COMPOSITION OF OIL SHALE ASHES FROM PULVERIZED FIRING AND CIRCULATING FLUIDIZED-BED BOILER IN NARVA THERMAL POWER PLANTS, ESTONIA

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The composition of oil shale ashes from pulverized firing (PF) and circulating fluidized-bed boiler combustion (CFB) systems at the Eesti and the Balti Thermal Power Plants was studied by means of quantitative X-ray diffraction, chemical analysis and scanning electron microscopy. The composition of ash varies systematically in the boiler gas pass, depending on the firing technology. PF ashes are dominated by free lime, whose content decreases from the furnace to the last fields of electrostatic precipitators. Same trends can be observed within residual fraction (i.e. mineral phases remaining in firing process) and Ca-silicates. Anhydrite, on the other hand, concentrates into the end of the gas pass. CFB ash shows more complex variations, and on several occasion the changes in certain phases are opposite to variations in respective PF ashes. Comparison of the phase composition of ashes from the same type of boilers in the Eesti and Balti TPP show remarkable differences in Ca-silicate phases. To our best knowledge, earlier mineralogical studies have not addressed compositional variations of ashes from two separate power plants. These differences are probably related to the heterogeneity of oil shale fuel, not so much to combustion temperature.

Introduction

The Estonian Thermal Power Plants (TPP) are fuelled by low-calorific kerogenous oil shale, which is characterized by high content of complex mineral residue. The amount of ash that remains after burning makes up 45–50% of the oil shale mass [1]. The formation of such a large amount of ash in boilers causes difficulties in heat-transfer and phase-separation processes, as well as in transport and deposition of ash [2].

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The two most powerful Estonian TPPs (the Eesti and the Balti TPP, together called Narva TPPs) use two different oil shale combustion technologies: pulverized firing (PF) and circulating fluidized-bed (CFB) technology [3]. The production of electricity and heat started in the Balti TPP and in the Eesti TPP in 1959 and 1969, respectively. The Balti TPP was put into operation in two stages. During the first stage (1959–62), 18 high-pressure TP-17 boilers (now stopped) were installed, and in the second stage (1963–65) 8 high-pressure TP-67 boilers were launched at the Balti TPP. All of these boilers operate on PF technology. The Eesti TPP, put into operation between 1969 and 1973, was equipped with 16 high-pressure TP-101 boilers [3]. In 2004 the old PF boilers in unit No. 11 in the Balti TPP and unit No. 8 in the Eesti TPP were replaced with new CFB boilers with the maximal power of 215 MW [4]. At present, 12 units (eight at the Eesti TPP and four at the Balti TPPs) are operative for electricity and heat supply. Each power unit is composed of two boilers and a condensing turbine. Currently 20 PF boilers and 4 CFB boilers are running at the Narva TPPs, with installed electric and thermal capacities of 2380 MW and 484 MW, respectively [5]. According to the Development Plan for the Estonian Electricity Sector until 2018 [6], the boilers using the PF technology will be partly shut down, partly replaced with CFB boilers, and 4 power units will be fitted with sulphur and nitrogen (oxides) capture devices by 2018, for higher efficiency and substantial fuel saving [7] in the CFB boilers and significant reducing of air pollution [4] of the renovated power units.

Different combustion conditions in the PF and CFB technologies cause remarkable differences in the phase composition as well as in chemical composition of ash fractions [*e.g.* 2]. Recently, Liira *et al*. [8] showed different hydration characteristics of CFB ashes compared to PF ash, which has already resulted in technological difficulties of ash deposition in the waste ash landfills. Different composition of ash fractions has significant influence on the potential application of ashes as secondary raw materials. In earlier decades, PF ashes have been extensively studied [2, 9–12], and used for the production of construction materials and cement [13], in road construction [14] and for liming of acid soils [15]. Potential industrial scale applications and possible environmental aspects of CFB ashes are, however, virtually unexplored. In this contribution we undertake a detailed parallel characterization of PF and CFB ashes in the Eesti and Balti TPPs, in order to examine the distribution of mineral and chemical components in different ash fractions. The results of this study are important for more efficient reuse of ash wastes produced at Narva TPPs.

Material and methods

The ash samples were collected from different points of the ash-separation systems of CFB and PF boilers at the Balti and Eesti Thermal Power Plant in

November the 5th, 2008. According to the information from the Narva TPPs, the moisture content of raw oil shale, used at this time as a fuel at the Balti and Eesti TPPs, was 13.3 and 10.24%, calorific value 8.55 MJ/kg (minimal calorific value 8.38 MJ/kg), and ash content 43% and 45.6%, respectively. The ash samples from the PF boiler of the Balti TPP were taken from the superheater, economizer, and from four electrostatic precipitator fields. At the Eesti TPP, ash from the PF boiler system was collected from furnace (bottom ash), super-heater, economizer, cyclone separator, and three electrostatic precipitator fields. The ash samples from CFB boilers of the Eesti TTP were taken from the furnace, INTREX, air-preheater, and four electrostatic precipitator fields. In the Balti TPP, in addition to the afore-mentioned ashes from the CFB system, samples were also collected from the superheater and economizer.

