Mineralogy and chemistry of conventional and fluidised bed coal ashes

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A b s t r a c t . Coal combustion residues represent very abundant inorganic waste materials. The change from conventional combustion of powdered North Bohemian brown coal to its combustion in fluidised bed boilers in several Czech power and heating plants calls for detailed mineralogical and geochemical characterisation of the combustion residues. The main differences between fly ashes from both combustion systems result from different burning temperatures and differing systems of desulphurisation (coeval with combustion / post-combustion). Both these factors influence the chemical and phase compositions as well as the speciation of trace elements. The study further shows that the validity of the surface enrichment model (Linton et al. 1975) can be limited.

K e y w o r d s : brown coal, power plant, conventional coal combustion, fluidised bed combustion, fly ash, mineral composition, trace elements, heavy metals

Introduction

Fly ash is a waste material, generated at a gigascale in the production of electricity and heat. Because of its chemistry and the amounts generated, it represents a potential major environmental concern. The mineralogy and chemistry allow it to serve as a source of materials for large-volume applications, low- as well as high-tech. The applicability of different fly ash types as a secondary source material is determined by their respective bulk mineralogies and chemistries. These result both from coal type and chemistry, and from the coal combustion process used. In the Czech Republic, two major technologies are used: conventional (combustion of pulverized coal in grate boilers) and fluidised bed combustion. The fluidised bed combustion (FBC), belonging to new, "cleaner" coal combustion technologies, generates coal combustion residues (CCRs) distinctly different from residues from conventional combustion. The differences occur in many aspects, involving mineralogy, major- and minor-element chemistry, mechanical and rheological properties.

The intended large-scale production of these materials has to be assessed carefully, at best assisted by mineralogical studies of the bonding of potentially hazardous elements (PHEs) and its durability. This article considers environmental aspects of the fluidised bed combustion of North Bohemian brown coal, as compared to conventional combustion.

More than 85% of power generation in the Czech Republic is realised through brown coal combustion. This coal is mined in the North Bohemian Coal Basin. Although its chemistry and mineralogy vary broadly, it can be generally described as high-S lignitous coal of relatively low calorific value (10–20 MJ.kg⁻¹). Large-scale combustion of this coal, performed in power plants not equipped with desulphurisation units in the past, has caused serious damage to the environment by introducing large volumes of sulphur dioxide and other hazardous compounds into the atmosphere. After 1989, the Czech government agreed to drastically decrease the emissions of sulphur dioxide. Desulphurisation of all power plants was accomplished in 1999; besides that, several power / heating plants were converted to fluidised bed combustion. In spite of the dramatic drop in gaseous emissions, neither the conventional boilers with wet or semi-dry limestone scrubbing, nor fluidised bed furnaces produce less solid CCR. Moreover, the volume of combustion residues is increased by additives or washing agents introduced into the burned coal (FBC) or flue gas (desulphurisation). The mineralogy and chemistry of fly ashes from conventional coal combustion are relatively well known, although mostly on bulk level, while FBC products (bottom ash, fly ash) are known to a much lesser degree. Bulk concentrations of trace elements in FBC ashes from North Bohemian lignite were studied by Smolík et al. (1998), a.o.

Material and methods

Material studied

This paper provides results of a detailed study of FBC ashes from a set of experiments performed in an atmospheric FBC pilot plant in Mazingarbe (France) with four model types of North Bohemian brown coal, differing in calorific value and sulphur content. The principal properties of the used coal types are given in Table 1.

The four coal types were combusted with four different additives (2 limestones ± lime, dolostone) under different oxygen inputs to the furnace (to meet two different emission limits). The total number of coal/additive/com-

Table 1. Principal properties of coal types used in the experiments.

Coal type / property	S3 (6)	S3/1 (2)	S4 (5)	V3 (4)	Average
Qr	14.69	17.09	16.08	16.21	15.74
Wtr	30.15	29.06	30.5	33.07	30.81
Ad	22.38	15.39	18.35	13.1	18.19
Sd	3.62	2.3	5.75	3.34	4.03
Smr	1.72	0.96	2.49	1.38	1.78

Explanation: Qr – calorific value (MJ.kg^{-1}), Wtr – water content of coal, Ad – ash content (wt%), Sd – sulphur content (wt%), Smr – specific sulphur content (gS/MJ).
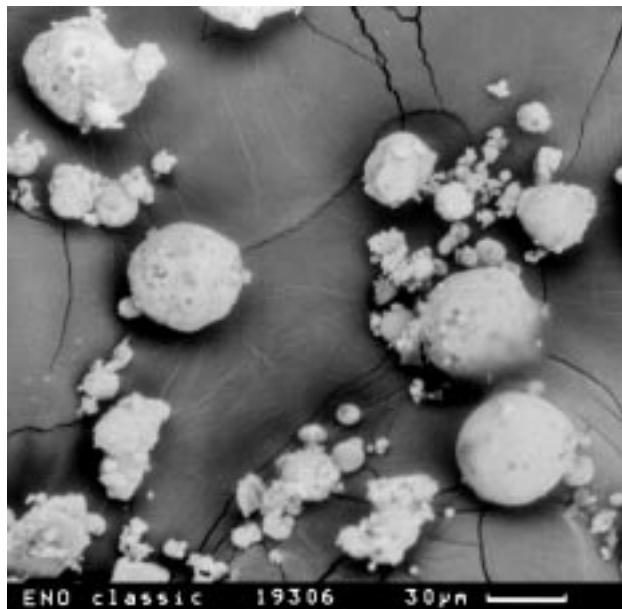

Fig. 1. Spherical nature of most particles of fly ash from conventional burning of North Bohemian brown coal. SEM – backscattered electron image (BEI).
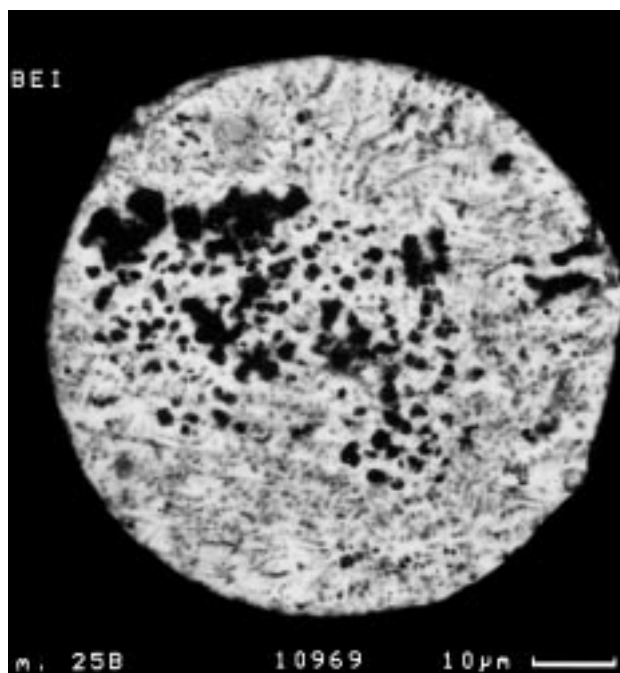

Fig. 2. A cross section of an ash particle composed of magnesioferrite (dark grey) and dicalciumferrite (brighter grey). SEM – BEI.

bustion conditions combinations was 18. Besides, an average coal was combusted in a conventional furnace. Other studied fly ashes from conventional grate furnaces come from power and heating plants of Poříčí, Dvůr Králové and Přerov n. Labem.

Coal and fly ash analysis

The bulk chemistry of coals and FBC ashes was determined by XRF analysis + wet chemistry (see Tables 2 and 3). Bulk mineralogy was determined by powder X-ray diffraction. Special attention was paid to the form of occurrence of toxic elements, which was assessed from the chemistry of individual coal and fly ash particles by grain-by-grain electron microprobe analysis, involving EDS determination of major components and WDS determination of trace elements. The results of microprobe analyses were processed by statistical methods (ANOVA, factor analysis, correlation analysis).

