Developments in CO$_2$ mineral carbonation of oil shale ash☆

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ABSTRACT

Solid waste and atmospheric emissions originating from power production are serious problems world-wide. In the Republic of Estonia, the energy sector is predominantly based on combustion of a low-grade carbonaceous fossil fuel: Estonian oil shale. Depending on the combustion technology, oil shale ash contains 10–25% free lime. To transport the ash to wet open-air deposits, a hydraulic system is used in which 10^7–10^8 cubic meters of Ca^{2+}-ion-saturated alkaline water (pH level 12–13) is recycled between the plant and sedimentation ponds. The goals of the current work were to design an ash–water suspension carbonation process in a continuous mode laboratory-scale plant and to search for potential means of intensifying the water neutralization process. The carbonation process was optimized by cascading reactor columns in which the pH progressed from alkaline to almost neutral. The amount of CO$_2$ captured from flue gases can reach 1–1.2 million ton at the 2007 production level of the SC Narva Power Plants. Laboratory-scale neutralization experiments were carried out to compare two reactor designs. Sedimentation of PCC particles of rhombohedral crystalline structure was demonstrated and their main characteristics were determined. A new method providing 50× greater specific intensity is also discussed.

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1. Introduction

Safely disposing of solid wastes and controlling atmospheric emissions are among the most serious problems caused by the extensive use of low-grade solid fuels in heat and power production. CO$_2$ sequestration by mineral carbonation of alkaline waste residues serves both causes, since after stabilization by carbonation the leaching behavior of the alkaline waste material is often improved.

Mineral carbonation was first proposed by Seifritz [1] and later developed by Dunsmore [2] and Lackner [3–6]. The aim was to accelerate natural weathering processes to an industrially acceptable level. At first, only natural Ca- and Mg-rich minerals such as serpentinite, olivine, wollastonite, and talc were considered as raw materials. Since 1998, the carbonation of industrial wastes such as steel slag, ash, and waste cement has also been studied [7–10]. Accelerated carbonation treatment can be used to promote the stabilization degree and to improve the leaching behavior of the alkaline waste materials [11–13].

In the Republic of Estonia, the primary energy source is Estonian oil shale, a local low-grade carbonaceous fossil fuel. Combustion of oil shale is characterized by high specific carbon emissions (29.1 ton C/TJ against 25.8 and 15.2 for coal and natural gas) because of the high mineral carbonate content. In Estonia, the power sector is the largest CO$_2$ emitter and is also a source of huge amounts of waste ash. Depending on the combustion technology (pulverized firing (PF) or circulating fluidized bed combustion (CFBC)), the ash contains up to 30 wt.% free Ca–Mg oxides. Ash fields with sedimentation ponds for ash separation and deposition cover an area of about 20 km^2 and hold approximately 15–20 million m^3 of water [14].

Previous research [14–17] has demonstrated the feasibility of utilizing the theoretical lime-based CO$_2$-binding capacity of oil shale ash in direct aqueous carbonation. The main technological stages of CO$_2$ mineral sequestration by waste oil shale ash [18] are direct aqueous carbonation of ash and neutralization of alkaline ash-transportation water with flue gases (Fig. 1).

Therefore, the aim of the current research was to use the results of continuous mode model experiments to develop a proposal for industrial-scale control of these two stages of CO$_2$ mineral sequestration using oil shale waste ashes from Estonian power plants.