The chemical composition of the ash samples was determined in the Certified ACME Laboratory (Vancouver, Canada) by the ICP-MS method with 4-acid digestion. The mineral composition of crystalline phases in ash was studied by using powder X-ray diffraction (XRD) on a Bruker D8 diffractometer. Micromorphology of ash fractions was investigated using a Zeiss DSM 940 scanning electron microscope (SEM) equipped with an Idfix Si-drift technology energy-dispersive analyser (EDS), and a scanning electron microscope Zeiss EVO MA 15.

Results

The chemical composition of all ash types is dominated by CaO, whose proportion varies form 26.4 to 54.5% in PF ashes and 26.4–49.1% in CFB ashes (Table 1). As reported earlier [2], the proportion of CaO decreases both in PF and CFB boilers along the boiler gas pass, from the average of 49.4% in bottom ash to 29.7% in the last fields of electrostatic precipitators (Fig. 1). The proportion of CaO was corrected for partial hydration into port-landite [$Ca(OH)_2$]. The average proportion of MgO is 4.75% (Table 1), which is considerably lower than 7–15% of MgO_{total} reported in earlier studies [*e.g.* 2]. Magnesium is mostly derived from the thermal decomposition of dolomite [$CaMg(CO_3)_2$], and the difference in those figures evidently follows variation in dolomite admixture in raw oil shale, depending on geological section used for mining. Al_2O_3 content in PF and CFB ashes remains in the range of 2–10.5%, showing an increasing trend in finer fractions and reaching maximum values in the last fields of electrostatic precipitators. The proportion of Fe_2O_3 is remarkably high (on average 4.3%) in all ash types. In PF ashes the Fe_2O_3 content is rather stable in different ash fractions, mostly between 4 and 5%. On the other hand, in CFB ashes the proportion of ferric oxide increases gradually from less than 3% in the bottom ash to more than 5% in electrostatic precipitators (Fig. 2). Variation in sulphur content agrees with the earlier studies and, as expected, the S

