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MICROANALYTICAL CHARACTERIZATION (AEM) OF GLASSY SPHERES AND ANHYDRITE FROM A HIGH-CALCIUM LIGNITE FLY ASH FROM GERMANY

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ABSTRACT

Lignite fly ash is known to have cementing properties. The heterogeneous composition of lignite fly ash complicates its utilization as an admixture to concrete. The reactivity of lignite fly ash is related to the occurrence of reactive glassy components and several cement phases. Glassy spheres and anhydrite in the micrometer and submicrometer range of lignite fly ash were analyzed with AEM methods. The main components of the glassy spheres are Al_2O_3, SiO_2 and CaO. The ratio of $Al_2O_3/(Al_2O_3+SiO_2)$ is constant for most analysis and indicates the origin of the glassy spheres from kaolinite. The calcium content of the spheres is rather variable. Leaching experiments led to the definition of three different compositional ranges of different reactivity. With decreasing CaO content the reactivity of the glassy spheres decreases. A major boundary at 25 wt-% CaO separates highly reactive glassy spheres from less reactive spheres. Calcium-free spheres with a $Al_2O_3/(Al_2O_3+SiO_2)$ ratio less than 0.45 show no reactivity. Anhydrite particles in the submicrometer range are often contaminated with aluminium in unknown binding form (presumable calcium aluminate, aluminium sulfate, or calcium aluminate sulfate). This aluminium is fixed in a highly soluble anhydrite environment and probably is the easy accessible elemental source for the first ettringite formation during the hydration reaction of lignite fly ashes.

Introduction

Germany produces annually about $10*10^6$ t of lignite fly ash. This material is mainly utilized for sanitary landfilling. Although this material has cementing properties its usage as an admixture to concrete, filler or resource is due to economical and compositional reasons rather restricted (1). Bambauer (1) reported a compressive strength up to 45 MPa after 180 days for portlandite blended lignite fly ash from eastern Germany. A better knowledge about the mineralogic and chemical composition of the fly ash could lead to an increased utilization of fly ash in the construction industry or as a resource for nonmetallics.

Lignite fly ashes are a heterogeneous mixture of mineral phases and amorphous glassy phases. Some of these phases possess cementing properties. Glassy spheres, free lime and anhydrite are the most prominent reactive phases. They are assumed to contribute the chemical constituents of the first newly formed mineral phases in the hydration process (1,2,3). The detailed knowledge about the elemental composition of these mineral phases could help to evaluate their reactivity and further to predict the setting behavior of certain fly ash samples.

The amount of noncrystalline glassy material in fly ash particles can be determined by differential XRD-methods (4,5) or differential wet-chemistry (6). The chemical composition of the glassy phase has been evaluated using the glass peak of XRD-diagrams (7). These methods assume a homogeneous composition of the glassy phase, and neglect the existence of glassy particles with varying chemical composition. Stevenson et al. (8) studied the microchemical composition of several North American fly ashes with AAS and SEM/EMPA methods. They found a correlation between the microchemical composition of ash particles and the clay mineral species in the raw coal. They emphasized the importance of the geological origin of the coal on the chemical composition of particles and correlations between certain elements. However, the fine grained nature of the material - commonly in the micrometer and submicrometer range - and the agglomerating process of particles during the high temperature coal conversion process limit the usage of conventional SEM-microanalysis or electron probe microanalysis (2,3,8,9).

Schreiter (6) has proposed a classification scheme for different types of glassy spheres. He considered particles soluble in concentrated hydrochloric acid more reactive than particles insoluble in this acid and termed the glassy spheres active and inert. This model helped in explaining the different reactivity of bulk fly ash samples from Germany. Homertgen and Odler (10) have studied the reactive behavior of several synthetic glasses in the system CaO-Al_2O_3-SiO_2 with a high aluminium content. They found a varying reactivity of the synthetic glasses dependant on chemical composition.

The objective of this study is the chemical characterization of single micrometer and submicrometer particles in fly ashes using the high spatial resolution of the analytical transmission electron microscopy (AEM). The reactivity of individual particles is determined by a sequential leaching process with acids in combination with AEM microanalysis. In this case the remainder in an acid solution is assumed to be less reactive than the dissolved particles. A general classification of the material was undertaken with XRD-methods and XRF-methods.