Table 2. Chemical composition of the coal types used in experiments (F and Cl in wt%, other trace elements in ppm).

Element	S3 (6)	S3/1 (2)	S4 (5)	V3 (4)	Average
F	0.017	0.017	0.019	0.019	0.018
Cl	0.021	0.02	0.019	0.018	0.020
As	385.8	251.6	517	288.5	393.0
Ba	227.5	138.7	89.8	170.2	159.0
Cd	8.6	1.8	3	65.4	18.6
Co	42.1	15.8	51.4	35.2	40.7
Cr	30	12.8	18.5	37.3	25.9
Cu	12.6	7.9	11.3	17.4	12.7
Ni	35.6	19.4	39.2	34.4	34.7
Pb	23.7	9.7	14.6	40.6	22.9
V	42.7	21.9	27.1	46.9	36.1
Zn	84.7	41.7	64.8	119	80.9

Table 3. Average values (95 % confidence intervals) of individual streams of CCR from all 18 FBC experiments.

|	Bottom ashes	Filter-trapped ashes	Cyclone-trapped ashes
CaO (%)	1.6 + 0.2	2.9 + 0.4	7.3 + 1.3
CaSO$_4$ (%)	35.2 + 1.8	20.7 + 0.5	16.6 + 12.3
CO$_2$ (%)	0.6 + 0.0	1.3 + 0.1	2.8 + 2.1
CaCO$_3$ (%)	1.3 + 0.1	2.8 + 0.2	6.8 + 5.0
residual CaO (%)	14.5 + 0.8	8.6 + 0.2	11.2 + 8.3
SiO$_2$ (%)	31.4 + 2.2	28.1 + 0.7	31.6 + 23.4
TiO$_2$ (%)	0.5 + 0.0	1.3 + 0.0	0.7 + 0.5
Al$_2$O$_3$ (%)	7.7 + 0.3	14.9 + 0.4	11.3 + 8.4
Fe$_2$O$_3$ (%)	4.1 + 0.1	12.8 + 0.3	8.7 + 6.5
MnO (%)	0.03 + 0.00	0.05 + 0.00	0.04 + 0.00
MgO (%)	1.0 + 0.1	4.3 + 0.5	3.1 + 2.3
Na$_2$O (%)	0.12 + 0.01	0.21 + 0.01	0.13 + 0.10
K$_2$O (%)	0.9 + 0.04	1.4 + 0.2	1.2 + 0.9
loss on ignition (%)	1.3 + 0.1	2.7 + 0.1	3.9 + 2.9
As (ppm)	665 + 163	1789 + 331	557 + 111
Ba (ppm)	102 + 33	187 + 61	119 + 80
Co (ppm)	28 + 5	98 + 23	97 + 34
Cr (ppm)	72 + 17	141 + 24	130 + 40
Cu (ppm)	38 + 15	61 + 9	53 + 15
Ni (ppm)	39 + 5	108 + 15	99 + 30
V (ppm)	87 + 16	224 + 24	154 + 55
Zn (ppm)	124 + 20	263 + 127	236 + 54
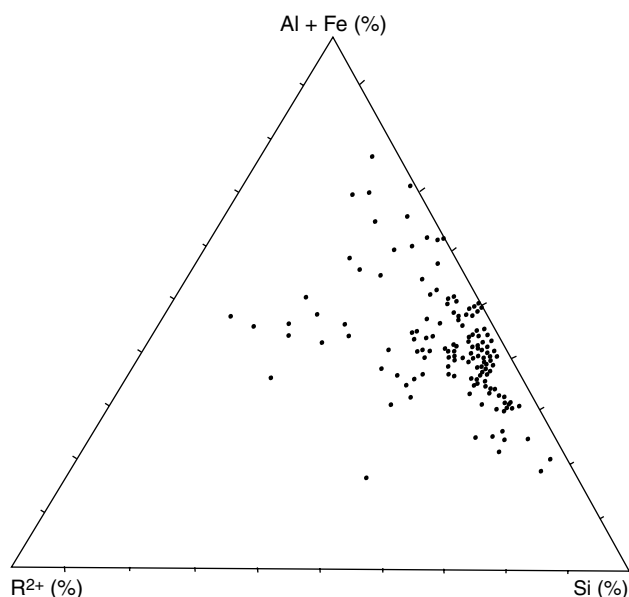
Fig. 3: Ternary plot of microprobe analyses of glass particles from conventional burning of North Bohemian brown coal.

Table 4. Speciation of trace elements in coals used in the experiments, as revealed by factor analysis of microprobe analyses of coal components.

Element	Main forms of occurrence	Minor forms of occurrence
Arsenic	in iron disulphides, minor part bonded directly in organic matter	in organic matter and accessory ore minerals
Baryum	in barite and crandallite group minerals	in K-feldspar, illite, kaolinite
Tin	in cassiterite	
Fluorine	in apatite, mica and clay minerals	in organic matter, amphibole
Phosphorus	in apatite and crandallite group minerals	in organic matter
Chromium	in clay minerals, mica, framboidal pyrite	in magnetite
Cadmium	in sphalerite	
Cobalt	in iron disulphides	in haematite
Manganese	in carbonates, iron oxides	
Copper	in chalkopyrite, admixture in pyrite	
Nickel	in pyrite, millerite	in organic matter
Lead	in galenite	
Thorium	in monazite, less in xenotime and zircon	
Vanadium	in clay minerals, organic matter	
Uranium	in uraninite	in organic matter, zircon
Zinc	in sphalerite	

Results

Mineralogy and geochemistry of North Bohemian brown coals

The CCR composition is controlled by the mineralogy of the combusted coal. From this point of view, the most important coal properties are the content and nature of iron disulphides and clay minerals. Iron disulphides are represented by pyrite and marcasite. Pyrite occurs in several genetic types, syngenetic as well as epigenetic. Among the syngenetic types, framboidal pyrite is the most common. The North Bohemian brown coals usually contain high amount of arsenic, which is one of the most hazardous trace elements involved in coal combustion – both due to its abundance in coal (usually several hundred, locally up to several thousand ppm) and to its volatility. The electron microprobe study of North Bohemian lignite revealed that arsenic occurs both in the coal matter and in pyrite. Of the pyrite types, vein-type epigenetic shows the highest As level (up to 3000 ppm). The speciation of other potentially hazardous elements revealed by electron microprobe study is summarised in Table 4. Notable is the affiliation of chromium with framboidal pyrite; Cr probably enters the structure of sheet silicates embedded within pyrite framboids.

The concentration levels of trace elements in North Bohemian brown coals were previously reported by Bouška et al. (1994), a.o.