Table 1. **Chemical composition of studied samples, wt%**

| Boiler type		Origin of ash	Al	Ca	Fe	Mg	K	Na	P	S	Ti
			weight %								
Balti Power Plant	PF	Superheater	3.07	34.20	3.25	2.98	2.07	0.056	0.063	1.69	0.207
		Economizer	2.97	33.33	3.31	3.00	2.04	0.059	0.061	1.62	0.200
		El. Precip 1	4.21	27.90	3.23	2.70	2.04	0.076	0.074	2.14	0.276
		El. Precip 2	4.07	29.89	3.42	2.85	1.98	0.070	0.073	2.00	0.276
		El. Precip 3	4.42	23.89	4.06	2.42	2.35	0.092	0.073	2.64	0.290
		El. Precip 4	4.26	23.44	3.92	2.44	2.37	0.091	0.077	2.60	0.284
	CFB	Furnace	1.26	34.48	1.99	2.78	0.69	0.028	0.045	3.77	0.079
		Intrex	1.48	33.12	2.42	3.45	0.78	0.037	0.061	7.37	0.095
		Superheater	3.89	24.46	3.38	2.64	2.28	0.097	0.060	2.62	0.259
		Economizer	4.09	22.53	3.51	2.66	2.16	0.083	0.066	2.45	0.264
		Air-preheater	3.47	25.46	3.46	3.00	2.36	0.075	0.069	3.44	0.234
		El. Precip 1	4.62	20.04	3.47	2.33	2.17	0.097	0.069	2.00	0.316
		El. Precip 2	5.18	20.37	3.68	2.54	2.35	0.108	0.078	2.11	0.369
		El. Precip 3	5.44	19.00	3.70	2.40	1.95	0.103	0.087	1.90	0.373
		El. Precip 4	5.55	21.21	3.73	2.98	2.24	0.093	0.106	2.61	0.372
Eesti Power Plant	PF	Furnace	2.28	38.21	2.82	2.16	1.12	0.039	0.059	1.41	0.163
		Superheater	2.74	36.03	2.82	2.71	1.39	0.046	0.057	1.96	0.198
		Economizer	2.62	37.99	2.93	2.85	1.22	0.044	0.062	1.53	0.188
		Cyclon	2.79	31.96	2.62	4.56	1.57	0.040	0.060	1.84	0.197
		El. Precip 1	4.19	25.15	2.53	3.41	2.02	0.082	0.077	2.76	0.276
		El. Precip 2	4.83	21.31	2.77	2.54	2.30	0.103	0.083	2.94	0.329
		El. Precip 3	5.27	18.52	2.72	1.97	2.50	0.130	0.100	3.80	0.365
	CFB	Furnace	1.06	31.21	1.82	4.02	0.67	0.016	0.045	2.29	0.069
		Intrex	1.09	17.39	1.34	2.88	0.63	0.020	0.041	4.32	0.109
		Air-preheater	3.38	22.52	2.46	3.18	2.37	0.063	0.060	2.65	0.229
		El. Precip 1	4.45	20.17	2.83	2.71	2.55	0.080	0.060	1.86	0.298
		El. Precip 2	4.65	19.81	2.91	2.69	2.65	0.080	0.061	1.84	0.307
		El. Precip 3	5.00	19.50	3.20	2.74	2.27	0.079	0.075	1.95	0.341
		El. Precip 4	5.44	20.20	3.40	3.10	2.29	0.075	0.095	2.42	0.366
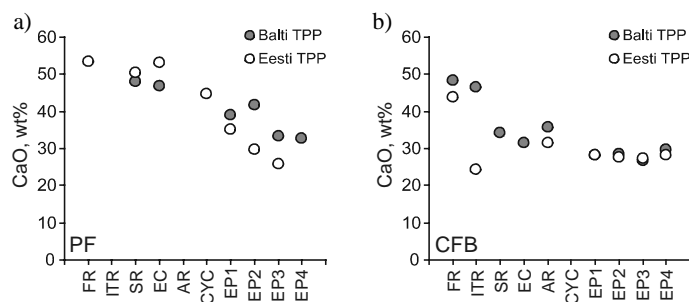
Fig. 1. Changes in CaO content. a) ash from pulverized firing boilers (PF), b) ash from circulating fluidized bed (CFB) boilers. Legend: FR – furnace, ITR – INTREX (in CFB boilers), SR – superheater, EC – economizer, AR – air preheater, CYC – cyclone, EP(1,2,3,4) – electric precipitator filters 1,2,3,4, respectively.
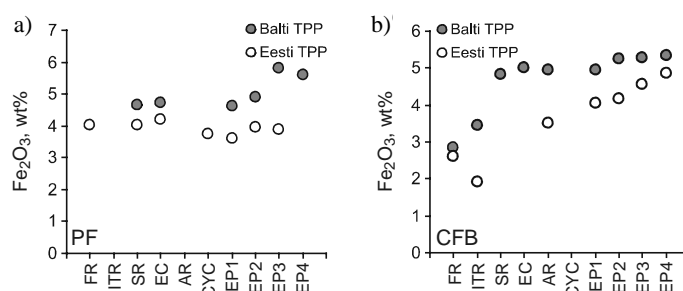
Fig. 2. Changes in Fe_2O_3 content. a) PF ash; b) CFB ash. Legend – see Fig. 1.

content is highest in the INTREX ash of the CFB boilers (Fig. 3), where near complete removal of SO_2 from flue gases occurs [16]. Separation of S along the boiler gas pass in PF ashes shows gradual enrichment in finer ash fractions (Fig. 3).
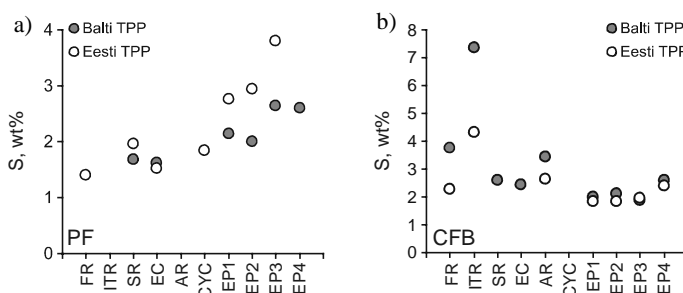

Fig. 3. Variations in sulphur content. a) PF ash; b) CFB ash. Legend – see Fig. 1.

The mineral composition as well as the average grain size of the unhydrated ash fractions vary systematically with the position in the ash removal system. The average grain size of ash fractions decreases along the boiler gas pass, being coarsest in furnace ash (~250 µm) and finest in the last field of electrostatic precipitators (~6 µm).The mineral composition of ash (Table 2) is dominated by lime (free CaO), varying from about 1.6% in CFB ashes to a maximum of 24.6% in PF ashes. Concordant to the chemical composition of the samples, the proportion of lime, in PF ashes at both power stations, shows a gradual decrease from the bottom ash towards electrostatic precipitators. In CFB ashes, however, the distribution of free CaO is more complex (Fig. 4). The proportion of lime in bottom ash is rather low compared to PF boilers, the lime reaches the maximum level in the economizer – air-preheater zone and thereafter decreases again through the fields of electrostatic precipitators (Fig. 4b). This variation is evidently related to the active sulphur binding following INTREX preheaters where