Methods

Sample Origin and Preparation

Fly ash samples for this study were taken from electrostatic precipitators of a power plant using a lignite fuel from the mining area south of Leipzig, Germany. The coals of this mining area formed in a continental environment with carbonaceous and evaporitic bed rocks. They are characterized by a high quartz, marcasite and gypsum content (11). The major clay mineral is kaolinite. Raw coal from this area contains 6.5 - 8.5 wt% mineral matter and 1.5 - 2.5 wt% sulfur. Fly ashes from this source were studied in detail by Enders (12). He found that the chemical and mineralogical composition of these fly ashes was constant within a one year period. Bambauer (1) compiled chemical and mineralogical data of fly ashes from all major German brown coal mining areas. For AEM work the submicrometer particles were enriched using a dry sieving process with a 20 μm sieve. The particles were transfered to copper grids using a California Measurements MPS-3 Cascade impactor.

Analytical Transmission Electron Microscopy (AEM)

The submicrometer particles were analyzed with a Philips EM 400T transmission electron microscope. Attached to microscope is a scanning-unit (STEM), which allows a very accurate positioning of the electron beam for X-Ray microanalysis. The diameter of the electron beam was usually 5 nm. In some cases the beam was enlarged (10 - 20 nm) to improve X-Ray excitation. The X-Ray spectra were recorded with a EDAX 9100/65 energy dispersive X-Ray microanalyzer. The energy resolution of the Si(Li) detector was 159 eV. The spectra were accumulated for 100 seconds. The results were processed following principles first proposed by Cliff and Lorimer (13) for standardless TEM-microanalysis. The accuracy of the system was tested with mineral standards and the systematic error was found to be less than 5 % compared to the ideal composition of the minerals. The upper size limit for particle analysis following the Cliff-Lorimer approach is 500 - 1000 nm. Glassy spheres in this size range were chosen using spherical morphology and a high Al and Si content as the criterion. Anhydrite particles were observed in different morphologies (pseudocubes, rounded, irregular subrounded). Therefore a high calcium and sulfur content was the criterion for particles classified in this group. For comparison reasons all of the data are reported and plotted in weight-percent.

Leaching Process

To evaluate the reactivity of individual fly ash particles the samples were treated with water, 1:1 diluted CH_3COOH, concentrated CH_3COOH, concentrated HNO_3, and concentrated HCl. 1 g of the sample was mixed with 30 mL acid in a glass bottle. The solutions were turned overhead for four days. Then the material was filtered and the remainder was analyzed with AEM-methods. The selection of the particles for analysis followed the criteria outlined above.

XRD, XRF and SEM work

Prior to AEM-work the samples were examined with SEM and XRD-methods. XRD-work was done with a Siemens D500 X-Ray spectrometer using Cu Kα-Radiation (40kV, 30mA) and conventional phase identification procedures described by Klug and Alexander (14).

Results

Mineralogic and Chemical Composition

The mineralogic composition and the fabric of the unfractionated fly ash samples were examined with XRD-methods and light microscopy. The results are outlined in Table 1. Minerals not altered in the high temperature process are termed residual minerals. Mineral phases produced by the high temperature process include glassy spheres and the devitrification products anorthite and gehlenite, anhydrite and free lime. Sometimes fly ash minerals are altered by secondary processes (hydration and carbonation) in or after the electrostatic precipitator which leads to the formation of calcite, gypsum or bassanite.

The fly ash samples are rich in quartz, anhydrite and glassy spheres. Quartz is enriched in the coarse fractions of the material, while anhydrite dominates the fraction less than 32 μm. Marcasite was found in the raw coal and rarely in magnetic concentrates from the fly ash. From reflected light microscopy it is evident that a rim of iron oxide shielded some marcasite from oxidation during the high temperature process. The chemical composition of the fly ash together with data from lasergranulometric grain size distribution are given in Table 2.

Analytical Electron Microscopy

The principal morphological features of the micrometer and submicrometer particles are outlined in FIG. 1. Pictures A and C show glassy spheres in SEM pictures. In FIG. 1 C

TABLE 1

Mineralogic Composition of the Fly Ash Samples from the Area South of Leipzig. (Fly ash minerals are classified according to their changes during or after the high temperature process. The asterisk marks compounds determined from ED-spectra.)

