Transformations in the solid and liquid phase at aqueous carbonization of oil shale ash

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Abstract

The oil shale based energy sector of the Republic of Estonia is related to huge waste flows - about 5 million tons of waste ash is landfilled annually by circulating in the system tens of millions of cubic meters of transportation water saturated with different salts. Due to the distinctiveness of oil shale, the waste ash is characterized by heterogeneous and complicated mineral composition. Ash contains, depending on combustion technology (currently both pulverized firing and circulated fluidized bed combustion are used), 10–20% of free lime as the most active compound. Contacting free lime with water leads to elevated pH values (pH>13) and makes landfilling of this ash by hydraulic transportation highly problematic. It has been shown that the negative environmental impact of high alkalinity of these flows could be equilibrated by using CO_2 from flue gases as a neutralizing agent. At the same time the emission of CO_2 is diminished.

Laboratory batch tests showed that by treating ash – water suspension with CO_2-containing flue gases, the most of the free CaO can be reduced to an acceptable level. Some aspects of processes deceleration during wet carbonization of ash have been elaborated. Part of the free CaO present is not accessible due to low porosity and the formation of reaction products on the surface of ash particles. Also, lowering the pH of carbonized ash suspension influences the composition of the liquid phase by increasing leaching of some of the ash components. The behaviour of $CaSO_4$ as one of the dominant Ca-compounds in ash has been elaborated.

Keywords: CO_2 mineralization, waste oil shale ash.

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1 Introduction

Extensive usage of low-grade solid fuels in the world energy production is accompanied by a variety of problems, including emission of greenhouse gases and safe deposition/utilization of solid wastes. Reducing CO_2 emissions is an actual problem, being recognized and investigated by numerous research groups all over the world. One of the options is CO_2 sequestration by mineral carbonation, considering both natural minerals (O`Connor and Dahlin, [1], Haywood et al., [2]) and alkali wastes (Teir et al., [3], Huijgen et al., [4], Anthony et al., [5], Kuusik et al., [6]) as CO_2 sorbents.

The other part of the problem is related to the stabilization and safe landfilling of alkaline wastes. Carbonization has been recognized to be an important weathering process affecting alkaline waste materials such as ashes from power plants (Soong et al., [7]; Back et al., [8]; Reddy et al., [9]), and MSWI bottom ash (Meima et al., [10], Ecke, [11]).

The above-mentioned problems concern also the Republic of Estonia, whose energy sector is predominantly (up to 67%) based on local low-grade fossil fuel – Estonian oil shale. Compared with other fossil fuels, oil shale contains more mineral CO_2 in the form of limestone and dolomite. During combustion of oil shale, high temperatures drive off CO_2 from carbonate minerals and forming ash contains considerable amounts of Ca and Mg oxides (15-30%), which in certain conditions can be the binders of CO_2. Since 1959 the main combustion technology of oil shale has been pulverized firing (PF); in 2004 a more suitable combustion method for low calorific fuel – the circulating fluidized bed combustion (CFBC) was also implemented. The differences between the temperature levels (higher in PF boilers and lower in CFBC boilers) for the new and old boilers influence the phase and chemical composition, as well as the surface characteristics and reactivity of ashes. The objective of this paper is to elaborate the mechanisms of processes deceleration and changes in leaching of some of the Ca compounds during wet carbonization of ashes at ambient conditions.

2 Materials and methods

Initial samples of ash were collected from different points of the ash-separation systems of CFBC and PF boilers at the Estonian Thermal Power Plant. The CFBC ash samples used for the research were named and marked as follows: intrex ash (CFBC/INT), economizer ash (CFBC/ECO), electrostatic precipitator ash – 1st field (CFBC/ESPA1). The PF ashes used were bottom ash (PF/BA), cyclone ash (PF/CA) and electrostatic precipitator ash – 1st field (PF/ESPA1).

