

## Reduction of CO<sub>2</sub> emissions by carbonation of alkaline wastewater

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### Abstract

In energy production based on combustion of fossil fuels, particularly the low-grade ones (lignite, sulphur-rich coal, oil shale etc.), huge amounts of alkaline wastewater are formed. This situation is characteristic for the Republic of Estonia where 59% of the need in primary energy was covered by local oil shale in 2006. Due to the calcareous origin of the mineral part of oil shale, its combustion yields lime-containing ashes (5–6 million tons annually, containing 10–25% of lime as free CaO) as well as enhanced amounts of CO<sub>2</sub> (up to 29.1 t C per TJ energy produced) as compared to coal combustion. To transport the ash into wet open-air deposits, a hydraulic system is used. As a result tens of millions of cubic meters of alkaline water (pH level 12–13) saturated by Ca<sup>2+</sup>-ions is recycling between the plant and sedimentation ponds. Before directing excessive water to nature it should be neutralized to a pH level accepted by environmental regulations (< 9). Related to this, the current work was targeted to develop possibilities for neutralizing wastewater with CO<sub>2</sub>-containing flue gases, leading to reduction of CO<sub>2</sub> emissions. Intensification of respective heterogeneous gas–liquid reactions and characterization of calcium carbonate (PCC) forming were other objectives of the study.

A cycle of laboratory-scale neutralization experiments using industrial wastewater samples and a model gas of flue gas composition has been carried out. Two different reactors – barboter-type columns and a dispergator-type phase mixer – have been comparatively examined. Sedimentation of PCC particles of *rhombohedral* crystalline structure has been shown and their main characteristics have been determined. A neutralization method having up to fifty times higher specific intensity has been proposed. According to calculations 970–1010 tons of CO<sub>2</sub> can be trapped and 2200–2300 tons of PCC per million cubic meters of water can be obtained.

*Keywords: carbon dioxide, alkaline wastewater, Ca-compounds, carbonation, precipitated calcium carbonate.*



## 1 Introduction

In several process industries, for example, in energy processing based on combustion of fossil fuels (coal, oil shale, brown coal etc) huge amounts of highly alkaline (pH 10–13) technological and wastewaters are formed. Such technological water is the circulating water used to carry ash formed during combustion to ash-fields. If limestone is used for SO<sub>2</sub> capture or when a limestone-containing fuel (such as oil shale) is burnt, the ash formed contains free lime and its transport water has a high concentration of Ca<sup>2+</sup>-ions. As a rule, before directing these wastewaters to natural water basins they have to be neutralized, decreasing their pH to the level fixed in environmental regulations (usually, below 9). Neutralization with strong mineral acids such as hydrochloric or nitric acid is well-known. The disadvantage of this method is usage of expensive reagents, release of notable quantities of acid anions to natural water and corrosion of equipment. Besides, due to the character of the neutralization curve (sharp decrease of pH around the equivalent point), a risk of reagent overdose exists. These disadvantages can be avoided by carbonation i.e. by using carbon dioxide for wastewater neutralization, which forms a weak carbonic acid at dissolution. In addition, calcium carbonate is formed in the process, which can be used as a separate product.

Carbonation of alkaline water is a heterogeneous process taking place via gas – liquid reactions. Carbonation methods can be divided into two groups. In the first case gaseous CO<sub>2</sub> is directed into water that is to be carbonized. As the gas-bubbles move through the water-layer, CO<sub>2</sub> is dissolved. This process is slow and to achieve appropriate rates, long residence time is needed, which requires big dimensioned barboter-columns. The rate can be increased by enlarging the area of phase contact, using different methods for dispersing gas bubbles. For example, specific rotating dispergator elements are used inside columns [1]. Carrying out the carbonation process under pressure is also well-known and used widely in food-processing industries [2].

The other group of methods uses injection of liquid phase into a chamber filled with CO<sub>2</sub> or into an adsorption column with rising gas flow. In the last case atomizers are used to intensify the process increasing the contact surface by reducing the liquid particle size. Industrial absorption columns are big dimensioned apparatus having a diameter of 5–6 m and height of 30–40 m. Neutralizing processes for alkaline wastewaters using liquid carbon dioxide as the neutralizing agent are also known, such as the SOLVOCARB<sup>®</sup>-process and respective apparatus of the company “Linde Gas” [3]. However, using commercial carbon dioxide at power plants where the flue gas contains 12–15% of CO<sub>2</sub> is not reasonable.