Coal	Fly ash		
	residual	newly formed	alteration
quartz	quartz		
kaolinite		glassy spheres	
		anorthite	
		gehlenite	
gypsum		anhydrite	gypsum
		freelime	bassanite
marcasite	(marcasite)	hematite	
		anhydrite	gypsum
organic origin		free lime	calcite
questionable origin		Ca-aluminate*	
		NH_4-sulfate*	
		Al-sulfate*	

a filled plerosphere demonstrates the importance of a high spatial resolution for chemical analysis of single particles in lignite fly ash. FIG. 1 B and 1 D show anhydrite crystals with a pseudocubic morphology. Typical energy dispersive X-Ray spectra of glassy spheres and anhydrite particles are given in FIG. 2. During AEM work in most spectra for glassy spheres a small peak of sulfur was detected. It was assumed that this sulfur is bounded in a surface layer of anhydrite. This sulfur content was used to recalculate the CaO content of the glassy spheres.

TABLE 2

Chemical Composition and Grain Size Distribution of the Examined Fly Ash.

major elements (wt%)		trace elements (ppm)	
SiO_2	39.81	V	189
TiO_2	1.13	Mn	1052
Al_2O_3	16.25	Cu	65
Fe_2O_3	8.26	Zn	29
MnO	0.14	Th	27
MgO	2.09	Cr	186
CaO	24.30	Pb	62
Na_2O	0.17	Rb	30
K_2O	0.43	Sr	1171
P_2O_5	0.10	Ba	3160
SO_3	6.72		
sum	99.40		

Grain size distribution

D10:	7.32 μm	D50:	42.14 μm	D90:	110.02 μm

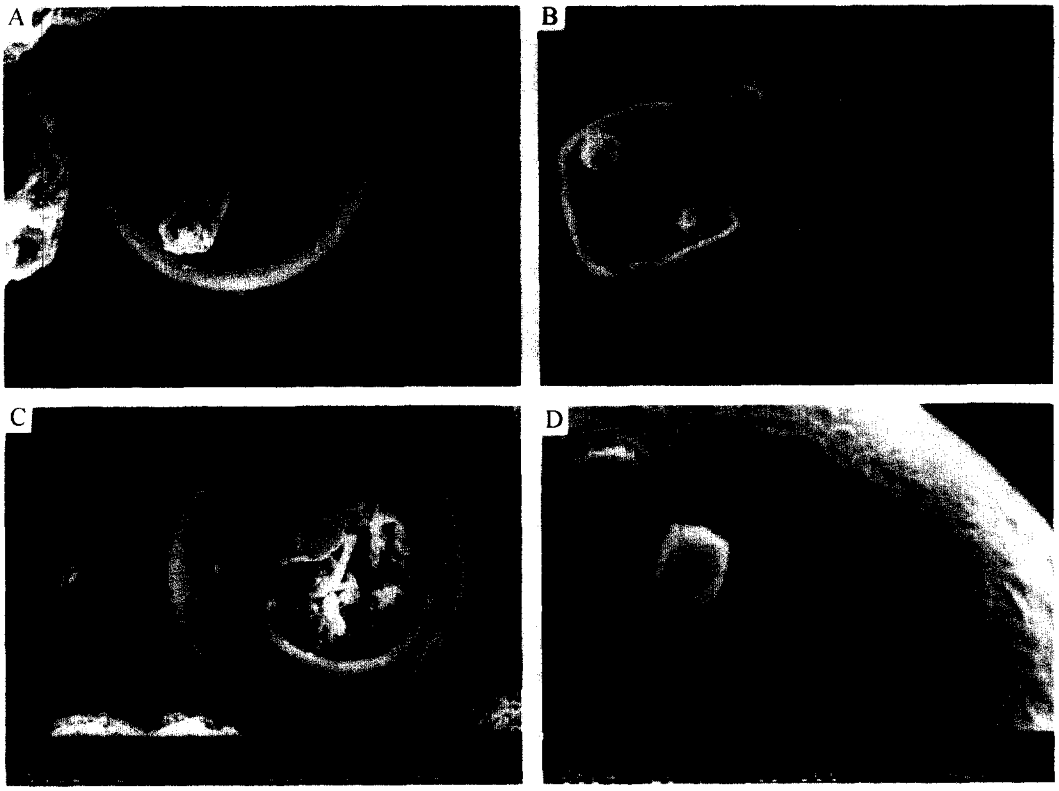

FIG. 1
SEM-Micrographs 1A and 1C show glassy sphere and a plerosphere. STEM-Micrographs 1B and SEM-Micrograph 1D display anhydrite crystals in pseudocubic morphology (1A, 1C, 1D - SEM-SE, 1B - STEM-SE)

