

MINERAL TRAPPING OF CO₂ VIA OIL SHALE ASH AQUEOUS CARBONATION: CONTROLLING MECHANISM OF PROCESS RATE AND DEVELOP- MENT OF CONTINUOUS-FLOW REACTOR SYSTEM

M. UIBU*, R. KUUSIK

Laboratory of Inorganic Materials
Tallinn University of Technology
5 Ehitajate Rd., 19086 Tallinn, Estonia

Ash containing considerable amounts of free lime as the most active component requires stabilization to assure safe landfilling. Using CO₂ from flue gases as a neutralizing agent, also the emission of CO₂ is diminished. The most extensive effect could be achieved by treating ash-water suspensions with CO₂-containing gas. As even minute amounts of extraneous substances present in water influence the extent and rate of lime solubility in water, the behavior of lime as the key component of ash in various conditions was studied and the mechanism of process deceleration was proposed. As the next step, a laboratory-scale continuous-flow reactor system for aqueous carbonation of oil shale ash and main considerations for industrial pilot-scale plant design were developed.

Introduction

Emission of greenhouse gases and safe deposition/utilization of solid wastes are among the most serious problems caused by extensive usage of low-grade solid fuels in the world heat and power production. CO₂ emissions could be decreased by reducing the usage of fossil energy sources, improving energy efficiency and/or by more intensive implementation of carbon capture and storage (CCS) technologies. CO₂ sequestration by mineral carbonation, considering both natural minerals [1, 2] and alkali wastes [3–5] as CO₂ sorbents, is a prospective option.

Carbonation of minerals is similar to natural rock weathering and involves permanent storage of CO₂ under the thermodynamically stable form of calcium and magnesium carbonates [6]. Mg- and Ca-rich silicates such as olivine, serpentine, talc and wollastonite are available worldwide and have

* Corresponding author: e-mail maiibu@staff.ttu.ee

the potential of sequestering the total amount of CO₂ emitted from the combustion of all the available fossil fuel reservoirs [7]. Unfortunately, because of very slow reaction rates the carbonation of natural minerals requires chemical additives and/or elevated pressures and temperatures [8].

One way of bypassing some draw-backs of accelerated carbonation of primary alkaline earth minerals is using alkaline waste residues from thermal processes or from construction and demolition activities as a feedstock. As these materials are often associated with CO₂ point source emissions and tend to be chemically more unstable than geologically derived minerals [9], they require a lower degree of pre-treatment and less energy-intensive operating conditions to enhance carbonation yields [9, 10]. Furthermore, after stabilization by accelerated carbonation, the leaching behavior of alkaline waste materials such as municipal solid waste incinerator (MSWI) bottom ash [11, 12], steel slag [4, 9, 13, 14], air pollution control (APC) residues [15, 16] and ashes from coal and oil shale power plants [17–19] is improved. This allows the usage of stabilized waste materials in civil engineering applications or for safer final disposal to landfill.

The energy sector of the Republic of Estonia is predominantly (up to 67%) based on local low-grade fossil fuel – Estonian oil shale [20]. Because of the high share of minerals present in oil shale, large amounts of ash are produced (45–47% of oil shale burnt, dry mass basis) and deposited in open-air ash ponds. Depending on the combustion technology, ash contains from 10 to 25% free Ca and Mg oxides and thereby it can be considered a CO₂ binder even under natural weathering conditions [21]. On the other hand, the ash is rich in free lime as the most active component, and because of that it requires stabilization to assure safe landfilling or further use. Using CO₂ from flue gases as a neutralizing agent, the emission of CO₂ is also diminished.

Aqueous batch-mode experiments showed [18] that oil shale ashes react readily with CO₂-containing gas mixture, though the carbonation extent depends on operating conditions. The aim of the current study was to study the factors influencing the behavior of lime as the key component of ash under various conditions and as the next step to develop a laboratory-scale continuous flow reactor system for aqueous carbonation of oil shale ash.

Materials and methods

Batch experiments and process deceleration studies

To establish hydration of lime and dissolution of Ca²⁺ ions in different conditions, aqueous ash (PF cyclone ashes, pretreated PF cyclone ashes and CFBC ash, Table 1) suspensions were prepared (solid/liquid ratio 1 : 10). Distilled water (DW), recirculation water (RW) from the ash-transportation system of Estonian Power Plant (pH = 13; TDS = 11.4 g/l; Ca²⁺ = 730 mg/l, SO₄²⁻ = 2.8 g/l; OH⁻ = 64.25 mmol/l) and carbonated recirculation water

Table 1. Chemical composition of initial PF and CFBC ashes (see also [23])

Ash	Description	CaO _i , %	CaO _f , %	CO ₂ , %	SO ₄ , %	SSA, m ² /g	d _{mean} , μm
PF07/CA	pulverized firing cyclone ash	50.16	23.44	1.49	4.59	0.44	43
PF07/CA*	slowly hydrated by the humidity of air during 8 months					1.18	
PF08/CA	pulverized firing cyclone ash	49.71	21.68	1.13	3.72	0.47	47
PF08/CA hydr	hydrated by water					1.48	
CFBC07/Mix12	circulating fluidized bed combustion ash	36.36	8.23	12.29	6.15	6.32	33
PF08/Mix	pulverized firing ash	49.69	22.43	5.07	3.96	1.62	47
CFBC07/Mix	circulating fluidized bed combustion ash	NA	12.38	9.92	NA	3.73	34

NA – not analyzed

(CRW; pH ~ 7.5; TDS = 6.8 g/l; Ca²⁺ = 450 mg/l; SO₄²⁻ = 2.7 g/l; HCO₃²⁻ = 60.75 mmol/l) were used as liquid agents. After 15-min stirring, the suspensions were filtered and the solid residue dehydrated at 105 °C.

Carbonation of ash-water (DW, RW, CRW) suspensions was carried out using a model gas whose composition (10% Vol. CO₂ and 90% Vol. air) simulated the proportion of CO₂ in flue gases formed during oil shale combustion. The carbonation was performed in an absorber (diameter 55 mm, water column height 100 mm) equipped with a magnetic stirrer to achieve better interfacial contact and a sintered glass gas distributor (pore diameter 100 μm) at room temperature under atmospheric pressure. The experiments went on until suspension pH reached 7.5. The degree of carbonation N_{CO₂} indicating how many times the amount of CO₂ entrained into suspensions exceeds the stoichiometric ratio (CaO/MgO + CO₂ = CaCO₃/MgCO₃) varied up to 5. After carbonation, the suspensions were filtered and the solid residue was dehumidified at 105 °C.

The samples were analyzed for chemical composition: Ca²⁺, Mg²⁺, SO₄²⁻ content (Spectrophotometer Spectrodirect, Lovibond Water Testing) and alkalinity were determined in liquid phase and CaO_f [22] and CO₂ were determined in solid phase. Specific surface area (SSA) was estimated with BET method at Sorptometer KELVIN 1042 (Costech Microanalytical SC). Scanning electron microscope Jeol JSM-8404 was used for surface observations. To determine the elemental composition of the ash particles, the samples were analyzed by high-resolution scanning electron microscope (Zeiss ULTRA 55 equipped with an angle selective backscattered detector (EsB) for compositional contrast) using an energy dispersive x-ray analysis (EDX) (Röntec EDX XFlash 3001 detector).

