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INVESTIGATING THE MINERALOGICAL COMPOSITION OF FLYING ASH PULPS FROM THE ASPECT OF WASTE QUALITY

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Abstract

Nowadays coal-based power plants have still a 25% share in energy production in Hungary. Consequently, professional treatment of the yearly accumulating large volumes of ash/flying ash is an important task from environmental, as well as national economic aspects. Since power plants have gradually switched during the recent years to hybrid- fluid technology, substantial part of sulphur accumulates in fine ash/flying ash. It is important to know in which form the sulphur component becomes absorbed in the flying ash–water pulp of approximately 1:1 mixing ratio. This study presents the thematic as well as temporal evolution of the detailed determination of mineralogical composition.

Keywords: flying ashes, chemical, mineralogical, strength tests.

1. Introduction

Sulphur as well as sulphur-dioxide released in the air through the combustion of fossil fuels – like coal – in thermal power plants pose a gradually aggravating environmental problem all over the world.

The highest sulphur-dioxide emission occurred in Hungary in the 80s[1], the fuel structure has changed since then, but coal-based power plants still have a 25% share in our energy production.

To combat air pollution these power plants have been equipped with electrostatic dust separators, practically stopping their dust release. Flue gas desulphurisers of 90–95% efficiency are much more expensive, they have not yet been introduced in Hungary. A less efficient, but substantially cheaper method is used for reducing sulphur-dioxide release in the Ajka power plant. The special procedure called hybrid-fluid combustion method together with the sulphur absorbing capacity of the applied coal's high carbonate content reduce sulphur-dioxide emission by 60–80%.

[1] SO_2 emission of coal combusting power plants: 654.1, 503.5 and 460.4 kt in 1980, 1985 and 1988, respectively

Using this technology the predominant part of sulphur content accumulates in the *flying ash.*[2] However, environmental authorities consider this accumulated flying ash *hazardous waste.* That was the reason why the EGI-Contracting Engineering Co. Ltd. regarded essential to learn the mineralogical composition of the water-mixed, hydraulically transported flying ash thick pulp deposited in case. Within this scheme, priority is given to the study of the sulphur's absorption mechanism as well as to trace the temporal evolution of the mineralogical composition and the pulp solidification.

2. Description of Flying Ash

From the point of view of energy production, our domestic coal supply is of rather poor quality. Generally, it features approximately 40% ash content, the yearly coal consumption of 8 – 10 million tons results thus in the formation of 3 – 4 million tons of clinker and flying ash, of which only 10 – 15% can be reused.

Sulphur is the most harmful component in coal. It is partially combustible and its burning damages the environment. Depending upon its origin the overall sulphur content of coal is composed of inorganic and organic constituents.

The inorganic constituent occurs most frequently in pyrite or in its modifications, as well as in a form bound in gypsum and anhydrite. Following combustion they accumulate in ash, without releasing their sulphur in gases.

Organic sulphur is generated by the anaerobic disintegration of living organisms through the action of sulphur bacteria. Geological conditions of the one-time swamp basin play an important role in the proliferation of sulphur microbes. Due to the action of lime dissolved from calcareous rocks the water of the swamp becomes alkaline, providing thus a suitable environment for abundant proliferation of sulphur bacteria (FEJÉR – OSWALD – SZÉLES, 1989). Consequently, there is a relationship between the sulphur content of ash/flying ash and the abundance of the denudation area in carbonate rocks during coal formation.

Considering sulphur content, the most unfavourable flying ashes among the investigated ones are those originating from the carbonate environment of the Transdanubian Central Range – Ajka (Cretaceous), Tatabánya, Inota (Eocene), whereas the lowest sulphur content can b=e observed in the Pliocene lignite of Mátra hills in a volcanic geological environment (*Fig. 1*).

Accordingly, high variation can be observed in the CaO and SO_3 content of flying ashes coming from different coal-based power plants studied (*Table 1*).

The cement industry uses so-called acidic flying ashes featuring a CaO + MgO : SiO_2 + Al_2O_3 ratio below one. All the investigated flying ashes belong to this group.

[2]Flying ash – it is the fine-grained component of the coal's ash content, released with flue gases from the boiler through waste-heat flues. In the case of coal dust combustion, 80 – 85% of ash is flying ash.