Fly ashes from conventional pulverized coal combustion

The mineralogy of fly ashes from conventional burning is controlled by the composition of non-combustible (ballast) coal minerals, the proportions and contents of individual mineral species in the coal, and the conditions in the furnace (oxidative/reductive atmosphere, temperature in the furnace and the homogeneity of its distribution, grain size of the ground coal, retention time of coal grains in the furnace, etc.). The principal feature of most con-
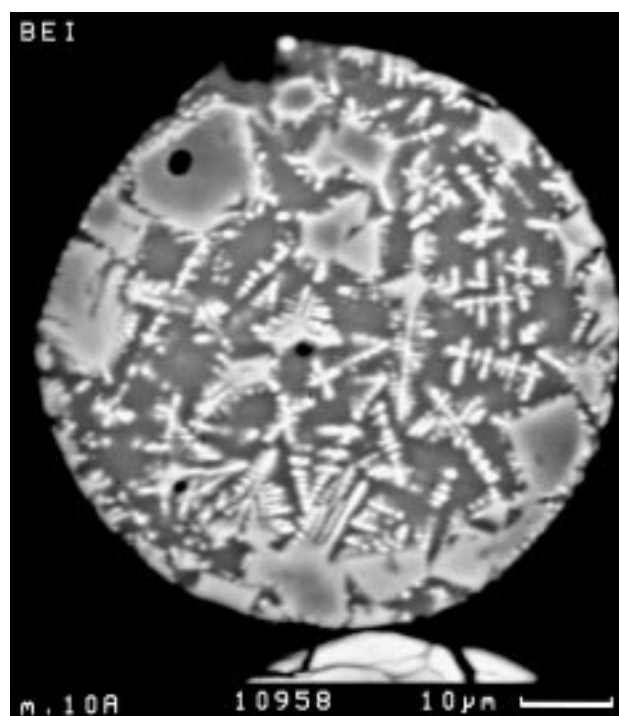

Fig. 4. A cross section of a fly ash glass particle with zoned Mg-spinel crystals (conventional burning, North Bohemian brown coal). SEM – BEI.
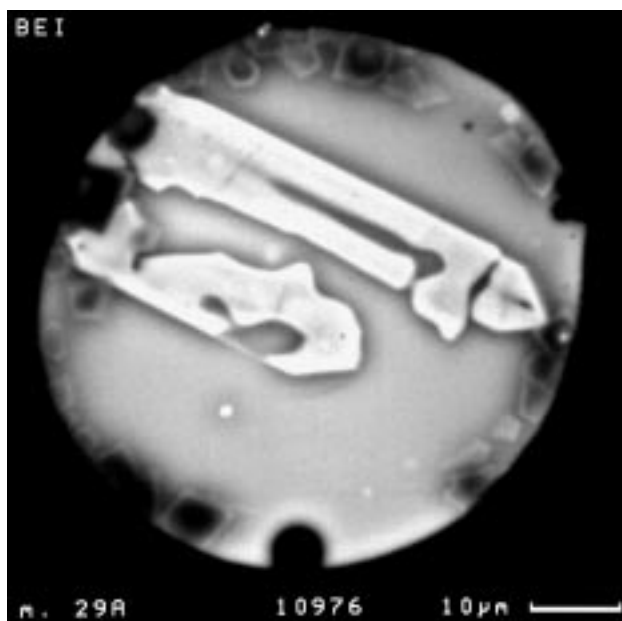
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Fig. 5. A cross section of a fly ash glass particle with zoned Mg-spinel crystals at the rim and zoned, corroded olivine crystals in the core (conventional burning, North Bohemian brown coal). SEM – BEI.
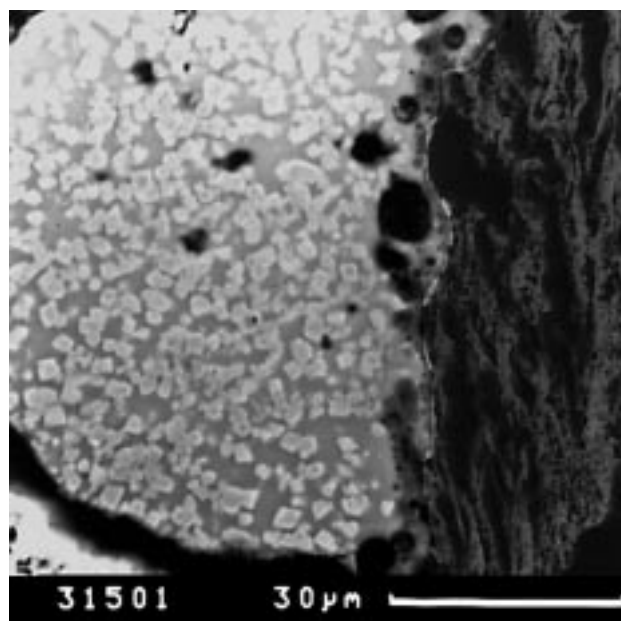

Fig. 6. A cross section of a compound fly ash particle: left part – glass with evenly distributed zoned spinel crystals, right – porous coke (conventional burning, North Bohemian brown coal). SEM – BEI.

ventional furnaces is the high temperature, usually between 1400 and 1500 °C.

Fly ashes from conventional coal combustion are characterised by a prevalence of spherical particles (Fig. 1), formed by glass matrices including crystals of mullite and spinel minerals (above all magnetite). Less common are spherules consisting of Ca- and Mg-oxides (di-calcium ferrite or Mg-ferrite – see Fig. 2). The glass matrix of the majority of fly ash particles shows a quite uniform chemistry, corresponding to illite or kaolinite, as shown by microprobe analyses plotted in Fig. 3. Ca-rich glass known from Lower-Saxony brown coal combustion residues (Enders 1995) was not observed. The most common phases in glass among them are spinel-type phases (mostly magnetite and hercynite), and various silicates – e.g. mullite, olivine, pyroxene, sillimanite, wollastonite, melilite. Spinels often occur as skeletal crystals and their aggregates (Figs 4–6). In many cases they display distinct zoning (Fig. 4), especially in Mg and Fe contents (the rims are distinctly richer in Fe). Similar zoning has been observed in crystals of olivine-type compounds (Fig. 5). Spinel crystals are either dispersed throughout the glass spherules (Figs 6, 7), or concentrated along particle rim

(Fig. 8). Magnetic spherules as either are often composed solely of magnetite crystals – octahedra (Fig. 9) or skeletal crystals (Fig. 10), forming feathery or fan-like aggregates (see Fig. 11). The spatial organisation of closely packed magnetite octahedra resembles very much that of pyrite framboids (Fig. 12), which represent the most common form of pyrite in the North Bohemian lignitous coal. It seems to be quite probable that at least a part of these magnetic beads were formed by direct conversion of framboidal pyrite into "framboidal magnetite".

Spinels in conventional fly ashes often adopt increased amount of certain toxic elements in their structure, both in the M^{2+} (Zn, Mn), and M^{3+} (V, Cr) positions. Other separately occurring crystalline phases of fly ash are cristobalite and haematite. The abundance of coke particles very much depends upon the conditions in the furnace; they are usually spherical and very porous. The overview of mineral-equivalents observed in conventional fly ashes from combustion of North Bohemian brown coal is given in Table 5.

The presence of certain phases in the studied fly ashes, however, indicates that the temperature of fly-ash formation, hence also the real temperature of combustion,

Table 5. The overview of mineral-equivalents observed in conventional fly ashes from combustion of North Bohemian brown coal.

Most abundant:	glass, quartz, mullite, char, magnetite, haematite, meta-kaolinite
Abundant:	rutile, plagioclase, sillimanite, MAGHEMITE, hercynite, spinel, magnesioferrite
Less common:	anatase, goethite, cristoballite, micas, olivine, pyroxene, barite, celestite, magnesioferrite, dicalciumferrite, pyrrhatite, sphalerite, gypsum (alteration product), IRON OXYSULPHIDE, siderite, ankerite, fayalite, wollastonite
Rare:	tridymite, K-feldspar, calcite, BA-MELILITE, (Ca,Ba,Sr) SULPHATE-ARSENATE, METALLIC LEAD +METALLIC TIN, MCKINSTRYITE ($Cu_{0.8}Ag_{1.2}S$), Ba-TUNGSTATE, Ba-TUNG-STATE-SULPHATE, Ba-TUNGSTATE-OXIDE, zircon, magnesian siderite, witherite, Ba_2SiO_4 (BARIUM OLIVINE), $SnCl_2$, AgCl, cassiterite, baddeleyite, ZINCITE (ZnO), LITHARGITE (PbO), BUNSENITE (NiO)

