Phase Composition of Solid Residues of Fluidized Bed Coal Combustion, Quality Tests, and Application Possibilities

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Received 2 April 1996

The scope of this paper is to focus the attention on the newly produced ashes – residues after fluidized bed coal combustion. The favourite phase composition of this material due to low combustion temperature of 850 °C exhibits very good cementitious properties. Fluidized ashes may be preferably used in the production of some types of Portland cement as a gypsum replacement and in cement-free concretes. The quality tests of this sulfo-calcareous material are proposed as well as some application possibilities.

In the last decades, new "clean" technologies in the production of electrical energy have been introduced, the most promising of which is fluidized bed coal combustion [1]. Here, ground coal is burnt together with limestone acting as a sulfur dioxide sorbent [2] at considerably lower temperature of 850 °C in comparison to the conventional boilers working at the temperatures within 1200 to 1750 °C, which strongly influences the phase composition of the solid residues produced.

The fluidized bed coal combustion proceeds either at the atmospheric pressure (AFBC) or under elevated pressure (PFBC), which also influences the chemical and especially the phase composition of the solid residues [3—6]. While PFBC technology has been used in three power plants worldwide so far, the AFBC boilers cover *e.g.* in Germany 7 % of the whole electricity production. The large volume of solid residues produced evokes both for economic and ecological reasons an interest in the research of their properties and utilization.

The bed ash and fly ashes from the separators are in fact mixtures of mineral components of the fuel and products of desulfurization. Besides limestone, also dolomite may be used as a sorbent, which, however, is less suitable for the use of this material in the civil engineering.

The aim of this paper is to inform the producers and users of this material about the advantageous composition and properties of solid residues of FBC technologies. Several rapid and concluded quality standard tests are recommended and some promising possibilities of the utilization of this material are proposed.

FUEL AND COMBUSTION PROCESS

For fluidized bed combustion, all kinds of coal are used: bituminous, subbituminous, lignite, and even solid wastes or slurry after coal mining. In the Netherlands, the wastes of coal mining are burnt to produce ash to replace cement in mortars and concretes, electricity is the by-product.

In the course of combustion, different chemical reactions and phase transformations take place. At first, free water evaporates followed by the escape of water bound in clay minerals. The temperature of their decomposition varies in different clay minerals, *e.g.* kaolinite loses bound water within 500 to 650 °C and converts to amorphous metakaolinite, which has a large specific surface area and exhibits high reactivity. The amorphous aluminosilicate phases and amorphous silica are mainly responsible for the hydraulic and/or pozzolanic reactivity of the ashes. Magnesium carbonate decomposes at the temperatures above 500 °C and calcium carbonate above 700 °C. Pyrite decomposes around 400 to 500 °C, which is associated with an oxidation of the sulfur and iron. The calcium oxide produced in the decomposition of limestone exhibits large surface and reacts readily with sulfur dioxide formed in the combustion process. In the presence of excessive oxygen, anhydrite II ($CaSO_4$) rather than calcium sulfite ($CaSO_3$) is formed. The excessive amount of the sorbent remains in the form of free lime in the AFBC process or as calcium carbonate in the PFBC process.

The low combustion temperature of 850 °C assures a high specific surface of the ashes and thus

Table 1. Chemical Analysis of Different Kinds of Fluidized Ashes (PFBC, AFBC) (in mass %)

