CZECH FLUID SULFOCALCIC ASH AND FLY ASH

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Sulfocalcic ash is formed during the fluidized bed combustion of coal in the presence of limestone. It differs from classical fly ash by its composition and properties. Sulfocalcic ash contains free CaO, CaSO$_4$ and partially sintered aluminosilicates. In contact with water, it produces Ca(OH)$_2$, expansive ettringite and a small amount of the CSH phase. There is little information about these ashes in the literature. At present, the possibility of using fluid sulfocalcic ashes is quite limited because of the formation of expansive ettringite. More research in the field of sulfocalcic ashes is a necessity because increasing quantities of this product are rejected by the energy-generation industry.

INTRODUCTION

Energetic products

The generation of the electric power by combustion of coal and the subsequent desulfurization of flue gases give rise to fly ashes, gypsum and fluidized-bed fly ashes. The volume of these products produced all over the world is huge. Fly ash is formed during the combustion of coal at temperatures exceeding 950°C (frequently above 1100°C). The gypsum (CaSO$_4$·2H$_2$O) mostly originates as a product of flue gas desulfurization processes based on washing by limestone. The two above mentioned materials have attracted a rather considerable attention as this is shown by published literature. The fly ash rejected during the fluidized-bed combustion of coal represents another product. The fluidized-bed combustion of coal in the Czech Republic as well as in some other countries is combined with the flue gas desulfurization by mixing pulverized coal with pulverized limestone. About 1.5 million tons of this type of fly ash is produced in the Czech Republic annually. Particles of fluidized-bed ash (called „Fluidized-bed ash and fluidized-bed fly ash for building trade applications" by the Czech standard CSN 72 2080) represent essentially solid residues arising during the fluidized-bed combustion of coal, a mixture of mineral components in coal and the desulfurization products resulting from reactions of sorbents (for in-stance, limestone or dolomite) with sulfur dioxide (their formation temperature does not exceed 850°C). However, different interpretations of the term „fluidized-bed fly ash" can be found in the technical literature (Table 1). In contrast to the fly ash, the fluidized-bed fly ash (according to the Czech standard CSN 72 2080) contains CaSO$_4$; therefore, the term „sulfocalcic ash" is more suitable for its characterization.

Table 1. Fly ash terminology.

Fly ash generated during the high-temperature combustion of coal	Fly ash
Fly ash generated during the fluidized bed combustion of coal	CFBC ash (circulated fluidized bed combustion) FBC ash (fluidized bed combustion)
Fly ash occurring during the fluidized bed combustion of coal with limestone	Partially sulfated CFBC ash Dry flue gas desulfurization product Soil shale CFBC ash Sulfocalcic ash
Product – a residue on the grate bar during the fluidized bed combustion of coal	CFBC spent bed material CFBC bottom ash

Mechanism of sulfocalcic ash formation

Two basic reactions take place during the combustion of pulverized coal and limestone at temperatures ranging from 800 to 950°C:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad CaO + SO_2 + \tfrac{1}{2}O_2 \rightarrow CaSO_4$$

The above processes are accompanied by limestone decomposition and the subsequent CaO sulfatization. The final product contains $CaSO_4$ (on the surface of the particles) and CaO (inside the particles) [1]. According to this idea, $CaSO_4$ particles surround CaO particles (pseudomorphoses from $CaCO_3$). A $CaSO_4$ layer forms around CaO if the $CaCO_3$ particle is compact. However, the sulfatization process is almost accomplished if the $CaCO_3$ particle presents fissures; in this case, the particles in question contain minimum CaO (Figure 1).
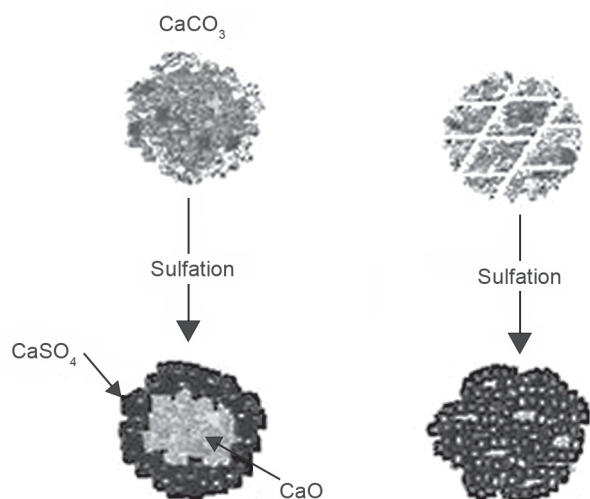

Figure 1. Hypothetical representation of limestone sulfatization at higher temperatures [1].

The combustion product is composed of a chemically heterogeneous mixture. $CaSO_4$ is present in the mixture in the form of high-temperature anhydrite AII, CaO as well as partially sintered alumino-silicate particles originating from incombustible coal components that have been subjected to dehydration or decarbonization during the combustion and which, eventually, sinter partially. In contrast to the fly ashes, no vitreous (liquid) phase arises during the combustion. However, a transformation into partially sintered products containing Si, Al, Fe and other elements takes place. In dependence on the coal composition, the product can also contain a variety of other minerals as, for example, quartz and hematite. Also the reaction products of CaO with incombustible parts of coal containing Si and Al minerals can be detected in the sulfocalcic fly ash. In this case, the formation of Ca silicates, aluminates and ferrites can take place to some extent.

A part of the sulfocalcic fluidized-bed fly ash drops to the grate bar of the combustion boiler where the particles conglomerate by giving rise to a denser product – bed fly ash.