2. Experimental

2.1. System ash–water–CO$_2$-containing model gas

Oil shale ashes formed in boilers using different combustion technologies (PF or CFBC) differ noticeably in their chemical reactivity toward acidic gases [19,20]. Batch experiments have revealed

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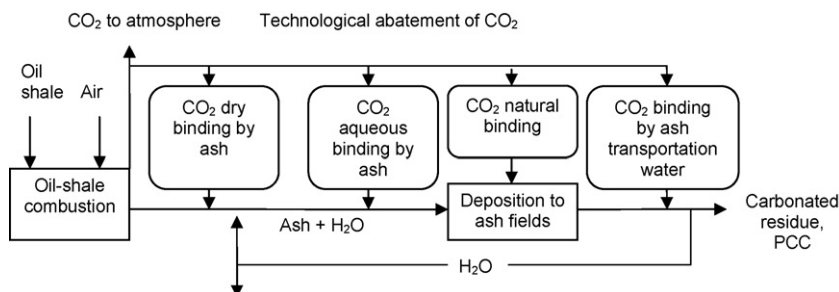   *E-mail address:* maiuibu@staff.ttu.ee (M. Uibu).

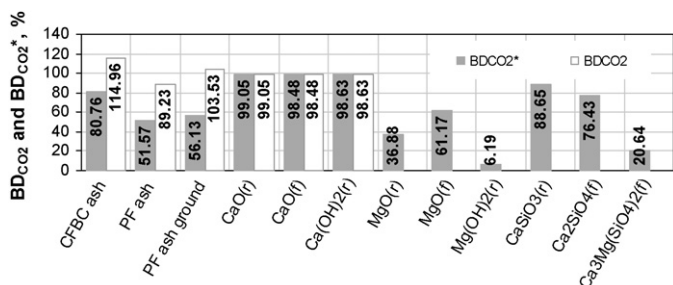Fig. 1. Concept for CO_2 mineralization by waste oil shale ash: prospects in oil shale based power production.

Fig. 2. Comparative reactivity of ashes and some model compounds (r—commercially purchased and f—freshly synthesized in the laboratory) towards CO_2 in batch reactor. Binding degrees calculated on the basis of the content of free CaO (BD_{CO_2}) and of all potentially CO_2-binding components in the initial sample ($BD_{CO_2}*$) [20].

that under the same conditions, CFBC ashes can be carbonated more completely than PF ashes (Fig. 2). The behavior of free lime as the key component of the ash has been elucidated and a rate controlling mechanism has been proposed [21]. Aqueous carbonation of PF ash, which is characterized by low porosity, depends to a great extent on the aqueous phase composition. The excess amount of SO_4^{2-}, CO_3^{2-}, or HCO_3^- ions present in the slaking water affects the extent and rate of lime solubility in water [22–24]. The process decelerates shortly after introducing the CO_2-containing model gas, leaving most of the free lime unreacted. As the dissolution of $Ca(OH)_2$ is diffusion controlled, reactions with CO_3^{2-}, HCO_3^-, and SO_4^{2-} tend to take place inside the pores and on the surface. The pores of the almost impermeable surface of PF ash can plug easily and the ensuing layers of $CaCO_3$ and $CaSO_4$ hinder both lime slaking and further carbonation (Fig. 3). The porous structure of CFBC ash particles supports fast and full hydration of lime as well as diffusion of Ca^{2+}-ions into solution, resulting in almost complete carbonation. These findings must be considered when planning continuous mode experiments.

Although free lime possesses the highest reactivity towards CO_2, the Ca-silicates ($CaSiO_3$ and Ca_2SiO_4) and periclase also take part in CO_2-binding reactions [18].

2.1.1. Materials and methods

A continuous flow reactor system was developed for treating oil shale ash–water suspensions with a CO_2-containing model gas (Fig. 4a). The continuous mode aqueous carbonation was optimized by cascading several reactor columns (water column height 0.7 m and volume 10 L) and setting the pH levels in the different reactors
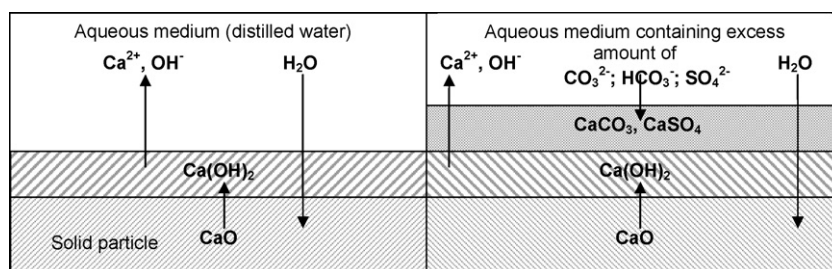