	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	C	S	Free lime	L. O. I.
Värtan, PFBC											
B P K	34.2	25.9	5.6	12.8	6.6	n	1.5	1.8	3.2	1.43	5.9
C P K	31.1	25.3	6.4	15.0	6.0	n	1.4	3.7	3.6	1.04	7.1
B P D	18.2	28.7	22.9	6.32	4.13	0.35	0.74	n	n	n	7.7
C P D	24.4	25.8	16.9	13.0	5.35	0.58	0.94	n	n	n	7.8
C P K < 40 μm	29.7	23.4	5.4	16.4	5.9	n	1.6	4.9	4.4	n	7.9
40—63 μm	31.7	27.9	7.8	13.4	7.0	n	1.1	1.8	3.3	n	4.7
63—90 μm	32.4	27.7	8.0	13.0	6.9	n	1.1	1.9	2.5	n	4.6
90—200 μm	35.2	28.1	8.6	11.6	6.1	n	1.0	2.0	1.9	n	5.5
Finspong, PFBC											
B P K	35.4	23.5	1.6	12.1	3.3	0.6	1.5	4.2	4.2	0.28	8.3
C P K	37.1	20.2	2.7	15.6	6.0	0.9	1.6	2.2	2.2	0.58	6.1
F P K	38.5	10.1	2.7	23.4	6.9	1.8	2.1	4.6	4.6	0.0	0.8
B S K	19.5	47.8	1.8	8.4	3.9	< 0.1	0.5	3.1	3.1	1.28	9.35
C S K	18.2	46.2	0.9	7.9	3.7	< 0.1	0.4	2.6	2.6	0.51	14.55
Leykam, AFBC											
B P K	27.2	37.7	2.0	13.6	3.6	n	1.1	1.5	4.9	20.0	5.2
C P K	29.6	35.5	3.0	17.0	5.1	n	1.4	1.2	3.7	16.3	3.5
Třinec, AFBC											
B W D	60.2	3.3	2.6	20.9	6.3	0.8	2.8	0.3	0.6	0.45	0.34
C W D	46.9	7.7	3.2	22.9	7.2	0.7	2.3	3.6	1.1	1.48	4.81
C W D < 40 μm	44.8	7.9	3.4	22.5	1.3	0.7	2.4	4.3	1.1	n	7.5
40—63 μm	48.4	8.9	4.3	21.0	1.0	0.7	2.6	0.9	1.7	n	1.5
> 63 μm	56.1	5.4	3.2	22.6	1.2	0.7	2.4	0.2	0.7	n	0.8

B – bed ash, C – cyclone fly ash, F – filter fly ash, P – Polish bituminous coal, W – coal wastes, S – Israel oil shale, K – sorbent calcite, D – sorbent dolomite, n – not determined.

a greater reactivity as compared to conventional fly ashes formed at combustion temperatures up to 1700 °C. These high-temperature residues often contain dead burnt lime which reacts slowly with water, which may be the cause of volume instability of composites produced from such ashes. The FBC solid residues do not contain nonreactive mullite, which is formed at the temperatures above 1150 °C in the amount up to 25 mass %.

THE CHEMICAL AND PHASE COMPOSITION OF FBC ASHES

During the FBC process, the relatively coarse bed ash is withdrawn separately from the finer cyclon fly ash. The finest fly ash is collected in the last separators – hose filters. Due to the different kinds of fuel used, the composition of solid residues varies considerably. The chemical composition of the sorbent influences the ratio of the components in the ashes in a low extent. The CaO/MgO ratio is given by the sorbent used (calcite or dolomite). The chemical composition of different kinds of FBC ashes of different origin is shown in Table 1. These results alone do not suffice for assessing the quality of the material produced. The overall amount of *e.g.* CaO found usually by X-ray fluorescence analysis is present as free lime or bound in the form of sulfate, carbonate or clay decomposition product. The value of loss on ignition (determined at 975 °C according to the European standard EN 196-2) includes the amount of residual carbon, rests of combined water and CO_2 bound in calcium (magnesium) carbonate. It is also important to distinguish between the divalent and trivalent form of iron, as the oxidation of the former is associated with the volume expansion [7].

A certain information is given even by the colour of the material. The pink or beige colour indicates the presence of iron sesquioxide, the greyish colour is caused by the presence of magnetite or, more usually, due to the unburnt carbon, the content of which may vary in a wide range between a few tenths up to more than 10 mass %. Due to its large specific surface area, variation in its amount may distinctly affect the amount of water required in the production of mortar or concrete mixes containing this ash.

The phase composition of the FBC ashes determined by X-ray powder diffraction analysis is shown in Fig. 1*a—d*, XRD patterns show distinct lines of anhydrite, calcite, and quartz. Hematite, magnetite, feldspar, and illitic clay decomposition products are present in small amounts. Approximately a half of the constituents is present in X-ray amorphous form. Useful information is also obtained by thermal analysis (DTA and TG). The phase composition of different fly ashes is presented in Table 2.

