CHARACTERIZATION OF OIL SHALE ASHES FORMED AT INDUSTRIAL-SCALE CFBC BOILERS

R. KUUSIK[*(a)], M. UIBU[(a)], K. KIRSIMÄE[(b)]

[(a)] Laboratory of Inorganic Materials
   Tallinn University of Technology
   5 Ehitajate St., Tallinn 19086, Estonia
[(b)] Institute of Geology, University of Tartu
   46 Vanemuise St., 51014 Tartu, Estonia

Combustion conditions in boilers with circulating fluidized bed differ dramatically from those in boilers with firing of pulverized oil shale. To determine the differences in chemical, grain and phase composition of ashes taken from different technological units of boilers, the samples were analyzed using chemical, fractional and quantitative XRD methods. SEM and BET methods were implemented for surface observations and porosity measurements. The comparative physical-chemical and phase characterization of the two above-mentioned kinds of ashes is presented.

Introduction

The unique pulverized-fired (PF) boilers developed and built during 1959–1965 are still working. PF boilers represent a result of joint effort of Tallinn University of Technology (Estonia), Taganrog boiler factory and planning and design institute *Teploelektroprojekt* (both Russia), a number of enterprises that belong to *Eesti Energia* Ltd. and also researchers, designers and exploiters from other institutions (in Estonia and Russia).

The exclusivity of PF boilers is emphasized by the fact that they burn low-calorific oil shale that contains much mineral matter of complicated chemical composition. This circumstance causes difficulties in heat-transfer and phase-separation processes as well as in transport and deposition of ash.

For that kind of material new circulating fluidized bed boilers characterized by advanced technology and less serious impact on the environment were developed and put into operation in last two decades [1]. The research and experimental activity began in the early nineties of the last century to investigate the possibilities to use circulating fluidized bed combustion (CFBC) technology for oil shale combustion [2, 3]. As a result, since the beginning of 2005 two 215 MW units with CFBC boilers have been put into commercial exploitation.

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[*] Corresponding author: e-mail *rein.kuusik@ttu.ee*

Examination of the ashes of experimental combustion has shown that noticeable differences in chemical and phase composition of ash as well as in reactivity and structure of particles can be expected because the temperature in CFBC boilers is considerably lower as compared to PF boilers. The properties of PF ashes have been investigated, and the results have been used as a basis for several large-scale applications like production of construction materials [4–7] and conditioning/neutralizing of soils [8], by recommendation of ash as SO_2 sorbent [9]. Also, the processes occurring during deposition of ash into landfills were explicated [10]. At present, developing industrial applications for CFBC ashes is hindered by insufficient data; and the aim of the current study was to partially fill up the gap.

Materials and Methods

To determine the differences in chemical, grain and phase composition of the ash, the samples were collected from different points of the ash-separation systems of CFBC and PF boilers at the Eesti Thermal Power Plant. During the period of sample collecting, the lower heating value, moisture and ash content of oil shale feed were 7.93 and 8.16 MJ/kg, 11.5 and 12.5%, 44.8 and 44.0% for CFBC and PF boilers, respectively.

The CFBC ash samples used for the investigation were named as bottom ash (CFBC/BA), intrex ash (CFBC/INT), economizer ash (CFBC/ECO), air preheater ash (PHA), electrostatic precipitator ash – fields from 1st to 4th (CFBC/ESPA 1–4), and mixture of ashes taken from common ash silo, whereby the ash is collected from different equipments before landfilling on ash fields (CFBC/Mix). The PF ashes used were: bottom ash (PF/BA), superheater ash (PF/SHA), economizer ash (PF/ECO), cyclone ash (PF/CA) and electrostatic precipitator ash – fields from 1st to 3rd (PF/ESPA 1–3).

The above-mentioned ash samples were analyzed using chemical, grain-size and quantitative XRD methods, as well as SEM and BET methods. Content of total CaO [11], free CaO [12], CO_2 (volume method), total MgO (AAS method), total sulphur and its bonding forms [13], loss on ignition at 900 °C (LOI) [14] and indissoluble residue in aqua regia (I.R.) were determined by chemical analysis.