Continuous flow experiments

Following the promising results achieved with a batch reactor, a continuous-flow reactor system for treating oil shale ash – water suspensions with CO₂-containing model gas has been developed (Fig. 1). Carbonation process was optimized by adding reactor-columns (water column height 0.7 m and volume 10 L). They worked in cascade; and pH levels were set from alkaline (reactors I and II) to almost neutral (reactor III) in different reactors. This prolonged the contact time of phases (ash, water, CO₂-containing model gas) for CaCO₃ precipitation at optimal conditions. Ash (CFBC07/Mix or PF08/Mix ash – see Table 1; flow-rate 2.6–3.5 kg/h) and water (tap water or circulating process water; flow-rate 26 L/h) were fed to the reactor-column I, from which the partly carbonated suspension was led to the next stages (reactors II and III) for deeper carbonation. The mechanic stirrer (1000 rpm) was equipped with extra impellers for achieving better interfacial contact and more homogeneous material flow. Suspension pH was controlled by adjusting the flow-rate of incoming CO₂. The amount of CO₂ entrained into reactors per stoichiometric ratio according to $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$ (N_{CO_2}) was calculated as the sum of 0.4–0.6 (N_{CO_2} in reactor I), 0.3–0.6 (reactor II) and 0.3–0.5 (reactor III) for PF ash (see Fig. 2) and the sum of 0.4–0.7 (reactor I), 0.2–0.5 (reactor II) and 0.6–1.1 (reactor III) for CFBC ash. Samples of suspension (sampler was located at the 35-cm distance from

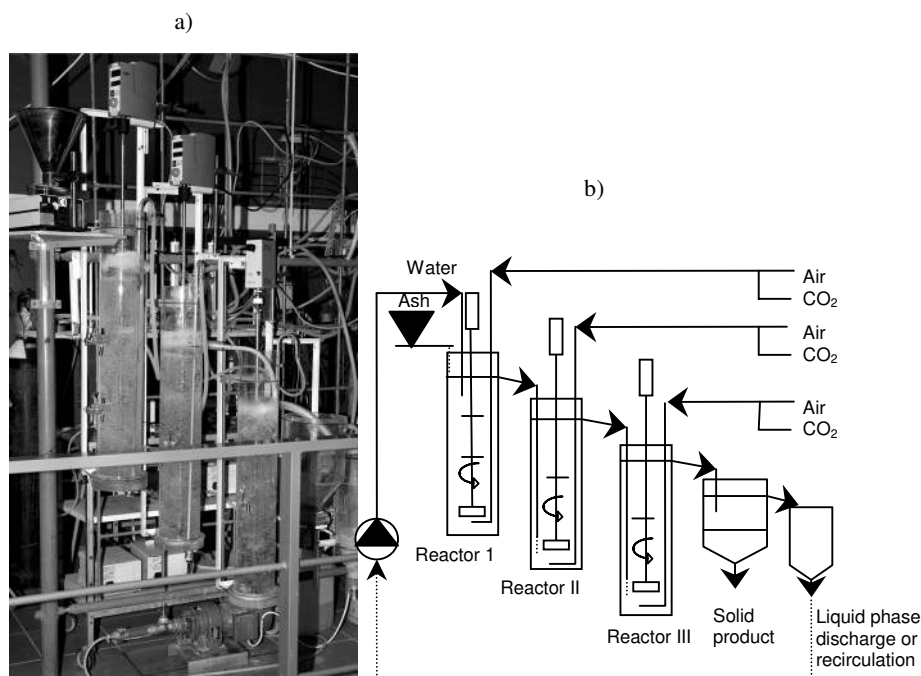


Fig. 1. Experimental setup (a – photo; b – scheme).

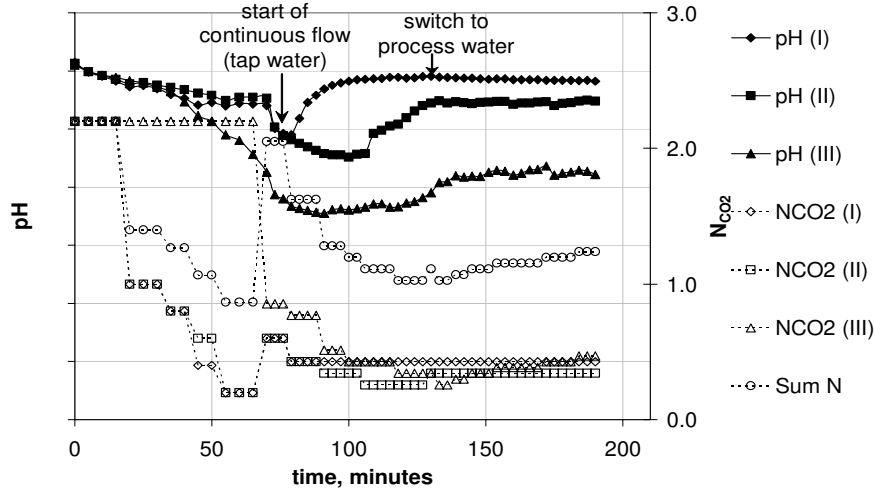


Fig. 2. Operating pH (reactors I to III) and N_{CO_2} regimes during carbonation of ash (PF08/Mix) in continuous mode.

the bottom of reactor-columns) were filtered and solid residue dehumidified at 105 °C. The liquid and solid phases were analyzed for chemical composition (content of free CaO [22] and bound CO_2 primarily). Effectiveness of the carbonation process was described by a CO_2 -binding degree (BD_{CO_2} , %) and a CaO-binding degree (BD_{CaO} , %). BD_{CO_2} shows which part of the theoretical CO_2 -binding capacity is utilized ((Eq. 1), where CO_2 is analytically determined CO_2 content of the sample and $\text{CO}_{2\text{max}}$ is the maximal possible CO_2 content of the sample, % according to (Eq. 2)). BD_{CaO} shows which part of free CaO as the most important CO_2 -binding component in ash is utilized ((Eq. 3), where CaO is analytically determined CaO content of the sample and CaO^i denotes the content of free CaO in the initial sample).

$$\text{BD}_{\text{CO}_2} = \frac{\text{CO}_2}{\text{CO}_{2\text{max}}} \cdot 100, \quad (1)$$

$$\text{CO}_{2\text{max}} = \frac{\text{CaO}^i \cdot 44/56 + \text{CO}_2^i}{100 + \text{CaO}^i \cdot 44/56} \cdot 100, \quad (2)$$

$$\text{BD}_{\text{CaO}} = \frac{\text{CaO}^i - \text{CaO}/(1 + \text{CaO}/56)}{\text{CaO}^i} \cdot 100. \quad (3)$$

Results and discussion

Batch experiments and studies of process deceleration

As shown earlier [23], oil shale ashes formed in boilers operating at different combustion technologies differ significantly by their chemical and phase composition as well as by physical structure and surface properties. In the context of CO₂ sequestration and ash stabilization, the availability of lime for hydration and carbonation reactions is of key importance.