All ash samples were analyzed using chemical, grain-size and quantitative XRD methods, as well as SEM and BET methods (ash properties are discussed in more detail in Kuusik et al., [12]). XRD data was collected in powdered unoriented preparations with a Dron-3M diffractometer using Ni-filtered Cu-Kα radiation. Digitally registered diffractograms were measured within the range of 2–50° 2θ, with 0.03° 2θ step size and 3 s counting time. The diffractograms were analyzed with the code Siroquant using full-profile Rietveld analysis. A scanning electron microscope Jeol JSM-8404 was used for surface observations and specific surface area (SSA) was determined with a BET–method at Sorptometer KELVIN 1042 (Costech Microanalytical SC). Porosity measurements were carried out with the high pressure Hg intrusion method with a porosimeter Quantachrome AutoScan-33 (pressure range 0.1-227 MPa, pore diameter range 6.5-1500 nm).

The carbonization of aqueous ash suspensions with model gas, whose composition (10% CO_2 and 90% air) simulated CO_2 content in flue gases formed at oil shale combustion, was carried out in an absorber (diameter 55 mm, water column height 60 mm) equipped with a magnetic stirrer for achieving a better interfacial contact and a sintered glass gas distributor (pore diameter 100 μm). Distilled water or ash transportation water (TDS=7.79 g/l, Ca^{2+}-ions previously precipitated) were used for preparing the suspensions. The solid/liquid ratio was 1/10. Experiments were carried out at room temperature under atmospheric pressure until the suspension reached a definite value of pH (10; 9; 8.5). After carbonization, the suspension was filtered and solid residue dehumidified at 105 ^{0}C; in the solid residue free CaO content and CO_2 were determined. SSA and pore distribution measurements were performed for investigation of the deceleration mechanism.

In order to elaborate leaching characteristics, ash (CFBC ash, CaO_{free}=8.0% and $CaSO_4$=12.75%) or model mixtures (CaO and $CaSO_4$ of analytical grade) were mixed with water. The solid/liquid ratio was 1/10 in the case of ash. For the model system the amounts of CaO and $CaSO_4$ were calculated based on the actual contents in ash. Contents of Ca^{2+}, Mg^{2+}, SO_4^{2-} (Spectrophotometer Spectrodirect, Lovibond Water Testing) and alkalinity were determined in the liquid phase to study leaching.

3 Results and discussion

3.1 Characterization of oil shale ashes formed at industrial scale boilers

Reactivity of waste ashes towards CO_2 was estimated by their chemical and phase composition (Tables 1, 2) as well as by physical structure of ash particles (Kuusik et al., [12]). XRD analysis indicated that, as compared to PF ashes, the CFBC ashes contain more calcite (4.0–14.6 and 2.0–5.7%, respectively) and less free lime (10.8–19.9 and 26.5–29.3%, respectively). Mg was found in both cases mainly as periclase (MgO). In CFBC ashes, silica compounds are mainly presented by quartz (up to 17.1%) and orthoclase-type K-feldspar (up to 12.5%), while PF ashes contain noticeably more secondary silicate – belite (up to 15.9%) and merwinite (up to 13.2%). Relatively higher content of secondary silicates can be explained by significantly higher temperatures (1250–1400^{0}C) used in PF boilers, which leads to the formation of melted phase initiating the reactions between free CaO and clinker minerals.

Comparison of SEM photos of ash samples shows that particles of CFBC ashes formed at moderate temperatures (750–800^{O}C) are characterized by an irregular shape as well as by a porous and uneven surface (Fig. 1a). The glassy

Table 1: Chemical composition and physical properties of CFBC and PF ashes.

	CFBC/ INT	CFBC/ ECO	CFBC/ ESPA1	PF/BA	PF/CA	PF/ ESPA1
CaO_{total},%	47.59	32.84	29.52	50.75	49.39	36.08
MgO_{total}.%	13.65	9.50	8.33	15.19	14.19	11.26
CaO_{free}, %	18.87	10.40	8.45	24.84	22.52	13.56
CO_2, %	1.23	5.48	4.60	2.75	0.70	1.16
SSA, m^2/g	2.61	6.89	8.00	1.75	0.36	0.61
Total intruded volume, cm^3/g	0.32	0.39	0.62	0.23	0.13	0.34
d_{mean},µm	95	27	25	115	48	24

Table 2: Mineral composition of CFBC and PF ashes, %.