Decomposition rate of carbonate part of oil shale (k_{CO_2}) was calculated as follows:

$$k_{CO_2} = 1 - \frac{CO_2''/A''}{CO_2'/A'} \tag{1}$$

where CO_2' and CO_2'' are the contents of CO_2 in the initial material (oil shale) and in the heated residue (oil shale ash), %, respectively; A' and A'' are the contents of ash (mineral part) in the same materials, %.

XRD data was collected in powdered unoriented preparations with Dron-3M difractometer using Ni-filtered Cu-$K\alpha$ radiation. Digitally

registered difractograms were measured within the range of 2–50º 2θ, with 0.03º 2θ step size and 3 s counting time. The difractograms were analyzed by code Siroquant [15], using full-profile Rietveld analysis [16]. Scanning electron microscope Jeol JSM-8404 was used for surface observations, and specific surface area (SSA) data was determined by BET–method at Sorptometer KELVIN 1042.

Results and Discussion

Chemical Analysis and Particle Size Distribution

Chemical analysis (Tables 1 and 2) showed that in both kinds of ashes (from CFBC and PF boilers) total content of CaO decreases along the flow sheet of boilers, being the lowest in the electrostatic precipitator ashes.

Table 1. **Chemical Composition (%) and Other Characteristics of CFBC Ashes**

Item	CFBC/ /BA	CFBC/ /INT	CFBC/ /ECO	CFBC/ /PHA	CFBC/ /ESPA 1	CFBC/ /ESPA 2	CFBC/ /ESPA 3	CFBC/ /ESPA 4	CFBC/ /Mix
CaO_t	49.39	47.59	32.84	35.17	29.52	28.01	28.17	28.88	33.28
CaO_f	11.86	18.87	10.40	12.18	8.45	8.15	7.01	2.82	10.33
MgO	9.25	13.65	9.50	10.77	8.33	8.70	9.35	9.35	9.50
CO_2	15.14	1.23	5.48	4.30	4.60	3.92	3.66	3.80	6.41
k_{CO_2}	0.476	0.957	0.810	0.851	0.841	0.864	0.873	0.869	0.778
I.R.	8.85	13.25	34.02	29.33	42.45	38.58	38.03	32.74	31.86
LOI 900 °C	16.4	0.26	4.9	4.69	5.87	4.52	4.43	5.94	7.60
S_t	4.53	7.76	2.32	3.31	1.71	1.78	1.81	2.23	2.46
$S_{sulphate}$	4.32	7.70	2.22	3.27	1.71	1.78	1.81	2.21	2.43
$S_{sulphide}$	0.1	0.02	0	0.013	0	0	0	0	0.03
SSA, m^2/g	2.06	2.613	6.893	5.398	8.00	8.68	8.63	7.92	7.11

Table 2. **Chemical Composition (%) and Other Characteristics of PF Ashes**

Item	PF/BA	PF/SHA	PF/ECO	PF/CA	PF/ESPA 1	PF/ESPA 2	PF/ESPA 3
CaO_t	50.75	54.71	48.00	49.39	36.08	30.62	26.85
CaO_f	24.84	23.08	16.04	22.52	13.56	7.20	5.85
MgO	15.19	7.81	8.24	14.19	11.39	10.13	7.65
CO_2	2.75	0.96	2.50	0.70	1.16	0.90	0.80
k_{CO_2}	0.905	0.967	0.914	0.976	0.960	0.969	0.972
I.R.	18.21	18.81	26.64	20.29	26.05	29.80	35.79
LOI 900 °C	4.15	2.41	3.58	1.11	1.90	1.90	1.88
S_t	1.27	1.98	2.52	1.33	2.74	3.50	3.67
$S_{sulphate}$	1.27	1.93	2.514	1.33	2.74	3.46	3.67
$S_{sulphide}$	0	0	0.006	0	0	0	0
SSA, m^2/g	1.75	0.503	0.438	0.36	0.61	0.86	1.09

The content of indissoluble residue (mainly quartz) increases along the ash separation system in both CFBC and PF ashes, being lower in bottom ashes and several times higher in electrostatic precipitator ashes.

