Pergamon

Cement and Concrete Research 32 (2002) 1823–1830

CEMENT AND CONCRETE RESEARCH

Effect of waste aluminosilicate material on cement hydration and properties of cement mortars

B. Pacewska[a], I. Wilińska[a], M. Bukowska[a], W. Nocuń-Wczelik[b,*]

[a]*Faculty of Civil Engineering, Mechanics and Petrochemistry, Warsaw University of Technology, ul. Łukasiewicza 17, 09-400 Płock, Poland*
[b]*Faculty of Materials Science and Ceramics, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Cracow, Poland*

Received 10 January 2002; accepted 23 May 2002

Abstract

The effect of waste material (catalyst used previously in catalytic cracking of petroleum in fluidized bed—fluidized bed cracking catalyst denoted as FBCC) on cement hydration kinetics was investigated in terms of fineness of this admixture. The compressive strength and microstructure of cement mortars were also examined. Variable percentage of this aluminosilicate admixture, originating from batches of quite different grain size composition, was introduced to cement pastes. Further on, cement mortars were produced using the material of higher activity, as it has been found in admixtured cement investigations. The waste was added as cement replacement or, partially, as sand replacement. The activity of waste catalyst was strongly related to the fineness—finer grains indicate better activity. In the presence of a FBCC admixture, the $Ca(OH)_2$ content decrease in cement pastes due to the pozzolanic reaction is observed. The surface area of hydrated paste becomes higher and, simultaneously, the mean pore diameter decreases, as compared to reference sample, without admixture. The strength improvement is observed particularly when the aluminosilicate material is introduced as partial sand replacement.

Keywords: Waste catalyst; Aluminosilicate; Hydration; Cement paste; Cement mortar

---

1. Introduction

The pozzolanic admixtures to cement used in concrete production can be classified depending on their origin—as natural or artificial ones. Among the latter, one should mention pulverized fuel ashes, silica fumes, burnt clays, coal shales and ground ceramic materials. The naturally occurring pozzolans are usually of volcanic origin, such as volcanic ashes, tuff, pumice, siliceous earth, clays and others [1]. Some of them can be effectively used only after thermal treatment [2].

Vitreous silicate phase silica occurring as opal and zeolites are the components of natural pozzolans, reactive towards the calcium hydroxide [3]. The zeolites are at least as active as the vitreous components of natural pozzolans [2]; their activity can be even higher [3,4] due to significant porosity and ion exchange properties. In the early stage of cement hydration, $Ca(OH)_2$ from hydrating paste is incorporated to zeolite structure as a result of cation exchange, however, the main pozzolanic process leads to the destruction of zeolitic skeleton structure with the formation of hydration product type C-S-H and hydrated aluminate phases [2]. As a result of pozzolanic reaction in the presence of zeolite, the amount of C-S-H in the hydration products increases, and, thus, it becomes more compact and dense—the microstructure of hardened cement matrix is significantly improved by the reduction of capillary pores. As a further consequence, the paste is more impermeable, particularly to the attack of chlorides and other corrosive media. Therefore, it reveals better corrosion resistance. The tightening of structure results also in strength increase [5].

It seems quite reasonable that the similar effect can be achieved by the use of waste aluminosilicate zeolitic catalyst as concrete admixture. Their implementation to cement mixture could be a good way of this waste utilisation. However, the concrete with this admixture must be carefully tested, and their properties should be well characterised.

The zeolitic catalysts are used in the petroleum industry in catalytic cracking process in fluidized bed. The back-out catalysts are subjected to waste disposal procedure, so they must be stored or utilised in some other way.

---

* Corresponding author. Fax: +48-12-633-15-93.
E-mail address: wiesia@uci.agh.edu.pl (W. Nocuń-Wczelik).

0008-8846/02/$ – see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0008-8846(02)00873-6

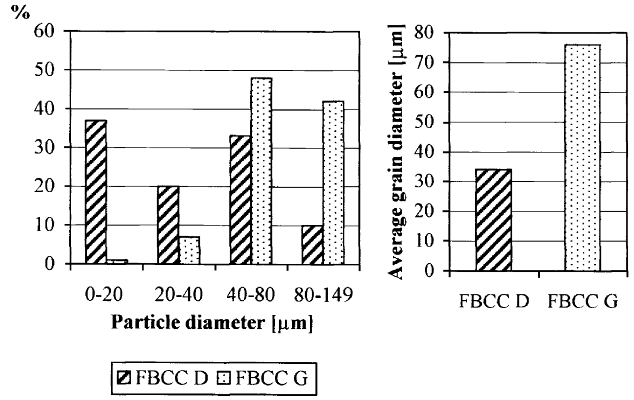

Fig. 1. Grain size distribution of FBCC D and FBCC G samples.

The fluidized bed catalytic cracking installations produce about 400 000 tons of used-up waste catalyst every year (worldwide annual output). The main part of this material is withdrawn because of the reduced activity. About 10% of the waste is collected in dedusting cyclones and electrofilters [6]. SiO_2 and Al_2O_3 are the main components of this material, irrespective of their source. Waste catalyst is only slightly contaminated with metals, including heavy metals, such as vanadium and nickel, occurring on the parts per million level.

There are some ways of waste catalyst practical implementation. Because of chemical composition and good thermal characteristics, it can be taken into account in the production of refractories and ceramic materials [7,8]. It can be also used as a filler in the production of asphalt or as a portland cement pozzolanic component [6].