Fig. 3. Reaction model for slaking of lime containing ash particles in aqueous sulfate and carbonate/bicarbonate solutions.
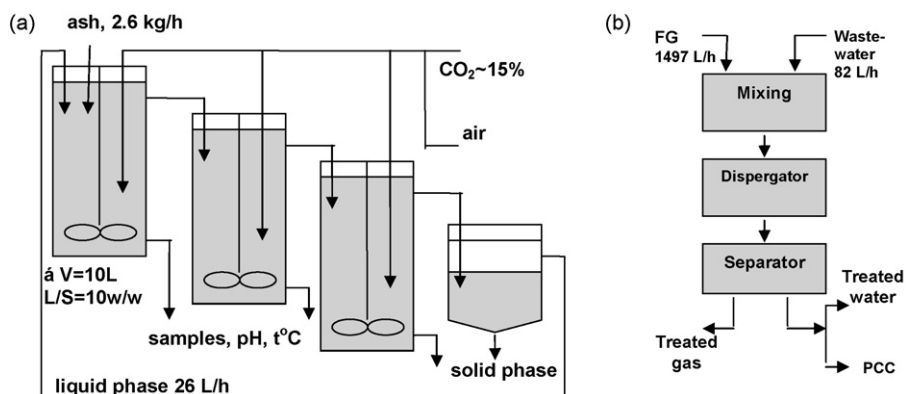

Fig. 4. Experimental devices for carbonation of ash suspension (a) and alkaline wastewater (b).

Table 1
Chemical composition and main characteristics of initial PF and CFBC ashes.

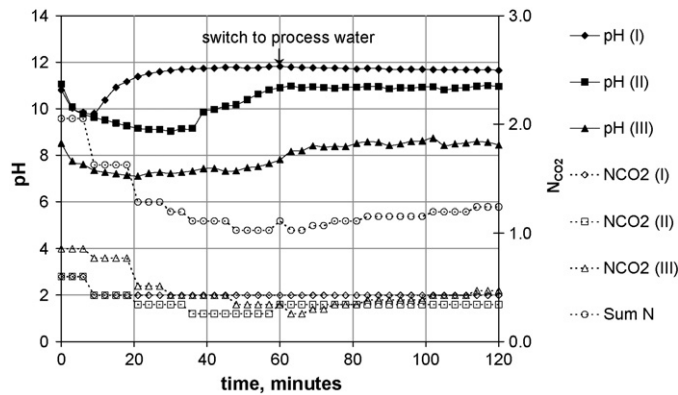| Ash	CaO_{total} (%)	CaO_f (%)	MgO_{total} (%)	CO_2 (%)	SSA (m^2/g)	d_{mean} (μm)
PF ash	49.69	22.43	6.49	5.07	1.62	47
CFBC ash	41.88	12.38	5.05	9.92	3.73	34

Fig. 5. Changes in pH (reactors I–III) and N_{CO_2} during carbonation of PF ash in continuous mode.

from alkaline (1st and 2nd reactor) to almost neutral (3rd reactor), prolonging the contact time of the phases (ash, water, and CO_2-containing model gas) under optimal conditions for $CaCO_3$ precipitation. The ash (Table 1) and water (tap water or circulating process water) were fed to the first reactor column from which the partly carbonated suspension was introduced to the subsequent stages (2nd and 3rd reactor) for deeper carbonation. A mechanical turbine-type stirrer (1000 rpm) was equipped with extra impellers to improve the interfacial contact and produce more homogeneous material flow. The pH of the suspension was controlled by adjusting the flow-rate of incoming CO_2. The mole ratio of CO_2 entrained into the reactors according to the equation $CaO + CO_2 = CaCO_3$ (N_{CO_2}) is depicted in Fig. 5. Samples collected from the bottoms of the reactor columns were filtered and the solid residue was dried at 105 °C. The liquid and solid phases were analyzed for chemical composi-