According to a SEM examination of ash samples, particles of CFBC ash formed at moderate temperatures (750–800 °C) are characterized by an irregular shape and a porous and uneven surface [23] while in the case of PF ash (formed at 1,250–1,400 °C), the glassy phase significantly affects the formation of particle shape and surface properties: the particles tend to have a regular spherical shape with a smooth surface (Fig. 3a). BET measurements revealed that, depending on the ash type, a ten-fold difference in specific surface area was observed: surface areas of CFBC ashes reached 6 m²/g, while the those of PF ash samples ranged between 0.4–0.5 m²/g (see Table 1; also [23]). These properties affect greatly the chemical reactivity of ashes. Apparently, the low porosity and small-sized pores (<3 nm) in PF

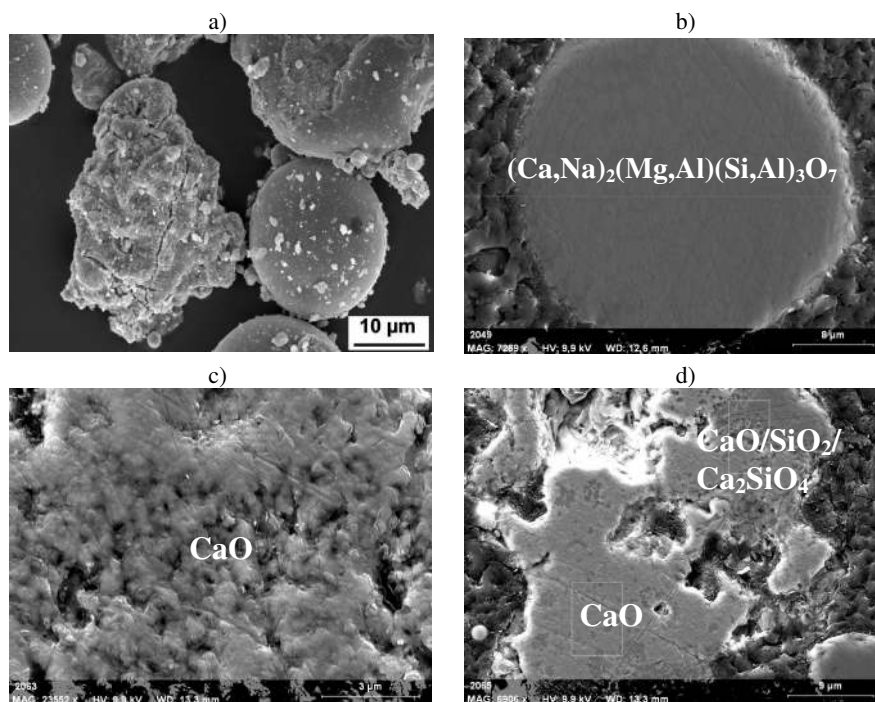


Fig. 3. Different types of particles present in PF cyclone ash (PF07/CA) and their chemical composition (SEM EDX analysis).

ashes limit the free CaO availability for reaction with CO₂, which can easily lead to process deceleration [19].

SEM analyses together with EDX element mapping revealed that particles of PF/CA can be divided generally into three types: spherical homogeneously melted ones – they contain Ca-Mg-Al-silicates: melilite (Ca,Na)₂(Mg,Al)(Si,Al)₃O₇, illite-smectite, merwinite (Ca₃Mg(SiO₄)₂) (Fig. 3b); slightly porous and uneven ones – these mainly contain free CaO (Fig. 3c) and partially melted ones – these contain lots of different phases (Fig. 3d; brighter and darker areas indicate different phases).

When PF/CA is immersed into DW, slaking of lime-containing particles occurs. As the water penetrates into the surface pores, heat of hydration is released which exerts internal expansive forces in the lime-containing particles (the molar volumes of Ca(OH)₂ and CaO are 33.078 and 16.79 mL/mol, respectively [24]) and causes them to fracture and disintegrate (Fig. 5a,b) [21]. The conversion of calcium oxide to calcium hydroxide is followed by the dissolution of calcium hydroxide to yield calcium ions and hydroxide ions on the surface of the particle and finally by the diffusion of calcium and hydroxide ions into the bulk of solution (Fig. 4) [25, 26]. The solution becomes strongly alkaline (pH = 12.9) and oversaturated with Ca²⁺ ions (Ca²⁺ = 1,400–1,500 mg/L, Table 2). The homogeneously melted particles are not affected by water (Fig. 5a) and are not likely to participate in carbonation reactions during short reaction times (15–45 min) in mild conditions (room temperature, atmospheric pressure, 10% CO₂ in model gas mixture). As a CO₂-containing model gas is bubbled through the ash-water suspension, a CaCO₃ precipitation reaction takes place (see Fig. 4). During carbonation, the pH and concentration of Ca²⁺ ions in the liquid phase stay on high level until carbonation of almost all free lime is realized (~2% of unreacted lime in solid residue, Table 2; Fig. 6a,b). Then pH of suspension liquid phase and concentration of Ca²⁺ ions decrease rapidly until stabilizing at pH ~ 7.5 and Ca²⁺ = 300–400 mg/L (Table 2, Fig. 6a).

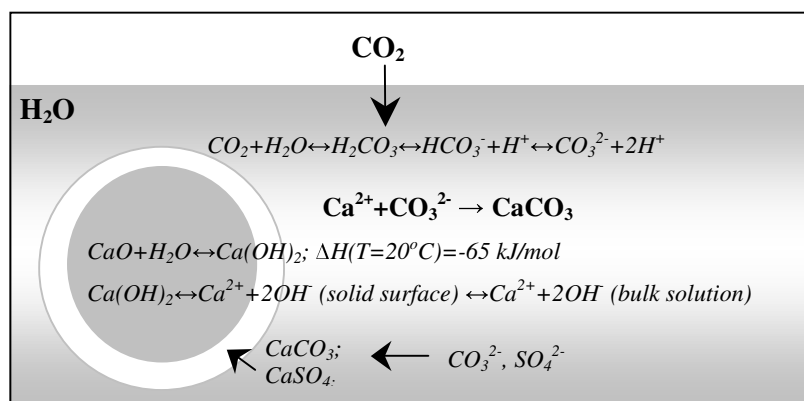


Fig. 4. Reactions of lime at CO₂ aqueous sequestration by oil shale ash.

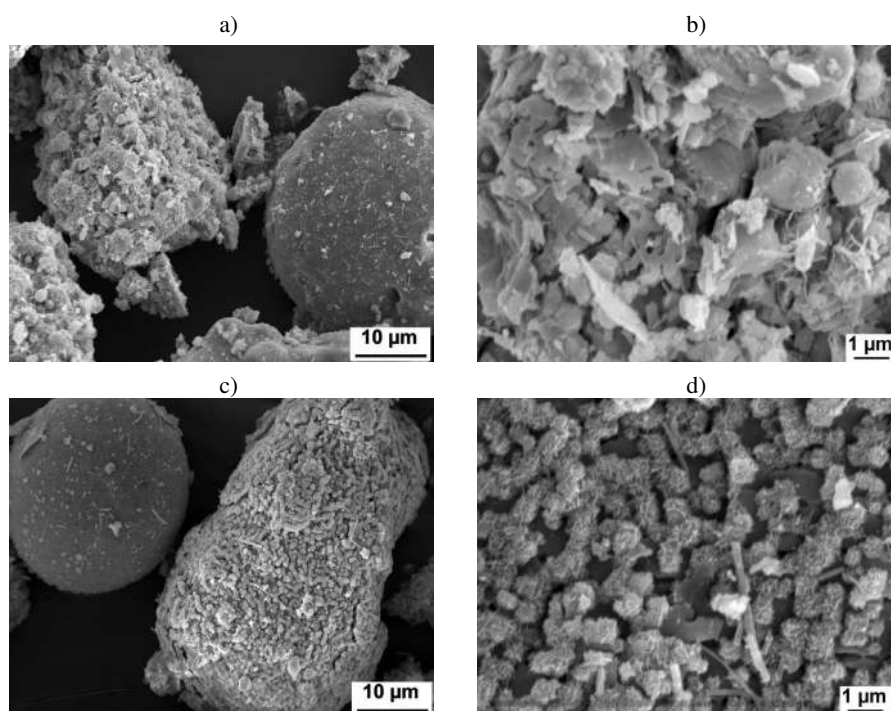


Fig. 5. SEM images of ash (PF07/CA) immersed into DW (a, b) or into CRW (c, d).