Compared to CFBC ashes, content of free CaO is considerably higher in PF ones (up to 24.84%). In CFBC ashes CaO content is relatively high in intrex ash, but decreases considerably in electrostatic precipitator ashes (down to 2.82%). Contrary to content of free CaO, CO_2 content is higher in CFBC ashes, being the highest in the bottom ash (up to 15.14%) and the lowest in intrex ash (1.23%). This indicates that oil shale carbonate part is far from being completely decomposed. The lowest rate of carbonate decomposition rate in the bottom ash (47.6%) could be explained by grain composition and inclusions of limestone into larger lumps of oil shale feed. Circulating of intrex ash particles between combustion chamber and intrex leads to nearly full (95.7%) decomposition of limestone as well as to desulphurization of flue gases.

Starting with economizer, the conditions for decomposition of carbonates become unfavorable, and the process stops. The particles that precipitate in economizer have previously been decomposed to the extent that depends on their size. In the case of PF technology, boiler temperatures are considerably higher (up to 1250–1400 °C) and carbonates are almost entirely decomposed that results in low CO_2 contents of PF ashes.

In CFBC ashes the content of total MgO is within the range of 8.33–9.25%. Compared to PF ashes (MgO_t = 7.65–15.19%) it is somewhat lower due to lower rates of carbonate decomposition. On the whole, the content of total MgO in analyzed samples is relatively high. This can be due to the use of dolomite-rich oil shale (MgO content in initial oil shale and in its laboratory-decomposed residues were 6.50 and 10.70%, respectively).

Sulphur content is highest in intrex ash (7.76%). It can be expected due to the most favorable temperature conditions for SO_2 binding in this part of the CFBC boiler system. In the case of PF ashes, sulphur content is higher in electrostatic precipitator ashes. The main part of sulphur is bound to sulphates. Traces of sulphides are present in CFBC/BA, CFBC/INT and CFBC/ECO samples.

The particle size of CFBC ashes varies in a very wide range (Table 3). Bottom ash is coarsest (~45% of particles have the diameter >0.63 mm), intrex ash particles are of average size (90% of particles have the diameter of 0.4–0.045 mm) and electrostatic precipitator ashes are finest (85–95% particles have the diameter less than 0.045 mm). Particle distribution of PF ashes (Table 4) is more homogeneous with less particles having the diameter over 0.63 mm. Bottom ash and superheater ash are coarsest (~75% of particles have the diameter of 0.1–0.63 mm). As expected, the electrostatic precipitator ashes are finest, with about 90% of particles having the diameter less than 0.045 mm.

The above-mentioned dissimilarities between chemical and fractional composition of different ash types for various combustion technologies are

caused by several circumstances, fractional composition of fuel fed to the boiler being the most important of them. For PF boilers the average median measure of fuel fed to the boiler is 35–60 μm, and the rest on sieves with aperture size 90 and 200 μm is 20–40 and 10–25%, respectively. Fractions differ noticeably by chemical composition [17]. The material fed to CFBC boilers belongs predominantly to the class 1–10 mm. Fine particles of pulverized oil shale and ashes melt and agglomerate forming larger particles, while in the case of CFBC the main part of fine fractions is formed as a result of intensive attrition of particles in fluidized bed.

