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Utilization of oil shale ash to prepare PCC: leachability dynamics and equilibrium in the ash-water system

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Abstract

In current study the oil shale ash consisting free lime have been considered as a source of Ca in the precipitated calcium carbonate (PCC) production. In connection with this approach, a set of laboratory experiments was carried out in order to investigate the leach ability dynamics and equilibrium of the main ions from oil shale ashes formed in boilers operating with different combustion technologies. The main characteristics of Ca distribution between phases have been established using different ash/water suspension ratios and diffusion coefficients determined. The effect of temperature on the Ca^{2+} equilibrium concentration was investigated. Data collected served as basis for modeling of the equilibrium and dynamics of leaching of Ca^{2+} ions.

© 2009 Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).Keywords: Oil shale ash; solid waste; precipitated calcium carbonate; Ca^{2+} -ions; mineralization; leachability; equilibrium; dynamics

1. Introduction

The use of oil shale as a fuel for power plants is common in China, Germany and Estonia. Power production based on oil shale combustion is, however, accompanied by high CO_2 emissions and by the formation of alkaline waste ash [1-3]. In the modern world, environmental protection issues substantially influence the energy sector, making the above mentioned problems particularly relevant in Estonia, where over 90% [4] of the basic power supply is provided by oil shale-fired thermal power plants. Power plants are the biggest polluters in Estonia, emitting annually thousands of tons of gaseous additives into the atmosphere and contaminating the landscape with alkaline pollutants [5]. Also, Estonian oil shale is characterized by a high content of mineral matter, which leads to the formation of large amounts of ash during the combustion process, which makes it highly desirable to develop effective usage of this waste.

Oil shale energetic is also the main source of CO_2 emissions in Estonia. In 2005, oil shale across all sectors of the economy was responsible for about 72 % of total Estonian energy-related CO_2 emissions [4]. In this aspect, a new

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direction in reducing the negative environmental impact of emissions is CO_2 mineralization, which is based on the CO_2 binding capacity of oil shale ashes and its water suspension [6-8]. An advantage of this process is not only abatement of CO_2 emissions, but also the possibility of the utilization of oil shale waste ash for PCC production. Production of new materials from oil shale ash helps to reduce the ash amount to be deposited as well as reduce its environmental impact, and gives extra value to the combustion product.

Ash from oil shale power stations contains 45 -52% of Ca oxides (including free CaO up to 30 wt-%) [3, 7]. And therefore the separation of free lime from oil shale ash and its application in PCC production is of particular interest. Although the carbonation of lime is well known [9], data about the specific characteristics of the carbonation process of free lime in oil shale ash and of its reactivity towards CO_2 are incomplete. The latter depends on the chemical composition and physical properties of the ash as well as on the conditions of the heterogeneous interaction of the ash with CO_2 . From multiple [3, 7, 10] studies it is known that the main part of the lime in oil shale ash can be neutralized by CO_2 from flue gases with the formation of calcium carbonate. Production of PCC from lime involves dissolving the Ca -ions (diffusion of Ca^{2+} ions into the solution), concentrating the lime milk and precipitation under controlled mixing and temperature conditions. Before this type of process can be applied on an industrial scale, basic and applied research must be carried out to fully understand the mechanisms involved.

Since accessibility of free CaO from ashes is essential for the carbonation process to take place, diffusion of Ca^{2+} ions into a solution is the primary stage. Consequently, leachability of other key ions and the effect of temperature on the Ca^{2+} equilibrium concentration are of importance and for this reason a set of laboratory experiments was carried out in order to investigate the leachability dynamics and equilibrium of Ca^{2+} and accompanying ions from oil shale ashes formed in boilers operating with different combustion technologies. Mathematical tasks of the present work included development of models for the description of Ca equilibrium distribution between phases and determination of an effective diffusion coefficient in the solid particle, which characterizes the resistance of mass transfer in Ca leaching.