tion [primarily the free CaO content [25] and CO_2 (volume method, GOU-1 gas analyzer)]. The effectiveness of the carbonation process was described by the CO_2-binding degree (BD_{CO_2}) and the CaO-binding degree (BD_{CaO}). BD_{CO_2} is an indication of how much of the theoretical CO_2-binding capacity is utilized (Eq. (1); where CO_2 is the analytically determined CO_2 content of the sample and CO_{2max} is the maximum possible CO_2 content of the sample in % according to Eq. (2)). BD_{CaO} expresses the degree of utilization of free CaO as the most important CO_2-binding component in ash (Eq. (3), where CaO_f is the analytically determined free CaO content of the sample and CaO_f^i denotes the content of free CaO in the initial sample).

$$BD_{CO_2} = \frac{CO_2}{CO_{2max}} \times 100 \tag{1}$$

$$CO_{2max} = \frac{CaO_f^i \times M_{CO_2}/M_{CaO} + CO_2^i}{100 + CaO_f^i \times M_{CO_2}/M_{CaO}} \times 100 \tag{2}$$

$$BD_{CaO} = \frac{((CaO_f^i - CaO_f)/(100 + (CaO_f \times M_{CaCO_3}/M_{CaO}))) \times 100}{CaO_f^i}$$
$$\times 100 \tag{3}$$

2.1.2. Results and discussion

Continuous mode carbonation of oil shale waste ashes was carried out at pre-set pH levels. The liquid phase compositions corresponded to the suspension pH and gave rather similar results with the both types of ash. Along with the high pH level of the first reactor, the liquid phase was oversaturated with Ca^{2+}-ions (1100–1500 mg/L), creating optimum conditions for CO_2 absorption. Determination of the solid phase composition indicated that
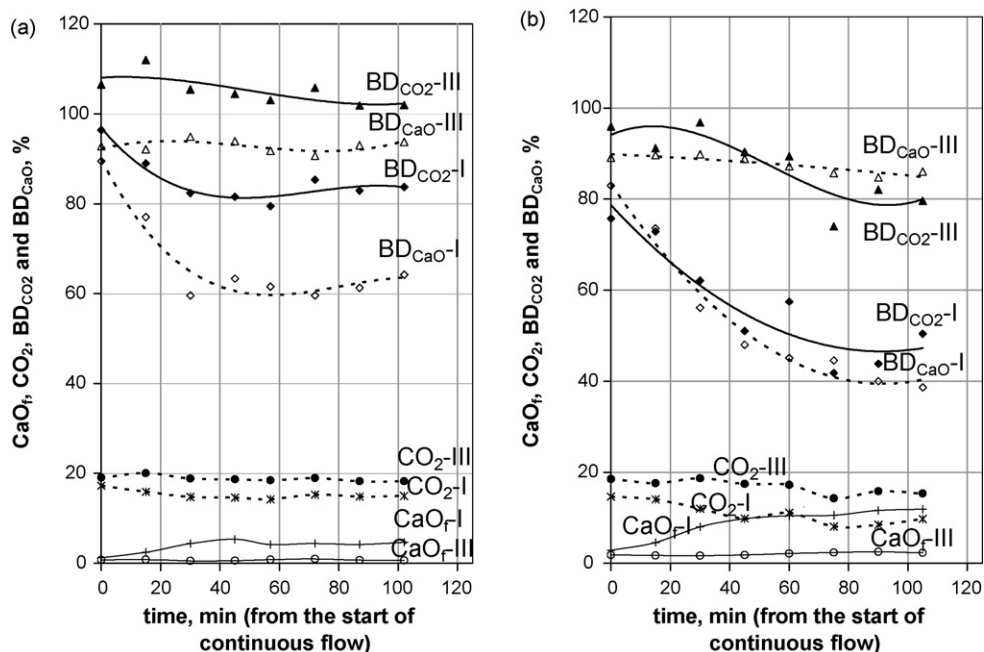