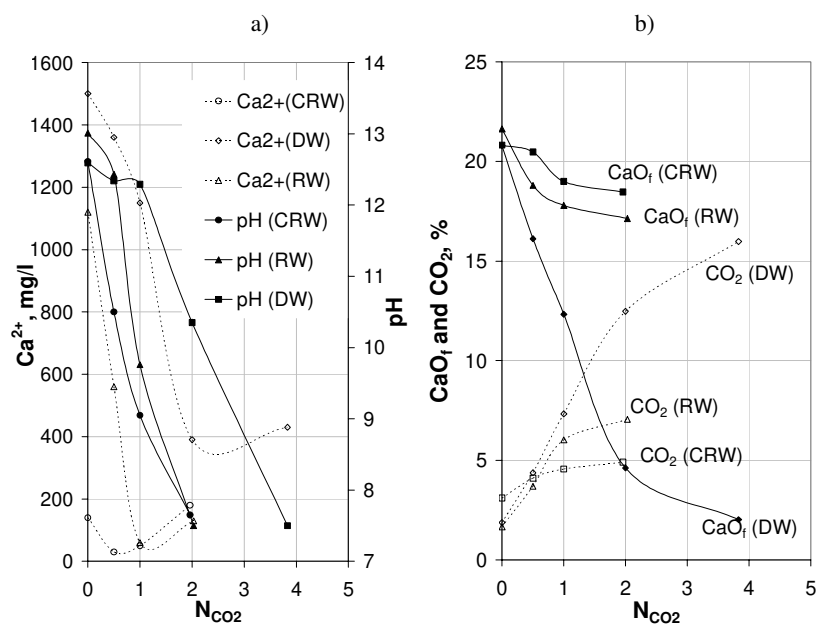


Fig. 6. Carbonation of aqueous suspensions of PF ash (PF07/CA): depending on: a) Ca²⁺ content and pH of liquid phase and b) CO₂ and free CaO contents in solid phase on the extent of carbonation (N_{CO2}).

Table 2. Carbonation of aqueous suspensions of oil shale ash: composition of liquid and solid phase

Suspension composition	Composition of liquid phase							Composition of solid phase			
	pH	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	OH ⁻	CO ₃ ²⁻	HCO ₃ ⁻	CO ₂	CaO _f	SO ₄	SSA
		mg/L			mmol/L				%		m ² /g
Ash + distilled water											
PF07/CA	12.9	1500	0	NA	56.5	2.0	0.0	1.87	20.80	3.70	1.95
PF08/CA	12.9	1400	0	980	54.0	2.0	0.0	2.24	18.83	2.88	1.62
Ash + recirculation water (pH = 13; TDS = 11.4 g/L; Ca ²⁺ = 730 mg/L, SO ₄ ²⁻ = 2.8 g/L; OH ⁻ = 64.3 mmol/L)											
PF07/CA	13.3	1120	0	NA	77.5	4.0	0.0	1.66	21.64	3.93	1.62
PF08/CA	13.3	1060	0	3030	75.5	7.0	0.0	1.71	21.53	3.41	1.10
PF08/CA hydr	13.3	1020	0	3285	66.0	8.0	0.0	1.63	21.65	3.32	2.60
Ash + carbonated recirculation water (pH ~ 7.5; TDS = 6.8 g/L; Ca ²⁺ = 450 mg/L; SO ₄ ²⁻ = 2.7 g/L; HCO ₃ ²⁻ = 60.8 mmol/L)											
PF07/CA	12.6	140	0	NA	25.0	7.0	0.0	3.10	20.82	4.16	2.21
PF08/CA	12.7	60	0	2805	15.5	15.0	0.0	2.62	22.36	3.62	1.77
PF08/CA hydr	13.3	1020	0	3110	71.5	7.0	0.0	2.96	19.66	3.47	4.01
Ash + distilled water + model gas (10% CO ₂ , 90% air)											
PF07/CA	7.5	430	18	NA	0.5	1.0	0.0	15.98	2.02	2.88	13.7
PF08/CA	7.5	340	36	826	0.0	1.0	1.5	13.61	4.54	2.54	10.22
CFBC07Mix12	7.5	520	78	NA	0.0	0.5	1.0	16.58	1.26	5.67	13.24
Ash + recirculation water (pH = 13; TDS = 11.4 g/L; Ca ²⁺ = 730 mg/L, SO ₄ ²⁻ = 2.8 g/L; OH ⁻ = 64.3 mmol/L) + model gas (10% CO ₂ , 90% air)											
PF07/CA	7.5	130	42	NA	0.0	5.0	22.5	7.05	17.14	3.84	2.96
PF07/CA*	7.5	310	30	4245	0.0	2.0	2.0	16.92	1.97	2.61	21.17
PF08/CA	7.5	140	24	3055	0.0	6.0	25.0	5.89	18.17	3.34	2.36
PF08/CA hydr	7.5	60	36	3440	0.0	4.0	12.0	11.99	6.97	2.71	5.06
CFBC07Mix12	7.5	400	24	NA	0.0	1.0	3.0	16.99	1.17	6.12	13.01
Ash + carbonated recirculation water (pH ~ 7.5; TDS = 6.8 g/L; Ca ²⁺ = 450 mg/L; SO ₄ ²⁻ = 2.7 g/L; HCO ₃ ²⁻ = 60.8 mmol/L) + model gas (10% CO ₂ , 90% air)											
PF07/CA	7.5	180	42	NA	0.0	3.0	30.5	4.9	18.47	3.92	2.08

* – ash was held in nonhermetical conditions for 8 months.

After carbonation (solid residue contains 30–36% CaCO₃) the ash particles are covered with a porous and permeable product layer (Fig. 7a), while specific surface area increased to 10–13 m²/g (see Table 2).