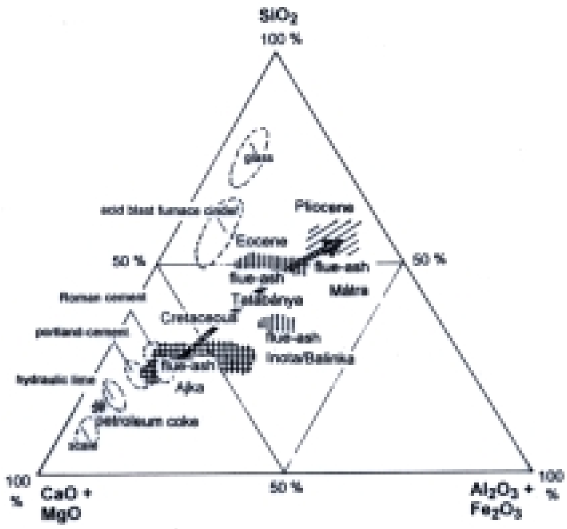

Fig. 1. Chemical feature of analysed flying ashes; variation in lime content as a function of the age of combusted coals

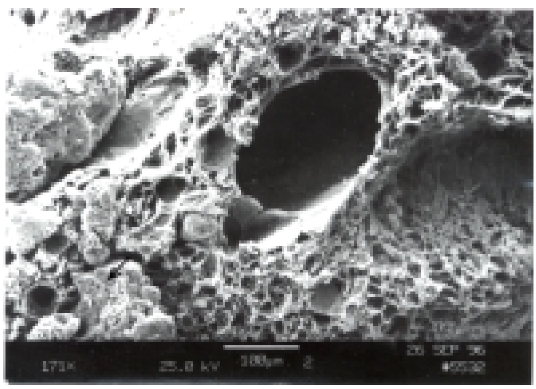

Fig. 2. Electron microscopic image of an amorphous flying ash grain of spongy structure magnified 171 times (Mátra Power Plant)

3. Investigation of the Mineralogical Composition of Thick Pulp

During the recent decades our coal-based power plants switched over to coal dust combustion of considerably higher efficiency. Subsequently, the clinker–flying ash residue was collected and transported as a diluted pulp of 1:5 – 1:10 flying ash : water ratio. It was stored in cases between 3 – 5 m high landfills. High water

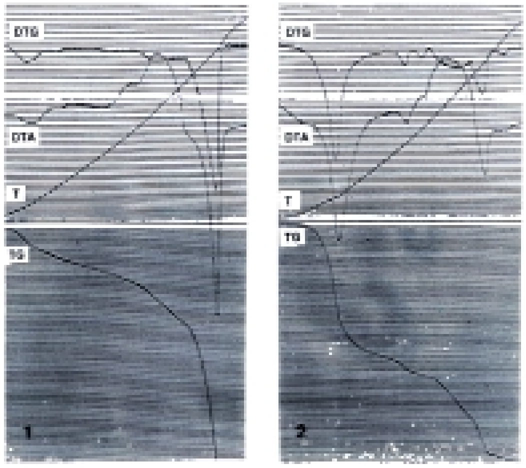

Fig. 3. Vertical differentiation of the mineralogical composition of coherent pulp on the basis of the derivatographic image; 1 – at the top of the pulp; 2 – at the bottom of the pulp (Ajka Power Plant)

Table 1. Chemical features of flying ashes from different coal combusting power plants

Power plant	CaO m %	SO_3 m %
Ajka	32.7	16.7
Inota	22.2	12.4
Mátra		
– clinker	6.2	4.3
– ECO flying ash	7.5	3.9
– Ljungström p.	6.1	0.4
filter p. 1995	9.5	6.3
1996	8.1	4.0
Tatabánya	14.9	8.4

Analyses were made by Erika Csányi in the Department of Construction Materials, Technical University of Budapest.

content caused serious environmental problems.

Elaboration of the so-called thick pulp technology started in the 1980s upon international examples. In this case the flying ash : water ratio equals approximately 1:1. Taking measures for producing uniform pulp mixtures must be therefore given special attention.