Fig. 6. Changes in CaO_f and CO_2 contents and CO_2- and CaO-binding degrees during carbonation of CFBC ash (a) and PF ash (b) in continuous mode.

after the first reactor 40–70% of the initial free CaO was utilized (BD_{CaO}; Fig. 6). The carbonation process was continued in the second reactor, in which the pH was decreased to 10–11 and the Ca^{2+}-ion content of the liquid phase was decreased to 500–800 mg/L. After the 2nd reactor 80–90% of the initial free lime was utilized. In the final stage (3rd reactor) of the ash carbonation process, the suspension pH was decreased to 7.5–9.0 and BD_{CaO} stabilized at 95% for CFBC ashes and 85–90% for PF ashes (Fig. 6).

The slightly higher values of BD_{CO_2} (over 100% in the 3rd reactor, although the free lime was not completely utilized) compared to BD_{CaO} suggest that other potential CO_2-binding components such as MgO and Ca-silicates also underwent CO_2-binding reactions (BD_{CO_2}; Fig. 6a). This tendency was not as apparent in the case of PF ash. Although switching from tap water to circulating process water did not have any noticeable effect on carbonation of CFBC ash, it had a negative influence on the processing of PF ash (the content of unreacted lime increased from 1.7% to 2.9%). Evidently, the low porosity of PF ashes [26] renders a portion of the free CaO inaccessible. The final products contained 0.6–2.0% of unreacted lime and 17–20% of CO_2.

In summary, we achieved a stable laboratory-scale process for continuous carbonation of oil shale waste ashes under optimal conditions for $Ca(OH)_2$ dissociation and $CaCO_3$ precipitation. Significant differences were observed in the reactivity of CFBC and PF ashes towards CO_2. While CFBC ash was almost completely carbonated in the continuous flow reactor system, PF ash will probably require pre- or extended treatment for more complete carbonation. Pretreatment of pulverized firing ash by grinding or hydration would make the free lime trapped inside ash particles more accessible by breaking the particles and/or increasing their porosity.

2.1.3. Considerations for the design of a pilot-scale plant

Full-scale operation (for instance at the SC Narva Power Plants) would require a plant capacity of 120 ton of ash/h. The initial intermediate scale should be 10–20 times less (6–12 ton/h). The operating parameters for the test plant include slurry-phase conditions (a water/solid weight ratio of approximately 10), atmospheric pressure, and ambient temperature. Operation of several lines in parallel provides greater process flexibility. In the case of four lines, the capacity of one line would be 30 ton/h and the total volume of the reactors would be approximately 300 m³.

The suspension pH was chosen as the main process control variable. To reduce the suspension pH to the optimum final value of 8.5 ± 0.3 in one line operating at 30 ton/h would require 20,000 (at a stoichiometric ratio N_{CO_2} of 1.0–1.2) to 30,000 m³/h ($N_{CO_2} = 1.5$) of flue gas containing 15% CO_2 by volume. An initial gas injection density of 100 m³/m² h could be achieved by adjusting the results of the laboratory experiments to produce a 3–5-fold increase in the liquid column height. A flow chart of the process is presented in Fig. 7.