The use of recirculation process water, which contains an excess amount of sulfate and/or carbonate ions (RW or CRW) significantly inhibits the lime slaking rate and the reactions that follow. When PF/CA is immersed into carbonated recirculation water (pH ~ 7.5, HCO₃⁻ = 60.75 mmol/L; SO₄²⁻ = 2.7 g/L) the Ca²⁺ ion concentration in the liquid phase drops to 60–140 mg/L (see Table 2) according to reaction (Eq. 4):



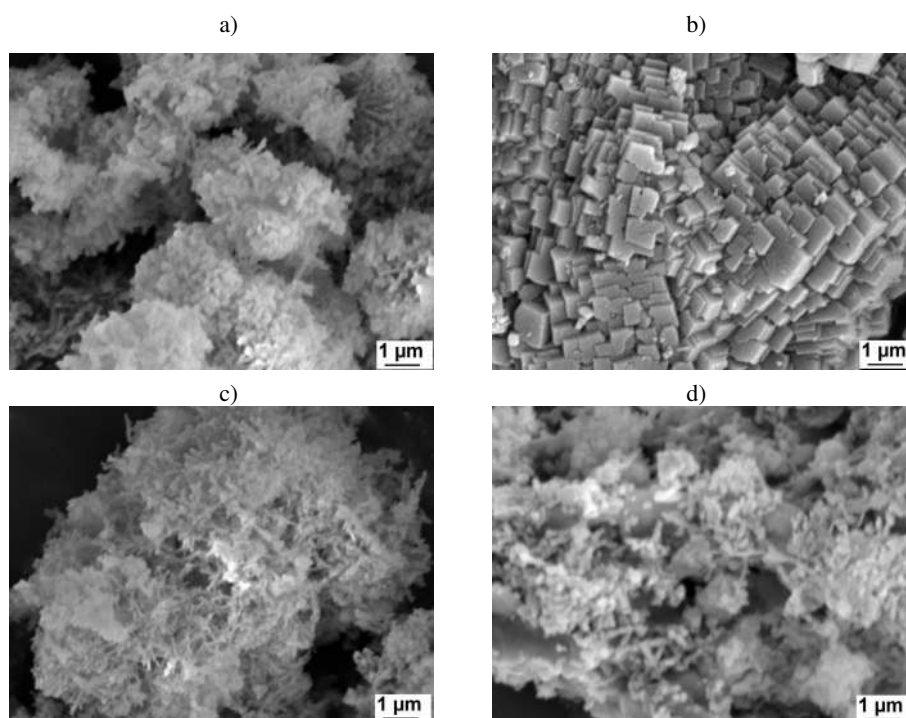


Fig. 7. SEM images of the carbonation products formed in the heterogeneous systems of: a) PF07/CA + DW + CO₂-containing model gas; b) PF07/CA + CRW + CO₂-containing model gas; c) CFBC07/Mix12 + DW + CO₂-containing model gas and d) CFBC07/Mix12 + RW + CO₂-containing model gas.

This indicates that hydration of lime-containing particles is already retarded.

In the presence of Ca²⁺ and OH⁻ ions the slaking rate reduces because the reaction is also controlled by the diffusion of calcium hydroxide away from the surface [26]. Carbonate and sulfate ions (>500 mg/L) present in the lime slaking water are known to form insoluble layers of both CaCO₃ and CaSO₄, which partially or completely coat the surface, thereby preventing further dissolution or at least slow it down [27]. At 0.01–0.05 M carbonate concentrations calcium carbonate forms a coherent film on the calcium hydroxide surfaces, thereby denying water access to the surface and preventing further dissolution of the slaked lime [28]. The SEM and EDX linescan analysis reveals that immersing ash particles into sulfate containing recirculation water causes sulfur compounds (obviously in the form CaSO₄) to concentrate on the surface layer (Fig. 8a,b). The layer of carbonates cannot be detected by EDX linescan analysis because the base material also contains carbon, but the solid phase analysis shows a slight increase in CO₂ content (1.1–1.5→2.6–3.1%, see Tables 1 and 2). The small-size pores of PF ash are easily blocked although the overall SSA may increase (0.4–0.5→1.1–2.2 m²/g; see Tables 1 and 2) due

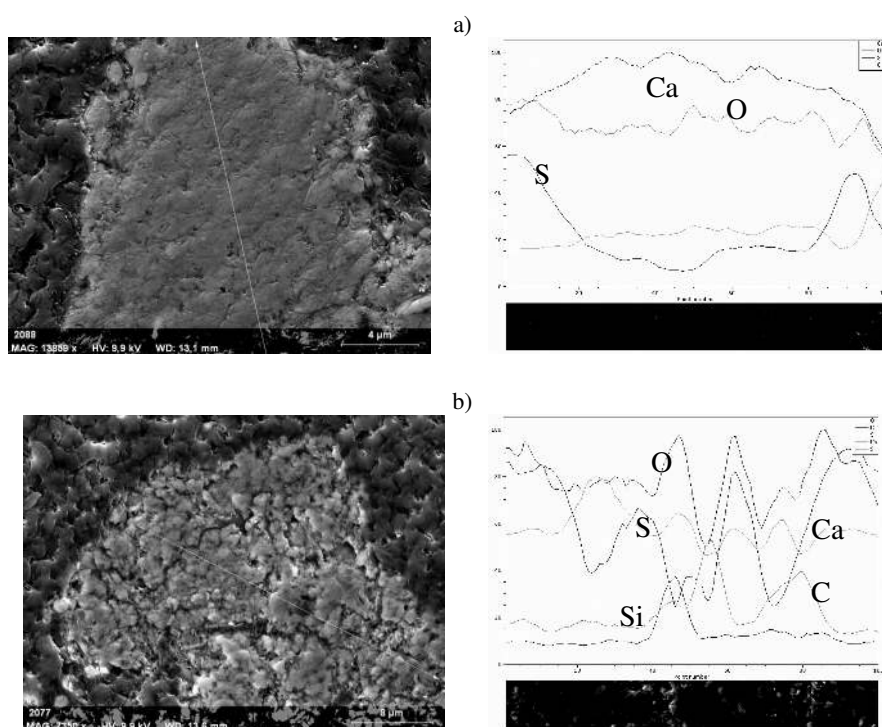


Fig. 8. SEM and EDX analysis of PF ash (PF07/CA) after a) immersing into carbonated recirculation water (CRW) and b) treatment with CO₂-containing model gas.

to precipitating reaction products (CaSO₄, CaCO₃). Surface observations also showed distinct differences between ash particles immersed into distilled water and carbonated recirculation water: instead of a hydrated surface layer formed by particle fracturing (see Fig. 5a,b) the cleaving of reaction products on the surface of particles seems to be more important (Fig. 5c,d).

The carbonation process decelerates shortly after introducing the CO₂-containing gas mixture into the ash-water (CRW, RW) suspension: the pH and Ca²⁺ content in liquid phase decrease rapidly (Fig. 6a) and the final product contains only 6–7% CO₂ and most of the free lime (17–18.5%) remains unreacted (Fig. 6b; Table 2). Process deceleration, which starts already during the hydration step, is the combined effect of two factors: low porosity of PF ash and high content of sulfate and/or carbonate ions in suspension liquid phase. Due to high concentration of dissolved salts in the recirculation water, the diffusion of Ca(OH)₂ away from the surface decelerates, which in turn reduces the slaking rate and causes reactions to take place inside the pores. Insoluble layers of precipitating reaction products easily plug the small-size pores of PF ash (see Fig. 4). The forming product layer is characterized by crystalline and impermeable nature

(Fig. 7b). Therefore, while operating with the continuous flow reactor, the composition of liquid phase contacted with ash should be monitored and carbonate/bicarbonate ions avoided.

PF ash hydration by water (PF08/CA hydr) or by air humidity (PF07/CA*) as a pretreatment causes ash particles to fracture and disintegrate. In turn, the SSA of ash as well as the average pore size increase [29], and the lime becomes more available for carbonation treatment (see Table 1). As a result, the aqueous carbonation process becomes less sensitive to liquid phase composition, and the final product contains less unreacted free lime (1.97–6.97%; see Table 2).