Table 3. **Grain-Size Composition of CFBC Ashes**

Ash type	Screenings, mm						
	+0.63	+0.4	+0.16	+0.1	+0.071	+0.045	−0.045
CFBC/BA	45.2	7.7	19.1	16.4	5.4	3.7	2.6
CFBC/INT	2.2	2.4	15.2	36.0	22.9	18.5	2.8
CFBC/ECO	–	–	–	1.4	2.8	20.1	75.8
CFBC/PHA	–	–	0.2	3.4	6.3	36.2	53.9
CFBC/ESPA 1	–	–	–	0.3	1.7	11.1	86.8
CFBC/ESPA 2	–	–	–	0.6	1.6	12.5	85.3
CFBC/ESPA 3	–	–	–	0.4	1.7	10.9	87.0
CFBC/ESPA 4	–	–	–	–	0.7	4.3	95.1
CFBC/MIX	1.7	0.8	3.3	4.4	3.3	13.1	73.3

Table 4. **Grain-Size Composition of PF Ashes**

Ash type	Screenings, mm						
	+0.63	+0.4	+0.16	+0.1	+0.071	+0.045	−0.045
PF/BA	5.3	9.9	37.8	25.4	6.1	8.8	6.6
PF/SHA	3.4	8.1	41.0	27.0	5.0	6.3	9.3
PF/ECO	2.6	1.4	14.2	25.7	10.2	19.6	26.2
PF/CA	–	–	8.4	23.6	13.2	27.1	27.7
PF/ESPA 1	–	–	–	1.8	1.4	4.5	92.3
PF/ESPA 2	–	–	–	0.3	0.5	0.7	97.4
PF/ESPA 3	–	–	–	–	–	0.7	99.3

Phase Composition

XRD analysis was carried out to determine the phase composition of CFBC and PF ashes (Tables 5 and 6). For some compounds the results of quantitative XRD were compared to those calculated on the basis of chemical analysis (Fig. 1). XRD analysis indicated that as compared to PF ashes CFBC ashes contain more calcite and less free lime. This agrees with composition expected on the basis of chemical analysis and considering different combustion conditions of oil shale. Calcite content in CFBC/BA is highest– up to 34.8%. Anhydrite ($CaSO_4$) content is highest in CFBC/INT. This was also confirmed by chemical analysis.

Table 5. **Mineral Composition of CFBC Ashes, wt.%**

Minerals	CFBC/ /BA	CFBC/ /INT	CFBC/ /ECO	CFBC/ /PHA	CFBC/ /ESPA 1	CFBC/ /ESPA 2	CFBC/ /ESPA 3	CFBC/ /ESPA 4	CFBC/ /Mix
Quartz SiO_2	8.9	5.6	17.1	17.7	16.8	17.9	15.3	12.1	13.8
Orthoclase$KAlSi_3O_8$	1.3	2.7	9.4	8.1	12.5	12.5	13.4	15.7	15.6
Albite $NaAlSi_3O_8$	1.6	2.7		tr.		tr.			
Illite + Illite-Smectite $Na,K_x(Al,Mg)2Si_4O_{10}(OH)_2 \cdot H_2O$	2.1	3.1	11.2	9.5	13.8	14.0	15.6	16.8	9.7
Belite Ca_2SiO_4	4.6	7.3	5.8	6.2	5.3	5.7	5.8	7.5	5.0
Merwinite $Ca_3Mg(SiO_4)_2$	4.7	5.2	3.0	3.0	3.7	4.0	4.3	4.2	3.0
Tricalcium aluminate $3CaO.Al_2O_3$	1.2	1.4	2.0	2.2	2.3	2.2	2.2	3.3	1.8
Dolomite $CaMg(CO_3)_2$	3.9								
Periclase MgO	4.2	7.0	3.8	4.4	2.7	3.3	3.4	3.3	3.8
Melilite $(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	1.0	3.6	1.6	1.5	1.2	1.5	1.8	2.6	2.0
Anhydrite $CaSO_4$	16.2	29.9	11.1	14.3	9.5	8.8	8.2	11.3	10.1
Gypsum $CaSO_4 \cdot 2H2O$		0.8	0.5						
Lime CaO	11.4	19.9	13.3	14.9	10.8	10.0	9.1	3.2	11.0
Calcite $CaCO_3$	34.8	4.0	14.6	12.6	13.5	12.6	12.6	13.6	18.1
Aragonite $CaCO_3$			0.8						
Portlandite $Ca(OH)_2$	1.7	2.1	0.7	0.8		Tr.		0.9	
Hematite Fe_2O_3	1.1	2.1	3.6	2.7	4.3	4.5	3.8	3.9	3.7
Pseudowollas-tonite $CaSiO_3$	1.4	1.8	1.9	2.1	3.6	2.5	3.4	2.2	2.3