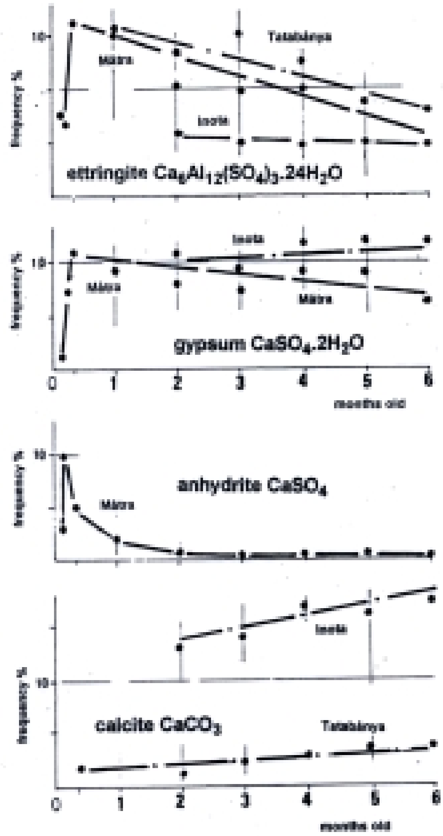

Fig. 4. Evolution of the pulp's mineralogical composition and its variation as a function of maturity

In order to determine the mineralogical composition of the thick pulp produced from fine-grained (0.002 – 2 mm) flying ash of variable chemical composition and solidified and absorbed under water we have completed three different wide-ranging instrumental studies.

– *X-ray diffraction method:* It can be used for determining the quality and the quantity of μ-sized, but crystalline components. (Instrument: PHILIPS DIFFRACTOMETER);
– *Thermic-gravimetric study:* It can be used for determining the quality and the quantity of crystalline and amorphous components modified at specific temperatures while heating (20 – 1000°C). (Instrument: MOM DERIVATOGRAPH);

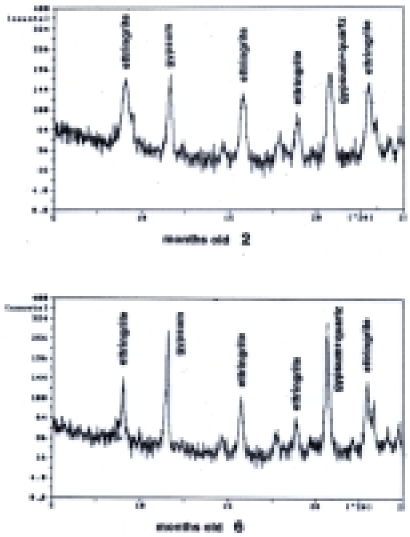

Fig. 5. Evolution of crystallisation rate as a function of the pulp's maturity on the basis of X-ray diffraction image (Mátra Power Plant)

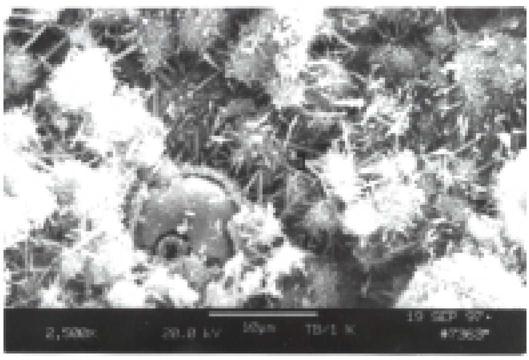

Fig. 6. Seeds of crystallisation on the surface of the fresh pulp. Electron microscopic image magnified 2500 times (Tatabánya Power Plant)

– *Electron microscopic study:* It can be used for the morphological study of the components of preparations covered with Au and C magnified at several thousand times, as well as for determining their chemical element composition on the basis of ED spectra. (Instrument: ARMAY 1830 I/T 6 SCANNING ELECTRON MICROSCOPE).

There are two factors impeding the determination of chemical composition:

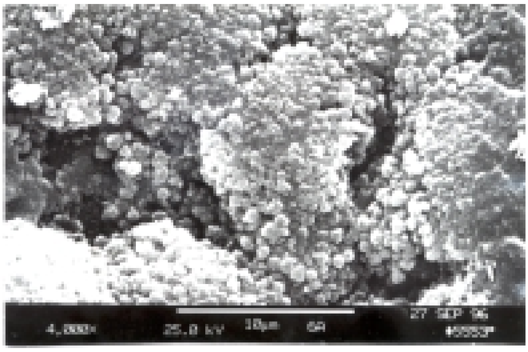

Fig. 7. Encrusting made up of stubby calcite crystalline accumulation developed on the pulp's surface. Electron microscope image magnified 4000 times (Tatabánya Power Plant)

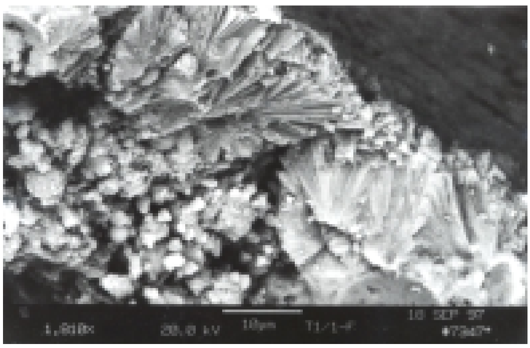

Fig. 8. Calcite layer of radial structure growing inside from the 30-days-old pulp's surface. Electron microscopic image magnified 1810 times (Tatabánya Power Plant)

– The initial flying ash features essentially amorphous components of glassy phase. X-ray analytic methods are inadequate for their identification (*Fig. 2*).