The composition of the glassy spheres in weight percent is shown in a triangular diagram of the main components in FIG. 3. The data points strictly follow a line with the $Al_2O_3/(Al_2O_3+SiO_2)$ ratio of kaolinite. This is clear evidence for the origin of the glassy spheres from kaolinite. This is consistent with previous results of Stevenson et al (8). The CaO-content of the particles is highly variable. Maximum values reach 60 wt% CaO. Analysis with a $Al_2O_3/(Al_2O_3+SiO_2)$ ratio different from kaolinite are sparse. The SEM/EDX analysis of Zschach (2) and Werner et al. (3) of glassy spheres from several fly ash samples from the former GDR including the one used for this study are included for comparison. Their data points for reactive glass particles (open symbols) show a deviation from the kaolinite line, which is probably due to the larger X-Ray excitation volume in SEM microanalysis with less spatial resolution. The filled symbols indicate their analysis for hydrochloric acid resistant glassy spheres, which were termed inert glass. Those are characterized by an increased silicon content and a decreased calcium content compared to the reactive glassy spheres (open symbols).

To evaluate the influence of elemental composition on the reactivity of the glassy spheres, a fly ash sample was treated with different acids and analyzed with AEM methods. In FIG. 4 the results of the leaching experiments are depicted. FIG. 4a gives an untreated sample (compare FIG. 3). One data point has the composition of a calcium aluminate. The sample plotted in FIG. 4b was treated with deionized water. The composition of the remaining glassy spheres