Table 6. **Mineral Composition of PF Ashes, wt.%**

Minerals	PF/BA	PF/SHA	PF/ECO	PF/CA	PF/ESPA 1	PF/ESPA 3
Quartz SiO_2	3.1	1.6	3.6	3.3	12.0	10.4
Orthoclase $KAlSi_3O_8$	6.6	9.7	2.5	1.7	3.8	9.3
Illite + Illite-Smectite $Na,K_x(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot H2O$			4.0	6.1		
Belite Ca_2SiO_4	13.5	20.3	15.9	15.9	12.3	11.7
Merwinite $Ca_3Mg(SiO_4)_2$	9.4	10.5	8.9	13.2	6.5	6.8
Tricalcium aluminate $3CaO.Al_2O_3$	2.3	3.3	2.0	2.2	2.8	3.8
Periclase MgO	7.9	3.8	3.8	8.7	8.5	5.8
Melilite $(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	17.8	12.6	18.9	5.8	3.3	3.2
Anhydrite $CaSO_4$	5.4	4.6	9.6	5.4	16.8	24.1
Lime CaO	26.5	24.1	19.0	29.3	28.1	14.3
Calcite $CaCO_3$	5.7	3.7	7.6	2.5	2.0	5.6
Portlandite $Ca(OH)_2$		3.3	2.5	3.1	1.0	0.8
Hematite $Fe2O3$	0.9	tr	1.1	1.1	1.6	1.7
Pseudowallastonite $CaSiO3$	0.9	2.6	0.7	1.6	0.8	2.3
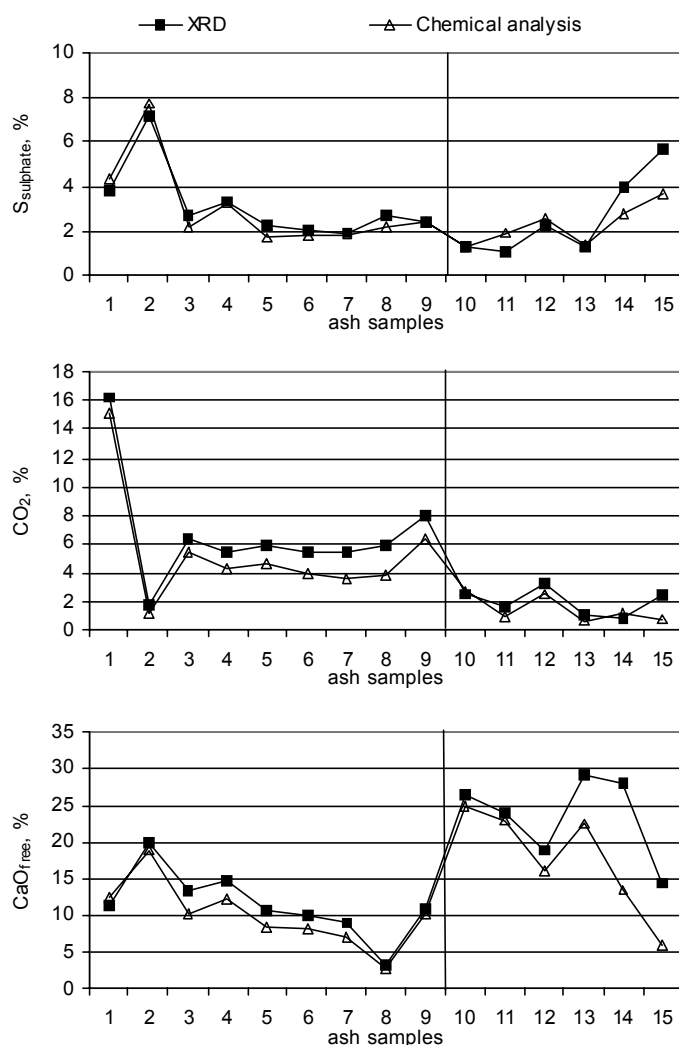
Fig. 1. Comparison of results of chemical and quantitative XRD analysis:
1 – CFBC/BA, *2* – CFBC/INT, *3* – CFBC/ECO, *4* – CFBC/PHA, *5* – CFBC/ESPA
1, *6* – CFBC/ESPA 2, *7* – CFBC/ESPA 3, *8* – CFBC/ESPA 4, *9* – CFBC/Mix,
10 – PF/BA, *11* – PF/SHA, *12* – PF/ECO, *13* – PF/CA, *14* – PF/ESPA 1,
15 – PF/ESPA 3