Minerals	CFBC/ INT	CFBC/ ECO	CFBC/ ESPA1	PF/BA	PF/CA	PF/ ESPA1
Quartz SiO_2	5.6	17.1	16.8	3.1	3.3	12.0
Orthoclase$KAlSi_3O_8$	2.7	9.4	12.5	6.6	1.7	3.8
Albite $NaAlSi_3O_8$	2.7					
Illite+Illite-Smectite $Na,K_x(Al,Mg)2Si_4O_{10}(OH)_2·H_2O$	3.1	11.2	13.8		6.1	
Belite Ca_2SiO_4	7.3	5.8	5.3	13.5	15.9	12.3
Merwinite $Ca_3Mg(SiO_4)_2$	5.2	3.0	3.7	9.4	13.2	6.5
Tricalcium aluminate $3CaO.Al_2O_3$	1.4	2.0	2.3	2.3	2.2	2.8
Periclase MgO	7.0	3.8	2.7	7.9	8.7	8.5
Melilite $(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	3.6	1.6	1.2	17.8	5.8	3.3
Anhydrite $CaSO_4$	29.9	11.1	9.5	5.4	5.4	16.8
Gypsum $CaSO_4·2H_2O$	0.8	0.5				
Lime CaO	19.9	13.3	10.8	26.5	29.3	28.1
Calcite $CaCO_3$	4.0	14.6	13.5	5.7	2.5	2.0
Aragonite $CaCO_3$		0.8				
Portlandite $Ca(OH)_2$	2.1	0.7			3.1	1.0
Hematite Fe_2O_3	2.1	3.6	4.3	0.9	1.1	1.6
Pseudowollastonite $CaSiO_3$	1.8	1.9	3.6	0.9	1.6	0.8

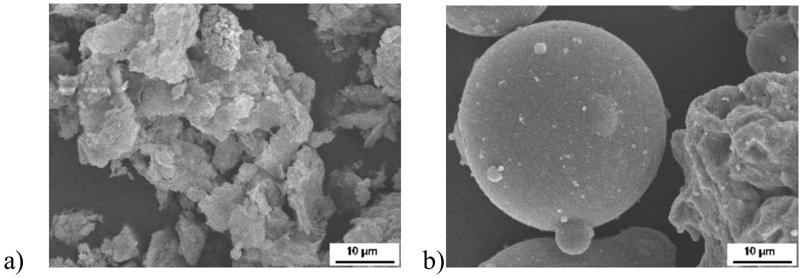

Figure 1: SEM pictures of CFBC (a-CFBC/ESPA1) and PF ashes (b-PF/CA), magnification 2000×.

phase is not formed. In the case of PF ashes, melting significantly affects the particle shape and surface properties: the particles are characterized by a regular spherical shape with a smooth surface (Fig. 1b).

BET measurements (Table 1) showed significant differences in the physical structure of CFBC and PF ashes – depending on ash type, the differences in SSA were up to a factor of ten. While SSA of CFBC ashes can reach 8.00 m^2/g, the SSA of PF ashes is within 0.36–1.75 m^2/g, which is caused by more intensive sintering of PF ashes at high boiler temperatures.

3.2 Transformations in the heterogeneous system CO_2 - ash - water: changes in the structure of ash particles

Laboratory batch tests (Table 3) showed that as compared to PF ashes, CFBC ash can be carbonized more deeply with lowering the content of free lime below 1%. In the case of PF ashes as less-porous materials, some of the free CaO present is not accessible, especially with PF/CA, which has the lowest porosity. Electrostatic precipitator ashes are most easily carbonized due to their finer fractional composition (Table 1). Ash transportation water characterized by a high concentration of dissolved salts also inhibits wet carbonization of ash. If ash transportation water was used for preparing the ash suspensions, the carbonization process stopped even earlier and most of the free CaO (8.3% Abs.) remained unreacted.

Pore distribution analysis of initial ashes showed that most of the pore volume of CFBC ashes (CFBC/ESPA1) is contributed by pores in the size range of 0.03-0.007 μm and 0.3-0.1 μm (Fig. 3a) as for PF ashes (PF/CA) the dominating pore diameter is considerably smaller – below 0.01 μm. Thereby, the PF ashes are expected to be more extensively influenced by the formation of reaction products on the surface of particles and pore plugging, which could lower mass transfer rates.