There is a variety of standards devoted to fly ash and delimiting its composition. The standards specify limits for the SiO_2 content, the content of active SiO_2 (CSN EN 197-1), the CaO content (CSA A3001) and the $SiO_2 + Al_2O_3 + Fe_2O_3$ content (ASTM C 618). All standards are quite strict as regards the SO_3 content – 3 to 5 % at the maximum.

The sulfocalcic fly ash does not meet the requirements specified in the above standards and, therefore, its application in the concrete production has not been permitted yet. No specific criteria for sulfocalcic (fluidized-bed) fly ash has been mentioned in the technical literature so far. Only Anthony et al [2] suggest the following mass criteria for the characterization of this type of fly ashes:

$$\frac{SiO_2 + Al_2O_3}{CaO_{total} + SO_3} \qquad \text{and} \qquad \frac{freeCaO}{SO_3}$$

The above criteria may be applied to the assessment of properties of sulfocalcic fly ashes.

Sulfocalcic ash analogy

In addition to sulfocalcic ashes produced in the Czech Republic there are similar sulfocalcic products occurring abroad. Products having compositions similar to (but not identical with) that of fluidized-bed fly ashes produced in the Czech republic are rejected in Canada during the desulfurization of flue gases from the combustion of petroleum coke. Canadian fly ashes contain 11 - 14 % SiO_2, 5 - 6 % Al_2O_3, 36 - 43 % CaO, 10 - 22 % free CaO and 1 - 2 % V_2O_5. The range of particle sizes is rather wide: coarse-grained particles larger than 100 μm predominate (the specific surface area BET ranging from 1.2 - 4.7 $m^2 \cdot g^{-1}$). The Canadian sulfocalcic fly ash possesses the tendency to harden but its volume is not stable after hardening. The fly ash is also sensitive to air moisture. The zonal character of particles is obviously due to the presence of vanadium oxide. The outer jacket of the particles is formed predominantly by $CaSO_4$, deeper layers are constituted of a mixture of $CaSO_4$ with CaO while the core is pure CaO [3]. Other sulfocalcic fluidized-bed products similar to fly ashes occurring during the desulfurization in the Czech Republic can be found in Estonia and Israel where they are produced during the combustion of oil-containing shales without desulfurization [4, 5]. These products are characterized by a high content of CaO (30 - 53 %), free CaO (10 - 25 %) and $CaSO_4$ (1 - 10 %). The products in question are prone to harden but their volume is not stable after hardening.

EXPERIMENTAL

The chemical composition of fly ashes was determined with the aid of the XRF analysis – spectrometer ARL 9400 XP (Thermo ARL, Switherland) while the XRD diffraction analysis – diffractometer PANanalytical X'Pert PRO(PANanalytical, Holland) with the PDF 2 database was applied to the determination of the mineralogical composition. As regards the sulfocalcic fly ashes, their chemical composition was complemented by the determination of the free CaO content by using a method described in the Czech standard CSN P 72 208. The fly ashes were further characterized by data obtained during the determination of the particle size distribution with the aid of the apparatus Mastersizer 2000 MU (Malvern Instruments Ltd., UK) as well as by porosity data obtained by Hg porosimetry AutoPore III (Micromeritics, USA). The character of fly ash particles was monitored with the aid of SEM comprising an EDX point-by-point analysis (Hitachi S4700, Japan). Fly ashes were used for preparation of the slurries (water coefficient ranging from 0.3 to 1.0) that were characterized by values obtained during the determination of their "standard" consistency according to the procedure described in Czech standards CSN 72 2071 and CSN 72 2080. The hydration process of the slurries was investigated by monitoring the release of the hydration heat in an isothermal calorimeter (TAM Air, TA Instruments, USA). The volume changes of the slurries that were taking place taking place during the hydration were determined by measuring directly length variations of experimental bodies with the dimensions of $4 \times 4 \times 16$ cm (gauge blocks were used for this purpose). The hydration products were characterized with the aid of a scanning electron microscope (SEM) with a point-by-point analysis (Hitachi S4700).

RESULTS AND DISCUSSION

Fly ash composition

Fly ashes from CEZ power plants were used for investigation, i.e. fly ashes and sulfocalcic ones occurring during the fluidized-bed combustion of coal mixed with limestone (flue gas desulfurization processes). The chemical composition of sulfocalcic fly ashes is given in Tables 2 to 4.

Table 2. Composition of fluidized-bed sulfocalcic fly ashes (XRF).

Oxide	w [%]				
	FK11 ÚP	FK11 LP	FK12 ÚP	FK12 LP	ETH 10
Al_2O_3	32.31	30.30	29.76	26.93	28.84
SiO_2	38.99	37.36	35.44	32.01	34.30
SO_3	4.99	7.44	6.07	7.29	7.69
CaO	8.84	13.68	14.81	22.56	16.51
Fe_2O_3	5.45	3.31	5.41	3.45	4.56
TiO_2	7.12	5.85	6.10	5.83	5.96

Table 3. Composition of fly ashes (XRF).

Oxide	w [%]		
	Silo A	S1	S2
Al_2O_3	35.55	35.60	35.32
SiO_2	51.63	52.08	52.13
SO_3	0.24	0.26	0.25
CaO	1.98	1.92	1.91
Fe_2O_3	5.15	4.72	4.90
TiO_2	1.79	1.76	1.74

Table 4. Concentrations of free CaO in fluidized-bed sulfocalcic fly ashes.