2.2. System wastewater–CO_2-containing model gas

2.2.1. Materials and methods

Neutralization of the alkaline ash-transportation water from the ash-transportation system of the Narva Power Plants (Ca^{2+} = 800–1020 mg/L; pH = 13.0–13.1) was carried out in a laboratory dispergator-type reactor (Fig. 4b), which provided effective mechanical mixing of the gas and liquid phases to increase the interfacial contact surface [27]. The initial ash-transportation water flowing at 82 L/h was treated with model gases flowing at 1497.4 L/h. The FG1 gas contained 15% CO_2 in air, while the FG2 gas contained 15% CO_2 and 0.07% SO_2 in air. After one carbonation cycle in a 1.5 stoichiometric excess of CO_2 (according to Eqs. (4) and (5)) the pH of the ash-transportation water was 10; after three cycles using a 4.5-fold excess the pH had decreased to 8. The experiments
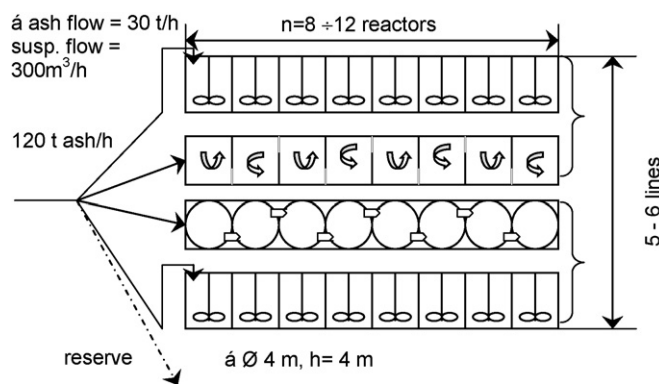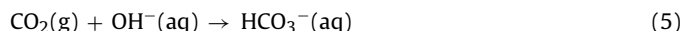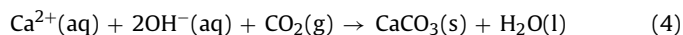

Fig. 7. Principle flow-sheet of industrial-scale ash carbonation plant.

were carried out at ambient temperature under atmospheric pressure. The calculated contact time was 1.25–3.75 s. After separation of the liquid and gas phases the gas was vented into the atmosphere and the liquid phase was either fed back into the reactor or to a filtration system where the solid reaction product was separated and dried at 105 °C.

$$Ca^{2+}(aq) + 2OH^-(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l) \qquad (4)$$

$$CO_2(g) + OH^-(aq) \rightarrow HCO_3^-(aq) \qquad (5)$$

To compare different technological approaches, a conventional barboter-type column was also examined. Carbonation of ash-transportation water with the FG1 and FG2 model gases at a flow-rate of 100 L/h was carried out in a laboratory absorber (water column height 500 mm, volume 0.6 L) equipped with a magnetic stirrer and a sintered gas distributor (pore diameter 100 μm). The experiments were continued until the pH of the treated wastewater reached 10 or 8. After treatment the suspension was filtered and the solid residue was dried at 105 °C.

The Ca^{2+} and SO_4^{2-} content were determined spectrophotometrically (Lovibond Spectrodirect). The TDS (microprocessor conductivity meter HI9032), pH (Precisa pH 900), and alkalinity [28] were also determined. The solid samples were analyzed for chemical composition and the surface morphology was examined using a scanning electron microscope (Jeol JSM-8404A). The particle size distribution was determined using a laser diffraction analyzer (Beckman Coulter LS 13320).

2.2.2. Results and discussion

Comparative experiments with the dispergator- and barboter-type reactors indicated that the alkaline ash-transportation waters reacted readily with CO_2-containing model gases FG1 and FG2, decreasing the content of Ca^{2+}-ions and pH (Table 2). In the case of the dispergator-type phase mixer, the Ca^{2+} ion content dropped to 10 mg/L after one carbonation cycle ($N_{CO_2} = 1.5$) and the pH decreased to the terminal level after three carbonation cycles ($N_{CO_2} = 4.5$). A dispergator-type reactor maximizes the gas–liquid contact surface, thereby promoting elevated mass transfer rates. Compared to a conventional barboter-type column, a 50-fold increase in specific intensity (q, m³/m³ h, calculated as the volume of processed wastewater per unit of volume of the reactor) was achieved. The filtered solid samples (PCC1–PCC6; Table 2) predominantly contained $CaCO_3$ (86–94%).