The chemical composition of fluidized bed cracking catalyst (FBCC) is very similar to those for some pozzolanic materials. Therefore, the investigation of mortars and concrete admixtured with this waste seems to be very promising. Beside our recent works relating to the use of FBCC as a component of concrete and its effect on cement hydration [9–12], there were also other reports [7,13–15].

In this report, however, the results of FBCC from the two batches of different fineness on cement hydration are shown. The strength and microstructure characteristics of mortars doped with admixture of higher reactivity is also given.

2. Materials and methods

2.1. Waste catalyst

FBCC is a porous, fine-grained aluminosilicate material of $SiO_2+Al_2O_3+Fe_2O_3$ content exceeding 90%, specific surface of about 100 m^2/g and mean grain diameter <80 µm. The two FBCC samples were taken into account:

- FBCC D—fine-grained material with mean diameter of 34 µm (collected from electrofilter);

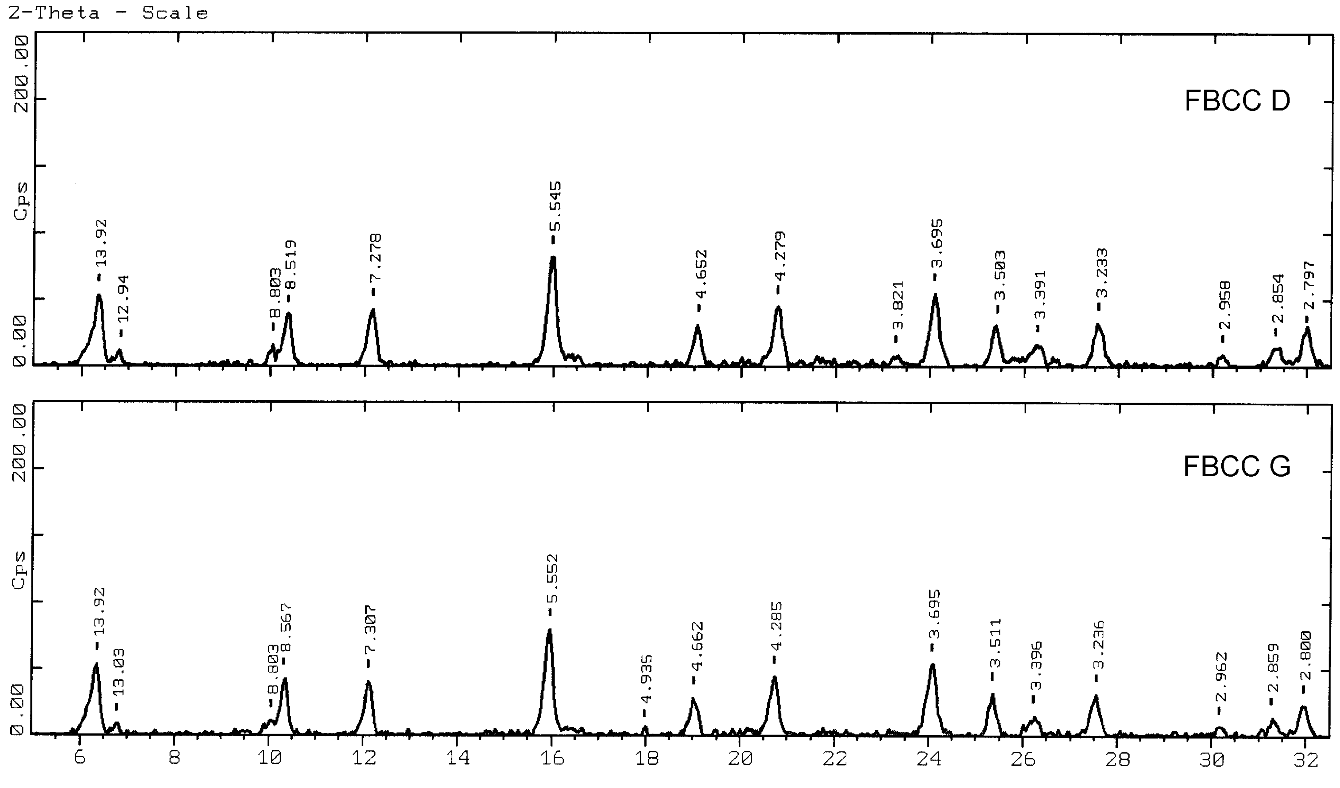

Fig. 2. XRD patterns of FBCC D and FBCC G samples.

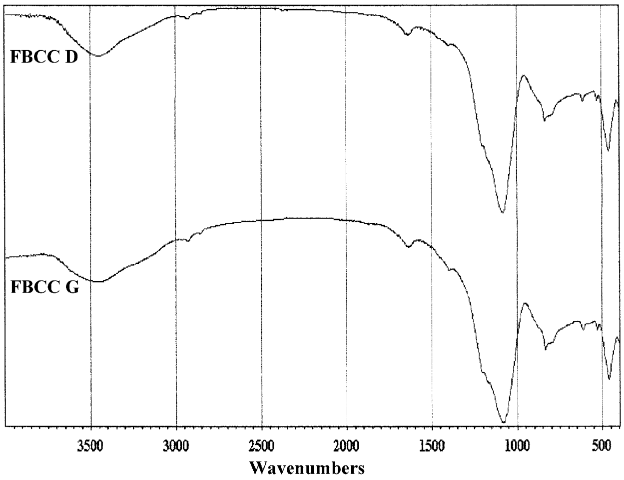

Fig. 3. IR spectra of FBCC D and FBCC G samples.

- FBCC G—coarse-grained material with mean diameter of 76 μm (collected from cyclone).