Porous structure of CFBC ash particles supports fast and full hydration of lime as well as diffusion of Ca²⁺ ions into solution, which results in almost complete carbonation. The results of carbonation do not depend on liquid phase compositions, hence the solid phase composition is almost identical to that of systems using distilled or recirculation water (CO₂ = 16.58–16.99%, CaO_f = 1.17–1.26%; see Table 2). In both cases the surface is covered with a fluffy and permeable product layer (Fig. 7c,d).

Continuous-flow experiments

Continuous-mode carbonation of oil-shale waste ashes was carried out at above mentioned pH ranges. The liquid phase compositions used corresponded to suspension pH and gave rather similar results for both kinds of ashes. Corresponding to the high pH level of reactor I, the liquid phase was oversaturated with Ca²⁺ ions (1,100–1,500 mg/L; Fig. 9). Thereby the most suitable conditions for CO₂ absorption were created. In the case of CFBC ash, the solid phase from reactor I contained 4–5% of unreacted lime and 14–16% of CO₂. This indicated that 65–70% of initial free CaO was utilized (BD_{CaO}, Fig. 10a). The indicators were somewhat lower for carbonated PF ash, which contained over 8% of unreacted lime – this shows that 55–65% utilization of free CaO was achieved (BD_{CaO}, Fig. 10b). The carbonation process was continued in the 2nd reactor, where pH and the content of Ca²⁺ ions in liquid phase decreased to 10–11 and 500–800 mg/L, respectively. About 80–90% of the initial free lime had been utilized after the 2nd reactor. In the final stage (3rd reactor) of the ash carbonation process, the suspension pH decreased to 7.5–9 and BD_{CaO} stabilized on the level of 95 and 90% for CFBC and PF ashes, respectively (Fig. 10). Somewhat higher values of BD_{CO2} (predominantly over 100% in the case of the 3rd reactor, although the free lime was not completely utilized) compared to BD_{CaO} showed that other potentially CO₂-binding components of ash, like MgO and Ca-silicates, took part in CO₂ binding reactions (BD_{CO2}; Fig. 10a). This tendency was not as apparent in the case of PF ash (see Fig. 10b). Although switching from tap-water to circulating process-water (pH = 8–10; Ca²⁺ = 400–700 mg/L; SO₄²⁻ = 1,000–1,600 mg/L; TDS = 1.0–1.7 g/L; CO₃²⁻/HCO₃⁻ = 1.5–3.5 mmol/L) did not have any noticeable effect on CFBC ash carbonation, – it had a decelerating influence on the

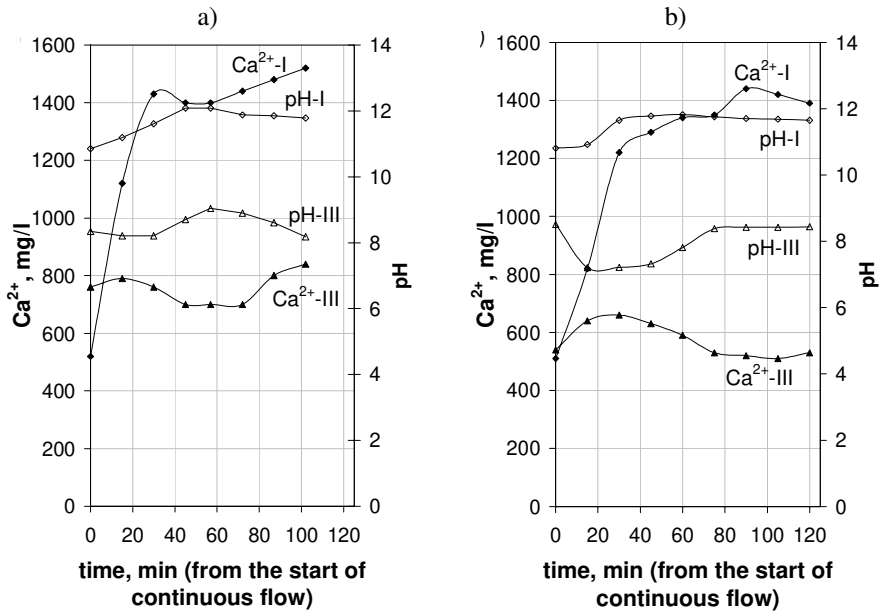


Fig. 9. Changes in Ca^{2+} ion contents and pH of suspension liquid phase during carbonation of *a* – CFBC and *b* – PF ash in continuous mode.

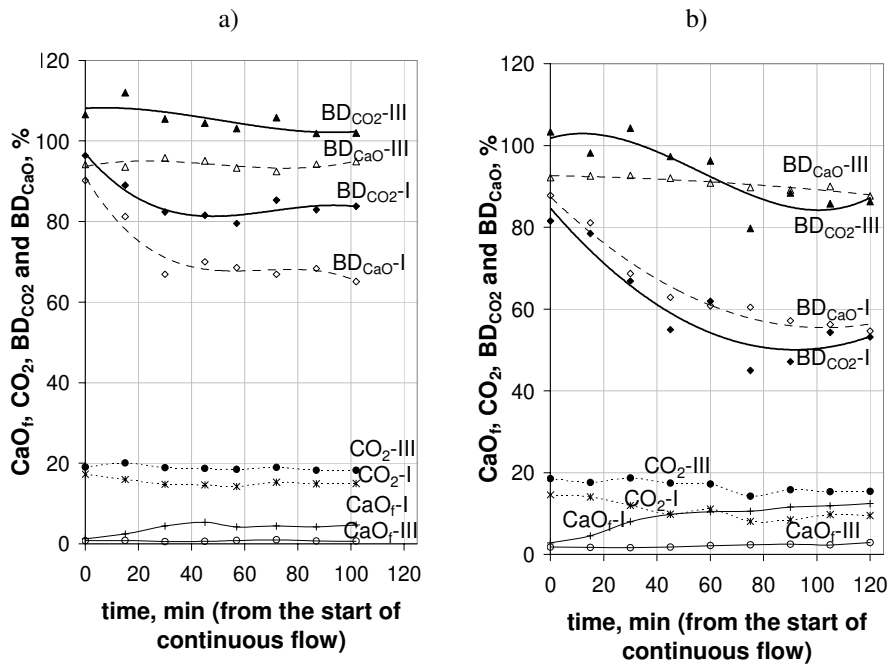


Fig. 10. Changes in CaO_f and CO_2 contents and CO_2 - and CaO -binding degrees during carbonation of *a* – CFBC and *b* – PF ash in continuous mode.

processing of PF ash (the content of unreacted lime increased from 1.7 to 2.9%). Evidently, in the case of PF ashes as nonporous materials [29], some part of free CaO is not accessible under these conditions. Final products contained 0.6–2.9% of unreacted lime and 17–20% of CO₂.