Generally, anhydrite concentration is somewhat lower in PF-ashes, being highest in electrostatic precipitator ones. Mg was found in both cases mainly as periclase (MgO), partially bound to carbonates (dolomite) or silicates (merwinite). Silica compounds in CFBC ashes are presented mainly with quartz and orthoclase type K-feldspar (up to 17.9 and 15.7% in electrostatic precipitator ashes, respectively). As indicated by the analysis of nonsoluble residue, concentrations of silicate compounds increase along the ash separation system.

a

b

c

d

e

f
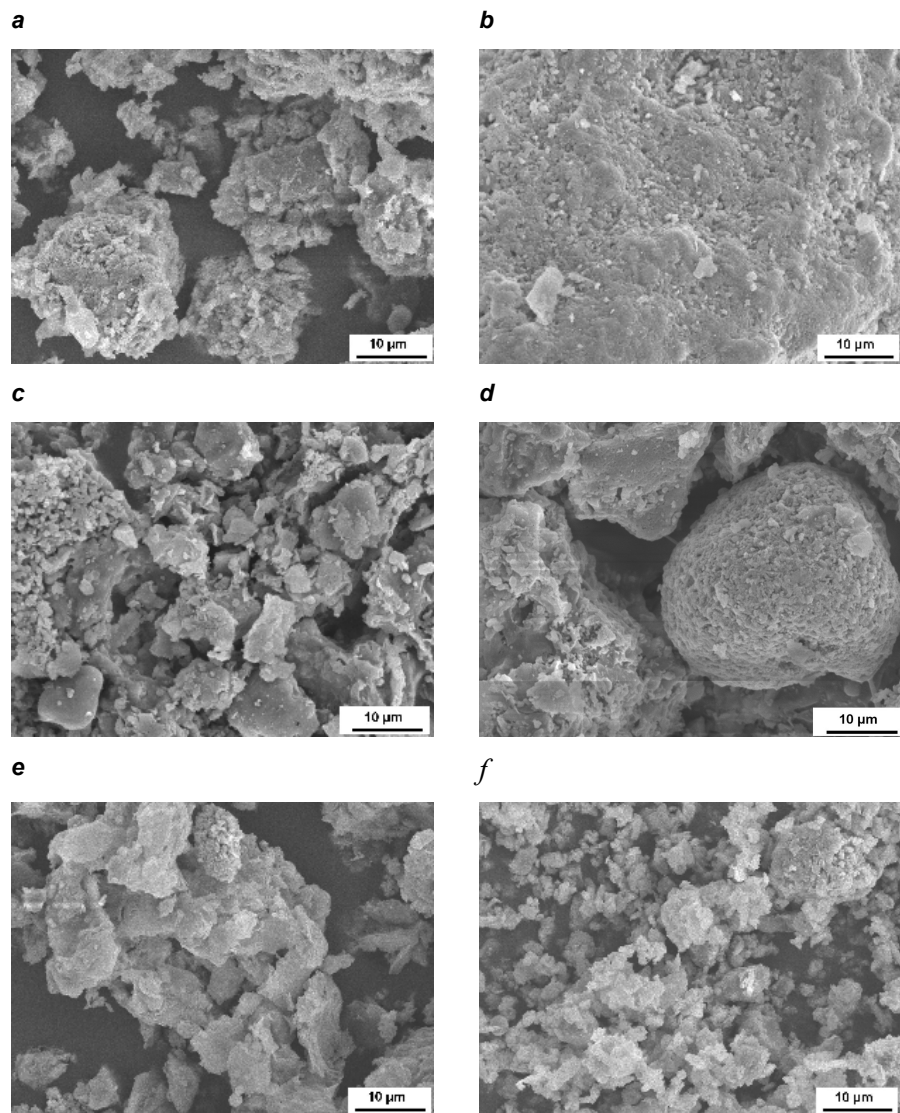
Fig. 2. SEM pictures of CFBC ashes, magnification 2000×, *a* – CFBC/BA (ground to <1 mm), *b* – CFBC/INT, *c* – CFBC/ECO, *d* – CFBC/PHA, e – CFBC/ESPA1, *f* – CFBC/ESPA4
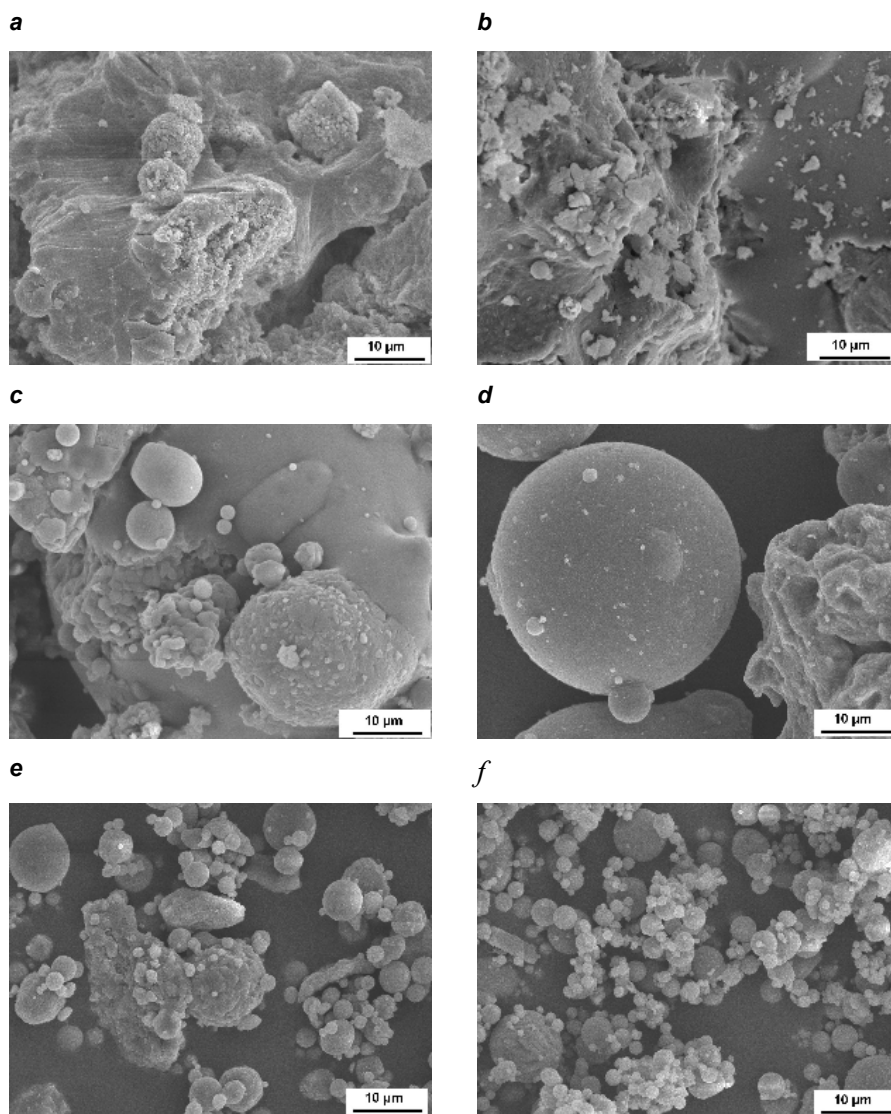
Fig. 3. SEM pictures of PF ashes, magnification 2000×; *a* – PF/BA, *b* – PF/SHA, c – PF/ECO, *d* – PF/CA; *e* – PF/ESPA 1, *f* – PF/ESPA 3