The physical and chemical properties of waste catalysts were presented in the previous report [9] (FBCC D used in reported studies [9] showed even higher fineness, with mean grain size of 21 μm).

The IR studies for FBCC D and FBCC G were done with the help of Mattson FTIR Spectrometer Genesis II in the range of wave numbers from 400 to 4000 cm^{-1}. The samples were prepared as KBr pellets. Phase composition was determined by the use of HZG-4C diffractometer (CuK_{α} radiation). The thermoanalytical studies were carried out for 20–30-mg FBCC samples, with the help of the TA Instruments SDT 32960 thermoanalyser, up to 1000 °C in Pt crucible, air atmosphere, at the heating rate of 10 °C/min.

2.2. Cement pastes

Cement pastes for calorimetric measurements and thermoanalytical studies were produced using standard portland cement CEM I 32,5 R [16] admixtured with FBCC D or FBCC G. Hydration kinetics was followed using the BMR differential nonisothermal–nonadiabatic calorimeter (constructed in the Institute of Physical Chemistry, Polish Academy of Science). The thermoanalytical studies of pastes were carried out with the help of Derivatograph 1500C in the temperature up to 1000 °C in Pt crucible, air atmosphere, at the heating rate of 10 °C/min, for 150-mg samples. Phase composition was determined by the use of a HZG-4C diffractometer (CuK_{α} radiation).

Calorimetric measurements were carried out on pastes produced from cement and FBCC admixtured in the amount of 0–35% by weight of cement. Further on, the cementitious materials with cement replacement were mixed with water, at a constant water-to-solid ratio (w/s) of 0.5, and were hydrated in BMR at an external temperature of 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 thermoanalytical studies were carried out for the pastes with 0, 10 and 20 wt.% FBCC added as cement replacement, at w/s = 0.5. The pastes were stored in sealed polyethylene containers. The hydration process was stopped using acetone. Dried samples were subjected to the DTA-TG measurements. The measurements focused on the determination of $Ca(OH)_2$ content in the paste, indicating the range of pozzolanic reaction.

2.3. Cement mortars

Cement mortars were prepared from portland cement CEM I 32,5 R, FBCC D and standard sand. Cement was

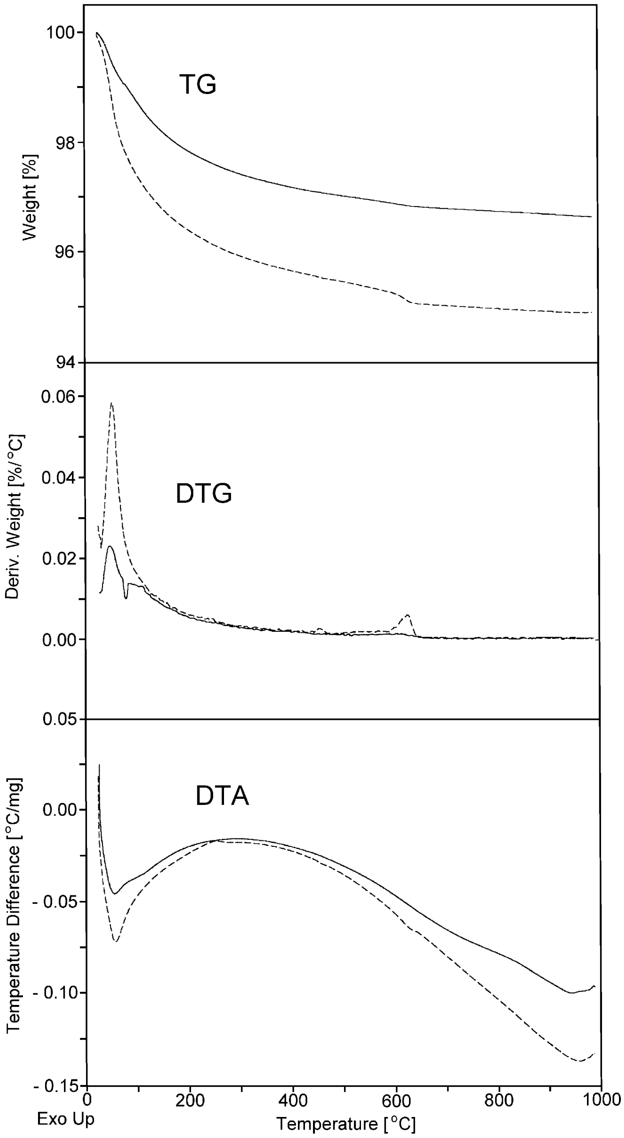

Fig. 4. TG, DTG and DTA curves for FBCC samples. (——) FBCC D, (- - - - - -) FBCC G.

admixtured with FBCC added in the amount of 0–35% (or 20%) by weight of cement, respectively, or as sand replacement. The standard mortars were produced following the Polish–European standard [17]. The following mixtures were produced:

- (sand + FBCC D)/cement = 3, w/c = 0.5 or w/c = 0.36—FBCC D admixtured as partial sand replacement—fine-grained filler;
- sand/(cement + FBCC D) = 3, w/s = 0.5 or w/s = 0.36—FBCC D admixtured as partial cement replacement.

In mortar preparation, the lignosulphonate–melamine–naphthalene type plasticizers were used in an amount enough to maintain constant consistency of fresh mortars, apart from the mortars with w/s = 0.5.

The 4 × 4 × 16-cm mortar bars were cured in standard conditions. The flexural/compressive strength was measured after 28, 90 and 270 days. Nine-month maturing samples were subjected to porosity and surface area determination. Porosity of mortars was determined by AUTOPORE-Micrometrics mercury porosimeter on 4–5.5-g samples.