Sulfocalcic fly ash	CaO_{free} [%]
FK12 ÚP	7.6
FK12 LP	8.8
ETH 10	6.9

Sulfocalcic fly ashes of Czech provenience contain predominantly 35 - 42 % SiO_2, 30 - 35 % Al_2O_3, 3 - 7 % Fe_2O_3, 5 - 8 % SO_3 and 5 - 10 % free CaO (Tables 2 and 3). In contrast to sulfocalcic fly ashes, the fly ashes are characterized by a substantially lower SO_3 content; furthermore, they do not contain any free CaO.

Grain size distribution of fly ashes

Differences in the grain size distributions of fly ashes and sulfocalcic ones are evident from Figure 2 and 3 as

Table 5. Parameters of grain size distribution for sulfocalcic fly ashes.

Fly ash	FK11 ÚP	FK12 ÚP	ETH10	ETH20
$d_{63.8}$ [μm]	36.7	36.3	28.9	26.6
d_{50} [μm]	27.1	23.0	15.2	16.1

Table 6. Parameters of grain size distribution for fly ashes.

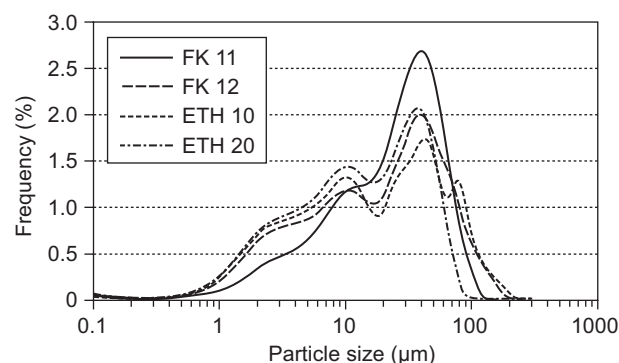| Fly ash	Silo A	S1	S2	K9
$d_{63.8}$ [μm]	42.9	41.0	32.9	35.7
d_{50} [μm]	28.9	27.6	20.7	24.6

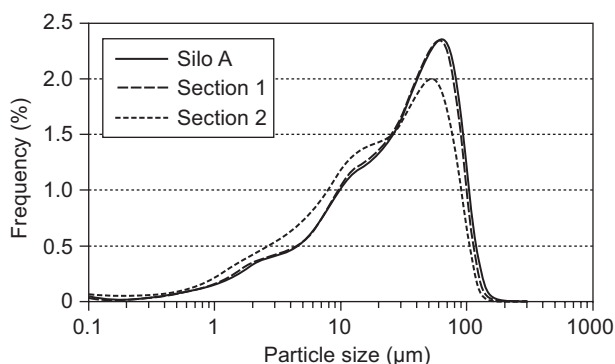Figure 2. Grain size distribution of fluidized-bed sulfocalcic fly ash.

Figure 3. Grain size distribution of fly ash.

well as from Tables 5 and 6. Sulfocalcic fly ashes rather represent a mixture of two fractions. On the contrary, the fly ashes are characterized by a monodispersed system of grain sizes.

Mineralogical composition of fly ashes

Mineralogical compositions of sulfocalcic and ordinary fly ashes differ substantially. This fact is due to the different temperatures of their origin (850°C for sulfocalcic fly ashes as compared to more than 950°C for the ordinary ones). The sulfocalcic fly ash contains crystalline phases of $CaSO_4$, CaO as well as coal residues (hematite, quartz). The X-ray diffraction does not show any presence of Si and Al compounds because of their amorphous character. $CaSO_4$ is present in the form of high-temperature anhydrite AII that occurs in two forms – as an insoluble (PDF 00-037-1496) and soluble (PDF 00-003-0162) compound. However, it is difficult to distinguish between these AII forms in sulfocalcic fly ashes. In addition to a vitreous (amorphous) phase (a broad diffusion peak) the ordinary fly ashes also contain minerals present in the coal or minerals formed during the combustion process as quartz, mullite, hematite, etc.
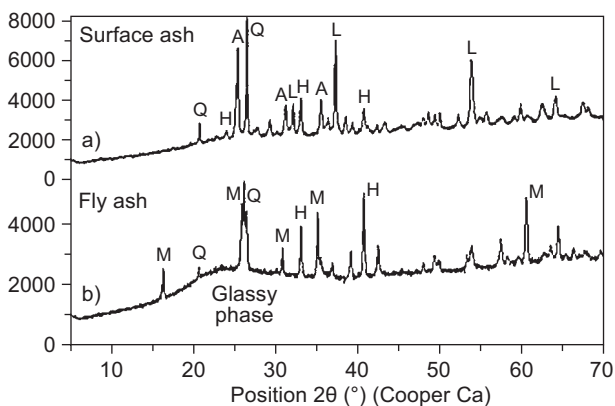
Figure 4. Diffractograms of fly ashes a) fluidized-bed sulfocalcic fly ash; b) ordinary fly ash (A…$CaSO_4$ anhydrite II, L…CaO, Q…SiO_2, H…hematite, Q…quartz, M…mullite).

Fly ash morphology

The morphology of sulfocalcic fly ashes and that of the ordinary ones differs because of the different temperatures existing during the combustion process. No melt forms in sulfocalcic fly ashes because of lower combustion temperatures (mostly below 850°C) and only a sintering process takes place. The character of sulfocalcic fly ashes is evident from pictures taken with the aid of a scanning electron microscope (Figure 5).

Sulfocalcic fly ashes contain predominantly $CaSO_4$, CaO as well as Al and Si compounds occurring as residues of incombustible materials present in the coal (Figure 5). Furthermore, there are also other minerals as quartz and hematite the presence of which is dependent on the coal composition. CaO present in sulfocalcic fly ashes exhibits morphology similar to that observed in softly calcined lime. Residues of layered structures of dehydrated and partially sintered argillaceous minerals are also present in sulfocalcic fly ashes. Their morphology and composition correspond to a metastable product formed during the firing of kaolinite (meta-kaolin).