The changes in porosity and pore distribution of ashes at different stages of processing were analyzed to elaborate the deceleration mechanism taking place during the carbonization process. During treatment, while ash containing free CaO went through hydration, leaching and carbonization processes, both the specific surface area and total intruded volume (TIV) of ash increased (Table 3, Fig. 2) as a contribution from reaction products. The deepness of carbonization did not influence noticeably the value of TIV (0.92-0.98 cm^3/g in the case of CFBC/ESPA1) ashes. The pore distribution analysis showed that the average pore diameter of hydrated and leached ashes was in the range of 0.007-0.04 μm (Fig. 3). Carbonized ashes had average pore diameter in the ranges of 0.007-0.03 μm and 0.08-0.3μm. At deeper carbonization (pH=8.5) in the case of PF ashes (PF/CA) the amount of bigger pores (pore diameter in the range of 0.08-0.3 μm) and the value of TIV started to decline.

However, there were no remarkable differences in pore size distribution of ashes carbonized up to definite pH level (Figure 3c). It seems that in the case of PF ashes as almost nonporous materials, the reaction products formed hinder

Table 3: Characterization of initial and carbonized ashes.

Ash		CaO$_{free}$, %	CO$_2$,%	SSA,m^2/g	TIV, cm^3/g
CFBC/ INT	Initial	18.87	1.23	2.61	0.32
	pH=10	1.48	13.08	16.54	0.73
	pH=9	1.13	13.5	13.05	0.63
	pH=8.5	0.94	15.14	20.56	0.72
CFBC/ ECO	Initial	10.4	5.48	6.89	0.39
	pH=10	1.03	11.84	15.35	0.64
	pH=9	0.5	13.1	14.76	0.63
	pH=8.5	0.42	13.2	15.02	0.57
CFBC/ ESPA1	Initial	8.45	4.60	8.00	0.62
	pH=10	0.84	10.75	17.16	0.98
	pH=9	0.33	11.72	15.00	0.92
	pH=8.5	0.38	12.88	15.88	0.94
PF/BA	Initial	24.84	2.75	1.75	0.23
	pH=10	2.07	13.00	9.58	0.45
	pH=9	2.14	15.93	10.27	0.56
	pH=8.5	1.57	17.12	13.18	0.51
PF/CA	Initial	22.52	0.7	0.36	0.13
	pH=10	4.25	10.88	6.26	0.32
	pH=9	3.20	13.89	11.27	0.63
	pH=8.5	3.24	13.16	7.20	0.32
	* pH=10	8.27	10.24	6.16	0.22
	* pH=8.5	8.13	10.13	5.01	0.22
PF/ ESPA1	Initial	13.56	1.16	0.61	0.34
	pH=10	1.53	9.66	10.71	0.71
	pH=9	0.58	11.91	13.20	0.91
	pH=8.5	0.40	12.15	11.45	0.87

*Ash transportation water was used for preparing suspension.

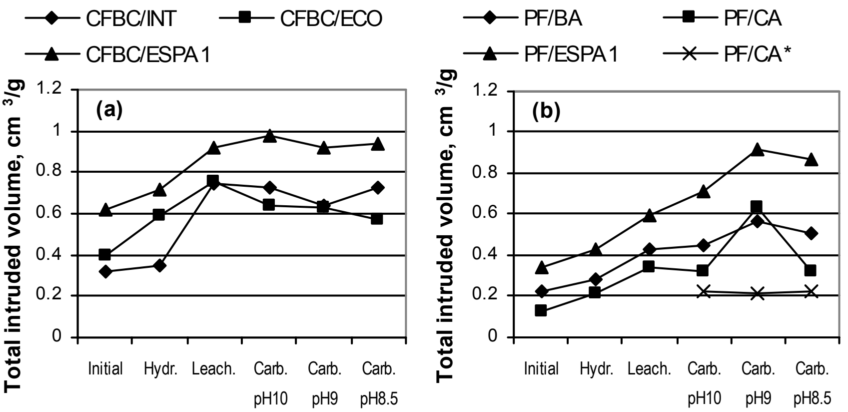

Figure 2: Changes in total porosity of (a) CFBC and (b) PF ashes during different stages of carbonization.