3. Results and discussion

3.1. Characteristics of waste catalyst

In Fig. 1, the results of FBCC D and FBCC G granulometric analysis are illustrated. In the case of FBCC D, the dominating fraction is in the range of 0–20 μm; 90% of the grains does not exceed 80 μm. On the other side, FBCC G main grain size fraction is in the range of 40–80 μm, and 90% of the grains is in the range of 40–149 μm. One can clearly see the significant difference.

The XRD and IR results, presented in Figs. 2 and 3, show no differences between the FBCC D and FBCC G samples. XRD plots of FBCC reveal the peaks of the zeolitic phase. The presence of amorphous substance cannot be excluded. IR spectra show the intensive band with a maximum at 1080 cm^{-1}, which can be attributed to the vibrations of O–Si(Al)–O. The presence of water is proven by a broaden 3450 cm^{-1} band.

FBCC D and FBCC G samples exhibit some different water content as it results from DTA-TG measurements (see Fig. 4). In the case of the FBCC G sample, a higher water loss may be related to higher amount of water, present both as adsorbed layer, zeolitic water and/or in the form of OH groups. An exothermic DTA peak, which could be attributed to the combustion of organic component, was not observed.

3.2. Cement pastes

3.2.1. Calorimetric measurements

The heat evolution curves for hydrating cements admixtured with waste catalyst are plotted in Figs. 5 and 6. One can easily notice that the heat evolution kinetics is strongly modified by the presence of FBCC and that the fineness of admixture is significant.

Calorimetric curve for 5% FBCC D almost interfered with that for neat cement paste; the main peak, attributed to the hydration of silicates, is somewhat broader. Small aluminosilicate particles act presumably as nucleation sites for hydration products, and the hydration is thus slightly modified. Taking into account the heat-evolved values (see Fig. 7), we can conclude that in the presence of fine-grained admixture not exceeding 5–10 wt.%, the hydration process is accelerated. Further increase of admixture content—over 10 wt.%—brings about the heat-evolved decrease, less

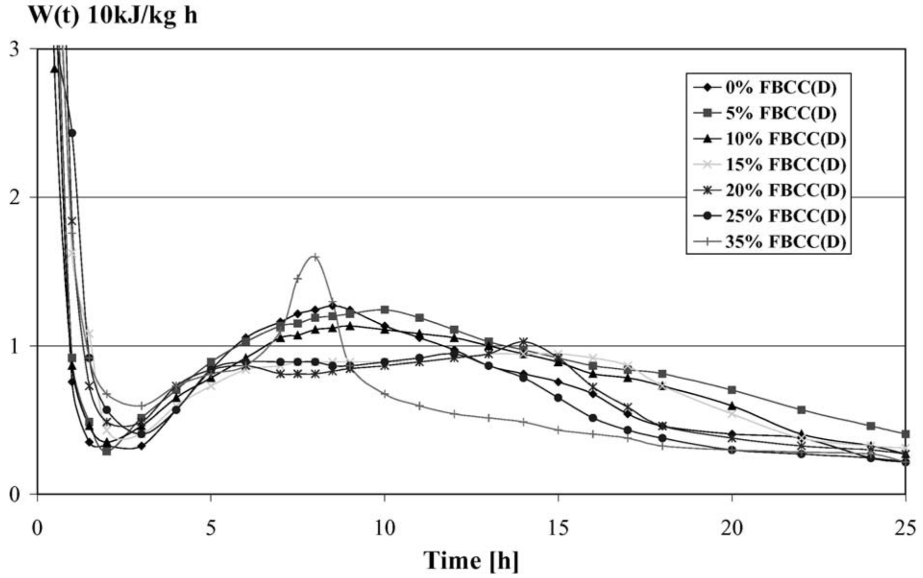

Fig. 5. Heat evolution curves for pastes admixtured with FBCC D.

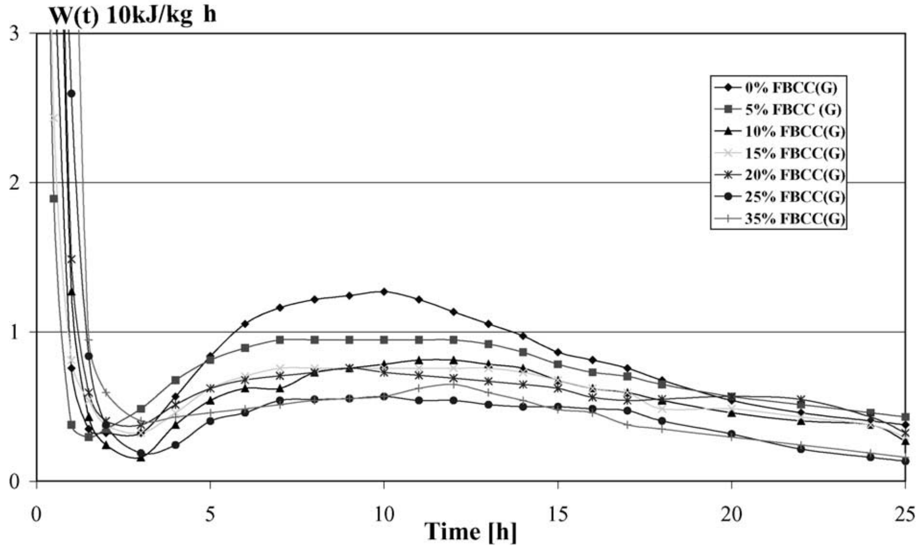

Fig. 6. Heat evolution curves for cement pastes admixtured with FBCC G.

pronounced, however, than the reduction of cement percentage in the hydrating sample. This can be attributed to the relative C-S-H and other products decrease when the binder is “diluted” with less active component than cement. At 35% FBCC D, the additional sharp peak appears, probably due to the formation of ettringite or other aluminate hydration products, based upon active alumina from admixture. Perhaps it is also the consequence of an unbalanced sulphate/aluminate content—at lower portland cement content, there is no sufficient gypsum set controlling agent for alumina from waste.