The data obtained with the aid of high-pressure mercury intrusion porosimetry indicate that the particles
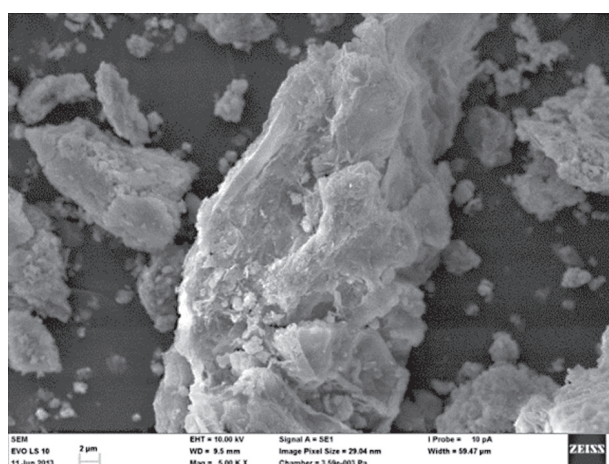
a)
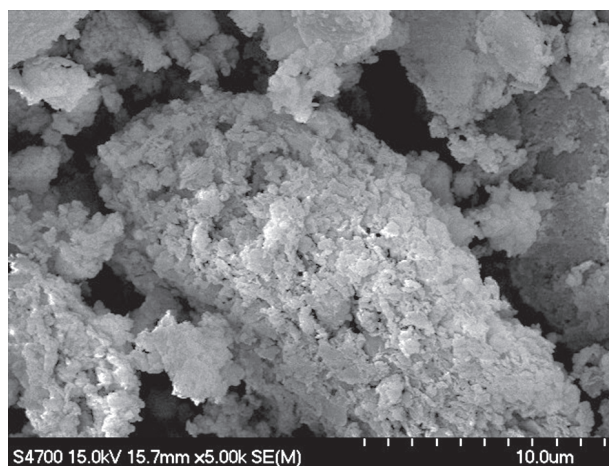
b)

Figure 5. SEM pictures of sulfocalcic fly ashes.

of sulfocalcic fly ashes are porous (Figure 7). The pores with a size of the order of micrometers occupy the largest volume. This is not the porosity in the true sense of the word because the particles aggregate to form clusters (Figure 5 and 6). Moreover, even the porosity of the layer formed by packed particles makes itself felt during the determination of this parameter with the aid of the mercury intrusion porosimetry. The porosity of sulfocalcic fly ashes is evidently interrelated with the CaO porosity (pseudo-morphoses from $CaCO_3$) and that of aluminosilicate clusters.

Particles of sulfocalcic fly ashes (BET analysis) possess a relatively large specific surface area (Table 7).

The morphology of fly ashes is rather manifold [6, 7]. The ordinary fly ash is a vitreous material containing predominantly Si, Al, Ca, Fe as well as a variety of other elements originating from incombustible components present in the coal (Figure 8). Furthermore, the fly ash also contains crystalline bodies as, for instance, quartz and mullite. The high-temperature combustion process above 950°C is accompanied by the formation of a melt

Table 7. Specific surface area (BET) of sulfocalcic fly ashes.