All in all, experiments of continuous-mode carbonation of oil-shale waste ashes in a laboratory-scale set-up under optimal conditions proved that stability of Ca(OH)₂ dissociation and CaCO₃ precipitation was achieved. The experiments confirmed the expected significant differences in the reactivities of CFBC and PF ashes towards CO₂. While CFBC ash was carbonated almost completely in the continuous-flow reactor system, deeper carbonation of PF ash probably needs a pre- or extended treatment. Pretreatment of pulverized-firing ash by grinding or hydration would make the free lime trapped inside ash particles more accessible for the reagents by breaking the particles and increasing the contact surface of particles. Also, it is important to monitor closely the content of sulfate and carbonate ions in the contacting liquid phase, as they form insoluble product layers on the surface of particles and thereby strongly inhibit the ash hydration process.

Considerations for design of an industrial-scale pilot plant

Considering real-scale production, for example at the Narva Power Plant, it is reasonable to choose the capacity of the test plant to be 120 t/h ash (Fig. 11). Solid:liquid ratio of the pulp to be processed is 1:10 being suitable according to the experiments. It is reasonable to divide total capacity of the test device into several lines as to guarantee higher flexibility for the process. In the case of four lines, the capacity of one line will be 30 t per hour, and the total volume of the reactors will be approximately 300 m³.

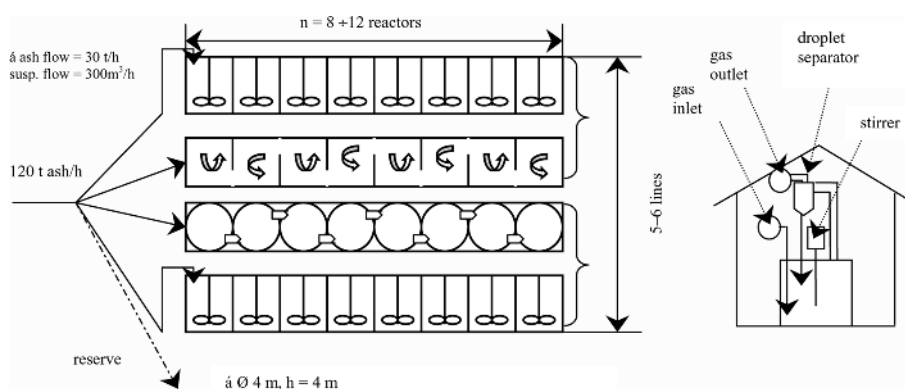


Fig. 11. Principle flow-sheet of pilot-scale ash carbonation plant.

A few important aspects should be taken into account when designing the pilot-scale plant:

- Suspension pH value was chosen to be the main indicator to control the process progress. To ensure optimal conditions for lime slaking and dissociation of Ca^{2+} ions into bulk solution, pH values should be carefully chosen for all the reactors composing the line, and also optimized during exploitation of the plant.
- To decrease suspension pH to the optimum final level 8.5 ± 0.3 at the capacity of one line 30 t/h, it is necessary to introduce 20,000 (at stoichiometric ratio $N_{\text{CO}_2} = 1.0\text{--}1.2$) to 30,000 $\text{m}^3/\text{h}^{\text{STP}}$ ($N_{\text{CO}_2} = 1.5$) of flue gases (content of CO_2 15% Vol).
- Gas injection density is recommended as the main factor determining reactor dimensions (suspension column height and reactor diameter). An initial value of $100 \text{ m}^3/\text{m}^2\cdot\text{h}$ could be recommended by adjusting the results of laboratory experiments to a 3–5-fold increase in liquid column height.
- The construction and working regimes of stirrers should be chosen carefully to avoid passive zones in the reactor column bottom. Also, the smooth-running suspension flow between reactors should be provided.
- Rotating impellers should avoid gravity settling of solid material which slows down vertical movement of gas bubbles at the same time. Inlet of flue gases should take place as deep in the reactors as possible as to guarantee a maximal and homogeneous interfacial contact (with a possible inlet of gas phase through stirrer shaft and impellers).
- Considering the large volumes of gas-liquid flows, the exiting gases should be passed through a droplet separator. As the process involves alkaline solutions containing Ca^{2+} ions and gases containing CO_2 , precipitations in gas inlet and outlet sections and equipments are highly possible and therefore periodical high-pressure cleaning is required.

Conclusions

Batch experiments and studies on deceleration of the aqueous oil-shale ash carbonation process showed the following:

- Aqueous carbonation of PF cyclone ash as the most typical PF ash depends to a great extent on the liquid phase composition.
- In the case of carbonation of PF cyclone ash–distilled water suspension, active dissolution and diffusion of Ca^{2+} ions into bulk of solution continues until almost all free lime is precipitated as calcium carbonate (~2% of unreacted lime in solid residue).

- In the case of the PF ash–recirculation water system, which contains an excess amount of sulfate and/or carbonate ions, the process decelerates shortly after introducing CO₂-containing model gas, and much of the free lime (17–18.5% Abs.) remains unreacted.
- During aqueous carbonation of ash, lime – as the most reactive component – goes through several steps: hydration, dissolution and diffusion of Ca²⁺ ions into bulk of solution and carbonation. Process deceleration, which starts already at the hydration step, is mainly caused by concurrence of two factors: low porosity of PF ash and high content of sulfate and/or carbonate ions in the liquid phase of suspension. Due to a high concentration of dissolved salts in recirculation water, diffusion of Ca(OH)₂ away from the surface decelerates, which in turn reduces the slaking rate and causes reactions to take place inside the pores. Also, precipitating reaction products easily plug small-size pores of PF ash. Carbonate ions and sulfate ions in the slaking water form insoluble layers of both CaCO₃ and CaSO₄, which partially or completely prevent further dissolution of CaO. Therefore, while operating with a continuous-flow reactor, the composition of the liquid phase contacting ash should be monitored and, if possible, sulfate and carbonate/bicarbonate ions avoided.
- Hydration of PF ash by water or by air humidity as pretreatment causes ash particles to fracture and disintegrate. In turn, the ash SSA as well as average pore size increase and lime becomes more available for carbonation treatment. As a result, the aqueous carbonation process becomes less influenced by the liquid phase composition, and the final product contains less unreacted free lime (1.97–6.97%).
- Porous structure of CFBC ash particles supports fast and complete hydration of lime as well as diffusion of Ca²⁺ ions into solution, and this results in almost complete carbonation. The effect of liquid phase composition on slaking and diffusion rates of Ca²⁺ ions and following carbonation reaction is not evident.

Continuous-flow experiments showed that:

- A continuous-mode laboratory-scale reactor system for treating aqueous suspensions of oil shale ash with CO₂-containing model gas was developed. The carbonation process was optimized by adding reactor-columns working in cascade and setting pH levels in different reactors from alkaline to almost neutral in order to attain optimal conditions for lime slaking, Ca(OH)₂ dissociation and CaCO₃ precipitation.
- The experiments confirmed significant dissimilarities in reactivities towards CO₂ of water-suspended oil shale ashes formed under different combustion regimes. While CFBC ash is carbonated almost completely in the continuous flow-reactor system, PF ash needs pre-

or extended treatment for deeper carbonation. Final products contained 0.6–2.9% of unreacted lime and 17–20% of CO₂.

- The main considerations and initial data for design of an industrial pilot-scale plant have been defined and compiled, and a principal flow-sheet has been proposed.

Acknowledgements

Authors express their gratitude to Dr. Valdek Mikli and to Dr. Olga Volobujeva for performance of SEM and EDX analysis as well as to SC Narva Elektriijaamad (Narva Power Plants) for partial funding of current investigation.