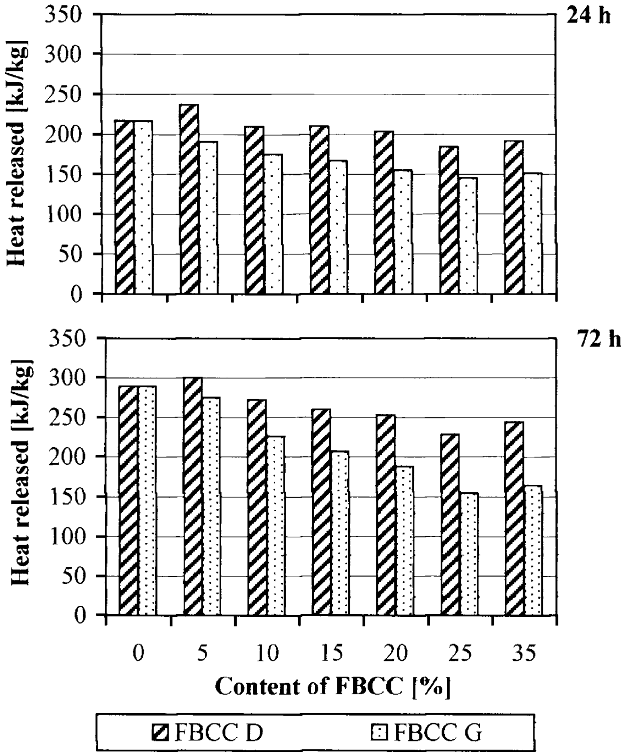

Fig. 7. Heat evolved within 24 and 72 h of hydration.

Quite different course of heat evolution curves is observed when the coarse-grained FBCC G is added. The curves are diffused and flat for mixtures with an increasing percentage of admixture—the hydration products form slowly, the heat evolved decreases more than the percentage of neat cement in the pastes (see Fig. 7). However, the somewhat similar effect of alumina from 35% admixture was also observed. Summarising the calorimetric data, one can say that the activity of aluminosilicate waste catalyst is strongly determined by fineness. It seems quite reasonable that this activity can be improved by additional grinding, as it was found by some other authors [13]. It is known that prolonged grinding is an effective method of pozzolanic activity modification in the case of natural pozzolanas [18].

3.2.2. Thermoanalytical studies

The examples of TG and DTG plots are shown in Fig. 8. On the TG curve for cement pastes, the three steps of weight loss, together with corresponding endothermic DTG peaks, are observed. In the range up to about 480 °C, the complex dehydration of C-S-H, sulphoaluminates and aluminates is observed. In the range from 480 to about 550 °C, dehydration of $Ca(OH)_2$ takes place, while over 550 °C, there is further dehydration, and close to 900–1000 °C, decomposition of carbonates and synthesis of silicates from decomposed products are observed.

In the case of pastes with FBCC, one can find an additional peak on DTG curve at temperature about 200 °C. This peak becomes stronger with percentage of admixture and hydration time. Presumably, it is related to the hydrated aluminate phase, formed from aluminosilicate admixture.

The estimation of $Ca(OH)_2$ content in hydrating systems was an important step in these studies (Fig. 9). Generally,