Sulfocalcic fly ash	BET
ETH 20	12.51 $m^2\ g^{-1}$
FK 12	8.09 $m^2\ g^{-1}$
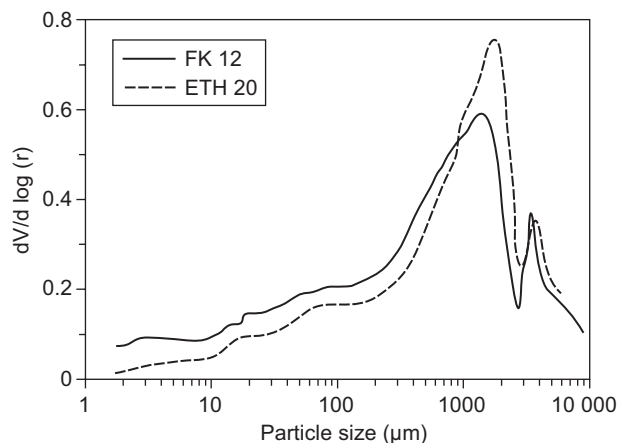
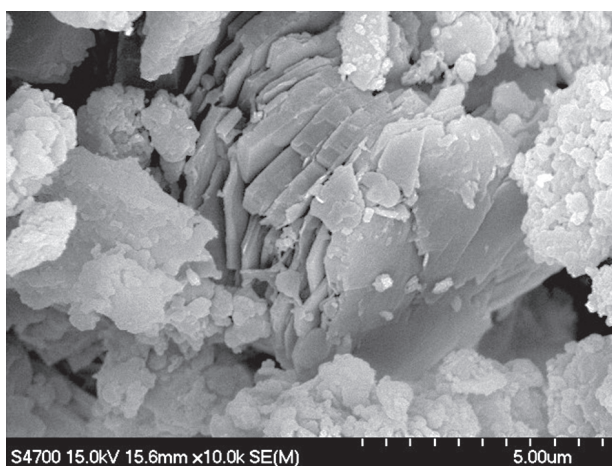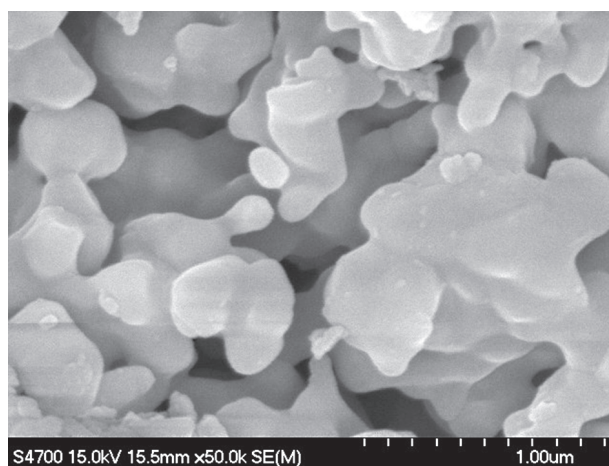Figure 7. Pore size distribution of in sulfocalcic fly ashes from mercury intrusion porosimetry.
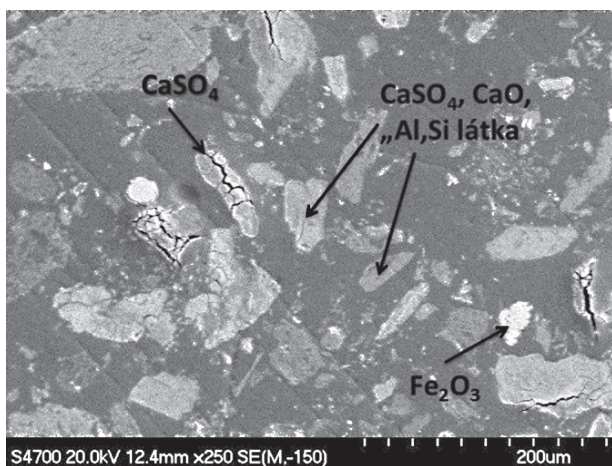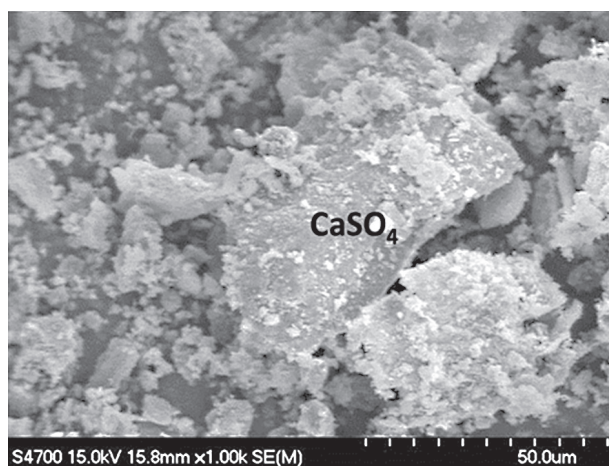
Figure 6. SEM pictures of the sulfocalcic fly ash: a) thin section; b) $CaSO_4$; c) layered amorphous structure of a Si, Al compound similar to that of metakaolin; d) CaO.
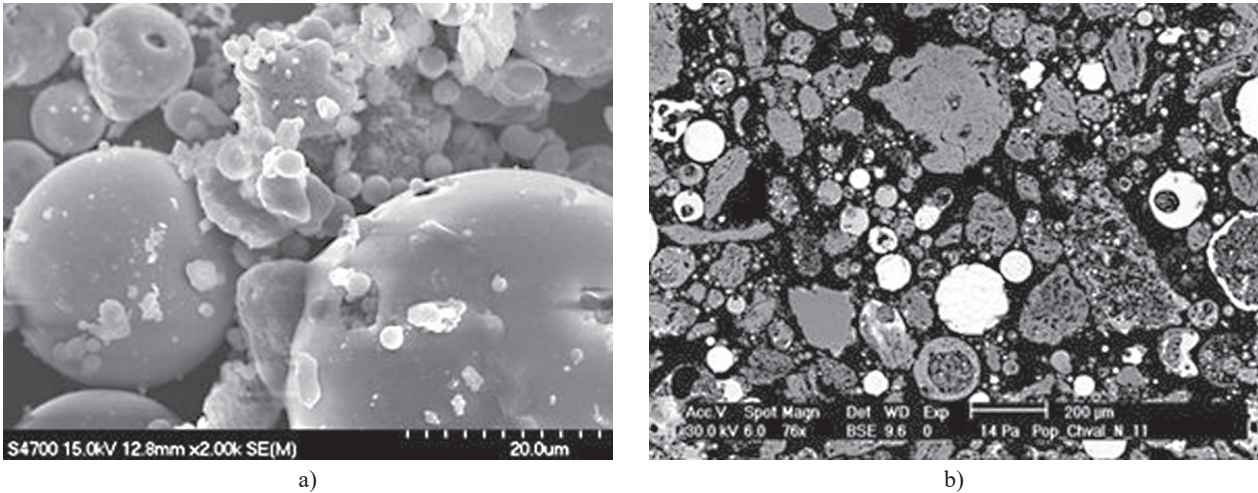
Figure 8. SEM pictures of the fly ash: a) plerospheres; b) polished thin section in BSE visualization (white areas corres-pond to high iron content).
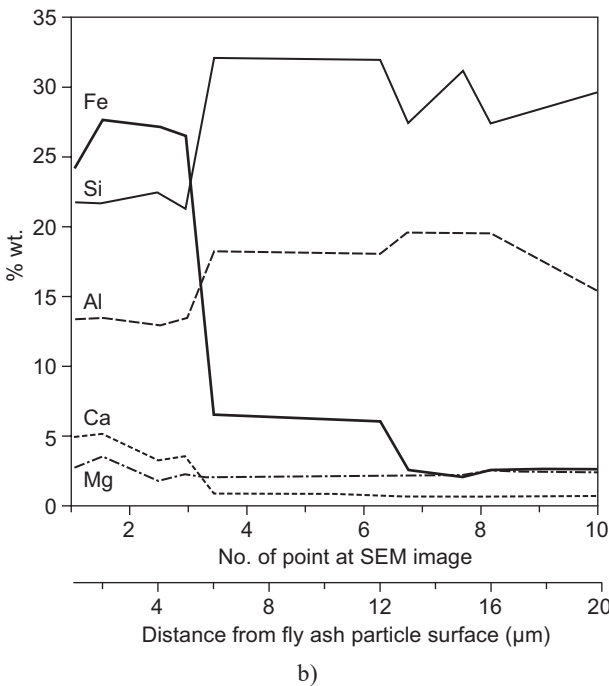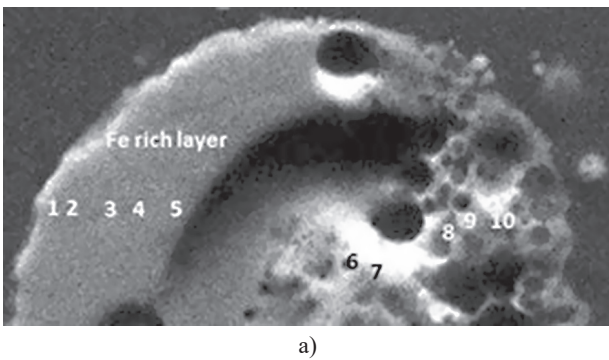