The end-point pH value of the carbonation did not influence the size of PCC particles formed in the dispergator-type reactor (Table 2). The samples are characterized by a homogeneous particle size distribution (median size ~5 μm). The presence of SO_2 in the gas mixture considerably influenced the size and shape of the particles: their median size increased noticeably due to agglomeration of particles (PCC3 and PCC4; Table 2). The agglomeration effect

Table 2
Wastewater treatment with model gases: composition of the solid and liquid phase.

| N_{CO_2}	Liquid phase							Solid phase	Particle size distribution		PCC sample
	pH	TDS (g/L)	Ca^{2+} (mg/L)	SO_4^{2-} (mg/L)	OH^-	CO_3^{2-} (meq/L)	HCO_3^-	$CaCO_3$ (%)	Mean (μm)	Median (μm)	
Wastewater treatment in dispergator-type phase mixer with FG 1											
1.5	~10	5.61	10	1980	2.0	24.0	0.0	86.01	5.263	5.184	PCC1
4.5	~8	6.33	30	2210	0.0	6.0	25.0	90.40	5.225	5.103	PCC2
Wastewater treatment in dispergator-type phase mixer with FG 2											
1.5	~10	6.43	10	2180	0.0	27.0	1.5	94.16	9.163	5.205	PCC3
4.5	~8	6.49	100	2340	0.0	7.0	24.5	93.22	27.38	8.381	PCC4
Wastewater treatment in barboter-type column with FG 2											
0.7	~10	6.39	10	2540	0.0	14.0	14.75	91.20	5.734	5.773	PCC5
1.04	~8	6.48	160	1922	0.0	0.0	42.5	88.25	7.715	7.883	PCC6
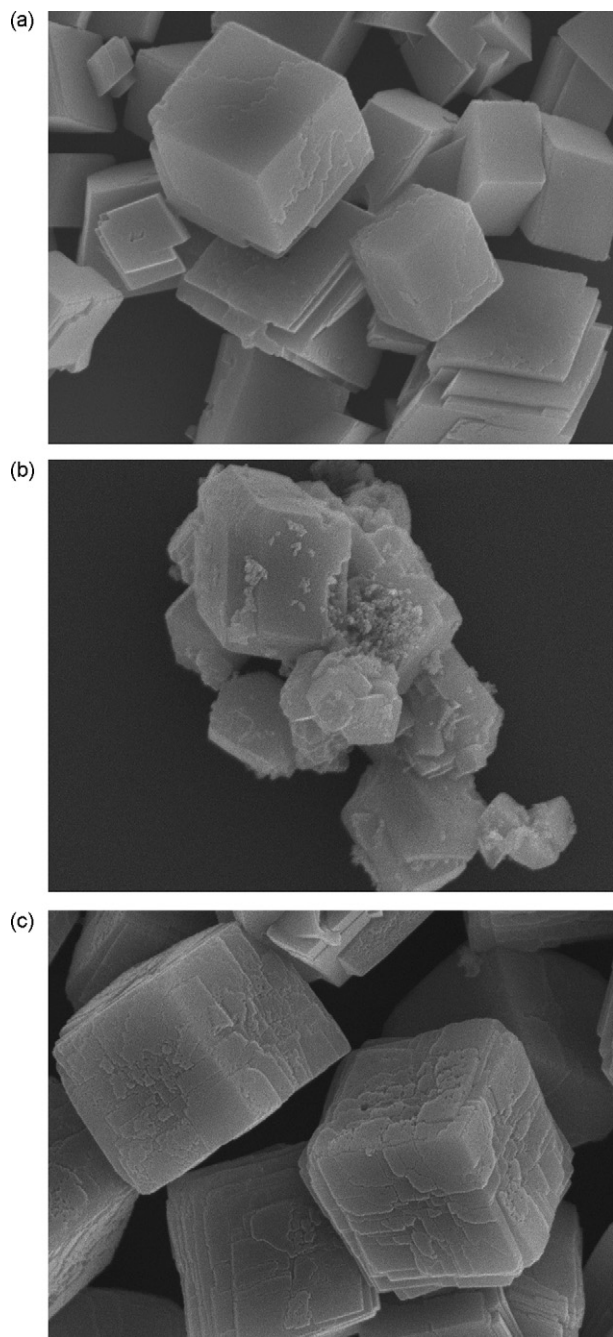
Fig. 8. SEM images of PCC samples formed at different conditions in dispergator-type phase mixer: (a) PCC1, (b) PCC4 and barboter-type column PCC6 (c), magnification 10,000x.