Because ashes are preferably used in powdered (ground) form, it was interesting to determine separately the chemical composition of individual fractions of the ash in question. Results in Table 1 and

Table 2. Combustion Technology and Phase Composition of Solid Residue (in mass %)

	High temperature combustion	Fluidized bed combustion	
		Atmospheric AFBC	Pressurized PFBC
θ/°C	> 1200	850	850
Glass phase	50—90	0	0
Mullite	3—20	0	0
X-Ray amorphous AS	0	30—50	30—50
Clay, shale	0	1—3	1—3
Feldspar	0—1	1—2	1—2
Dead burnt lime	0—3	0	0
Free reactive lime	0	5—22	0—2
Periclase	0—1	0—2	0—2
Hematite	2—20	3—10	3—15
Magnetite	2—10	4—15	2—6
Anhydrite II	0—2	10—25	10—25
Calcite	0	0—1	10—15
Quartz	2—8	3—10	3—10

Fig. 1*a*—*d* document great differences in the chemical and phase composition. The grindability of some constituents (*e.g.* anhydrite) is easier, other constituents (quartz) are harder and form a considerable part of coarser fractions.

The reactivity of the powdered material is always strongly influenced by the particle size and specific surface area. Therefore, the standards EN and ASTM prescribe to determine the fineness of ashes by the sieve analysis.

REACTIVITY OF FBC ASHES

The PFBC ashes differ from AFBC ones considerably [4—7] first of all due to the absence of free lime, which may exceed in the latter 15 mass %. The amount of anhydrite and amorphous aluminosilicate is similar in both of the materials. Therefore, after addition of water to AFBC ash, ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, is formed. Due to the lack of lime in using PFBC material, ettringite is formed only in a minute amount. This influences the early strengths of the hardened material. Another new formation responsible for the final strengths of the composite is amorphous CS(A)H gel. Using PFBC ashes, the addition of lime, Portland cement or clinker is desirable to stimulate the ettringite and CS(A)H phases formation.