Table 2. **Mineral composition of studied samples, wt%**

Balti Power Plant			Quartz SiO_2	Lime CaO	Portlandite $Ca(OH)_2$	Calcite $CaCO_3$	Anhydrite $CaSO_4$	Melilite $(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	Periclase MgO	C2S β-Ca_2SiO_4	Merwinite $Ca_3Mg(SiO_4)_2$	Wollastonite $CaO{\cdot}SiO_2$	Adularia $KAlSi_3O_8$	Hematite Fe_2O_3	Illite $KAl_2(Si_3AlO_{10})(OH)_2$	C3S Ca_3SiO_5	Akermanite $Ca_2MgSi_2O_7$	C4AF $Ca_2(Al,Fe^{3+})_2O_5$	Rankinite $Ca_3Si_2O_7$	Sylvite KCl	Dolomite $CaMg(CO_3)_2$
	Boiler type	Origin of ash										weight %									
	PF	Superheater	9.2	19.9	12.0	15.2	7.1	6.5	4.2	8.9	4.9	2.4	6.2	3.5				1.4			
		Economizer	9.2	17.5	8.7	14.7	5.4	8.8	4.6	11.5	4.1	2.4	8.4	3.2							
		El. Precip 1	14.9	17.1	6.8	9.9	10.2	3.3	4.1	12.4	5.6	2.5	8.6	4.5							
		El. Precip 2	15.2	16.8	9.2	11.2	9.4	6.1	3.7	10.5	5	2.7	7.2	3.1							
		El. Precip 3	15.7	14.2	6.7	13.9	12.9	3.9	2.9	8.9	3.8	3.6	9.3	4.3							
		El. Precip 4	15.2	13.3	17.0	12.1	10.6	3.1	2.8	8	4	1.9	8.1	3.4						0.6	
	CFB	Furnace	4.9	4.5	2.6	43.4	12.5	2.5	3.7	6.5	3.4	1.4	4.2	3.4	tr.					tr.	6.9
		INTREX	6.1	9.9	12.3	7.6	27.7	13.7	5.9	4.9	2.9	0.8	4.7	3.4							
		Superheater	18.9	6.7	3.5	17.5	9.7	9.6	3.1	4.5	2.7	1.4	9.0	5.9	7.6						
		Economizer	19.9	7.2	2.3	16.9	9.2	8.5	3.2	3.9	2.8	1.5	9.2	6.3	9.1						
		Air-preheater	17.0	10.5	4.2	11.6	13.1	10.3	3.9	4.2	2.8	1	8.6	6.3	6.5						
		El. Precip 1	19.3	7.8	2.5	12.9	7.8	10	2.4	4.9	2.9	1.6	11.2	7.2	9.7						
		El. Precip 2	17.1	6.1	2.3	12.5	8.5	10.5	2.9	5.3	3.2	1.3	14.9	7.1	8.4						
		El. Precip 3	15.1	1.8	2.0	11.6	8.7	12.5	2.4	6.9	4.3	1.3	16.3	7.8	9.4						
		El. Precip 4	10.4	0.0	1.7	15.9	14.6	2.3	3.2	10.5	2.4		13.5	7.5	5.5		0.8		6	tr.	

		Quartz SiO_2	Lime CaO	Portlandite $Ca(OH)_2$	Calcite $CaCO_3$	Anhydrite $CaSO_4$	Melilite $(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	Periclase MgO	C2S $\beta\text{-}Ca_2SiO_4$	Merwinite $Ca_3Mg(SiO_4)_2$	Wollastonite $CaO{\cdot}SiO_2$	Adularia $KAlSi_3O_8$	Hematite Fe_2O_3	Illite $KAl_2(Si_3AlO_{10})(OH)_2$	C3S Ca_3SiO_5	Akermanite $Ca_2MgSi_2O_7$	C4AF $Ca_2(Al,Fe^{3+})_2O_5$	Rankinite $Ca_3Si_2O_7$	Sylvite KCl	Dolomite $CaMg(CO_3)_2$
PF	Furnace	2.6	21.1	13.5	6.4	5.4	11.3	2.9	19.1	4.8		5.1	1.8		2.4	1.4	2.1	4.1		
	Superheater	4.1	19.6	13.6	3.3	8.9	10.6	3.69	17.6	5.7		4.6	2		2.9	1.2	2.3	4.1		
	Economizer	4.5	24.6	14.8	4.4	6.9	7.8	4	16	5.7		3.6	1.8		2.6	1.1	2.3			
	Cyclon	6.8	24.6	8.9	4.2	9.5	4.5	8	13.9	6.7		4.3	2.2		2.7	1.1	2.6			
	El. Precip 1	11.2	18.9	2.6	4.3	16	3.2	6.4	12.4	4.3		8.9	3.9		3.3	1.7	2.9			
	El. Precip 2	13.0	15.3	1.9	4.7	21.4	2.9	3.9	9.9	3.4		10.8	5		3.3	1.8	2.7		tr.	
	El. Precip 3	8.8	9.2	1.0	4.2	26.9	3.6	2.6	11.8	3.6		12.3	5.1		2.7	2.3	3.2		1.7	
CFB	Furnace	4.1	2.9	3.5	51.2	7.5	2.4	5.1	3.9	1.9		4.5	2.1		1	8.7	1.2			
	INTREX	4.8	3.5	2.3	6.5	15.8	3.5	4.7	4.3	1.7		5.2	1.5		0.1	1.5	0.7			
	Air-preheater	17.4	12	5.7	13.3	12	3.5	4.8	5.5	2.1		11.5	4.4	5.9	0.6	0.8	0.6			
	El. Precip 1	19.4	11.6	2.4	13.4	8.4	2.3	2.9	5.3	2.1		14.1	5.4	9.7	1.4	0.8	1.0			
	El. Precip 2	19.9	10.2	2.6	12	8.3	2.2	2.9	5.5	2.3		14.5	5.6	10.6	1.5	0.9	0.9			
	El. Precip 3	17.6	7.2	2.3	10.9	9.9	2.7	3.1	7.8	3.1		15.0	6.8	9.8	1.5	0.9	1.3			
	El. Precip 4	11.3	1.6	1.5	12.9	13.1	3.3	3.8	11.2	4.6		13.9	7.7	10.2	1.8	1.2	2.0			