The method described in [4] is based on a gas–liquid reaction taking place in a column filled with coal ash (contains free lime), water slurry or eluate into which CO<sub>2</sub>-containing flue gas is directed through a distributor. One product of the process is calcium carbonate. Carbonation takes place at bubbling flue gas through the ash–water slurry requiring prolonged duration of phase contact (20 min) and, hereby, a big dimensioned reactor.

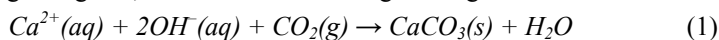


Formation of highly alkaline wastewater is also characteristic for the industry of the Republic of Estonia, where more than 90% of electric energy is produced by combusting local carbonate-rich fuel–oil shale [5]. This brings along the formation of CO<sub>2</sub> emissions and waste ash, which contains 10–30% of free Ca and Mg oxides [6], in the annual amounts of 11–13 and 5–6 million tons, respectively. Sedimentation ponds of the hydrosystem for water separation and transportation have a volume 15–20 million m<sup>3</sup> covering an area of about 20 km<sup>2</sup> [7]. The water that reaches the ash fields is oversaturated with Ca<sup>2+</sup>-ions (1000–1400 mg/L), after sedimentation the Ca<sup>2+</sup>-ion content in circulation water has dropped to 400–800 mg/L [8]. Taking this into account, the aim of the current research was to reduce CO<sub>2</sub> emissions, to clarify intensification possibilities of carbonation of alkaline wastewater with CO<sub>2</sub>-containing flue gases and to give the first characterization of the formed PCC.

## 2 Materials and methods

### 2.1 Theoretical considerations and calculations

Neutralization of alkaline wastewater, which contains Ca<sup>2+</sup>-ions with CO<sub>2</sub>-containing flue gases, results in the following heterogeneous reactions:



Dissolution of CO<sub>2</sub> in water depends on the pH, because forming H<sub>2</sub>CO<sub>3</sub> (CO<sub>2</sub>\*H<sub>2</sub>O) dissociates to CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> and, herewith, the overall concentration of dissolved carbon C<sub>CO2</sub> increases together with the amount of HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>-ions formed. Fractional amounts of carbonate species in solution depending on its pH are presented in Fig 1. This distribution diagram shows that at higher pH levels more CO<sub>2</sub> can be dissolved due to the formation of hydrogen carbonate or carbonate ions. Around the targeted pH value of wastewater (below 9), CO<sub>2</sub> is found in the solution mainly as HCO<sub>3</sub><sup>-</sup>. Therefore, the amount of CO<sub>2</sub> necessary to neutralize the alkaline wastewater can be calculated according to Eq (2).

As the wastewater also contains Ca<sup>2+</sup>-ions (300-1200 mg/L), determining the actual demand of CO<sub>2</sub> is more complex. Contact between Ca<sup>2+</sup>-ions and CO<sub>2</sub> leads to precipitation of CaCO<sub>3</sub>, which is practically insoluble at pH ≥ 9. Along with the formation of calcium carbonate, alkalinity of the solution also diminishes according to Eq. (1). In the case of high Ca<sup>2+</sup> concentrations (600-1200 mg/L) and lower pH values (pH<12.4), the stoichiometric amount of CO<sub>2</sub> needed for CaCO<sub>3</sub> precipitation is also sufficient for wastewater neutralization. Higher pH values of the initial solution require more CO<sub>2</sub> to neutralize extra OH<sup>-</sup>-ions according to Eq. (2). So, the overall CO<sub>2</sub> demand can be calculated as the combination of CO<sub>2</sub> amounts needed for precipitation of Ca<sup>2+</sup>-ions and neutralization of OH<sup>-</sup>-ions (Fig. 2).



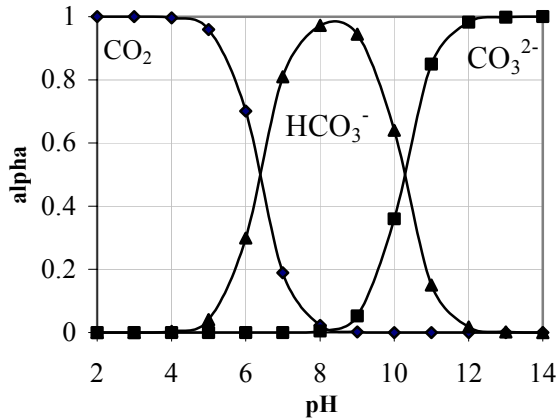


Figure 1: Dependence of the fractional amounts of all carbonate species on the pH of the solution.