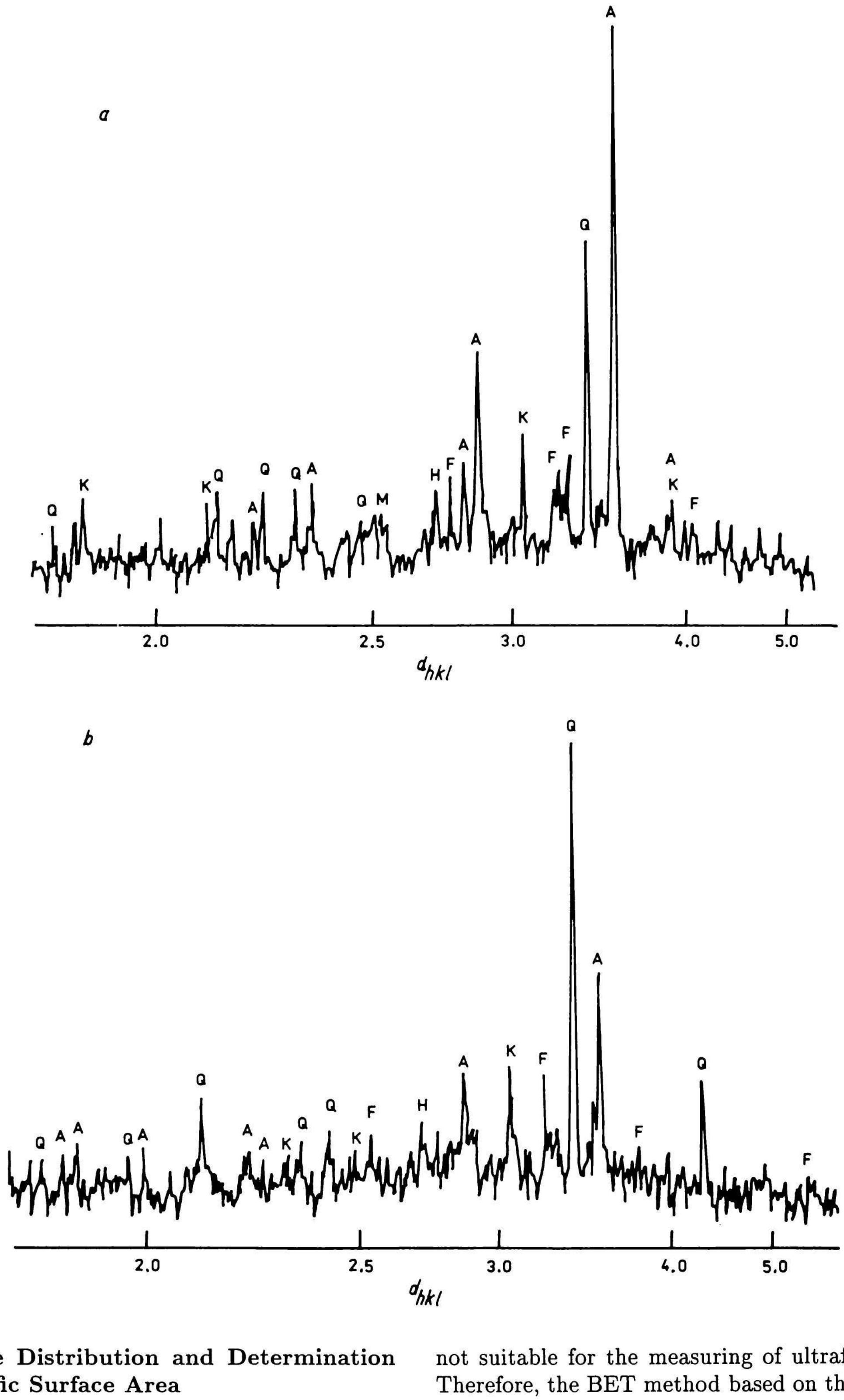
To improve the microstructure and performance, combination of FBC ash with ground granulated blast furnace slag is promising, the latent hydraulicity of the latter is evoked by lime and anhydrite in the FBC ashes. The relatively high content of anhydrite in the FBC ashes makes it possible to replace partially or fully gypsum in Portland cements, which enables to produce Portland fly ash cements or pozzolana cements.

QUALITY TESTS AND ANALYSIS OF FBC ASHES, STANDARD DOCUMENTS

Fluidized bed combustion solid residues have been produced in larger volumes only in the last decade. So far, specifications have not been developed for assessing the quality of this material. Moreover, the new European standards EN 450, 196, and 197 do not describe this material as a possible constituent for cement and/or concrete production. French standards included into the family of fly ashes a new category – sulfocalcareous solid residues, other national standards have the possibility to introduce some new materials into the introduction of the document.

European standard EN 197-1 describes 25 types of cements divided into 5 classes, which may contain following additives to the Portland clinker: granulated blast furnace slag, natural or industrial pozzolans, siliceous or calcareous fly ash, calcined shale, limestone, microsilica and natural or industrial calcium sulfate (dihydrate, hemihydrate or anhydrite). All these additives must meet certain limiting conditions. Comparing these limits with the composition of FBC ashes, it is obvious that this material, which is in fact a mixture of some above-mentioned additives, needs different criteria.

Since it is the mineralogical composition, and not the chemical composition, which would govern the pozzolanic and cementitious behaviour of a mineral admixture, classifications and restrictive specifications emphasizing the chemical composition are more of a hindrance than a help in promoting the use of FBC ashes as admixtures in cement and concrete industries [8]. New classifications and rapid tests relating to the desired performance criteria and to the microstructure of the hydrated mixes of binders in mortars and concretes are urgently needed.