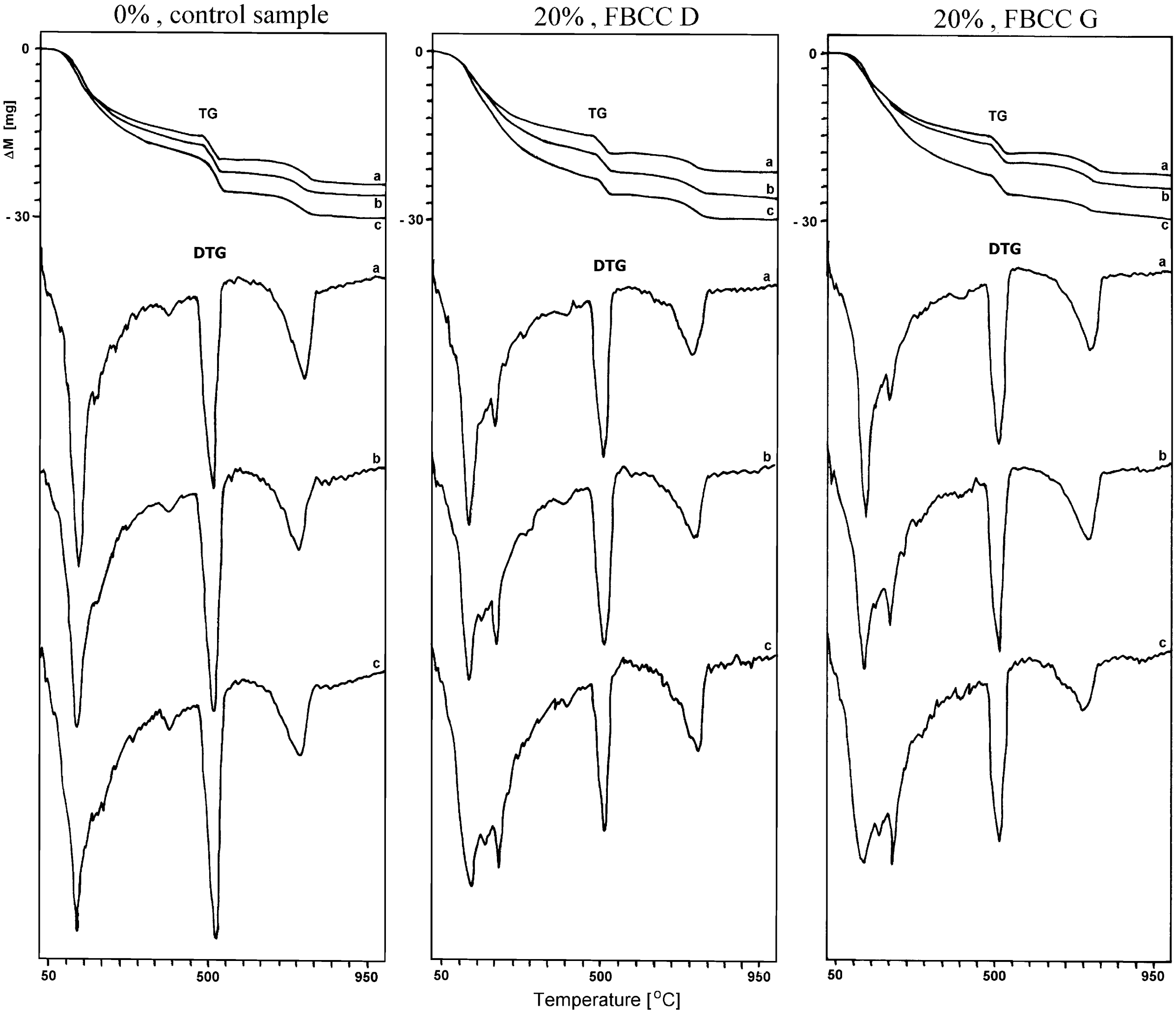

Fig. 8. TG and DTG curves for cement pastes after 3 days (a), 7 days (b) and 28 days (c) of hydration (constant sample mass: 150 mg).

the reduction of $Ca(OH)_2$ with time, in the presence of FBCC was found. This is partially due to the cement replacement by FBCC. At longer hydration time, the $Ca(OH)_2$ decreases more than the percentage of cement in the initial sample due to pozzolanic reaction. The skeleton structure of waste catalyst has many acid sites, and it is able to combine effectively the calcium ions, as it has been pointed out by other authors [13]. One cannot exclude the mechanism similar to that occurring in natural zeolitic pozzolanas, consisting of the destruction of zeolitic pozzolana structure with the formation of hydration products: C-S-H and hydrated aluminates [2].

Considering the $Ca(OH)_2$ contents in pastes modified by FBCC D or FBCC G, one can find that the differences are not significant, particularly when the 10% admixture content is discussed. Pastes with FBCC G exhibit slightly higher $Ca(OH)_2$ content as compared to those with FBCC D. Therefore, a little higher pozzolanic activity of fine-grained FBCC is proven.

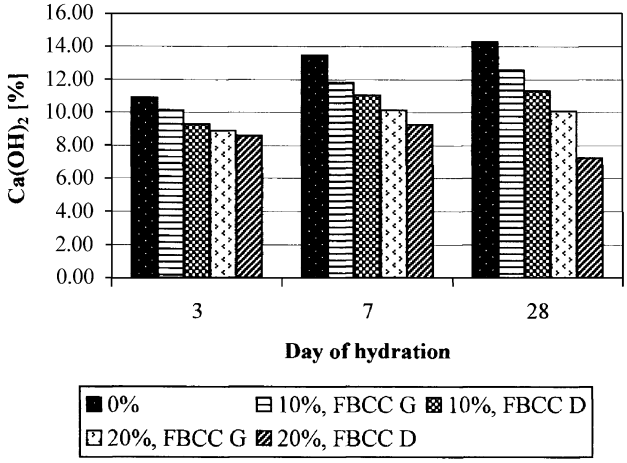

Fig. 9. $Ca(OH)_2$ content in cement pastes.

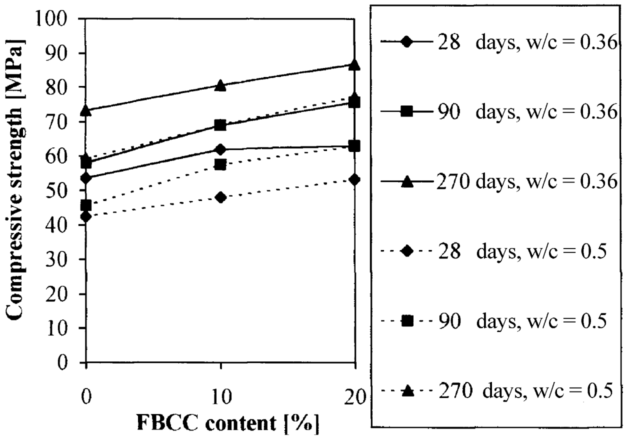

Fig. 10. Compressive strength of mortars admixtured with FBCC D calculated as partial sand replacement.

Higher pozzolanic activity of fine-grained FBCC was proven earlier by the compressive strength tests for mortars with 25% FBCC D of average grain value 21 μm and FBCC G, at additional water content to stabilise the consistency of mortar [9].