Compared to CFBC ashes, PF ones contain less quartz and orthoclase and notably more secondary silicate phases – belite (up to 20.3% in superheater ash) and merwinite (up to 13.2% in cyclone ash). Relatively higher content of secondary silicates can be explained by significantly higher temperatures used in PF boilers – they initiate binding of free CaO which leads to the formation of clinker minerals.

Basing on relatively good correlation between the results of chemical and quantitative XRD analysis (first used for analyzing oil shale ashes), it can be concluded that the latter can be used for preliminary express analysis.

Surface Observations

Comparison of SEM photos of ash samples investigated shows that particles of CFBC ashes formed at moderate temperatures are characterized by irregular shape as well as by porous and uneven surface (see Fig. 2). The effect of attrition could be shown by bigger particles of intrex and air preheater ashes (see Fig. 2*b,d*). The glassy phase is not formed. In the case of PF ashes, the glassy phase significantly affects the formation of particle shape and surface properties: the particles are characterized by regular spherical shape with smooth surface (see Fig. 3). It was shown that along the ash separation system the porous irregular-shaped particles are replaced by regular smooth spherical particles (electrostatic precipitator ashes).

The results of BET measurements confirmed the significant difference in the physical structure of CFBC and PF ashes depending on ash type: up to ten times (see Tables 1 and 2). While specific surface area of CFBC ashes can reach 8.68 m^2/g, the SSA of PF ashes is in range 0.36–1.75 m^2/g.

Conclusions

1. Oil shale ashes, formed in boilers operating at different combustion technologies, differ significantly by their chemical and phase composition as well as by surface properties.

2. The sharp difference in the operating temperature and fuel particle size results in different behavior of calcium- and sulphur-containing compounds. Due to considerably higher temperature when using PF technology, the rate of carbonate decomposition is as high as 97–98%, being moderate (47–96%) in the case of CFBC. Content of free CaO is higher in PF ashes (up to 24.84%), while in CFBC ashes it is relatively high only in intrex ash (18.87%), but decreases considerably in electrostatic precipitator ashes (down to 2.82%). In both CFBC and PF ashes the content of total CaO decreases and the content of indissoluble residue increases along the ash separation system.

3. In the case of CFBC, the binding of gaseous SO_2 occurs in combustion chamber and intrex of the boiler, leading to high sulphur content of bottom (4.53%) and intrex ash (7.76%). The major part of sulphur is

bound to sulphates. In PF the bound sulphur is more uniformly distributed between different kinds of ashes, being highest in precipitator ashes (3.67%).

4. Quantitative XRD measurements verified the most part of the results of chemical analysis. Compared to PF ashes, CFBC varieties contain more calcite (up to 34.8% in bottom ash) and less lime. Silica compounds in CFBC ashes are mainly presented with quartz (up to 17.9%) and orthoclase type K-feldspar (up to 15.7%), while PF ashes contain noticeably more secondary silicate – belite (up to 20.3%) and merwinite (up to 13.2%).

5. Surface observations of CFBC and PF ashes show that particles of CFBC ashes are characterized by irregular shape and porous and uneven surface. In the case of PF ashes the glassy phase can be observed, and the particles are characterized by regular spherical shape and smooth surface. The value of specific surface area of CFBC ashes is up to ten times higher than in the case of PF ashes.

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