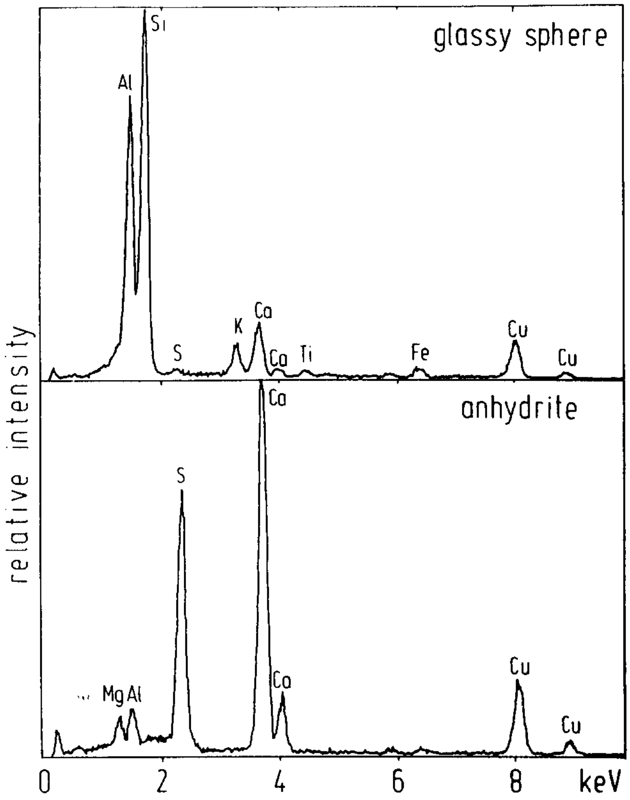

FIG. 2
Typical STEM-EDX-spectra for glassy spheres and anhydrite

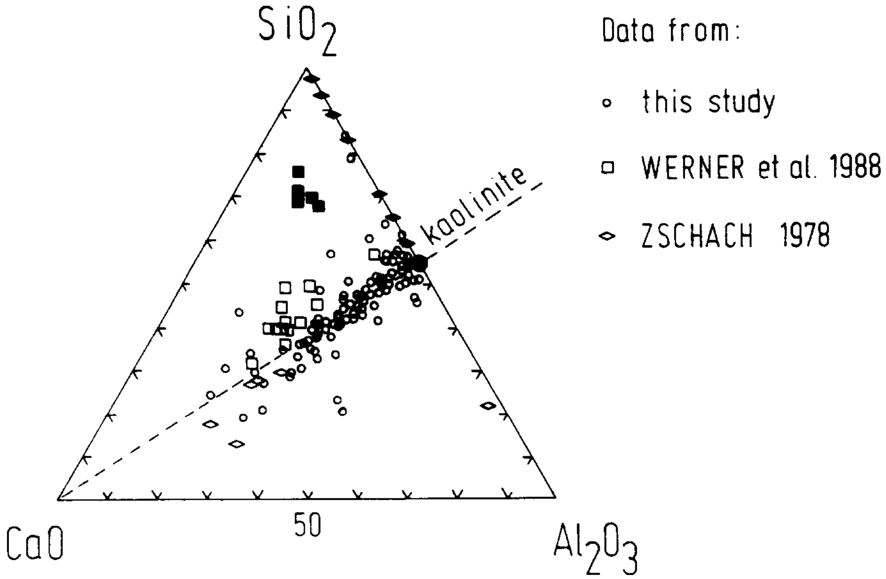

FIG. 3
Triangular diagram of 125 STEM-EDX analysis on glassy spheres. Open symbols mark data of Zschach (2) and Werner et al (3) for reactive glassy spheres. Filled symbols mark their data for inert glassy spheres (Data is plotted in wt%)

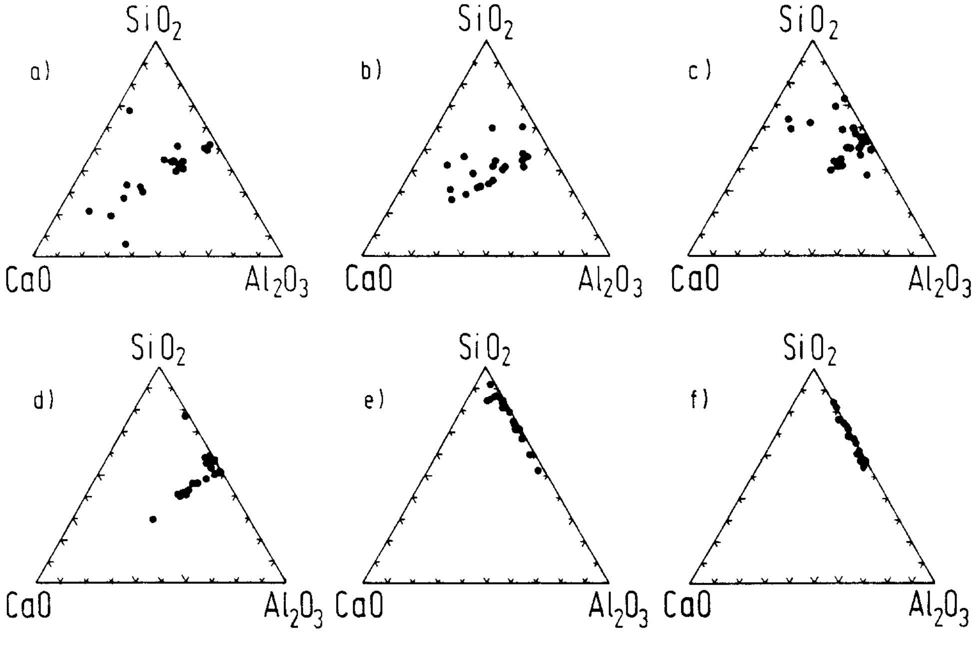

FIG. 4
Results of the leaching experiments. (a - untreated, b - deionized water, c - 1:1 diluted CH_3OOH, d - conc. CH_3OOH, e - conc. HNO_3, f - conc. HCl)

was barely changed compared to the untreated sample (FIG. 3, FIG 4a). A slightly decreased Al content indicated by a slight deviation from a kaolinitic composition is probably due to an increased solubility of aluminium in the presence of sulfate anions (15). Besides the residual glassy spheres this sample showed widespread formation of ettringite and gypsum, clearly indicating hydration reactions. FIG. 4c gives an sample treated with 1:1 diluted acetic acid (CH_3OOH). High calcium particles were completely dissolved, some particles lost some of their aluminium. The maximum remaining CaO content of the particles is 25 wt%. This dissolution effect is more obvious in the sample treated with concentrated acetic acid (FIG. 4d). In samples treated with concentrated nitric acid and concentrated hydrochloric acid only a few glassy spheres were left. They are almost calcium free and they are characterized by a $Al_2O_3/(Al_2O_3+SiO_2)$ ratio less than 0.45. This could be due to an enrichment of high Si-rich particles during the leaching process or an elemental change of single particles by exsolution of aluminium. From the rare occurrence of high Si-particles in untreated samples (FIG. 3, FIG. 4a) the later seems to be more probable.