Eesti Power Plant

Fig. 4. Changes in free lime (CaO) content . a) PF ash and b) CFB ash. Legend – see Fig. 1.

CaO, formed from the thermal decomposition of calcite and dolomite, reacts with SO_2 in flue gases. In contrast to lime, the proportion of anhydrite ($CaSO_4$) increases in PF boilers from about 5% in bottom ash to the maximum levels of ~13% and ~27% in electrostatic precipitators at the Balti and Eesti TPP, respectively (Fig. 5a). As expected from chemical analyses, anhydrite is at maximum in INTREX ash of the CFB boilers and slightly increased in the last fields of electrostatic precipitators (Fig. 5b).

There is a significant difference in the phase composition of major secondary Ca-silicate phases in ashes formed at the Eesti and Balti TPPs. In the Balti TPP the Ca-silicates are represented by C2S (belite – β-$CaSi_2O_4$), merwinite [$Ca_3Mg(SiO_4)_2$] and wollastonite type phases ($CaSiO_3$). The Ca-silicate composition of the ashes produced at the Eesti TPP, however, includes also C3S (Ca_3SiO_5) and rankinite ($Ca_3Si_2O_7$) type phases. The difference is also evident in the appearance of akermanite ($Ca_2MgSi_2O_7$) and C4AF [$Ca_2(Al,Fe^{3+})_2O_5$] in all types of ashes of the Eesti TPP (Table 2). Nevertheless, the distribution of Ca-silicate phases in boiler gas passes at both TPPs shows similarities upon the firing technology. In PF boilers, the proportions of Ca-silicate phases decrease along the ash separation tract (Fig. 6a). On the contrary, in CFB boiler system, the proportion of Ca-silicates is rather uniform in the first half of the ash removal system, and increase nearly exponentially in the electrostatic precipitators (Fig. 6b).
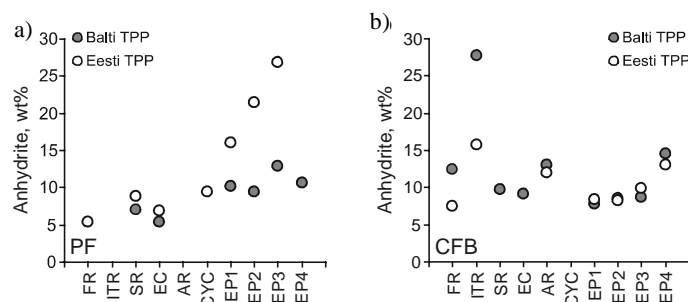
Fig. 5. Variations in anhydrite content. a) PF ash and b) CFB ash. Legend – see Fig. 1.
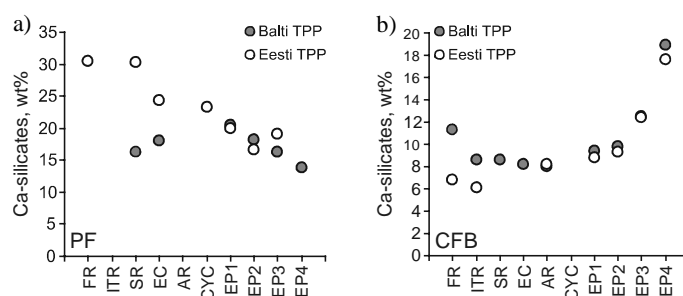
Fig. 6. Changes in the content of combined Ca-silicates, which include C2S, wollastonite, merwinite, C3S and rankinite. a) PF ash and b) CFB ash. Legend – see Fig. 1.