increased with decreasing pH. The PCC4 sample was not homogeneous, containing particles ranging from 3 to 310 μm.

Shape and surface observations confirmed the results of the particle size distribution analysis. The shape of PCC particles from the dispergator-type reactor was influenced noticeably by the extent of carbonation as well as by the presence of SO_2. Regularly structured particles of PCC were formed in the high pH region in an SO_2-free environment (Fig. 8a). In the presence of SO_2 most of the individual particles merged into agglomerates (Fig. 8b). The PCC samples from the barboter-type reactor were characterized by more homogeneous particles with a distinctive regular rhombohedral crystal structure (Fig. 8c) and somewhat larger particle size (median size 6–10 μm; Table 2).

Alkaline Ca^{2+}-containing wastewater from an oil shale ash transport system can be used as a calcium source for the production of PCC characterized by a regular rhombohedral structure and a homogeneous particle size (~5 μm) distribution. To avoid agglomeration of the particles and redissolution of $CaCO_3$, the neutralization process with production of PCC should be divided into two stages, $CaCO_3$ precipitation and separation at high pH values followed by decreasing the residual alkalinity of the wastewater to acceptable levels (pH ~ 8–8.5). A pilot-scale installation for the neutralization of alkaline wastewater with CO_2 from flue gas using commercially available dispergators (>5–10 m³ of water/h) has been proposed [27].

3. Conclusions

The main technological challenges associated with CO_2 mineralization using oil shale wastes have been studied. A continuous mode laboratory-scale reactor system for treating oil shale ash–water suspensions with CO_2-containing model gases was developed. The carbonation process was optimized by operating the reactor columns in a series cascade. The pH levels in the reactors ranged from alkaline to almost neutral. This produced optimal conditions for $Ca(OH)_2$ dissociation and $CaCO_3$ precipitation. The significant dissimilarities in the CO_2 reactivity of water-suspended oil shale ashes formed during different combustion processes have been experimentally confirmed. While the CFBC ash was almost completely carbonated in the continuous flow reactor system, the PF ash would require pre- or extended treatment for deeper carbonation. The final products contained 0.6–2.0 wt.% of unreacted lime and 17–20 wt.% of bound CO_2. In the SC Narva Power Plants (Estonia), approximately 1–1.2 million ton of CO_2 could be captured from flue gases at the 2007 production level.

Comparative experiments with dispergator- and barboter-type reactors indicated that the deeply alkaline, Ca^{2+}-saturated ash-transportation waters reacted readily with CO_2-containing model gases. Rapid neutralization (pH < 9) accompanied by the formation of the useful by-product $CaCO_3$ occurred. The dispergator-type phase mixer provided intensive stirring and effective mechanical mixing of the gas and liquid phases, resulting in an increase in the

interfacial contact area and up to 50-fold increase in specific intensity. The size and structure of the $CaCO_3$ particles was influenced by the end-point pH value of the carbonation process as well as the flue gas composition and the type of reactor used. According to the current results, wastewater from the oil shale ash transport system can be used as a calcium source for the production of PCC. Further optimization of process conditions is required to produce PCC of fine and homogeneous particle size.

Acknowledgements

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