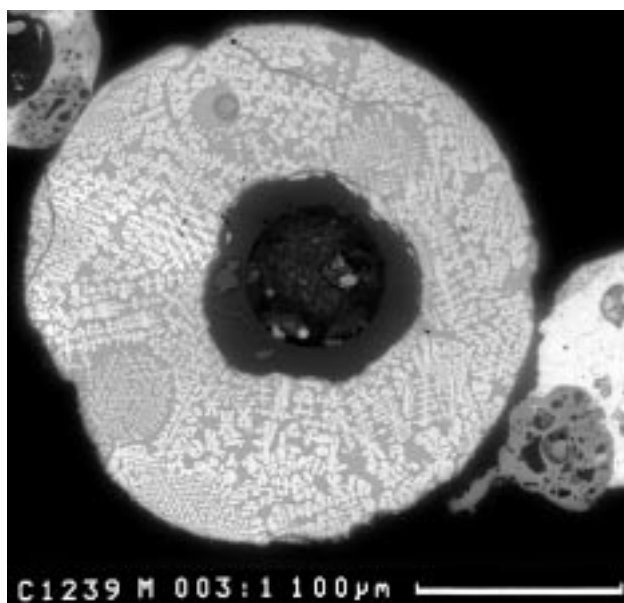Notice: regular font – a previously found mineral; CAPITALS – minerals discovered by the author

Fig. 7. A cross section of a hollow glass – magnetite particle, probably composed of several smaller spherules (conventional burning, North Bohemian brown coal). SEM – BEI.

Fig. 9. Hollow fly ash particle (conventional burning, North Bohemian brown coal) formed by magnetite crystals. SEM – secondary electron image (SEI).

was locally markedly lower than the usual 1400–1500 °C. One of them is the abundance of irregular glass particles, embedding clay aggregates, quartz, pyrite, pyrrhotite, sphalerite, i.e. minerals that cannot withstand the above temperatures unaltered. The presence of Ag-Cu sulphide (analogue to mineral mckinstryite) indicates that the transformation temperature of some coal/fly ash grains can be as low as 500 °C. Additional evidence of quite low temperatures of particle formation is the presence of Ca-Sr-Ba arsenates/sulphates (for composition see below). Ac-

cording to the experiments performed by Hirsch et al. (2000) at temperatures of 570–830 °C and in the absence of particulates, arsenic initially condenses as As_2O_3 rather than thermodynamically favoured As_2O_5. As(V) was only observed by them at these temperatures when calcium was added to the system, leading to the formation of calcium arsenate. It was concluded that the formation of arsenic(V) in combustion systems requires either the oxidation of As_2O_3, which appears to be a kinetically limited process, or the presence of reactive calcium compounds. This means that arsenic should form at the usual firing temperatures volatile As_2O_3 during combustion of low-
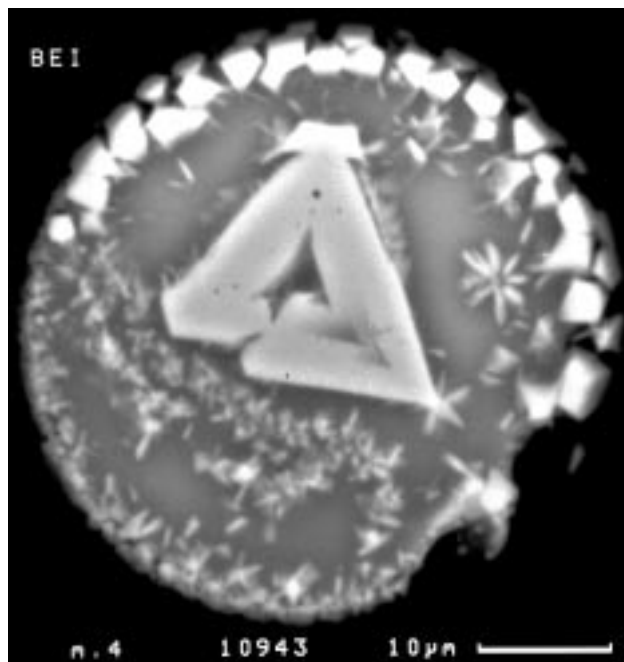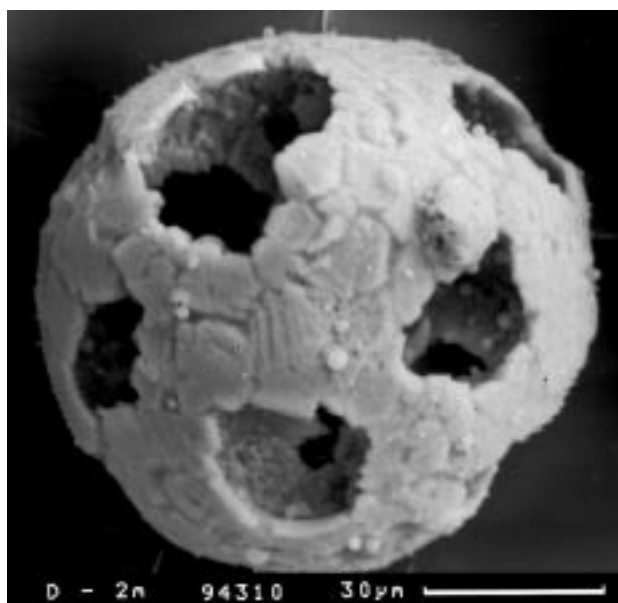

Fig. 8. A cross section of a glass spherule with spinel (magnetite) crystals arranged along the rim. Large crystal in the centre is also spinel. Fly ash from conventional burning of North Bohemian brown coal. SEM – BEI.a
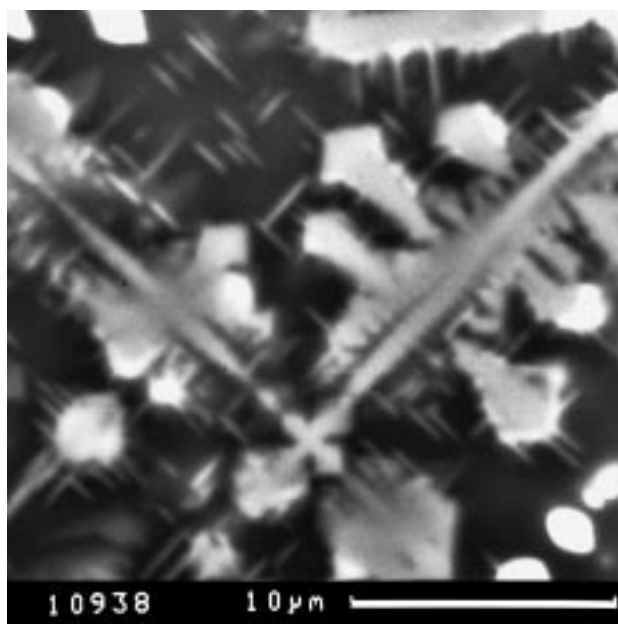