3.3. Cement mortars

3.3.1. Compressive strength

The results of compressive strength measurements for mortars produced with FBCC D, doped as cement or sand replacement, are given in Figs. 10 and 11. Firstly, a commonly known relationship between w/c ratio and compressive strength was proven again, and further on, a significant modification of strength by the use of FBCC admixture was found. At FBCC D used as sand replacement, compressive strength increase (as compared to reference samples) was observed, while in the case of cement replacement, less or more lower strength values were noted. However, the 90-day results, with w/c = 0.36, were clearly higher. Therefore, we can conclude that FBCC D added as sand replacement plays a role of active microfiller, but it is not sufficiently reactive to replace cement.

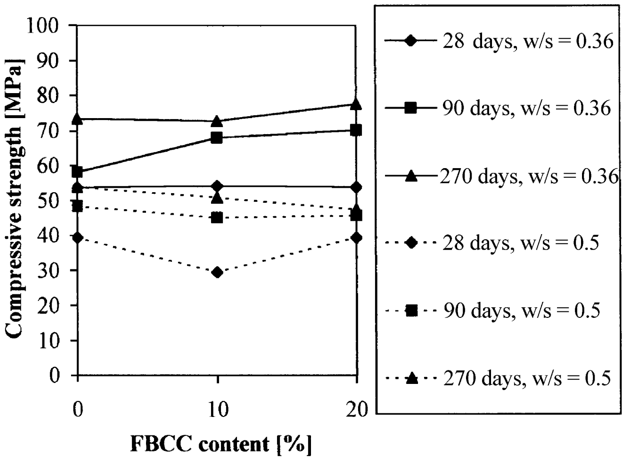

Fig. 11. Compressive strength of mortars admixtured with FBCC D calculated as partial cement replacement.

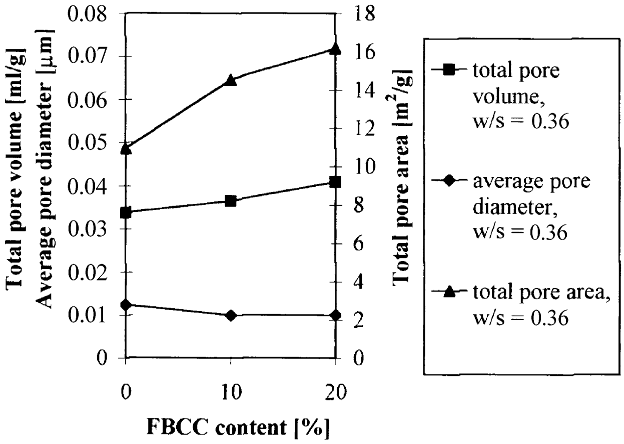

Fig. 12. Parameters of structure for 9-month curing cement mortars admixtured with FBCC D calculated as partial cement replacement. The numerical values on the left axis relate both to pore volume in [ml/g] and pore diameter in [μm] (see text).

The compressive strength improvement in the presence of FBCC as partial aggregate replacement was also found for concretes [9], either at FBCC D of higher fineness (average grain size = 21 μm) or at FBCC G admixture. Obviously, the FBCC component of higher fineness gave better strength development.

However, one should mention that in the presence of highly dispersed and porous FBCC material, the workability of fresh concrete mixture is getting worse, hence, careful control of water amount and/or use of plasticizers is needed.

3.3.2. Porosity

The results of porosity measurements for 9-month curing mortars, produced at w/s and w/c ratio = 0.36 as well as at w/c = 0.5, are shown in Figs. 12 and 13. The total pore volumes, mean pore diameters and surface areas were taken into account. No substantial differences were observed in most

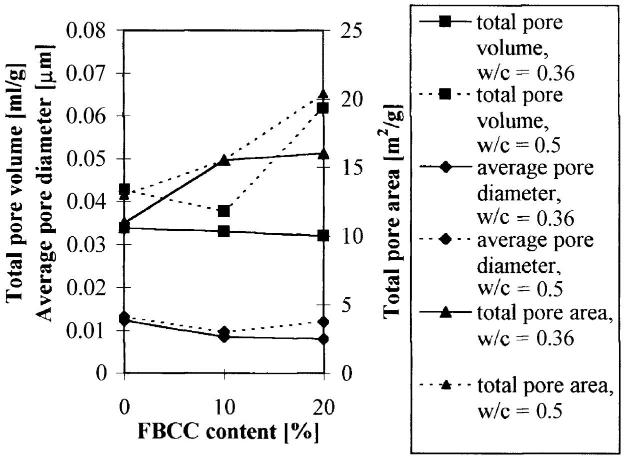

Fig. 13. Parameters of structure for 9-month curing cement mortars admixtured with FBCC D calculated as partial sand replacement.

cases between the admixtured and reference samples. In the case of mortars produced at w/s = 0.36, in which the FBCC D was used as partial cement replacement, some slight porosity increase, from 0.034 to 0.041 ml/g, was noticed for 20% FBCC D, together with the reduction of mean pore diameter, from 0.0123 to 0.0101 μm, and surface area increase. For mortars produced at w/c = 0.36 with FBCC added as partial sand replacement, clearer simultaneous total pore volume and mean pore diameter reduction, to 0.032 ml/g and 0.008 μm, respectively, with surface area increase at increasing FBCC D content was found (see Fig. 13). On the other side, for those mortars produced at w/c = 0.5, in which FBCC D was also used as partial sand replacement, the total pore volume and surface area increase for the same FBCC D 20% content was pronounced further on (see Fig. 13).