Figure 9. SEM picture of a polished thin section showing both a fly ash particle (cenospheres) and a curve characterizing the dependence of the compound concentrations on the distance from them particle surface (the investigation was carried out with the aid of the point-by-point SEM/EDX analysis).

with a high Si and Al content. A part of alumino-silicate melt with high iron content can often be found on the surface of fly ash particles (Figure 9). The particles are mostly compact, with a sealed porosity inside.

Hydration of sulfocalcic fly ashes

The hydration products of the sulfocalcic fly ash and those of the ordinary ones are quite different. The ordinary fly ash almost does not react with water and the hydration products are only present in mixtures with $Ca(OH)_2$, $CaSO_4$ or with the clinker (as this occurs in Portland-composite cements).

The mixing of the sulfocalcic fly ash with water is accompanied by water penetrating into its porous structure. A rather large water coefficient (0.8 to 1.2) must be used to achieve an acceptable workability of the fly ash slurry because of the ash porosity. Bodies possessing a measurable strength (a couple of MPa approximately) can be prepared despite this fact.

At first, a quick reaction of water with CaO takes place during the hydration:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (a)$$
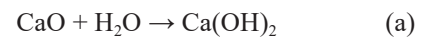
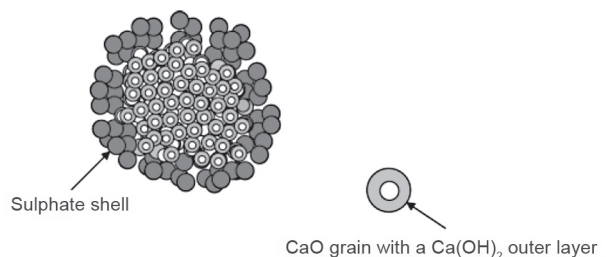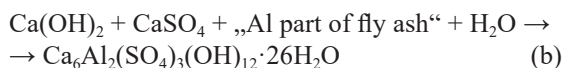An expansion takes place inside the particle and fissures are generated (Figure 10) because the molar

Figure 10. Conceptual representation of the beginning of sulfocalcic ash hydration [8].

volume of $Ca(OH)_2$ is larger than that of CaO. The $CaSO_4$ layer cracks thus facilitating further access of water. The reaction of CaO with water is fast because the character of calcium oxide present in sulfocalcic fly ashes does not differ from that of the soft-burnt lime.

In the subsequent stage, $Ca(OH)_2$ reacts with $CaSO_4$ as well as with a part of aluminate-containing fly ash by giving rise to ettringite (the ettringite was termed earlier as $3CaO·Al_2O_3·3CaSO_4·32H_2O$):

$$Ca(OH)_2 + CaSO_4 + „Al\ part\ of\ fly\ ash" + H_2O \rightarrow$$
$$\rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}·26H_2O \quad\quad (b)$$

This process is corroborated by the data obtained with the aid of X-ray diffraction analysis (Figure 11). The reaction is accompanied by expansion (Figure 12) that obviously finishes at the moment when all $Ca(OH)_2$ formed has been converted into the ettringite [8]. In later stages, the ettringite is transformed partially into complex Ca, Al carbonate-hydrates or into even more complex compounds as the woodfordite: $Ca_6Al_2(SO_4,SiO_4,CO_3)_3(OH)_{12}·26H_2O$ (Figure 11). Theoretically, also the hydration $CaSO_4\ AII + H_2O \rightarrow CaSO_4.H_2O$ can take place. $CaSO_4\ AII$ reacts slowly

Figure 12. SEM picture of acicular ettringite in slurry of sulfocalcic fly ash (the water coefficient 1.0) kept in water for 14 days.
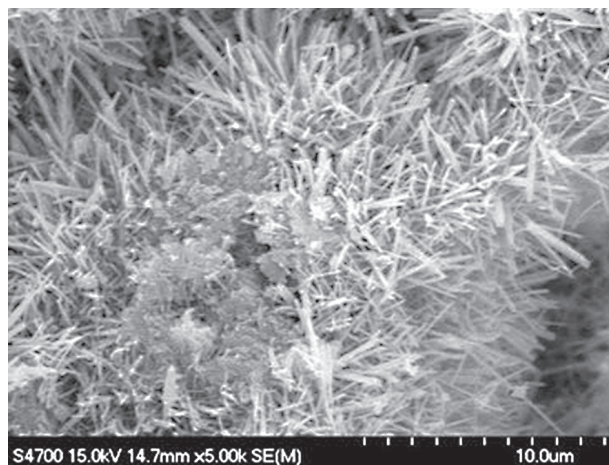