Fig. 10. A close-up of a cross section of a glass particle with skeletal, dendritic Mg-Fe spinel crystals (white – pure magnetite). Fly ash from conventional burning of North Bohemian brown coal. SEM – BEI.
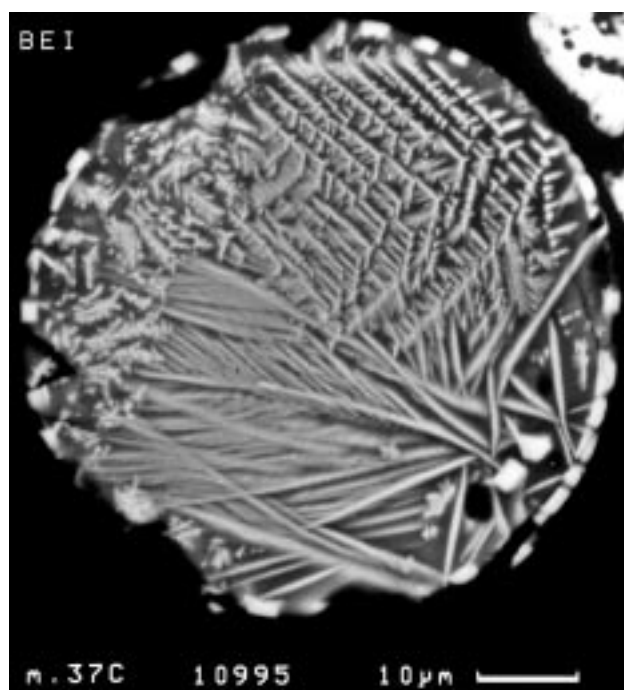
Fig. 11. A cross section of a glass spherule with abundant magnetite laths, arranged in fan-like aggregates. Fly ash from conventional burning of North Bohemian brown coal. SEM – BEI.

calcium coal, while coals high in calcium yield calcium arsenites and arsenates. All the studied ash samples contained only minor calcium contents (0.6–2.5 % CaO); thus the presence of Ca-Sr-Ba arsenates/sulphates is probably rather an evidence of a low formation temperature.
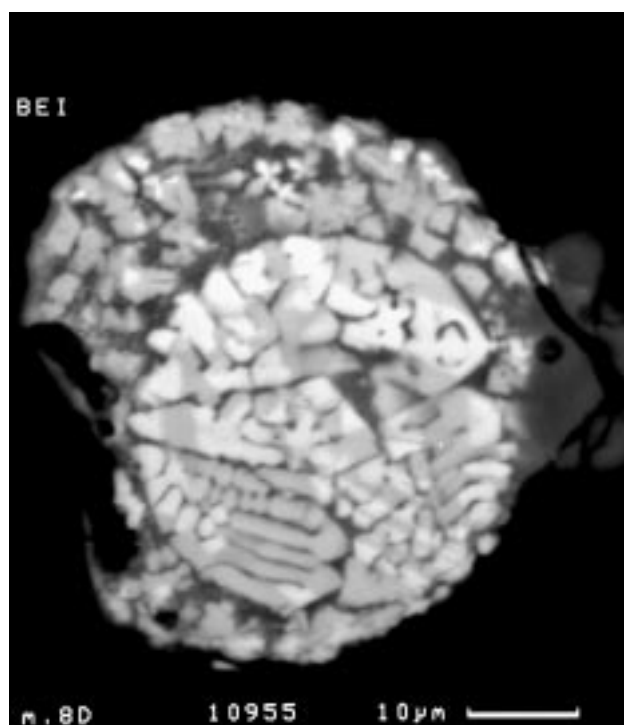

Fig. 12. A cross section of a matryoshka-style magnetic fly ash particle composed of magnetite (white) and Mg-spinel (grey). Fly ash from conventional burning of North Bohemian brown coal. SEM – BEI.

6

The mode of occurrence of trace elements

In the residues from conventional combustion of North Bohemian brown coal, trace elements have been observed to occur in the following forms:

Arsenic was found mostly in sulphates-arsenates of calcium, strontium and barium, forming small (usually 1–5, maximum 12 microns in diameter), isometric particles with radiate textures. Their observed presence in fly ashes supports the deduction of Hirsch et al. (2000) that calcium embedded in silicate fly ash may be capable of forming calcium arsenate, and their relative abundance in high-As fly ashes indicates that the extent of this reaction, taken as unclear by them, can be relatively wide.

Another form (not observable by electron microprobe study, but highly probable) is the surface enrichment described as the principal mode of occurrence of volatile elements by Linton et al. (1975). Arsenic levels in the most common phases – glass, SiO_2 polymorphs, spinel minerals – are well below the microprobe detection level (100 ppm); in some cases, concentrations slightly exceeding that level were found in haematite.

Barium occurs in a variety of mineral phases: barite, Ba silicate ("Ba-olivine"), barium arsenate-silicate, barium phosphate-silicate, celsian, Ba-Fe aluminosilicate analogous to melilite, barium carbonate (witherite), barium tungstate-sulphate, barium oxide-tungstate. Their compositions, given as empirical formulae:
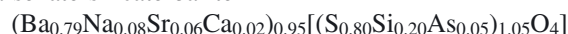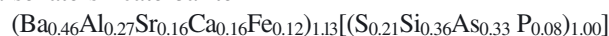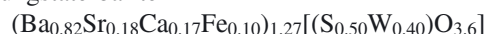
barite

$Ba_{0.97}Ca_{0.03}(SO_4)$

silicate-barite

$(Ba_{0.94}Sr_{0.09}Al_{0.08}Ca_{0.04}Fe_{0.03})_{1.17}[(S_{0.73}Si_{0.29})O_{4.12}]$

arsenate-silicate-barite

$(Ba_{0.79}Na_{0.08}Sr_{0.06}Ca_{0.02})_{0.95}[(S_{0.80}Si_{0.20}As_{0.05})_{1.05}O_4]$

arsenate-silicate-barite

$(Ba_{0.46}Al_{0.27}Sr_{0.16}Ca_{0.16}Fe_{0.12})_{1.13}[(S_{0.21}Si_{0.36}As_{0.33}P_{0.08})_{1.00}]$

tungstate-barite

$(Ba_{0.82}Sr_{0.18}Ca_{0.17}Fe_{0.10})_{1.27}[(S_{0.50}W_{0.40})O_{3.6}]$

Ba oxide-tungstate

$(Ba_{1.22}Fe_{0.39}Sr_{0.23}Al_{0.17}Pb_{0.03})_{2.032}[(O/WO_4)]$

Ba-feldspar (celsian)

$(Ba_{1.08}Fe_{0.07})_{1.14}[(Si_{2.00}Al_{1.69}Fe_{0.31})_{4.0}O_8]$

Ba-Fe melilite

$(Ba_{1.41}Fe_{0.42})_{1.83}(Fe_{0.86}Al_{0.14})_{1.0}[(Si_{1.41}Al_{0.59})_2O_7]$

witherite

$BaCO_3$
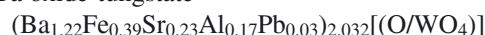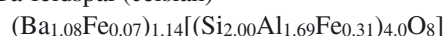
Cadmium is mostly present in spinels: these form fine crystalline (sometimes skeletal) inclusions in glass spheres; less often individual grains. Sphalerite, which sometimes survives combustion, may contain elevated concentrations of Cd. Cadmium in this form is more likely to be released in aqueous media than Cd fixed in spinels.

Copper occurs in Ag-Cu sulphides, which are unstable above 300 °C (indication of low firing temperature inside some coal particles). They are decomposed by aqueous solutions. Whereas Ag, released on decomposition by
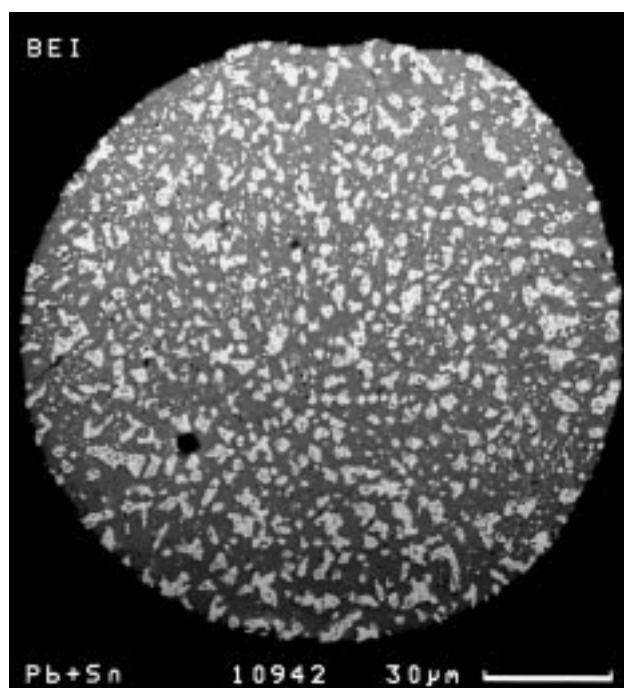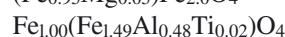
Fig. 13. A cross-section of a fly ash particle, formed by pure lead (lighter) and pure tin (darker). Fly ash from conventional burning of North Bohemian brown coal. SEM – BEI.