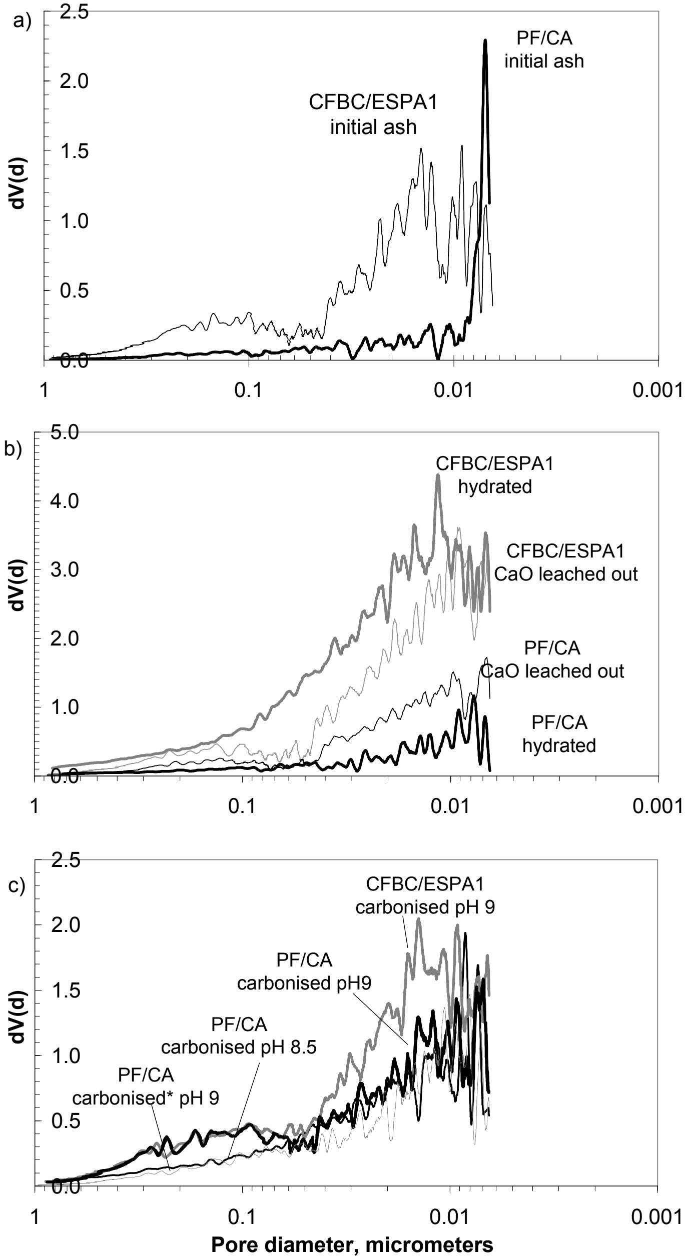

Figure 3: Changes in pore size distribution at hydration, leaching and carbonization of ashes (* - aqueous carbonization process carried out in ash transportation water).