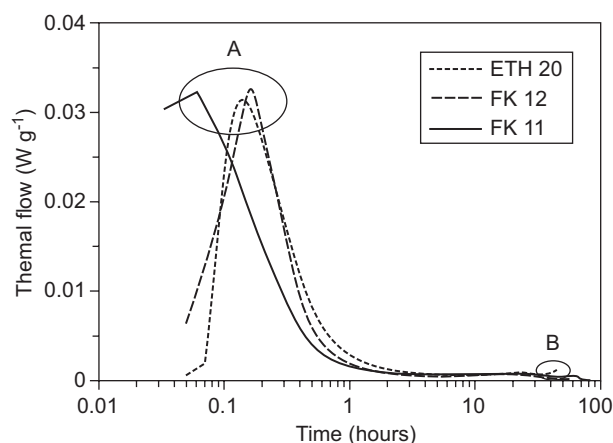Figure 11. Diffractogram of hydrated fluidized-bed sulfocalcic fly ash after 120 days in water.

Figure 13. Curves showing the release of heat during the hydration of sulfocalcic fly ash slurries.

with water and this reaction is accelerated by the presence of $Ca(OH)_2$ triggered by free CaO present in the fly ash. Nevertheless, the occurrence of $CaSO_4.H_2O$ in hydration products of the sulfo-aluminate fly ash could not be demonstrated. It seems that the ettringite is always formed preferentially.

A longer exposure of ettringite to atmospheric CO_2 may also result in its decomposition into limestone, $CaSO_4.H_2O$, Al_2O_3 gel and water [10] as per following reaction:

$$3CaO·Al_2O_3·3CaSO_4·32H_2O + CO_2 \rightarrow$$
$$\rightarrow 3\ CaCO_3 + 3\ CaSO_4·2H_2O + Al_2O_3·nH_2O +$$
$$+ (26\text{-}n)H_2O \quad\quad (c)$$

No hydration products of the type $CaCO_3$ and $CaSO_4·2H_2O$ could be detected in the hydrated sulfocalcic fly ash.

SEM pictures of hydrated sulfo-aluminate fly ash point to the presence of ettringite as a major hydration product (Figure 12).

The character of both initial hydration stages (a) and (b) is exothermic; they can be observed on curves showing the development in the generation of hydration heat (Figure 13).

Two regions of heat release could be identified on calorimetric curves of hydrating sulfocalcic fly ashes. The first release of heat could be observed during the first hour when the thermal phenomenon was probably due to the hydration of free CaO into $Ca(OH)_2$ as well as to the crystallization of the ettringite (the A region),

Table 8. Values of total reaction heat determined during the hydration of sulfocalcic fly ashes.

Sulfocalcic fly ash	w	Total reaction heat [$J·g^{-1}$]
FK 11 LP	0.30	225
FK 12 ÚP	0.80	310
ETH 20	0.80	150
FK 12 LP	0.50	370

or to the formation of a C–S–H phase. The second release of heat started in the period ranging from 24 to 70 hours but, nevertheless, the heat development was not very pronounced in this case. This phenomenon may be in relation with the development of the C–S–H phase (the B region).

The integration of the curves characterizing the heat fluxes yielded values of the total reaction heat expressed in joules per 1 gram of fly ash (Table 8).

The values of hydration heat obtained by measurement agree qualitatively with those obtained for Canadian flue ashes by revealing an obvious relationship between the content of free CaO and the release of hydration heat [11].

Rheological properties of fly ash slurries

A good workability of sulfocalcic fly ashes and the achievement of an acceptable consistency require a substantially larger water coefficient as compared with
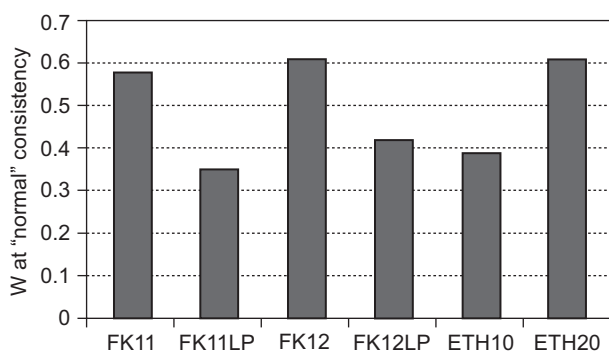

Figure 14. Rheological properties of sulfocalcic fly ash slurries (75 % fly ash + 25 % Portland cement).
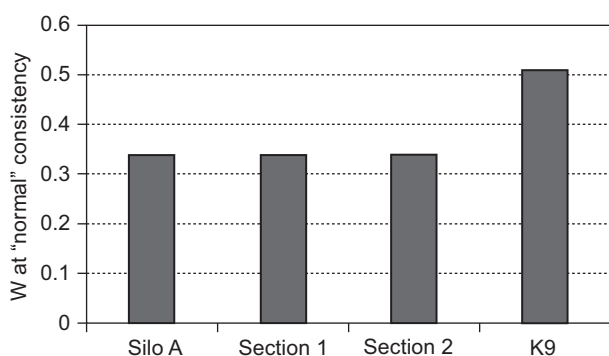

Figure 15. Rheological properties of the ordinary fly ash (75 % fly ash + 25 % Portland cement).