– Flying ash/ash constitutes the residue of coal combustion at 700 – 900°C, thus it is not suitable for thermic analysis, however, it has already an important role in the investigation of thick pulp formed from it. Quality specification is hindered at this point by the fact that sulphur with high environmental impact is absorbed essentially in water- bearing sulphate minerals featuring overlapping thermic-gravimetric peaks.

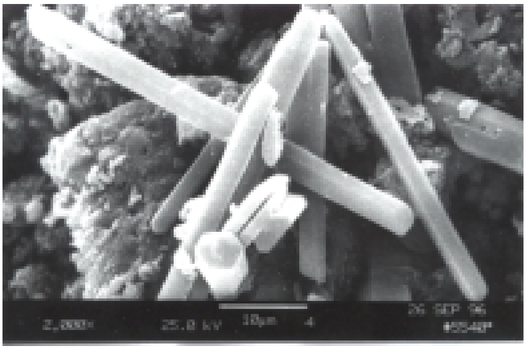

Fig. 9. Gypsum crystals of specific form developed on the surface of the free wall of the superficial cavity. Electron microscopic image magnified 2000 times (Mátra Power Plant)

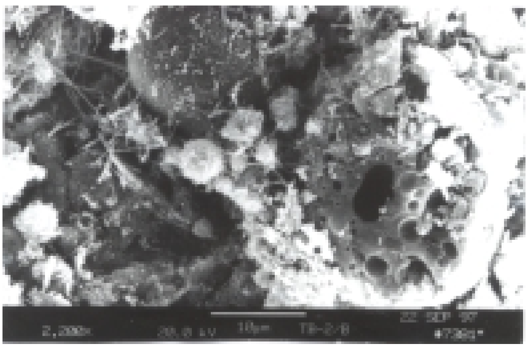

Fig. 10. The inner structure of the fresh pulp is made up of a set of irregular, spherical, amorphous components. Electron microscopic image magnified 2200 times (Tatabánya Power Plant)

3.1. Character of the Mineralogical Composition of Flying Ash Pulp

Samples of variable mixing ratio, size and maturity have been put at our disposal for studying their mineralogical composition. This heterogeneous distribution provided a practical aspect to the investigation.

Mineralogical composition of the flying ash/ash depends basically on the substance of the combusted coal and the overburden. Using the new technology changes this picture by feeding limestone grist in the combustion zone at hybrid-fluid combustion. The hence increased lime content modifies the process of crystallisation, resulting in a pulp of more favourable viscosity and flow property.

Fig. 11. Crystallisation initiated in the pulp's interior with Ca and Al silicate laminae. Electron microscopic image magnified 3040 times (Tatabánya Power Plant)

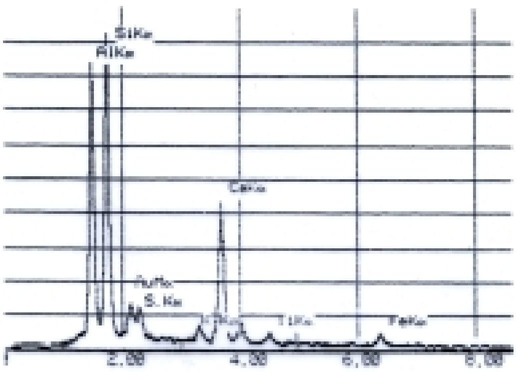

Fig. 12. Laminar mineral precipitation presented in *Fig. 11*. Upon ED spectrum it is Ca and Al silicate (Tatabánya Power Plant)

A remarkable phenomenon was observed on the studied, solidified flying ash thick pulp samples, the surface of the test preparations was namely covered by mm thick calcite-gypsum crust.

Investigation of small samples prepared from the flying ash of the Mátra Power Plant showed that homogenising the pulp of this flying ash of lowest lime content was not successful. We have revealed a considerable difference between the mineralogical composition of the superficial and the average test material of the 6 samples taken from one mixing (*Table 2*). The following experiments with larger samples resulted already in more homogeneous mixtures.