This experiment allows the definition of three different types of glassy spheres in the studied fly ash (Table 3). Type I consist of highly reactive high Ca particles. Their rapid dissolution in acetic acid is evidence for high reactivity. Additionally, the occurrence of free lime inclusions in the glass matrix is assumed. Type II includes particles with an intermediate reactivity and a CaO content ranging from 0 - 25 wt%. Particles with CaO $\approx$ 0 and a $Al_2O_3/(Al_2O_3+SiO_2)$ ratio less than kaolinite show no reactivity. The importance of kaolinite as the precursor of the glass particles can be evaluated from the kaolinitic $Al_2O_3/(Al_2O_3+SiO_2)$ ratio of the reactive glassy spheres (Table 3).

In the water treated sample ettringite formed within four days (FIG. 4b). During this period the elemental composition of the glassy spheres stayed almost constant. This calls for a second aluminium source for the fast ettringite formation. In this study the chemical composition of sulfate rich microparticles was determined with AEM methods (FIG. 1 B, 1C). The results are listed in Table 4. Most of the particles are contaminated with aluminium, although their major

TABLE 3

The Composition of Different Types of Glassy Spheres

	CaO [wt%]	$Al_2O_3/(Al_2O_3+SiO_2)$	reactivity
high-Ca-spheres	>25	±0.45	high, inclusions
low-Ca-spheres	<25	±0.45	low
Ca-free-spheres	± 0	<0.45	inert
kaolinite	0	0.45	none

element chemistry clearly indicates an origin from heated gypsum (Table. 3). The maximum aluminium content of single particles reaches 33 wt%. From the kaolinitic $Al_2O_3/(Al_2O_3+SiO_2)$ ratio one can easily exclude glassy spheres as a possible explanation for this aluminium contamination. Therefore glassy spheres can not be the heterogeneous seeds for the calciumsulfate rich particles. Due to the small size of the particles it was not possible to determine the binding-form of this aluminium. The rapid reaction of the material makes highly reactive mineral phases like calcium aluminate, aluminium sulfate or calcium aluminate sulfate (16, $C_4A_3\overline{S}$) the most probable candidates. The occurrence of $C_4A_3\overline{S}$ in lignite fly ashes has been reported by McCarthy et al (17, 18). This aluminium is included in a very easily soluble matrix of anhydrite and it is probably an easy accessible source for the ettringite formation.

TABLE 4

Results of 65 AEM Microanalysis on Sulfate rich Particles. Reported are Minimum, Maximum, Average values and the Standard deviation (sd). All data in wt%.

	minimum (wt%)	maximum (wt%)	average (wt%)	sd (wt%)
SiO_2	0.0	12.8	2.2	3.2
TiO_2	0.0	2.4	0.2	0.4
Al_2O_3	0.0	33.8	7.1	7.2
FeO	0.0	20.6	3.3	4.3
MnO	0.0	0.9	0.1	0.2
MgO	0.0	25.6	3.2	4.4
CaO	18.4	53.0	36.2	5.9
K_2O	0.0	8.1	0.3	1.0
As_2O_3	0.0	1.8	0.1	0.3
SO_3	19.5	62.0	47.5	9.7
$CaO+SO_3$	49.3	100.0	83.8	12.7
$Al_2O_3/(Al_2O_3+SiO_2)$	0.0	1.0	0.77	0.2

Conclusions

The fraction <20 μm of a Ca/S rich fly ash was examined with AEM methods. The high spatial resolution of this instrument allowed very accurate analysis of submicrometer particles. Glassy spheres have a variable chemical composition. The $Al_2O_3/(Al_2O_3+SiO_2)$ ratio indicates their general origin from kaolinite as the major clay mineral in the given lignite coal. With decreasing CaO content and decreasing $Al_2O_3/(Al_2O_3+SiO_2)$ ratio of the spheres the reactivity decreases. The fast formation of ettringite in these fly ashes is probably related to the occurrence of aluminium included in calcium sulfate-rich particles in unknown binding form. The most probable crystalline candidates for this material are calcium aluminate, aluminium sulfate or calcium aluminate sulfate ($C_4A_3\bar{S}$). The composition of the submicrometer particles has a major influence on the reactivity of fly ashes. This data might help evaluating the impact of varying composition of microparticles on the cementing properties of fly ashes.

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