Particle Size Distribution and Determination of the Specific Surface Area

The relatively coarse bed ash can be used as received or ground, if its use as a binder is presumed. Because of the fineness of some fly ashes, the sensitive automatic analyzers for measuring also submicrometer particle size distribution are preferred. The specific surface area measured by the Blaine method is not suitable for the measuring of ultrafine particles. Therefore, the BET method based on the principle of nitrogen adsorption is recommended. For the fineness determination, the sieve analysis by the wet method (sieve 0.045 mm) in EN 451-2 is prescribed. Because of the presence of reactive lime and anhydrite, for AFBC ashes water-free liquid must be used. For some material, dry classification or sieving gives acceptable results.

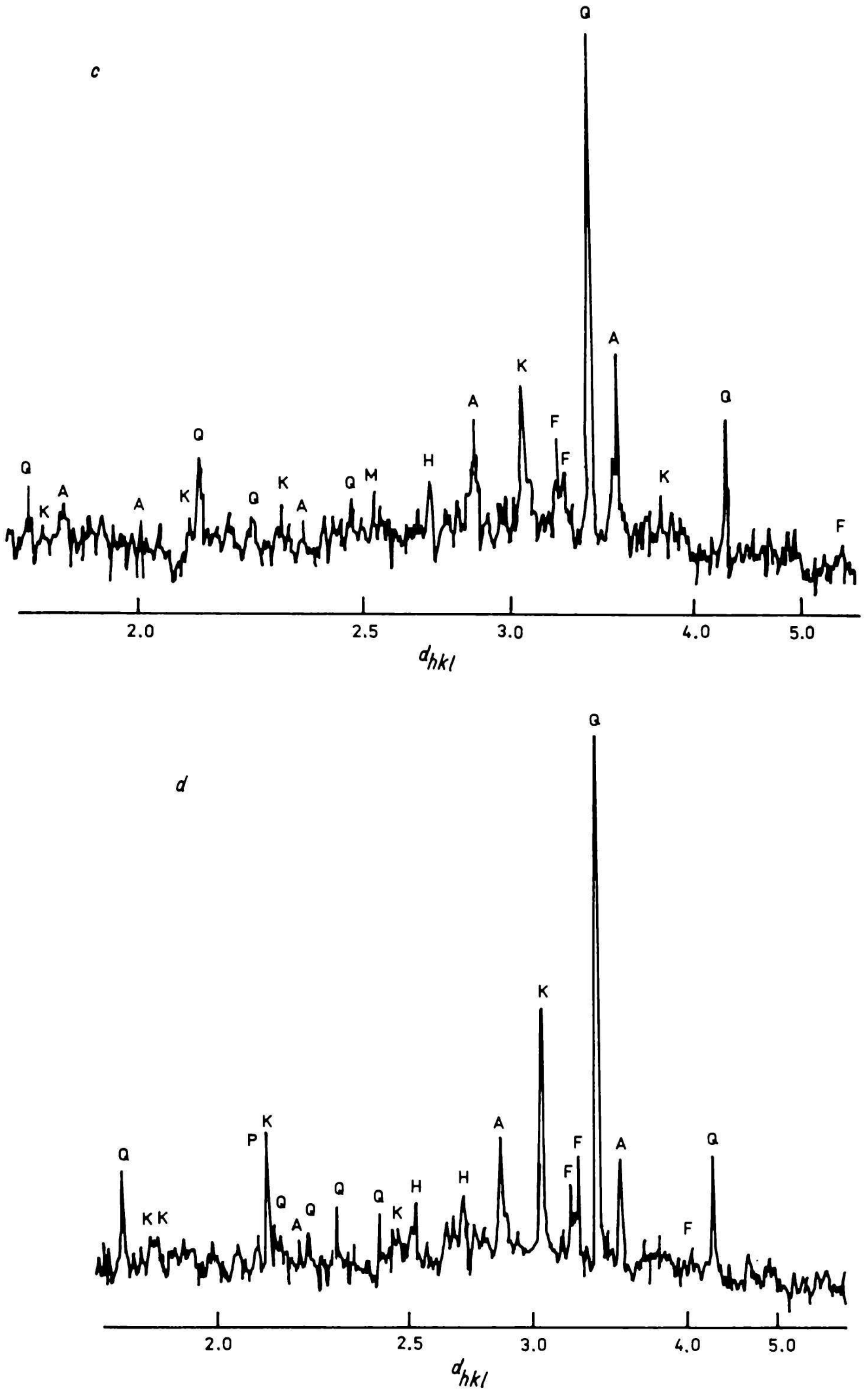


Fig. 1. X-Ray diffraction patterns of fractions of cyclone fly ash (PFBC Värtan, see Table 1). *a*) < 40 μm; *b*) 40—63 μm; *c*) 63—90 μm; *d*) 90—200 μm. Q – quartz, K – calcite, A – anhydrite, M – magnetite, H – hematite, F – feldspar, P – periclase.

Loss on Ignition, L. O. I.

The outcome of the L. O. I. determination depends on the temperature employed. New EN and ASTM standards prescribe an arbitrary value of 975 ± 25 °C. One has to keep in mind that several processes take place in the material: the whole amount of unburnt carbon is oxidized at temperatures below 700 °C. At about 500 °C, the decomposition of magnesium carbonate takes place, at 540 °C divalent iron in magnetite is oxidized, which is accompanied by the appropriate increase in mass. The decomposition of calcium carbonate begins at around 700 °C. The decomposition of anhydrite takes place at temperatures above 1150 °C, and so this phase remains unchanged. To determine unburnt carbon in the presence of carbonates (always in PFBC material), it is necessary to decompose limestone by acid prior to L. O. I. determination.

Determination of Residual Carbon

The most convenient and accurate determination of the free carbon and the total carbon (including CO_2 from carbonates) can be performed by the automatic analyzers based on the infrared spectroscopy determination of liberated CO_2, preferably with the simultaneous determination of sulfur. Alternatively, unburnt carbon can be determined after the decomposition of the sample by an acid, which removes CO_2 from carbonates.