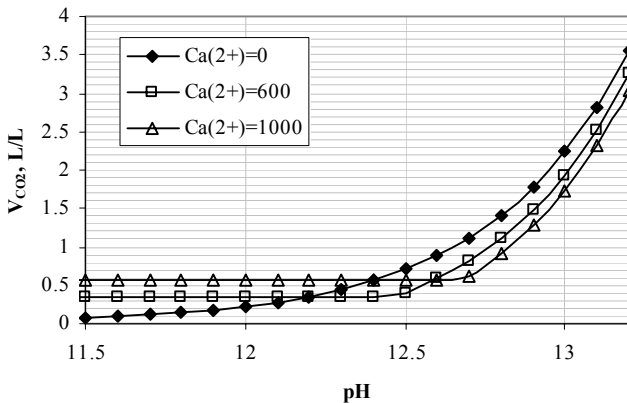


Figure 2: The amount of  $\text{CO}_2$  needed for precipitation of  $\text{Ca}^{2+}$ -ions and neutralization of  $\text{OH}^-$ -ions.

## 2.2 Dispergator-type phase mixer

Recirculation water from the ash transportation system of an Estonian Power Plant was used for laboratory experiments. The wastewater contained 800–1020 mg/L  $\text{Ca}^{2+}$ -ions; and its pH was 13.0–13.1. Neutralization of alkaline ash transportation water was carried out in a laboratory dispergator-type batch device (Figure 3a), which provides intensive stirring and good mechanical mixing of gas and liquid phases to increase interfacial contact surface [9]. The initial ash transportation water (flow-rate 82 L/h) was treated with model gases (flow-rate 1497.4 L/h) having flue gas  $\text{CO}_2$  ( $\text{SO}_2$ ) content: FG 1 (15%  $\text{CO}_2$  in air) or FG 2



(15% CO<sub>2</sub> and 0.07% SO<sub>2</sub> in air). It was determined that the pH of the treated wastewater decreased to 10 after one carbonation cycle at CO<sub>2</sub> excess (amount of CO<sub>2</sub> passed per stoichiometric amount according to Eq (1) and (2))  $N_{\text{CO}_2}=1.5$  and to 8 after three cycles at  $N_{\text{CO}_2}=4.5$ . The experiments were carried out at an ambient temperature under atmospheric pressure and the contact time of phases was 1.25-3.75 sec. After separation of the liquid and gas phase the gas was directed into the atmosphere and the liquid phase was either led back into the reactor or to filtration, where the solid reaction product was separated and dried at 105°C.

### 2.3 Barboter-type column

In order to compare different technological approaches, a conventional barborter-type column (Figure 3b) was also used. Carbonation of alkaline wastewater with model gases FG 1 and FG 2 (flow-rate 100 L/h) was carried out in the laboratory absorber (water column height 500 mm, volume 0.6 L) equipped with a magnetic stirrer (for achieving better interfacial contact) and a sintered gas distributor (pore diameter 100 µm). The experiments lasted until the pH of the treated wastewater reached 10 or 8. The gas phase was analyzed by a gas analyzer (TESTO 350) to determine the residual concentration of SO<sub>2</sub>. After treatment the suspension was filtered and solid residue dehumidified at 105°C.

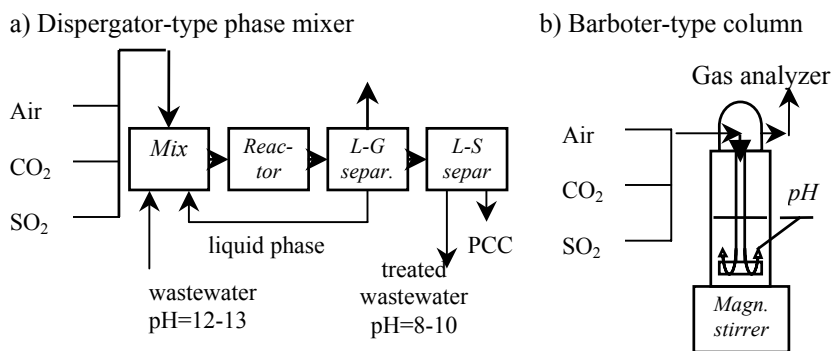


Figure 3: Experiment setup for alkaline wastewater carbonation.