Residual fraction is mainly composed of quartz, K-feldspar, and minor undecomposed calcite in PF ashes, and also additionally dehydroxylated clay minerals, calcite and traces of dolomite in CFB ashes. A proportion of non-carbonate residual fraction (expressed as the sum of quartz, K-feldspar and clay minerals) increases in PF ashes monotonously along the boiler gas pass (Fig. 7a). In CFB ashes, however, the proportion of non-carbonate residue increases in separation system from the bottom ash to the first (second) field of electrostatic precipitator and thereafter decreases towards the last field of electrostatic precipitator (Fig. 7b). The undecomposed fraction of the carbonate phases (mainly calcite) is considerably higher in CFB ashes, reaching 40–50% in bottom ash, but decreasing rapidly in subsequent ash separation points (Fig. 8).

Micromorphology of the ash fractions shows considerable differences in ashes formed in PF and CFB boilers. The PF ashes are, in most cases, characterized by large portion of spherical glassy and/or hematite particles with a clump of aggregated particles (Fig. 9). The relative proportion of the spherical particles increases from the bottom ash to ash fractions separated in electrostatic precipitators. Ash particles in CFB ashes, however, show only rarely spherical morphology, and ash is composed of porous aggregates
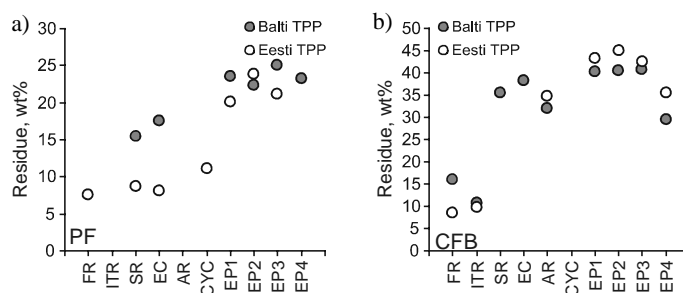
Fig. 7. Changes in residual fraction: quartz, K-feldspar, clay mineral illite and hematite. a) PF ash and b) CFB ash. Legend – see Fig. 1.
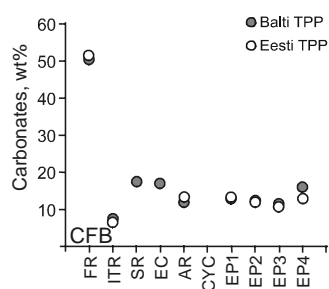
Fig. 8. Variations in carbonate content in CFB boiler ashes. Legend – see Fig. 1.
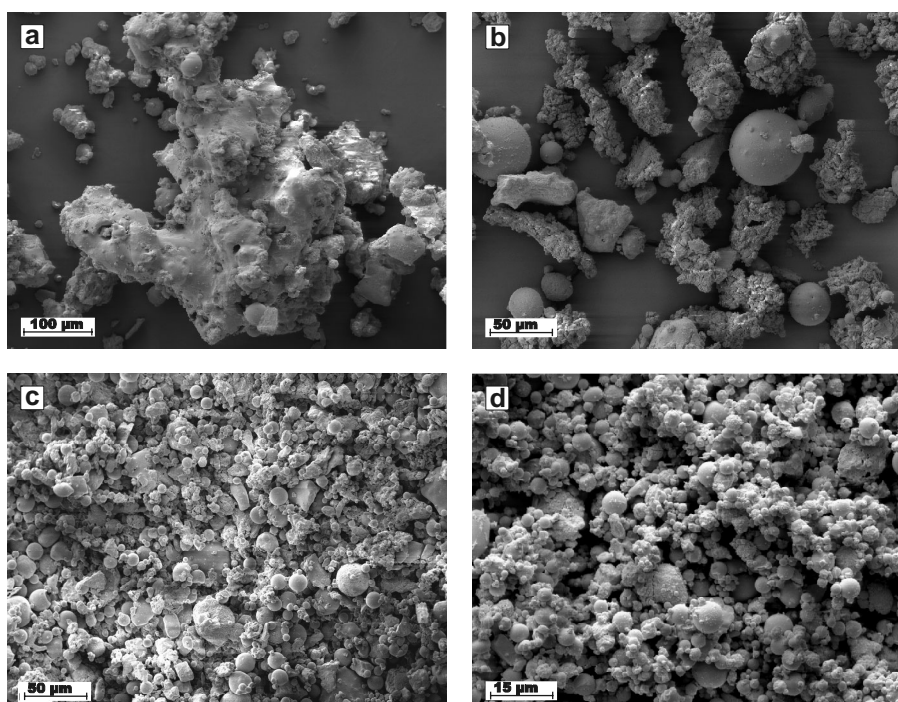