Fig. 14. A cross-section of an irregularly shaped particle composed of magnetite (the darkest crystals), tungstenian barite (medium-grey laths) and barium tungstate (white interstitial phase). Fly ash from conventional burning of North Bohemian brown coal. SEM – BEI.

aqueous solutions, precipitates soon, Cu may travel farther. Copper was also occasionally found in spinel phases at low levels (0.0X%).

Chromium is a common minor component in several oxide, spinel species (including magnetite) and maghemite. With the exception of maghemite, chromium is quite firmly fixed. Traces of chromium were also detected in glass and in some sulphates.

Iron occurs in pyrrhotite (FeS) and iron oxysulphide (FeOS), as ferrites (dicaldumferrite, etc., easily decomposed); as magnetite and other spinels, haematite, maghemite, siderite, olivine, and in numerous aluminosilicate phases embedded in glass. Phases with iron as the major component often contain high concentrations of some heavy metals. The least harmful appears to be the presence of these elements in spinel minerals, where chromium can replace M^{3+}. The variability of spinel phases is shown by the following empirical formulae:
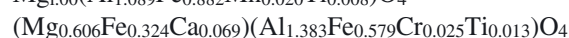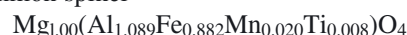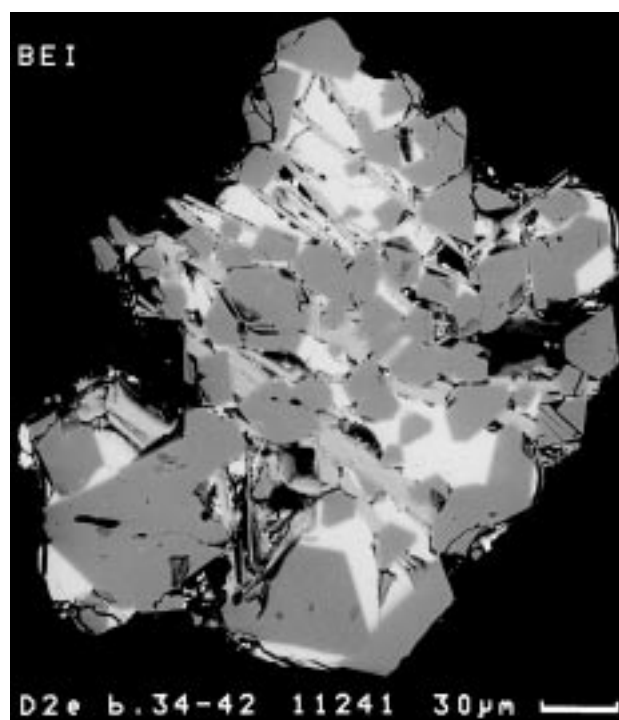
magnetite

$(Fe_{0.95}Mg_{0.05})Fe_{2.0}O_4$

$Fe_{1.00}(Fe_{1.49}Al_{0.48}Ti_{0.02})O_4$

$Fe_{1.00}(Fe_{1.94}Al_{0.62})O_{3.90}S_{0.10}$

hercynite

$Fe_{1.00}(Al_{1.403}Fe_{0.507}Ti_{0.026})O_4$

common spinel

$Mg_{1.00}(Al_{1.089}Fe_{0.882}Mn_{0.020}Ti_{0.008})O_4$

$(Mg_{0.606}Fe_{0.324}Ca_{0.069})(Al_{1.383}Fe_{0.579}Cr_{0.025}Ti_{0.013})O_4$

Ni-Fe spinel

$(Ni_{0.82}Co_{0.07}Zn_{0.06}Cd_{0.05})(Fe_{1.79}Al_{0.08}Sn_{0.07}Ti_{0.05})O_{4.01}$

Lead was found to form spherical to oval particles

5–110 microns in diameter, composed of graphically intergrowing pure lead and pure tin; lead appears to be the "host" phase (Fig. 13). Scarce occurrences of PbO (lithargite-like) coatings were observed.

Nickel is present in several forms. A part of the bulk content is usually fixed in refractory spinels, which are ac-
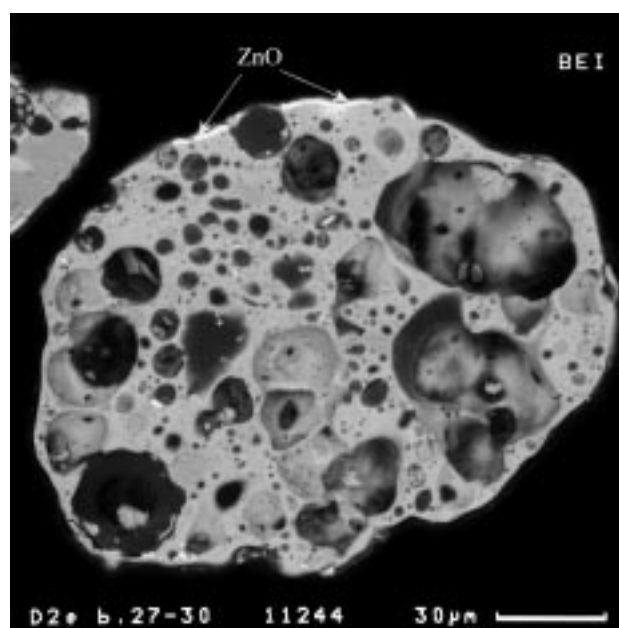

Fig. 15. A cross section of a porous glass particle with a thin crust of condensed ZnO. Fly ash from conventional burning of North Bohemian brown coal. SEM – BEI.
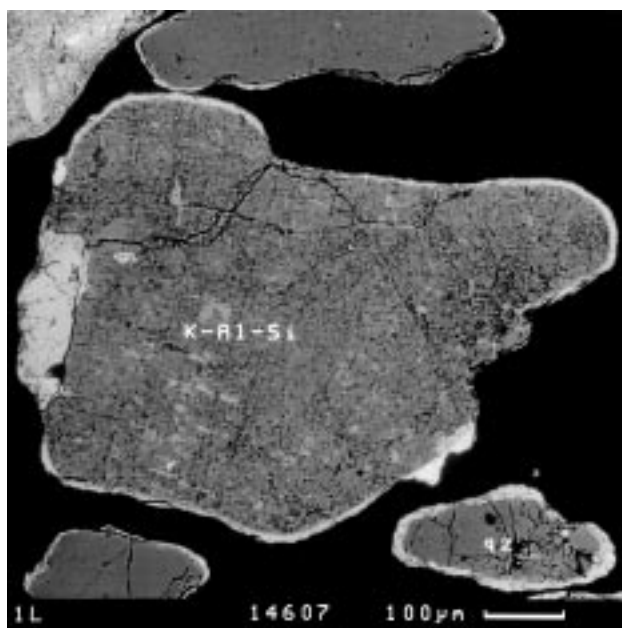
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Fig. 16. A cross section of a K-feldspar/quartz grain, encrusted by haematite. Fly ash from fluidised bed combustion of North Bohemian brown coal. SEM – BEI.
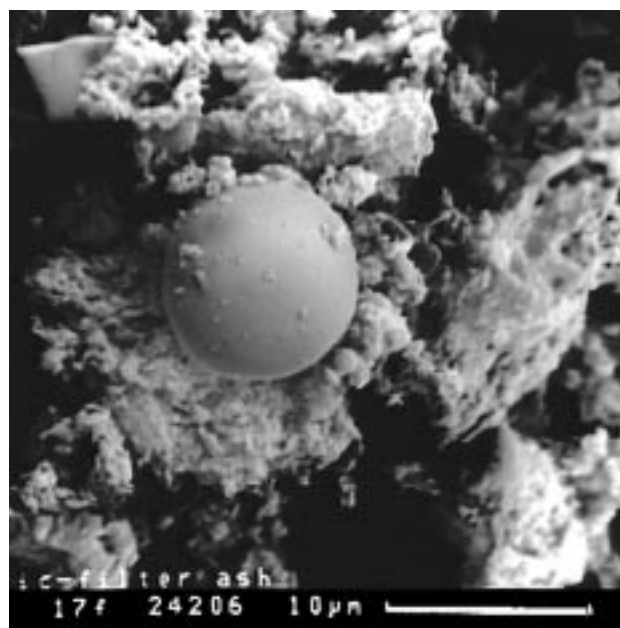