Determination of Calcium Oxide

The content of CaO as determined by X-ray fluorescence analysis covers its presence in different phases, which is not sufficient for the appreciation of the tested material. The free lime present in AFBC ashes is determined according to EN 451-1 after its extraction into the mixture of ethyl acetate and 2-butanol volumetrically by hydrochloric acid solution. If a certain amount of calcium hydroxide may be present, the titration after extraction into saccharate solution is preferred. The content of calcium carbonate can be determined with sufficient precision by measuring the volume of CO_2 released during the decomposition of the sample by HCl. Another modification of this method is based on the determination of the mass loss after the decomposition with HCl. Good results can be obtained by thermogravimetric analysis, the mass loss in the interval of 650 to 900 °C determines the amount of the CO_2 released. The very important determination of calcium sulfate (anhydrite) is performed by the calculation from the SO_3 content. The content of CaO possibly bound in the form of calcium aluminosilicates is considered to be small. Modern automatic analyzers determining simultaneously carbon and sulfur content after the thermal decomposition of the sample are very advantageous.

Determination of Sulfates

The amount of sulfate present is usually estimated from the sulfur content of the coal, which determines the amount of sorbent addition. Calcium sulfate can be determined also directly by quantitative X-ray analysis. The European standard EN 196-2 recommends the gravimetric method. The SO_3 bound in calcium sulfate may be determined by TG analysis as the mass loss between 1100 and 1250 °C. The automatic analyzer mentioned above is most convenient.

Determination of Divalent Iron

Significant amounts of divalent iron may be expected in AFBC ashes where it is present in the form of magnetite. Its determination is important as the oxidation to iron(III) oxide may be accompanied by an expansion of mortar or concrete containing such ash [7]. The determination of Fe^{2+} is based on the oxidimetric titration with dichromate after the decomposition of the sample by hydrochloric acid in the absence of air.