In the liquid phase, pH, the Ca<sup>2+</sup> content [10], SO<sub>4</sub><sup>2-</sup> content (spectrophotometer Spectrodirect Lovibond), TDS (microprocessor conductivity meter HI9032) and alkalinity [11] were determined. Solid samples were analyzed for chemical composition as well as for surface properties and particle size distribution. Surface observation of particles was carried out using the scanning electron microscope Jeol JSM-8404A. The laser diffraction analyzer Beckman Coulter LS 13320 was used for particle size distribution analysis.

3 Results and discussion

3.1 Carbonation of wastewater

Comparative experiments with dispergator- and barbوتر-type reactors indicated that alkaline ash transportation waters (pH=13.0-13.1, Ca<sup>2+</sup> content 800-1020 mg/L) react readily with CO<sub>2</sub>-containing model gases FG1 and FG2, decreasing the content of Ca<sup>2+</sup>-ions and pH value (Fig. 4 and Table 1). In the case of

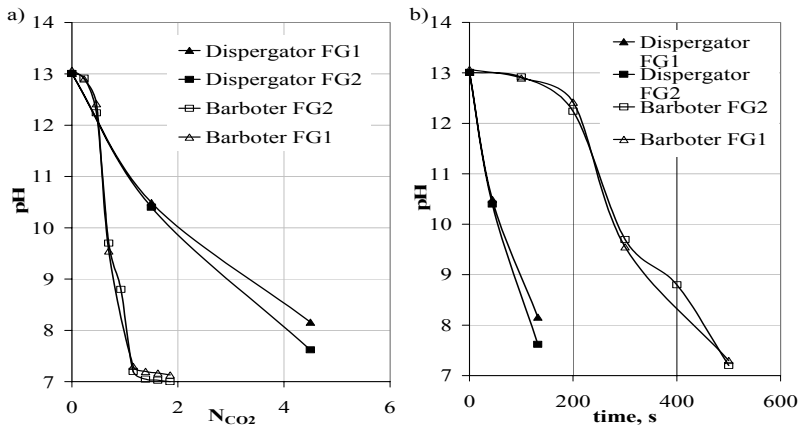


Figure 4: Changes in wastewater pH during carbonation as a function of a) CO<sub>2</sub> excess N<sub>CO2</sub> and b) time (calculated on 1 L of alkaline wastewater).

Table 1: Wastewater treatment with CO<sub>2</sub> and SO<sub>2</sub>-containing model gases: composition of solid and liquid phase.

	Liquid phase							Solid phase	PCC sample
N <sub>CO2</sub>	pH	TDS	Ca <sup>2+</sup>	SO <sub>4</sub> <sup>2-</sup>	OH <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	CaCO <sub>3</sub>	
		g/L	mg/L		mmol/L			%	
1. Wastewater treatment in dispergator type phase mixer with FG 1 (CO <sub>2</sub> +air)									
1.5	~10	5.61	10	1980	2.0	24.0	0.0	86.01	PCC1
4.5	~8	6.33	30	2210	0.0	6.0	25.0	90.40	PCC2
2. Wastewater treatment in dispergator type phase mixer with FG 2 (CO <sub>2</sub> + SO <sub>2</sub> +air)									
1.5	~10	6.43	10	2180	0.0	27.0	1.5	94.16	PCC3
4.5	~8	6.49	100	2340	0.0	7.0	24.5	93.22	PCC4
3. Wastewater treatment in barboter type column with FG 1 (CO <sub>2</sub> +air)									
0.7	~10	6.30	5	960	0.0	22.5	6.5	87.95	PCC5
1.04	~8	6.54	135	1200	0.0	0.0	32.5	84.77	PCC6
4. Wastewater treatment in barboter type column with FG 2 (CO <sub>2</sub> + SO <sub>2</sub> +air)									
0.7	~10	6.39	10	2540	0.0	14.0	14.75	91.20	PCC7
1.04	~8	6.48	160	1922	0.0	0.0	42.5	88.25	PCC8