Fig. 17. A scarce spherical particle among irregularly shaped particles of fly ash from fluidised bed combustion of North Bohemian brown coal. SEM – SEI.

tually refractory phases. A certain amount of Ni is sometimes bonded to the glass phase (potentially decomposable during long-term storage). The most interesting but less abundant form of Ni is a separate NiO phase occurring in intergrowths with Ba tungstate crystals (Fig. 14). This phase could become dissolved under acid conditions.

Silver occurs in the form of AgCl and copper-silver sulphide. Both phases can easily decompose and release Ag in the environment.

Tin is present as pure metal, intergrown with metallic lead, in residual cassiterite, as a minor component in spinel, and in SnCl$_2$. Only Sn linked with the last form is likely to be liberated in aqueous solutions.

Tungsten occurs as barium tungstate-oxide or barium tungstate-sulphate phases (Fig. 14), which have not been described in fly ash yet.

Vanadium accompanies some oxidic iron phases, mainly magnetite and maghemite. The latter is a quite reactive compound, and vanadium (as well as chromium) contained in maghemite can be released on decomposition easier than that bonded to magnetite or haematite.

Zinc occurs either in sphalerite, or as an admixture of the gahnite component in some spinel species. In both cases it may be accompanied by cadmium. Zinc was also observed in thin (0.X–1.2 μm) coatings on the surface of some ash particles (Fig. 15).

The important information acquired through this extensive microprobe study is the relative abundance of "concentrated" forms of trace elements in fly ash from conventional coal combustion. Earlier studies devoted to fly ash concluded that the increase in some trace elements in finer classes is solely a result of condensation of volatile elements on the surface of all particles. Neither

the original (Linton et al. 1975) hypothesis, nor a modified version (Smith et al. 1979), accounted for the presence of volatile elements in the form of proper minerals, or as an appreciable admixture in other phases. This author has found many phases containing high amounts of elements considered as volatile (Pb, Sn, As, Zn) or transient (semi-volatile – Ni, Cu, Ba, Sr). The most interesting of these are spheres formed of pure Pb and pure Sn. Calculation shows that such a particle, 20 microns in diameter, contains an amount of lead equivalent to a 10 nm surficial layer enriched in Pb to 500 ppm (maximum value found by Lichtman and Mroczkowski 1985), deposited on 400 000 particles of the same diameter. It is therefore evident that the presence of such particles rich in some trace elements can dramatically influence the mass balance of these elements, i.e. decrease the proportion of this element, which condensed on the surface of all particles. Similar behaviour was observed in other volatile as well as transient toxic elements, e.g. arsenic, tin, tungsten, and especially barium. Some of the very recent studies focused on the volatile toxic elements in coal combustion expect their existence in larger particles (Senior et al. 2000).

The content of volatile elements (As, Pb, Zn) in fly ashes from conventional coal combustion is lower than in fluidised bed ashes (Mumford and Lewtas 1982, Morgan et al. 1997); the difference represents the amount of volatilised elements escaping with flue gas into the environment.

Due to the entry of many potentially hazardous elements into the structure of crystalline phases that are very stable under ambient disposal conditions, more than 70% of all studied potentially hazardous elements are insoluble

in aqueous solutions likely to come into contact with them (rainwater, subsurface water). This applies, above all, to spinel-forming elements like chromium, vanadium, nickel and zinc, although zinc was also found in the form of ZnO coatings on the surface of fly-ash particles. The contents of trace elements in glass in most cases are much lower than those of crystalline phases occurring in glass globules, which corresponds to their low melt/spinel (olivine, melilite) partition coefficients. The only exclusion may be copper; its contents in North Bohemian brown coals are generally low (8–17 ppm).

Fluidised bed combustion ashes

Mineralogy of FBC ashes

The mineralogy of FBC ashes is very different from that of ashes from conventional burning, reflecting the distinctly lower combustion temperatures and the presence of alkaline additives. Although the so-called bottom ash (coarser ash particles collected at the bottom outlet from the FBC furnace) and fly ash collected by textile filters or cyclone collectors differ in proportions of the main mineral constituents, their mineral composition is generally the same. It is characterised by the presence of mineral components of coal, which are either not altered and crystalline (quartz, feldspars), or only slightly thermally altered and amorphous (metakaolinite, metaillite). Other characteristic components of FBC ashes are products from the reaction of sulphur dioxide from decomposed iron disulphides with additives (Mg and/or Ca carbonates and oxides). Among the crystalline components of FBC ashes, anhydrite is the most abundant (17 to 30% in average; some bottom ashes contain over 45% of anhydrite). Microprobe analyses of calcium sulphate aggregates show in most cases the atomic ratio Ca/S ~ 2–3 : 1.

The differences between filter- and bottom ashes are most distinct in the percentage of haematite. The finer ash fractions (trapped by baghouse filters or cyclone collectors) contain usually at least 3 times as much haematite as the bottom ash. Haematite forms by oxidation of iron disulphides in the coal; if the oxygen influx in the furnace is low, maghemite can form as well. Magnetite is usually not formed under the conditions of the fluidized bed combustion. The iron oxides either preserve the original form of the precursor pyrite (including the delicate texture of framboidal aggregates), or form thin rims on grains of all other phases of the ash (see Fig. 16), especially in the bottom ash. The rims formed probably from pyrite and clays finely dispersed in the organic matter, which entered a semi-plastic state and become "glued" to the surface of coarser grains of unreacted additive as well as quartz or feldspar. This FBC analogue to surface enrichment processes in conventional coal combustion has a lower enrichment ratio. The elements enriched are those speciated in haematite – V, As, Co.
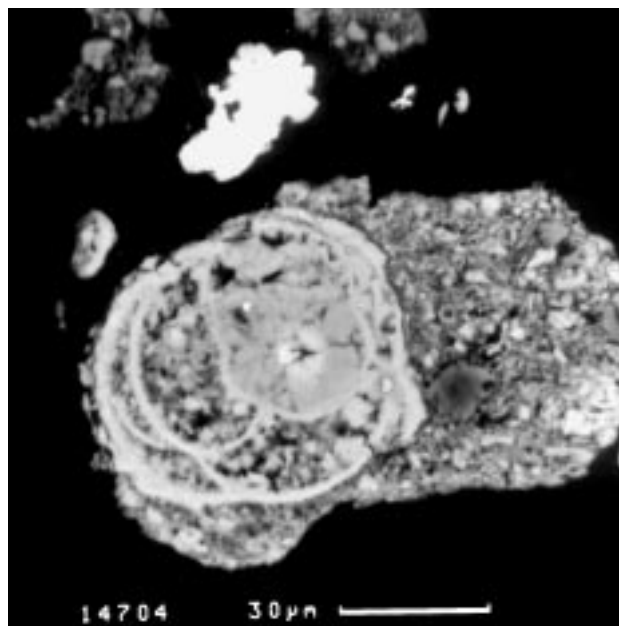

Fig. 18. A cross-section of partially reacted limestone particle with a relict of Foraminifera sp. Fly ash from fluidised bed combustion of North Bohemian brown coal. SEM – BEI.