Determination of the Pozzolanic Activity

Pozzolanic activity of the powdered material expresses its ability to react with calcium hydroxide in the presence of water to form hydrates possessing cementitious properties. High-lime fly ashes (AFBC) have self-hardening properties. Because the reactivity of the powdered material depends also on its fineness, it is important to test the material in the form as it will be used. For assessing the pozzolanic activity, a variety of different methods has been developed. More favourable methods ASTM C 311 or European standard EN 450 describe the determination of the strength activity index where the compressive strength of the control ordinary Portland cement (OPC) mortar is compared with the strength of a mixture where a given part of OPC is replaced by fly ash, at ages of 28 or 90 days. Due to the higher content of sulfates, for the tests of FBC ashes, modified procedure was proposed [9] using Portland clinker and gypsum to meet the total SO_3 content of 3.5 mass %.

Volume Changes of the Hardening FBC Composites

One of the fundamental reactions in setting and hardening of mortars and concretes containing FBC ashes is the formation of ettringite, which may cause expansion (unsoundness) of the material. To assess the volume changes, the LeChatelier test according to the EN 196-3 is the most suitable. The expansivity caused by the reactive free lime only cannot be expected, the effect of hydration of magnesium oxide present in the form of periclase may be determined by the autoclave test. A certain expansion may also be expected if the ashes contain the distinct amount of divalent iron.

SOME POSSIBILITIES OF THE UTILIZATION OF FBC ASHES

At present, the largest amount of ashes produced by conventional or fluidized combustion process [5, 6, 10] is used as the backfill of spaces left from coal mining and different structural fill amending mine soils. Other possibilities are in the use of ashes in land reclamation, sludge stabilization, waste management, base constructions of communications, waste water treatment and in their use in mortars and concretes.

To prevent the contamination of ground waters by toxic components which may be present in the ashes, the analyses of the leachates of the material must be performed. It is necessary to comment that the new hydrate phases formed after the mixing of the FBC ashes with water show not only lower solubility than the components in the starting material, but they even exhibit ion-exchanging properties, so that the leachates after a certain period approach potable water in their quality. The higher electrical conductivity is caused by the presence of Ca^{2+} and SO_4^{2-} ions due to the higher solubility of anhydrite present. The presence of free lime may significantly increase the pH of the leachates of the fresh ashes (FA), but the alkalinity decreases during storage. Many recent papers present the utilization of FA in agriculture [10].

The best utilization of FBC ashes is in mortars and concretes, where they fully assert their cementitious properties. The coarse bed ash can be used as received as an aggregate or in the ground form as a binder. The extraordinarily good properties are exhibited by the finest fly ash from the last separators (hose filters) in mortars and concretes as ultrafine particles, which ranges the hardened composites into the DSP material group. Due to the higher content of anhydrite, fluidized ashes can successfully be used for replacing the gypsum in Portland fly ash cement or pozzolana cement. Cement consisting of 45 mass % of Portland clinker and 55 mass % of PFBC cyclone fly ash exhibits only around 10 % lower 28-d compressive strength than the reference OPC standard specimen [9]. Using ultrafine hose filter fly ash, the mixture of clinker and 30 mass % of FA brings about the 40 % increase in strength compared to the reference OPC standard. Very good results were obtained in preliminary experiments with cement-free mortars and concretes, in which ground granulated blast furnace slag was chemically activated by the anhydrite and lime present in FBC residues [6].

The promising strengths do not suffice, good performance must be proved by complementary tests on long-term durability, freeze-thaw resistance, deterioration, steel reinforcement corrosion, changes in microstructure in time, *etc.* Results of these experiments will be presented in the next publication.

CONCLUSION

The composition of bed ash and fly ashes from the separators originating by fluidized bed coal combustion technologies differs especially by the phase composition from conventional "high temperature" fly ashes. Due to the higher content of anhydrite, lime (limestone), amorphous quartz, and aluminosilicates, they possess cementitious properties and can be used preferably as binders. Their best use proved to be the replacement of gypsum in producing Portland fly ash cement and pozzolana cement, as well as in the cement-free mortars and concretes. The standard tests of this sulfo-calcareous material are urgently needed.

Acknowledgements. The authors wish to thank the Grant Agency of the Czech Republic for the sponsoring of this work and the ABB Carbon Energi, Stockholm and Třinec Iron Works, CZ, for delivering of the samples of ashes.

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Translated by J. Brandštetr