2. Materials and Methods

The ashes studied were formed in boilers operating with different combustion technologies. The ashes and ash-mixes were collected from different points of pulverized firing (PF) or fluidized bed combustion (FBC) boilers at Estonian power plants. The main characteristics of ashes and the average content of the basic elements are presented in Table 1 and 2 respectively. Solid material composition was determined by IRIS Intrepid II Inductive Coupled Plasma Spectrometer (Thermo Electron Corporation, software: TEVA: thermo elemental validated analysis). Solid material was initially dissolved in 65% nitric acid in a pretreatment module (GWB Pressurized Microwave Decomposition). Particle size distribution was measured by LS 13 320 Multi-Wavelength Particle Size Analyzer with Aqueous Liquid Module System (Beckman Coulter, Miami, Florida) using ethanol solution.

Table 1. The main characteristics of oil shale ashes

PF ash	CaO_{total} %	CaO_{free} %	CO_2 %	Particle mean diameter, μm
PF1 (TP6/EE/2BI/BA/2K-A)	57.2	30.0	8.34	250.0
PF2 (TP6/EE/BI/CA/K.2-A)	50.2	23.4	7.72	
PF3 (TP6/Mix)	-	23.2	4.23	
FBC ash				
FBC1 (KK6/EE/8BI/EF1/K1)	27.9	8.0	3.50	26.5
FBC2 (KK6/EE/8BI/Mix11-14)	38.1	7.6	16.15	
FBC3 (KK6/Mix12)	-	9.6	8.29	

Table 2. Average content of the basic elements present in oil shale ash (per g of ash)**

Ash type	Ca	Mg	Fe	Al	S	K	Mn	Na	Zn	Si	Cr	Cu	Ni	Pb	V	
	g/g						$\mu g/g$									
PF1	0.425	0.038	0.03	0.015	0.018	0.007	545	540	155	70-100	25	20*	5	13	20	
PF3	0.380	0.047	0.03	0.023	0.019	0.010	600	580	120	70-100	35	12	<5	38	30	
FBC1	0.215	0.033	0.02	0.034	0.024	0.017	385	890	≈30	100-150	45	10	10	30	38	
FBC3	0.265	0.037	0.02	0.026	0.033	0.013	445	640	≈30	80-120	40	12	5	20	30	

*in some samples ≈100 $\mu g/g$; ** [Cd,Co]=0 $\mu g/g$

Experiments were carried out in a laboratory-scale batch reactor using ash/millipore water suspensions by varying solid/liquid mass ratios from 1/1250 to 1/10. Suspensions were mixed at fixed temperature during 1-180 minutes depending on the objective. Samples were taken with a syringe and filtered (0,45 μ m). Main parameters measured in filtrate (\approx 100 ml) were: pH (Precisa pH 900), TDS (total dissolved solids), conductivity (HI9032 Microprocessor Bench Conductivity/TDS/NaCl/Fertilizer/OC/OF meter with RS 232), Ca, K, Na, Mn, Mg, Al, Fe, several heavy metals (ICP Termo IRIS Intrepid II XDL), SO_4^{2-} (Ion chromatograph Dionex DX-120 Computer program: Peaknet DX -120), and SO_3^{2-} , S^{2-} (spectro photo meter SpectroDirect Lovibond).

3. Results and Discussion

3.1. Leachability dynamics of Ca^{2+} and main ions at fixed temperature

Preliminary experiments with different ash types showed changes of Ca^{2+} , SO_3^{2-} and S^{2-} ion concentration (in terms of millipore water) in the first 10 minutes. Based on preliminary data, 1, 3, 5, 7, and 10 - minute periods were selected for more detailed investigation. Experiments were carried out at room temperature (\approx 23 $^{\circ}$ C) with an ash/millipore water mass ratio of 1/10.

Experiments with both types of ash showed that millipore water pH increased rapidly from 7.0 to 12.2 (Figure 1, a) during the first minute of ash-water contact and remained at this value through the entire process. Total dissolved solids content (TDS) (Figure 1, b) reached a value of 5.4 – 6.2 g/L by the end of the third minute in case of both ash types.