Inversely, the bottom ash contains more grains of unreacted or partially metamorphosed additive (lime, limestone, dolostone) than the finer ash fractions. The amorphous portion of both fractions of FBC ashes corresponds to thermally altered clay minerals (metakaolinite, metaillite). The temperature in the furnace, ranging between 840 and 870 °C, is not high enough for the clay minerals to recrystallise. The melting of silicate coal minerals is very limited at these temperatures, and glass particles are therefore very scarce in FBC ashes (Fig. 17).

The imperfect action of heating on the additive grains and their stoichiometric excess over the sulphur dioxide produced by sulphides decomposition result in incomplete conversion of carbonates to oxides (Fig. 18). The combustion residues then contain residual calcite and portlandite. In the case of dolostone additive periclase is formed. Their presence increases the pH of ash leachates to 10–12, especially in the bottom ashes. Most heavy metals are not mobile under such conditions, which makes the FBC ashes a safe material for most potential uses. In some cases, the potential environmental threats can be further reduced by changing the other major parameter, redox conditions. Thus, Dutré et al. (1999) have shown that oxidative pre-treatment of arsenic-bearing fly ash can significantly decrease As solubility.

Forms of occurrence of trace elements in FBC ashes

The mode of occurrence of trace elements in FBC ashes was studied both by electron microprobe and by sequential extraction. Factor analysis of the microprobe analyses yielded several latent variables, corresponding to "mineral" components (see Tab. 6).

Tab. 6. Loadings of the four most prominent factors (factor analysis of spot microprobe analyses of FBC ashes – (Varimax rotation).

Variable/ Factor	alumino-silicates	Fe oxides	Ca sulphate/ oxide	Ti minerals
Co	–0.04	0.35	–0.55	0.17
Ni	–0.17	–0.39	0.34	–0.14
Cr	0.37	0.04	0.06	0.17
V	0.25	–0.48	0.07	0.78
As	–0.18	0.07	0.13	0.00
Zn	–0.03	0.30	–0.11	0.14
Ba	0.56	–0.24	0.2	–0.39
SiO_2	0.88	–0.05	0.09	–0.37
Al_2O_3	0.76	–0.17	–0.08	–0.19
Fe_2O_3	0.01	0.75	–0.69	0.47
MnO	0.17	0.4	–0.09	0.05
K2O	0.69	–0.21	0.05	–0.3
Na_2O	0.52	0.15	0.06	–0.25
TiO_2	0.2	–0.52	0.02	0.81
CaO	–0.81	–0.37	0.54	–0.21
SO_3	–0.79	–0.35	0.47	–0.25
% of variability explained by the factor	31	21.8	17.2	13.1

The *aluminosilicate factor* corresponds to thermally metamorphosed (amorphous) clay minerals, micas and feldspars; the highest loadings for this factor have Cr, V and Ba. The same factor and PHE association were found in coals, confirming that the bonding of these elements remains unchanged during FBC. The second factor, corresponding to *iron oxides*, shows increased correlation (expressed as factor loading) with Mn, Co and Zn. The third most important factor – *Ca sulphate/oxide* – has only a medium loading of Ni (and low or zero loadings of other trace elements), which corresponds to generally low level of trace elements in these phases. The least important factor corresponds to refractive *Ti-oxides* and is characterised by a high correlation with vanadium. Altogether, these four factors explain 83% of the overall variability in elements analysed.

Table 7. Results of sequential extraction of FBC ashes, expressed as percentages of trace elements fixed in individual fractions.

Fraction	As	Ba	Co	Cr	Cu	Ni	V	Zn
Mobile	0.1	8.1	1.6	0.8	1.1	0.0	0.9	0.0
Exchangeable (sulphate)	15.0	14.8	4.0	6.2	5.0	3.4	6.3	11.5
Fe-oxide	28.4	21.6	12.2	20.4	1.4	10.0	43.1	23.4
Refractory	56.5	55.5	82.3	72.7	92.6	86.6	49.7	65.0

Sequential extraction tests represent another, this time bulk-level view on the mode of occurrence of trace elements in fly ashes. The results obtained within the presented research show that the bonding to sulphates, expressed as exchangeable fraction, is increased in As and Ba (around 5%), while the Fe oxide fraction fixes large portions of vanadium (43%), arsenic (28%) and zinc (23%). The majority of all studied trace elements are bonded to refractory fractions, such as silicate minerals. The lowest proportion (from 50 to 65%) of this bonding was found in V, Ba, As, and Zn. Similar results were obtained by Van Herck et al. (2000), a.o.

Conclusions

The differences in mineralogy and geochemistry of residues from the North Bohemian brown coal combustion are summarized in Table 8. The summarisation clearly shows that the differences between residues from coal combustion in conventional furnaces and in fluidised bed furnaces are very distinct, especially in respect to their phase composition. A detailed knowledge of the phase composition is important for the consideration of the possible usage of the combustion residue as raw material. Besides, the "mineral" composition also controls the mode of occurrence of potentially hazardous elements

Table 8. Summary of the differences between classical and fluidised bed ashes.

Factor or process	Classical combustion	Fluidized bed combustion
Usual combustion temperature	1400–1500 °C	820–850 °C
Coal grain heating rate	1 °C . s^{-1}	1000 °C . s^{-1}
Furnace retention time	seconds	> 20 minutes
Input materials	coal	coal + additive
Mineral melting/glass formation	massive	scarce
Volatilization	Hg, Se, Pb, ZnO, $Ba(OH)_2$, As_2O_3 etc.	none
Ash grain forms	globular, rounded	irregular, rather sharp-edged
Grain size	smaller than original (thermal shock fragmentation)	original
Thermal metamorphism	strong	weaker
Recrystallisation	abundant	scarce
Mineral neoformation	massive, many species	massive, limited to a few species
Change of trace element bonding	massive	limited
Major phases	glass, mullite, anortite, quartz, cristoballite, magnetite and other spinels, gehlenite	haematite, quartz, metaillite, metakaolinite, anhydrite, periclase, lime, portlandite
Prevalent Fe oxide	magnetite	haematite
Amorphous phases	glass	metaillite, metakaolinite
Neoformation of mineral phases	extensive, many phases	extensive, few phases (anhydrite, meta-clays)
Changes in PHE speciation	distinct	limited
Concentrations of volatile elements	lower (major portion escapes with flue gas)	higher (up to 95 % of the amount present in coal)
Surface enrichment	pronounced, high	visible, lower

contained in the coal and concentrated by combustion in the solid residues.

In the combustion *residues from conventional brown coal burning*, the levels of potentially hazardous elements are generally lower, and in case of elements that can enter the spinel structure also sufficiently safely fixed. The greatest danger is associated with volatile elements that condense on the surface of the finest fly ash fractions (5–0.X μm).

The residues from *fluidised bed combustion* are due to lower firing temperature mineralogically much closer to the mineral components of coal. Low temperature prevents element volatilization and makes the solid combustion residues strongly enriched in potentially hazardous elements. The high alkalinity of the ashes, caused by the addition of sulphur dioxide neutralizing agents into the furnace, is a beneficial feature, as most of the hazardous trace elements (especially heavy metals) form compounds insoluble at high pH.

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