REFERENCES

1. O'Connor, W. K., Dahlin, D. C., Nilsen, D. N., Rush, G. E., Walters, R. P., Turner, P. C. CO₂ storage in solid form: a study of direct mineral carbonation // Proc. 5-th International Conference on Greenhouse Gas technologies, Cairns, Australia, 2000.
2. Haywood, H. M., Eyre, J. M., Scholes, H. Carbon dioxide sequestration as stable carbonate minerals – environmental barriers // *Environ. Geol.* 2001. Vol. 41. P. 11–16.
3. Teir, S. Reduction of CO₂ emissions by producing calcium carbonates from calcium silicates and steelmaking slags. Thesis of Licentiate in Technology, Helsinki University of Technology, Espoo, 2006.
4. Huijgen, W. J. J., Witkamp, G.-J., Comans, R. N. J. Mineral CO₂ sequestration by steel slag carbonation // *Environ. Sci. Technol.* 2005. Vol. 39. P. 9676–9682.
5. Kuusik, R., Veskimäe, H., Kaljuvee, T., Parts, O. Carbon dioxide binding in the heterogeneous systems formed by combustion of oil shale. 1. Carbon dioxide binding at oil shale ash deposits // *Oil Shale.* 2001. Vol. 18, No. 2. P. 109–122.
6. IPCC Special Report on Carbon Dioxide Capture and Storage; Intergovernmental Panel of Climate Change – Cambridge University Press, Cambridge, United Kingdom and New York, USA, 2005; 443 p.
7. Lackner, K. S. Carbonate chemistry for sequestering fossil carbon // *Annual Review of Energy and Environment.* 2002. Vol. 27. P. 193–232.
8. Gerdemann, S. J., O'Connor, W. K., Dahlin, D. C., Penner, L. R., Rush, H. Ex situ aqueous mineral carbonation // *Environ. Sci. Technol.* 2007. Vol. 41, No. 7. P. 2587–2593.
9. Huijgen, W. J. J., Comans, R. N. J. Carbonation of steel slag for CO₂ sequestration: leaching of products and reaction mechanisms // *Environ. Sci. Technol.* 2006. Vol. 40, No. 8. P. 2790–2796.
10. Huijgen, W. J. J., Comans, R. N. J. Carbon dioxide sequestration by mineral carbonation: Literature review. – ECN-C-03-016. Energy Research Centre of the Netherlands, 2003.

11. Van Gerven, T., Van Keer, E., Arickx, S., Jaspers, M., Wauters, G., Vandecasteele, C. Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling // *Waste Manage.* 2005. Vol. 25. P. 291–300.
12. Arickx, S., Van Gerven, T., Vandecasteele, C. Accelerated carbonation for treatment of MSWI bottom ash // *J. Hazard. Mat.* 2006. Vol. B137. P. 235–243.
13. Stolaroff, J. K., Lowry, G. V., Keith, D. W. Using CaO and MgO-rich waste streams for carbon sequestration // *Energy Convers. Manage.* 2005. Vol. 46. P. 687–699.
14. Kodama, S., Nishimoto, T., Yogo, K., Yamada, K. Design and evaluation of a new CO₂ fixation process using alkaline-earth metal wastes // *Proc. 8-th International Conference of Greenhouse Gas Control Technologies, Trondheim, Norway, 19–22 June, 2006; Elsevier Ltd.: Trondheim, Norway, 2006; 5 p. [CD-ROM].*
15. Baciocchi, R., Poletini, A., Pomi, R., Prigiobbe, V., Von Zedwitz, V., Steinfeld, A. CO₂ sequestration by direct gas-solid carbonation of air pollution control (APC) residues // *Energy & Fuels.* 2006. Vol. 20, No. 5. P. 1933–1940.
16. Baciocchi, R., Poletini, A., Pomi, R., Prigiobbe, V., Zedwitz-Nikulshyna, V., Steinfeld, A. Performance and kinetics of CO₂ sequestration by direct gas-solid carbonation of APC residues // *Proc. 8-th International Conference of Greenhouse Gas Control Technologies, Trondheim, Norway, 17–22 June, 2006; Elsevier Ltd: Trondheim, Norway, 2006; 5 p. [CD-ROM].*
17. Kuusik, R., Veskimäe, H., Uibu, M. Carbon dioxide binding in the heterogeneous systems formed at combustion of oil shale. 3. Transformations in the system suspension of ash – flue gases // *Oil Shale.* 2002. Vol. 19, No. 3. P. 277–288.
18. Kuusik, R., Uibu, M., Toom, M., Muulmann, M.-L., Kaljuvee, T., Trikkel, A. Sulphation and carbonization of oil shale CFBC ashes in heterogeneous systems // *Oil Shale.* 2005. Vol. 22, No. 4 Special. P. 421–434.
19. Uibu, M., Uus, M., Kuusik, R. CO₂ mineral sequestration in oil shale wastes from Estonian power production // *J. Environ. Manage.* 2008, Vol. 90, No. 2. P. 1253–1260.
20. Kallaste, T., Liik, O., Ots, A. Possible energy sector trends in Estonia. Context of Climate Change. – Stockholm Environment Institute Tallinn Centre: Tallinn, 1999; 180 p.
21. Uibu, M., Kuusik, R., Veskimäe, H. Seasonal binding of atmospheric CO₂ by oil shale ash // *Oil Shale.* 2008. Vol. 25, No. 2. P. 254–266.
22. Reispere, H. J. Determination of free CaO content in oil shale ash // *Transact. Tallinn Polytechnical Institute, series A.* 1966. No. 245. P. 73–76 [in Estonian].
23. Kuusik, R., Uibu, M., Kirsimäe, K. Characterization of oil shale ashes formed at industrial-scale boilers // *Oil Shale.* 2005. Vol. 22, No. 4 Special. P. 407–420.
24. Outokumpu HSC Chemistry for Windows. Chemical Reaction and Equilibrium Software with Extensive Thermochemical Database. Version 4.0. License Ser. No. 40050 for Tallinn University of Technology.
25. Domingo, C., Loste, E., Gomez-Morales, J., Garcia-Carmona, J. Calcite precipitation by high-pressure CO₂ carbonation route // *J. Supercrit. Fluids.* 2006. Vol. 36, No. 3. P. 202–215.
26. Ritchie, I. M., Xu, B.-A. The kinetics of lime slaking // *Hydrometallurgy.* 1990. Vol. 23, No. 2–3. P. 377–396.
27. Potgieter, J. H., Potgieter, P. P., de Waal, D. An empirical study of factors influencing lime slaking. Part II: Lime constituents and water composition // *Water SA.* 2003. Vol. 29, No. 2. P. 157–161.

28. Xu, B.-A., Giles, D. E., Ritchie, I. M. Reaction of lime with carbonate containing solutions // *Hydrometallurgy*. 1998. Vol. 48, No. 2. P. 205–224.
29. Uibu, M., Trikkel, A., Kuusik, R. Transformations in the solid and liquid phase at aqueous carbonization of oil shale ash // *Proc. ECOSUD VI*, 4–7 Sept. 2007, Coimbra, Portugal, 2007; *WIT Transactions on Ecology and Environment*: 4–7 Sept. 2007, Coimbra, Portugal, 2007; P. 473–483.

Presented by A. Siirde

Received September 11, 2008