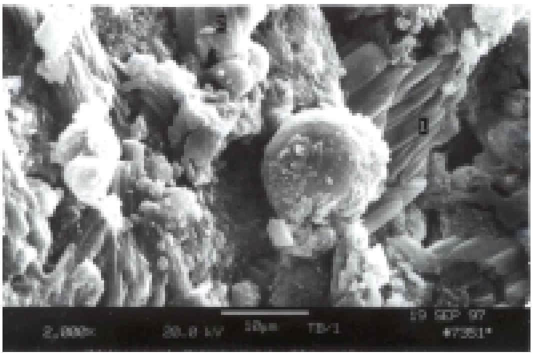

Fig. 13. Cementation made up of Ca-Al silicate (1) and calcite (2) brought about inside the mature pulp. Electron microscopic image magnified 2000 times (Tatabánya Power Plant)

Table 2. Heterogeneous features of the flying ash thick pulp mixture (30-days-old cohesion)

Sample character	Content of principal minerals %		
	Calcite $CaCO_3$	Gypsum $CaSO_4 \times 2H_2O$	Ettringite $Ca_6Al_2(SO_4)_3 \times 24H_2O$
superficial sample 6 items	4 – 6	14 – 32	2 – 6
average sample 6 items	1 – 2	4 – 12	6 – 17

We carried out a detailed study on a 40 cm high solidified (bound for 6 months) pulp block. Upon processing the results we stated that following the deposition a considerable difference occurs between the mineralogical composition of the superficial and deeper strata of the pulp (*Table 3*). As compared to the superficial lime precipitation (79% calcite) calcite content is reduced as low as to 27% in the bottom of the large sample (40 cm depth). At the same time, substantial enrichment in sulphur can be observed with increasing depth absorbed to sulphate minerals. Moreover, precipitation of portlandite ($Ca(OH)_2$) and calcium-hydro-silicate (*Fig. 3*) should be also noted at this point.

The referred differentiation is also reflected in the mass-composition characteristics of the thick pulp. Measurements showed with deepness an increase in bulk density and basic water content and a decrease in connected, active porosity (*Table 4*). It hints at favourable conditions concerning the permeability of the pulp case for a possible dissolution.

Simultaneously with our investigations similar results were summarised by Black & Veatch Engineering Services GmbH, as well as by the staff of the Leopold

Table 3. Vertical differentiation in the mineralogical content of the petrolcoke/brown coal flying ash thick pulp (6-months-old cohesion)

Sample position	Content of principal minerals %					
	Calcite $CaCO_3$	Gypsum $CaSO_4.2H_2O$	Anhydrite $CaSO_4$	Ettringite $Ca_6Al_2(SO_4)_3.24H_2O$	Portlandite $Ca(OH)_2$	Hillebrandite $CaSiO_4.H_2O$
superficial	79	2	1	2	3	–
10 cm depth	48	3	5	8	4	–
20 cm depth	42	4	6	16	10	6
30 cm depth	37	5	7	16	14	10
40 cm depth	27	7	5	21	19	7

Mixing ratio of petrolcoke/brown coal equals 1:10. Combustion took place in the hydro-fluid boiler of the Ajka Power Plant.

Table 4. Mass-composition characteristics of the petrolcoke/brown coal flying ash thick pulp (6-months-old cohesion)

Sample position within the block		Unit weight kg/m^3		Basic water content	Active porosity
		air dry	water saturated	V %	V %
upper part:	5 – 10 cm	1306	710	59.5	71.6
middle part:	20 – 25 cm	1389	751	64.8	70.3
lower part:	30 – 35x cm	1426	799	62.7	67.7

Franzens University of Innsbruck.

The large number of tests indicated that the amount of crystallised calcite, anhydrite, gypsum and ettringite was highly variable as a function of the type of flying ash. At the same time, it has to be stressed that regardless of the type of flying ash, in addition to quartz and wide-spread ferrous minerals, like goethite, siderite and hematite, a large number of other, mainly artificial minerals precipitate amounting to some percents, as follows:

– some other sulphate and sulphite minerals: bassanite, hannebachite;

– clinker minerals: bredigite, brownmillerite, gelenite, mayenite, wollastonite

– calcium-hydro-silicates: afwillite, foshagite, hillebrandite, neokite, okenite, tobermorite, xonotlite.

