day of the hydration process. Cement pastes containing this additive exhibited the highest compressive strengths. The highest

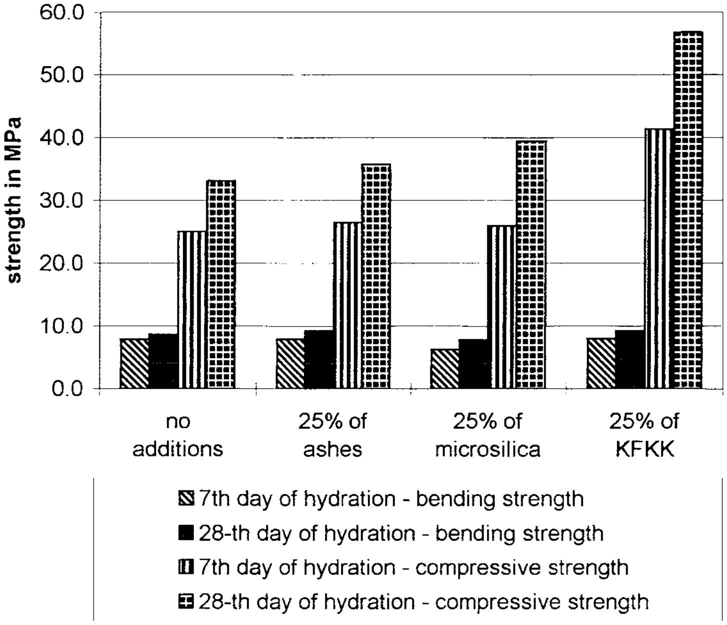

Fig. 5. Strength of cement pastes.

bending strengths were observed in pastes containing additions of either fly ashes or KFKK. Pastes containing microsilica additives exhibited reduced strengths, as compared with the controls, probably because of insufficient vibration treatment of the paste resulting from its considerable viscosity.

4. Conclusions

To sum up, it is possible to state that the performed experiments have shown no signs of unfavorable effect of KFKK on the properties of cement pastes, and the results were very promisive. The studies have been shown that KFKK, similarly to microsilica and fly ash, combine with other components of the pastes in chemical reactions.

Under the experimental conditions the KFKK accelerated considerably the hydration process. The hydration is a strongly exothermic process, owing to which the cement paste sets much more rapidly. The hydration process reminds that observed with natural pozzolana compounds, where the mechanism of the process consists in dissolving the crystalline zeolite. Comparison of the results obtained for samples containing KFKK with those for samples containing silica dusts has shown that the pozzolanic properties (ability of binding with $Ca(OH)_2$) of the spent catalyst is comparable with that of microsilica. The presence of aluminium–calcium carbonates suggests that one may expect a favorable effect of the spent catalyst additions on mechanical strength of concretes. Compressive strength of the pastes was the highest for samples containing the spent catalyst, both after the 7th and 28th days of hydration.

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