the slurries based on ordinary fly ashes (Figure 14 and 15). The difference in the workability of sulfocalcic fly ashes and the ordinary ones is due to the different character of their particles. Also the porosity and, hence, the water absorption of sulfocalcic fly ash particles play an important role in this case.
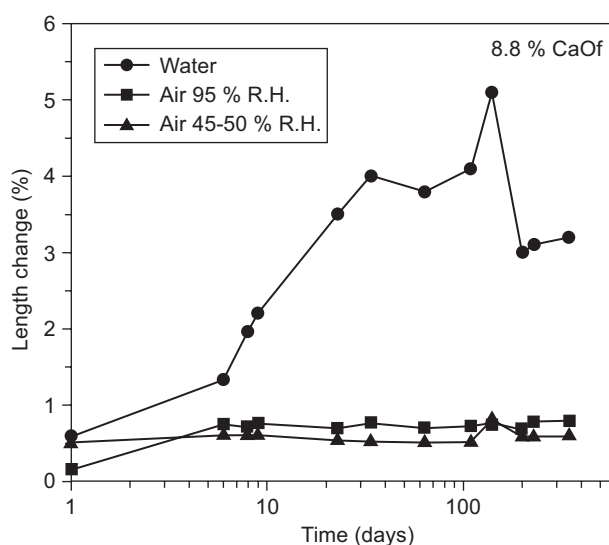

Figure 16. Volume changes of a 4×4×16 cm body; sulfocalcic fly ash containing 8.8 % free CaO.

Volume changes

Volume changes in hardening slurries of sulfocalcic fly ashes manifest themselves by expansion. The expansion takes place particularly during their exposure to water. The volume changes drop to minimum values if
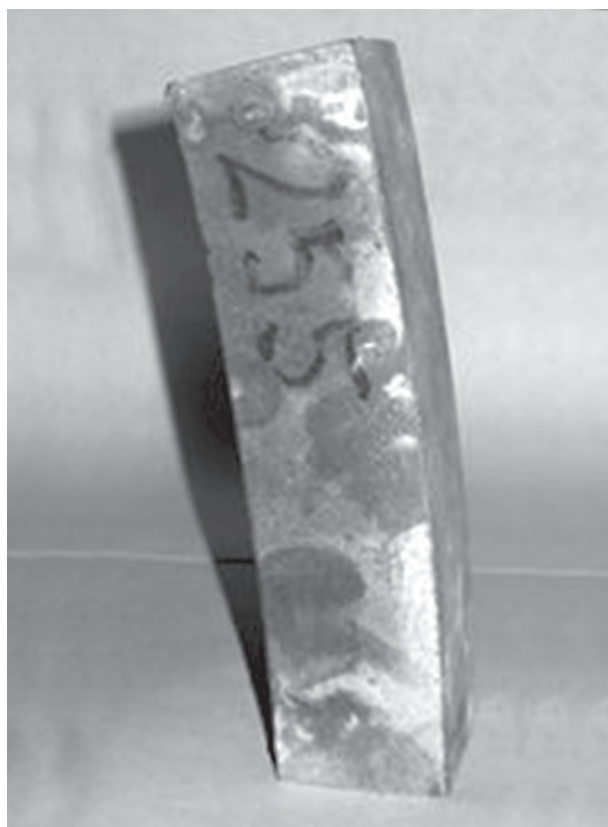

Figure 17. Deformation (induced by macroscopic expansion) of a sulfocalcic ash slurry with a water coefficient equal to 1.0, kept in water for 14 days.

the slurries are kept in air or in a humid environment. A typical character of the expansion taking place in hardened sulfocalcic ash slurry is shown in Figure 16.

The expansion taking place in sulfocalcic ash slurries eventually results in the body destruction (Figure 17).

It is obvious that the expansion related to the ettringite formation takes place as long as there is still some $Ca(OH)_2$ available (from free CaO). This fact is confirmed by data supplied by the X-ray diffraction analysis: no $Ca(OH)_2$ was found in sulfocalcic fly ash subjected to a long-term hydration after a detectable expansion could no longer be measured.

The reaction of alite hydration in mixtures of Portland cement with sulfocalcic fly ash is also a source of $Ca(OH)_2$. This fact makes a long-term formation of the secondary expansive ettringite possible until the moment when all $CaSO_4$ present in the sulfocalcic fly ah has been used up by the reaction. The risks associated with the use of sulfocalcic fly ash as an admixture to Portland cement are related to this fact because there is a danger that the concretes based on these mixtures would not preserve their volume stability.

CONCLUSIONS

There is much less data about sulfocalcic fly ashes in the technical literature as compared to the information on ordinary fly ashes. However, more pieces of systematic information about the composition and the reactivity of their individual constituents are needed for a potential utilization of fluidized-bed sulfocalcic fly ashes. The composition of sulfocalcic fly ashes differs from that of the ordinary ones ($CaSO_4$ content, free CaO content), the character of particles is different and also their porosity is not the same. Another difference consists in the different behavior during their hydration: the sulfocalcic fly ashes react directly with water whereas only a minimum reaction of ordinary fly ashes with water could be observed. The use of sulfocalcic fly ashes as admixtures to Portland cement is associated with a danger consisting in the formation of secondary ettringite, which results in a poor volume stability of hardened bodies. The possibility of using fluidized-bed sulfocalcic fly ashes is rather limited at present. This type of fly ashes might be used in such applications when the expansion during the hardening process would exert a negligible influence (for instance, the soil stabilization).

More research into the sulfocalcic fly ashes is necessary and desirable because of the increasing quantities of this product being rejected by coal-fired power plants.

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