Fig. 9. SEM pictures of PF boiler ashes. a) furnace ash, b) cyclone ash, c) EP1 ash, d) EP3 ash.

of irregular particles whose grain size gradually decreases along the ash separation tract (Fig. 10). Similar morphological characteristics of PF and CFB ashes were noticed by Kuusik *et al.* [2].
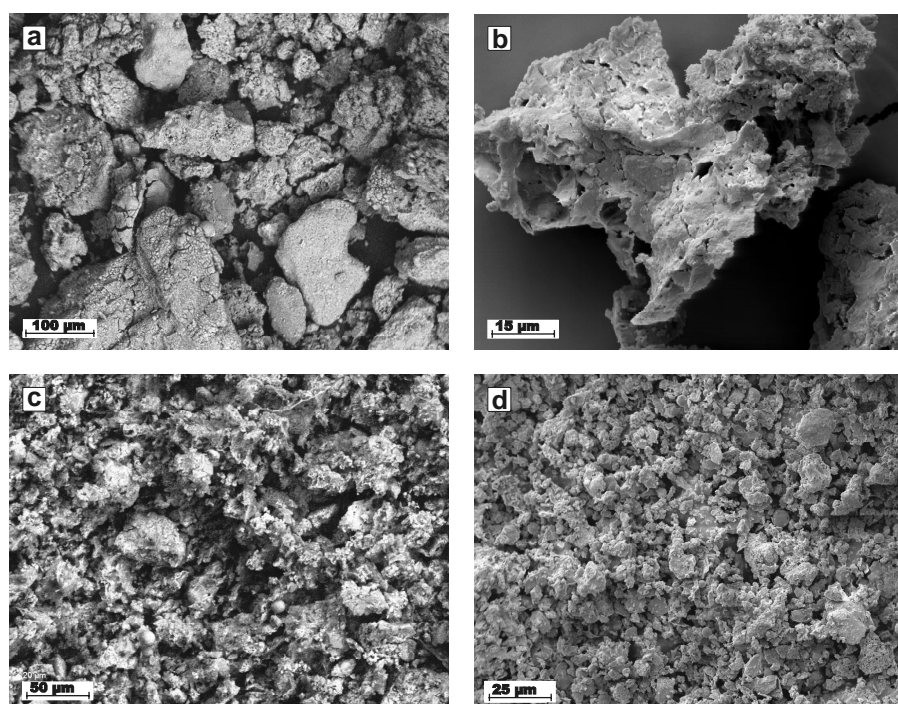
Fig. 10. SEM pictures of CFB boiler ashes. a) INTREX ash, b) cyclone ash, c) EP1 ash, d) EP3 ash.

Discussion

The compositional and morphological variations between PF and CFB ashes are principally controlled by firing temperature differences between combustion technologies, and by grain size differences of oil-shale fuel. The pulverized-firing technology exploits high-temperature combustion, where the nominal burning temperature inside the furnace chamber reaches 1350–1450 (up to 1500) °C, whereas in the circulating fluidized-bed combustion the optimum temperature in furnace chamber is about 850 °C [3]. These temperature differences have a major influence on the mineral matter decomposition and subsequent reactions. The high-temperature combustion process in the PF boilers ensures major decomposition of carbonate mineral phases (dolomite, calcite) and melting of clay minerals that form a source for reactive silica as well as aluminium, thus controlling the formation of secondary Ca-silicate and Ca-Al-silicate phases. The firing temperature in CFB boilers allows thermal decomposition of dolomite, but only partial decomposition of calcite. Also, the clay mineral phases are preserved, but they loose physically bound (including in interlayer position) water and for most part of the chemically bound hydroxyl groups. As a consequence, PF ashes are enriched with respect to free CaO and secondary Ca-silicate

phases, but CFB ashes contain a higher share of residual mineral phases. A specific characteristic of CFB ashes is the higher concentration of sulphur that is mainly concentrated into the INTREX ash in the form of anhydrite ($CaSO_4$). This phenomenon is caused by nearly complete desulphurization of flue gases by the prolonged contact/reaction of ash particles circulating between combustion chamber and INTREX chamber, which also ensures high decomposition rate of carbonate minerals [17].