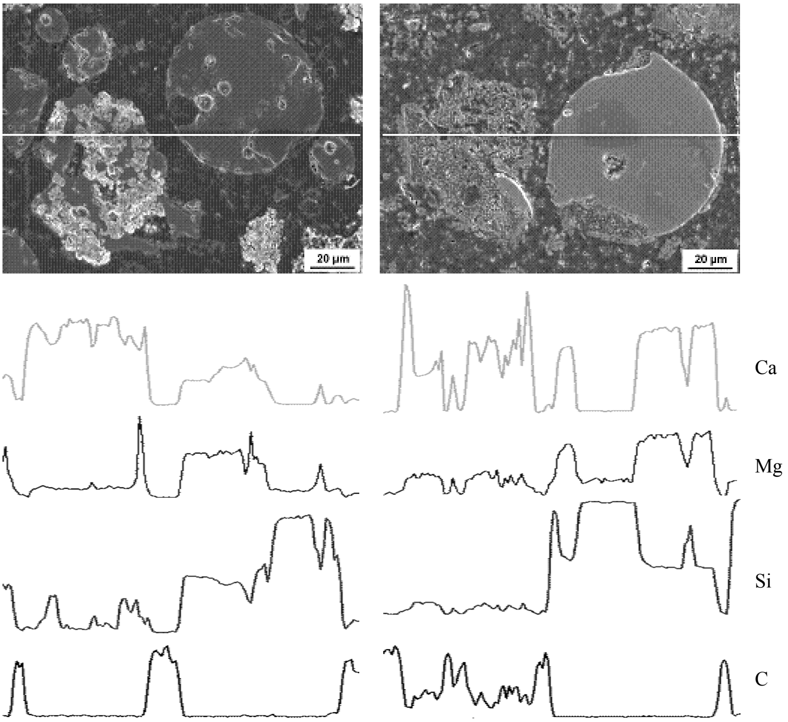

Figure 4: SEM and EDAX analysis of initial ash (PF/CA) and carbonized ash (on left).

reactions with CaO. It was verified also by SEM and EDAX linescan analysis that carbonized particles were covered with a perceptible layer of $CaCO_3$ (Fig. 4). Also, as the initial ash particles contain noticeable amounts of Ca-silicates, which participate at lower pH in carbonization reactions (Kuusik, et al., [13]), the SiO_2 released can block the pores of ash particles.

3.3 Transformations in the heterogeneous system CO_2 - ash - water: leaching of CaO and $CaSO_4$ at different pH levels

Ashes contain considerable amounts of free CaO (8-25%) and $CaSO_4$ (5-30%) (Tables 1, 2) which significantly influence the composition of the liquid phase while contacted with water: the liquid phase becomes deeply alkaline (pH>12) and saturated with Ca^{2+} and SO_4^{2-} ions. Laboratory experiments showed that the content of Ca^{2+} decreased significantly during carbonization due to the formation of more stable $CaCO_3$ (Fig. 5). Also, the content of SO_4^{2-} decreased to some extent (1190 and 847 mg/l, respectively) indicating possible co-precipitation of $CaSO_4$. At deeper carbonization to pH<8 the concentrations of Ca^{2+} and SO_4^{2-} started to rise again (to 480 and 1107 mg/l, respectively). The amount of Mg^{2+} ions in the solution became evident and bicarbonate ions appeared. Experiments with model systems ($CaSO_4$-CaO - H_2O - CO_2) confirmed the same tendencies.

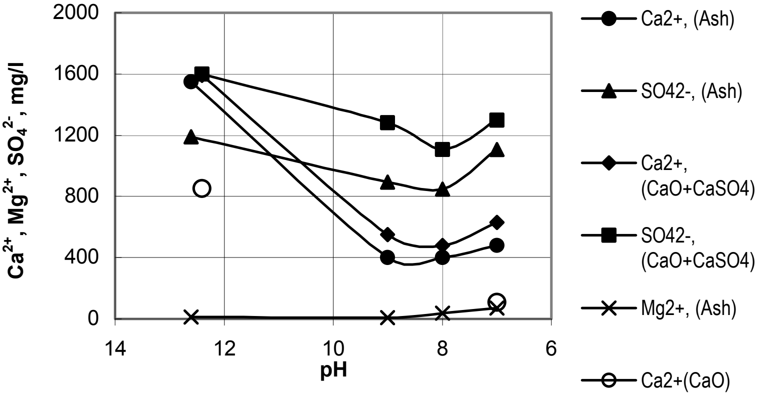

Figure 5: Changes in liquid phase composition during carbonization of aqueous suspensions of ash and model compounds.

Therefore, while using a wet carbonization method for stabilizing the ashes, it is recommended to keep final pH in the range of 8...9 – going to lower values would increase the leaching of some ash components.

4 Conclusions

The deceleration mechanism of the wet carbonization process of two kinds of oil shale ashes has been elaborated. The CFBC ashes, characterized by a porous and uneven surface as well as higher SSA values and larger pores, can be carbonized more deeply with lowering the content of free CaO below 1%.

Due to low porosity and small sized pores, the PF ashes are rather extensively influenced by product ($CaCO_3$) formation on the surface of particles. Evidently, in this case the formation of reaction products leads to the plugging of pores in extent hindering the leaching of lime and diffusion of Ca^{2+}-ions.

The carbonization process is also controlled by a liquid phase – by the pH of ash – water suspension. At lower pH values carbonization process may decelerate due to the increase in solubility of calcium carbonate and sulphate.

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