3.2. Temporal Evolution of the Pulp's Mineralogical Composition

It is well known from the cement industry that some important chemical processes occur within a short period following mixing. Starting from this concept we set out our tests using fresh 4-, 5-, 7- and 10-days-old samples and followed by more mature 1-, 2-, 3-, 4-, 5- and 6-months-old ones.

With regard to the thick pulp produced from different types of flying ash and at different mixing ratios, it can be stated that *precipitation of minerals starts very quickly and its first main phase is over within 30 days.* During our investigations we learned the results of the report made by the Laboratoire Matériaux Durabilité des Constructions of Toulouse on studying calcium-sulphite flaying ashes which came to the same conclusions.

The interpretation of flying ashes from different power plants showed that precipitation and subsequent substantial rise in the amount of ettringite, gypsum and anhydrite occurred quickly, within a few days following mixing (*Fig. 4*). Ettringite decreases afterwards, gypsum stagnates or slightly decreases as well, anhydrite decreases considerably, whereas calcite features a slight increase.

In addition to the changes in mineralogical composition *an increase in the crystallisation ratio* of minerals can also be witnessed with peaks on X-ray diffractograms becoming explicitly prominent (*Fig. 5*).

Major changes and a well-expressed evolution can be also traced upon the morphological study of pulp samples with different degrees of maturity under electron microscope.

Morphological analyses and tests of the element composition (ED spectrum) were carried out on thick pulp samples of 5 – 180-day maturity. Several preparations were made both from the surface and the interior of the pulp.

Crystallisation starts very rapidly on the pulp surface resulting in the formation of several-mm thick white encrusting. Initially, it is a loose, dense accumulation of several μm needle-thread-like crystals, simultaneously impregnating some grains with unbroken cementing crust (*Fig. 6*).

With regard to pulps of high lime content a massive, unbroken, μm-sized crystalline, calcite layer forms on the surface (*Fig. 7*). Subsequently it develops a calcite layer of radial structure growing inside from the surface (*Fig. 8*).

Some beautiful, 30 – 50 μm-sized gypsum crystals of specific form frequently develop on the edge of the cavities of still loose pulp and in its interior (*Fig. 9*).

After a few days, the interior of the pulp features loose structure including grains of different sizes and forms. Apart from frequently porous grains of irregular form, the occurrence of regular spherical sets is a characteristic feature (*Fig. 10*). On the basis of ED spectrum pictures they represent the amorphous phase of Ca and Al silicates. The occurrence of needle- and thread-like crystalline phase is of subordinate importance.

The 60-days-old samples are more solid, they feature higher degree of cementation. Significantly altered and crystallised forms of silicate components also appear as cementing agents (*Figs 11 – 12*). Nevertheless, calcite and occasionally gypsum in the matrix are more prominent (*Fig. 13*).

The gradual cementation of the pulp components is obviously well reflected in the related strength properties as well (*Table 5*).

Table 5. Variation in the strength of thick pulp as a function of water content and maturity (Tatabánya Power Plant)

Maturity of the pulp	Air dry unit weight kg/m^3	Water content m %	Air dry pressure strength N/mm^2
10-days-old	1635	56.4	1.348
2-months-old	1265	24.5	2.268
	1069	8.0	2.485

Analyses were made by Endre Árpás and Gyula Emszt in the Department of Engineering Geology, Technical University of Budapest.

4. Summary

The knowledge of the composition and attitude of the high amount of flying ash released yearly by power plants is of crucial importance from environmental and national economic aspects as well.

The high number of mineralogical investigations realised since 1995 on flying ashes of different chemical and technological features and maturity gave answers to several important questions:

- It can be stated that the sulphur content of combusted coals is closely associated with the amount of limestone occurring in the denudation area being the scene of coal evolution. Coal-bearing sequences of high carbonate content have higher sulphur amount.
- Pulps of higher carbonate content feature lower viscosity, they are easier to transport and homogenise.
- Important vertical differentiation can be observed in the deposition of thick pulp resulting in different mineralogical composition and physical properties. Obviously, the lower level of thick pulp collected in the pulp case is more massive and hygroscopic.
- Precipitation of minerals starts already in the first hours following pulp mixing. Initially a thin, but significant crust forms on the surface.
- The main phase of the development of principal mineral associations takes place during the 30 days after pulp mixing. Subsequently, cementation and the increasing degree of crystallisation are the most characteristic phenomena.

– Within a few months the sulphur content of the pulp becomes absorbed in minerals and a substance of good quality develops applying underwater storage.

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