According to Ots [3] the proportions of the different ash fractions in an averaged ash flow are: 39.3% bottom-slag ash, 3.1% superheater ash, 4.7% economizer ash, 32.2% cyclone ash and 13.5, 3.1, 0.7% of ash from electro-static precipitators 1, 2 and 3, respectively. Separation of the phases (either secondary or residual) along the boiler gas pass depends mainly on the particle size of the phases. Ash particles, whose free-fall velocity is lower than upward directed flue gas velocity are carried away from the furnace chamber through heat transfer surfaces by flue gas and are consequently separated depending on the boiler units in superheater, economizer, air-pre-heater, cyclon separator or in electrostatic precipitatiors. The coarsest or heavier particles precipitate onto the bottom of the furnace [3]. This separation mechanism suggests that the different firing technologies do not control only phase composition of ash but influence also particle size of the phases. Secondary Ca-silicates, forming at high-temperature conditions in the PF boiler, evidently form large (partially inter-melted?) aggregates, which are concentrated in coarse ash fractions that are removed in the first zones of the ash removal system. Our results show that at lower firing temperatures, in CBF boilers, the secondary Ca-silicate phases exist in the form of discrete and fine particles that are preferentially removed in the electrostatic pre-cipitators. On the contrary, the anhydrite particles in PF ashes are of fine grain size and occur mostly in ash separated by the electrostatic pre-cipitators. In CFB boilers, anhydrite is mostly found in INTREX ash, where anhydrite appears as a shell on unreacted CaO cores [18, 19], thus, forming relatively large particles, which are removed at large part in the INTREX chamber and to somewhat lesser degree in adjacent zones.

Comparison of the phase composition of ashes of the Eesti and Balti TPPs revealed differences in ashes formed at these power plants. The differences in ash composition are particularly seen in the composition of Ca-silicate phases. In the Balti TPP secondary Ca-silicates are represented mainly by β-C2S (belite), merwinite and wollastonite; while in the Eesti TPP also C3S, rankinite, as well as C4AF and akermanite are found.

Earlier mineralogical studies have addressed the qualitative [20] and quantitative [2] composition of ashes sampled at the Eesti TPP. Paat and Traksmaa [19] report only qualitative composition of the two fly ash fractions (cyclone and cloth filter) of the Balti TPP. The difference between ashes from two separate TPPs has not been shown before. The systematic difference in the composition of secondary Ca-bearing phases, which is evident both in PF and CFB ashes, suggests that this variation relates to the

composition/quality of the oil shale fuel used in boilers, not to technological differences.

The Eesti TPP is fed by oil shale mostly derived from the underground Estonia mine in the central part of the Estonia deposit of the oil-shale basin. The Balti TPP, on the other hand, uses oil shale mainly extracted by open-cast mining from Narva quarry in the easternmost part of the deposit. Calorific value of raw oil shale in both fields is nearly the same (7–9 MJ/kg), probably only slightly higher in Narva quarry [21]. The mineral composition of oil shale inorganic part is dominated by calcite, dolomite and terrigenous mineral phases (clay minerals, quartz, K-feldspar), and minor pyrite (Table 3). The content of terrigenous fraction in oil shale beds varies typically between 20 and 50%, while the proportions of carbonate minerals ranges from 50–75% [22]. Vingisaar *et al.* [22] indicate that the proportion of dolomite in the carbonate fraction of oil shale is somewhat higher in the northern part of the central field and also in the eastern area. The average content of MgO in the western part of the Estonia deposit is 2.6% and 1% in oil shale beds and carbonate rock intercalations, respectively; whereas the MgO content in eastern part of the deposit is in average 3.9% in oil shale beds and 2.5% in carbonate rock [22]. Dolomitic carbonate fraction of oil shale, which is decomposing at higher rate, would enhance the reactions between reactive CaO and silicate phases and the formation of variety of Ca-silicate and Ca-silicate-aluminate phases. Nevertheless, the content of MgO, which is the direct product of dolomite thermal dissociation, is not statistically higher in ashes from the Balti TPP compared to the Eesti TPP (Table 1), and further studies are needed for the confirmation and understanding of this phenomenon.

Table 3. Mineral composition of oil shale (unpublished data by Liidia Bityukova, 2010) compared with values reported by Vingisaar *et al*. [22]. Data are presented in wt%, tr – trace amount, n.d. – not determined

Sample/ mineral	Kiviõli 1	Kiviõli 2	Viru	Content range [22]
	weight, %			
Quartz	12.6	7.8	12.7	4–18
Calcite	36.0	60.4	33.8	30–70
Dolomite	14.7	7.8	17.7	5–30
K-feldspar	9.1	3.5	9.4	1–2
Albite		tr.		n.d.
Chlorite	5.8	2.1	3.3	0–3
Illite	14.6	11.1	19	5–36
Pyrite	6.1	6.9	4.1	n.d.
Gypsum	1	tr.		n.d.

Conclusions

The composition of oil shale ashes from the pulverized firing (PF) and circulating fluidized-bed boiler combustion (CFB) boilers at the Eesti and Balti TPPs shows a systematic variation in the boiler gas pass depending on the firing technology. PF ashes are dominated by free lime, whose proportion decreases from the furnace to the last fields of electrostatic precipitators. Ashes from CFB boilers show more complex variations, and on several occasion different phases change contrary to PF ashes. Comparison of the phase composition of ashes from the same type of boilers in the Eesti and Balti TPPs shows remarkable differences in Ca-silicate phases, which can be interpreted rather by the variation in oil shale fuel used at these TPPs than by combustion technology.

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