the dispergator-type phase mixer the content of  $\text{Ca}^{2+}$ -ions dropped notably – to 10 mg/L after 1 carbonation cycle ( $N_{\text{CO}_2}=1.5$ ) and the pH value decreased to the acceptable level (about 8) after 3 carbonation cycles ( $N_{\text{CO}_2}=4.5$ ). The dispergator-type reactor promotes dissolution of  $\text{CO}_2$  and the following dissociation of  $\text{H}_2\text{CO}_3$ , which raises the rate of neutralization (Fig. 4b), but due to the short contact time of phases (1.25 s per cycle) dissolution of  $\text{CO}_2$  is not completed and higher  $\text{CO}_2$  excess  $N_{\text{CO}_2}$  is needed (Fig. 4a) as compared to the conventional barboter-type column. Nevertheless, by using the dispergator-type reactor an increase in specific intensity ( $q$ ,  $\text{m}^3/\text{m}^3 \cdot \text{h}$ ) of up to 50 times, calculated as the volume of processed wastewater per unit of volume of the reactor, was achieved. It was found that the filtered solid samples (PCC1–PCC8, see Table 1) contained predominantly  $\text{CaCO}_3$  (85–94%). The distribution of sulphate ion between the liquid and solid phases needs further analysis.

### 3.2 Characterization of PCC

The PCC samples obtained were analyzed for particle size distribution and surface properties. Results showed that the end-point pH value of carbonation does not influence the size of PCC particles formed in dispergator type phase mixer (PCC1 and PCC2, Table 2). The samples can be characterized by homogeneous particle size distribution: median size  $\sim 5 \mu\text{m}$  and mean/median ratio  $\sim 1$ . The presence of  $\text{SO}_2$  in the gas mixture considerably influenced the size of particles (PCC3 and PCC4, Table 2): the median size of particles increased noticeably due to agglomeration of particles reaching 8–9  $\mu\text{m}$ . Additionally, the agglomeration effect escalated with decreasing pH. The sample of PCC4 was not homogeneous, containing particles in the size range of 3–310  $\mu\text{m}$ . The PCC samples from the barboter-type reactor (PCC5–PCC8, Table 2) had somewhat bigger particle sizes, which was also influenced by the extent of carbonation: median size was  $\sim 6 \mu\text{m}$  and 8–10  $\mu\text{m}$  at  $\text{pH} \sim 10$  and  $\text{pH} \sim 8$ , respectively. The presence of  $\text{SO}_2$  had a minor influence on the size distribution characteristics of PCC.

Table 2: Particle size distribution of PCC samples.

	Dispergator-type phase mixer				Barboter-type column			
	PCC1	PCC2	PCC3	PCC4	PCC5	PCC6	PCC7	PCC8
Mean, $\mu\text{m}$	5.263	5.225	9.163	27.38	6.074	9.524	5.734	7.715
Median, $\mu\text{m}$	5.184	5.103	5.205	8.381	6.169	9.632	5.773	7.883
Mean/Median	1.1015	1.024	0.995	3.267	0.985	0.989	0.993	0.979
	Average size, $\text{m}^{-6}$							
<10%	0.632	0.567	0.880	1.196	0.374	0.789	0.384	0.623
<25%	2.315	2.111	4.895	4.001	3.273	5.728	2.937	4.454
<50%	5.184	5.103	9.205	8.381	6.169	9.632	5.773	7.883
<75%	7.797	7.885	13.32	15.01	8.923	13.54	8.457	11.16
<90%	9.972	10.1	16.71	96.55	11.23	16.77	10.69	13.78



Shape and surface observations confirmed the results of the particle size distribution analysis. The shape of PCC particles from the dispersator-type reactor was influenced noticeably by the extent of carbonation as well as the presence of  $\text{SO}_2$ . Regularly structured particles of PCC were formed at the high pH region in a  $\text{SO}_2$ -free environment (Fig. 5a). Extending the carbonation process led to cleaving of particles (Fig. 5b). In the presence of  $\text{SO}_2$  most of the individual particles were merged forming agglomerates (Fig. 5c).

The PCC formed in the barboter-type column can be characterized by more homogeneous particles with a distinctive regular rhombohedral crystal structure as compared to the particles formed in the dispersator-type reactor. Shape and surface characteristics were not noticeably influenced by the extent of carbonation or presence of  $\text{SO}_2$  in the model gas (Fig. 5d-f).