The porosity and, particularly, strength results prove that the effect of FBCC as active microfiller-high surface area can be attributed to the formation of "excess" gel-like C-S-H formed from an admixtured component. Thus, the microstructure of mortar is modified by FBCC D.

Obviously, the strength of mortars is significantly affected by the parameters of pore structure, for example, total porosity.

4. Summary

(1) Waste aluminosilicate material—catalyst from fluidized bed cracking installation (FBCC) can play a role of active microfiller when used in hydrated cementitious mixtures. Its modifying effect depends upon its fineness and content in mortar/concrete.

(2) FBCC materials used in this work, originating from the batches differing significantly with their fineness, show no substantial differences dealing with phase composition, as studied by IR and XRD, but only variable loss on ignition as heated up to 1000 °C (DTA-TG measurements).

(3) Material of high fineness shows better activity (FBCC D, average diameter = 34 μm), and when used in low quantity (5–10 wt.%), it may be considered as a cement substitute. Five percent of FBCC brings about the heat evolved on hydration increase, while at higher content (> 10%), the heat-evolved value decreases, as compared to the reference sample without admixture. In the case of 35% FBCC D, a significant increase of heat-evolved value and a rapid growth of heat evolution peak on the calorimetric evolution curve is observed, as compared to the data for paste admixtured with 25% FBCC D. This is presumably the consequence of intensive formation of hydrated aluminate product, based on alumina from waste catalyst.

(4) Material of coarser grains (FBCC G, average diameter: 76 μm) shows lower activity, and when added to hydrated cement paste, the heat-evolved value after 24 and 72 h of hydration reduces more than the percentage of cement replaced by the aluminosilicate material. As we can expect, the improvement of admixture effect should be achieved by additional grinding.

(5) In the presence of FBCC, $Ca(OH)_2$ content in cement paste is reduced, as compared to the reference sample. This is the consequence of pozzolanic reaction, as well as partial cement replacement. Lower $Ca(OH)_2$ contents in FBCC D-admixtured result from higher pozzolanic activity of a fine-grained material.

(6) FBCC D used as 20% partial cement replacement slightly reduces the compressive strength of mortars. However, when used as partial sand replacement, it gives higher strength, as compared with values for reference mortars.

(7) FBCC D-admixtured mortars show lower average pore diameters and higher surface area than the reference material, irrespective of the composition of mortar, that is, when admixture is used either as cement or as sand replacement.

References

[1] J. Piasta, W.G. Piasta, Concrete, Arkady, Warszawa, 1997 (in Polish).

[2] H.F.W. Taylor, Cement Chemistry, Thomas Telford Publ., London, 1998.

[3] W. Kurdowski, Cement Chemistry, PWN, Warszawa, 1991 (in Polish).

[4] R. Sersale, 7th ICCC Paris, t.I, s. IV-1/3, Paris, 1980.

[5] S.Y.N. Chan, X. Ji, Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes, Cem. Concr. Compos. 21 (1999) 293–300.

[6] E. Furimsky, Spent refinery catalysts: Environment, safety and utilization, Catal. Today 30 (1996) 223–286.

[7] N. Su, H.-Y. Fang, Z.-H. Chen, F.-S. Liu, Reuse of waste catalysts from petrochemical industries for cement substitution, Cem. Concr. Res. 30 (2000) 1773–1783.

[8] A. Escardino, J.L. Amoros, A. Moreno, E. Sanchez, Utilizing the used catalyst from refinery FCC units as a substitute for kaolin in formulating ceramic frits, Waste Manage. Res. 13 (6) (1995) 569–577.

[9] B. Pacewska, M. Bukowska, I. Wilińska, M. Swat, Modification of the properties of concrete by a new pozzolan—a waste catalyst from the catalytic process in a fluidized bed, Cem. Concr. Res. 32 (1) (2002) 145–152.

[10] M. Swat, J. Kubissa, W. Kubissa, Waste catalyst as an effective concrete component, Inz. Bud. 4 (1997) 180–182 (in Polish).

[11] B. Pacewska, I. Wilińska, J. Kubissa, Use of spent catalyst from catalytic cracking in fluidized bed as a new concrete additive, Thermochim. Acta 322 (1998) 175–181.

[12] B. Pacewska, I. Wilińska, M. Bukowska, Hydration of cement slurry in the presence of spent cracking catalyst, J. Therm. Anal. Calorim. 60 (2000) 71–78.

[13] J. Payá, J. Monzó, M.V. Borrachero, Fluid catalytic cracking catalyst residue (FC3R) an excellent mineral by-product for improving early-strength development of cement mixtures, Cem. Concr. Res. 29 (1999) 1773–1779.

[14] N. Su, Z.-H. Chen, H.-Y. Fang, Reuse of spent catalyst as fine aggregate in cement mortar, Cem. Concr. Compos. 23 (2001) 111–118.

[15] J. Payá, J. Monzó, M.V. Borrachero, Physical, chemical and mechanical properties of fluid catalytic cracking catalyst residue (FC3R) blended cements, Cem. Concr. Res. 31 (2001) 57–61.

[16] Polish/European standard PN-EN-196-1, Cement–common cement–composition, specifications and conformity evaluation.

[17] Polish standard PN-85/B-04500, Building mortars—examination of physical characteristics and mechanical strength.

[18] C. Shi, R.L. Day, Comparison of different methods for enhancing reactivity of pozzolans, Cem. Concr. Res. 31 (2001) 813–818.