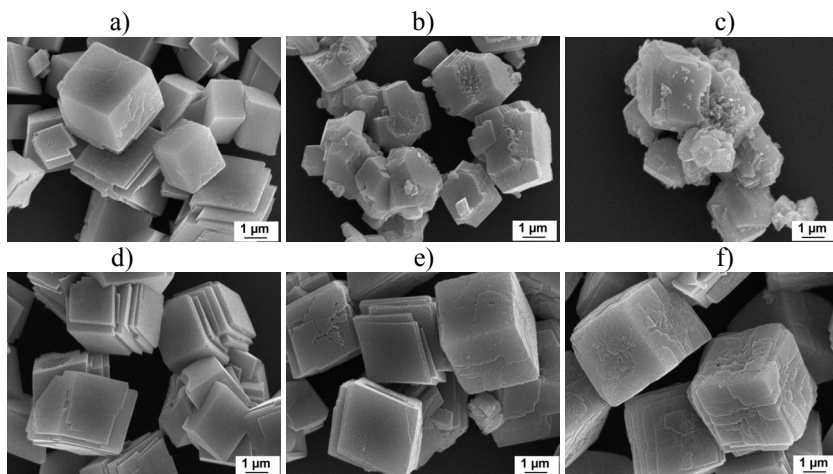


Figure 5: SEM images of PCC samples formed at different conditions in the dispersator-type phase mixer: a - PCC1, b - PCC2, c - PCC4 and the barboter-type column: d - PCC5, e - PCC6, f - PCC8.

According to thermodynamic calculations [12] precipitation of  $\text{CaCO}_3$  in the system wastewater–flue gas can be expected at the starting stage of interfacial contact at high pH values. At pH 7.5–9 the binding capacity of the liquid phase is almost utilized and the increase in  $\text{CO}_2$  binding is mainly due to the increase in the amount of dissolved  $\text{CO}_2$  and formed  $\text{HCO}_3^-$ . Also, at deeper carbonation to  $\text{pH} < 9$ ,  $\text{CaCO}_3$  becomes soluble in water and the concentration of  $\text{Ca}^{2+}$ -ions in the solution starts to rise again as is shown in Table 1. Therefore, to avoid agglomeration of the particles and redissolution of  $\text{CaCO}_3$ , the alkaline wastewater neutralization process with production of PCC should be divided into two stages: first,  $\text{CaCO}_3$  precipitation and separation at higher pH values and second, decreasing the residual alkalinity of wastewater to an acceptable level ( $\text{pH} \sim 8$ –8.5). Producing PCC of specific properties is a complicated process, which needs further research to obtain better understanding of the influence of different conditions on the crystallization processes.



## 4 Conclusions

According to calculations 970–1010 tons of CO<sub>2</sub> can be trapped and 2200–2300 tons of PCC per million cubic meters of wastewater can be obtained.

Comparative experiments with dispergator- and barboter-type reactors indicated that alkaline ash transportation waters with pH=13.0–13.1 and Ca<sup>2+</sup> content 800–1020 mg/L) react readily with the CO<sub>2</sub>-containing model gas of flue gas composition. Rapid neutralization accompanied by forming of useful by-product CaCO<sub>3</sub> with the following decrease in pH value to an acceptable level (pH<9) was shown. In the case of the dispergator-type phase mixer, which provides intensive stirring and good mechanical mixing of gas and liquid phases increasing interfacial contact surface, an increase in specific intensity of up to 50 times was achieved as compared to the barboter.

In the case of the dispergator-type reactor the shape and structure of PCC particles were influenced by the end-point pH value of carbonation – particles formed at a higher pH value were characterized by a more regular crystal structure and homogeneous size distribution (median size ~5 µm). The presence of SO<sub>2</sub> in the gas mixture influenced the size and shape of particles: due to extensive agglomeration, which escalated with decreasing pH, the median size of the particles increased noticeably. The PCC from the barboter-type reactor was characterized by more homogeneous particles of distinctive regular rhombohedral crystal structure and somewhat larger particle size as compared to samples from the dispergator-type reactor. The size and shape of particles were not influenced by the presence of SO<sub>2</sub> in the gas mixture.

According to the preliminary results, Ca-rich wastewater from the oil shale ash transport system can be used as a sorbent for reduction of CO<sub>2</sub> emissions as well as a calcium resource for PCC production.

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