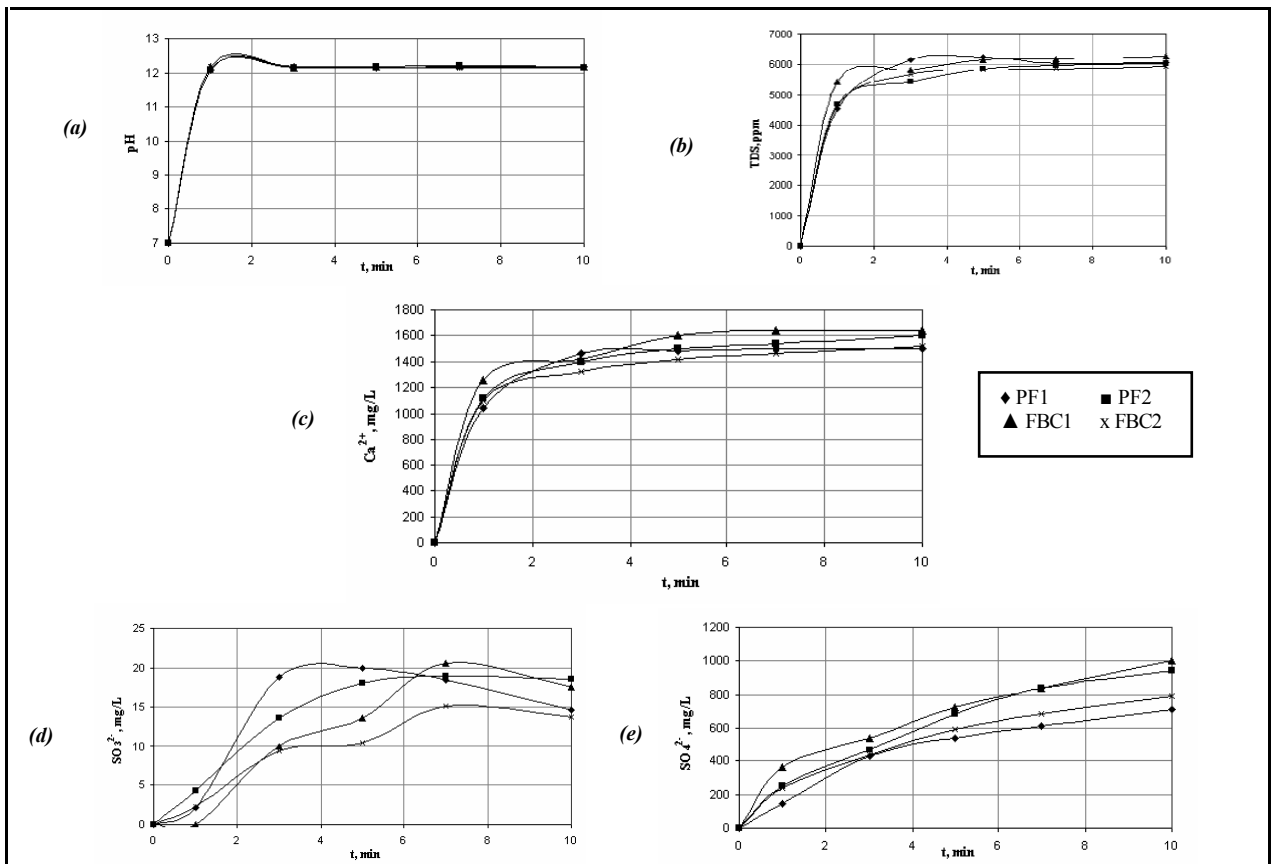


Figure 1. Changing dynamics of pH (a) and TDS (b) values and concentration curves of Ca^{2+} (c), SO_3^{2-} (d) and SO_4^{2-} (e) -ions during water contact with different kinds of ashes during the leachability experiments

Ca^{2+} -ion equilibrium concentration (~860 mg/L depending on temperature) is reached rapidly during the first minute of oil shale ash-water contact (Figure 1, c). Extending the contact time by a few minutes resulted in a about two times high supersaturation of the solution with Ca^{2+} ions: PF1–1500 mg/L, PF2–1600 mg/L, FBC1–1640 mg/L, FBC2–1520 mg/L. This finding is an important positive outcome in the context of the PCC production process.

Although there was no significant difference in the Ca^{2+} concentration in filtrate from different kinds of ashes, a slightly lower Ca concentration (1500 mg/L) in case of coarse PF1 ash was observed, which indicates the influence of ash particle size on Ca^{2+} diffusion extent into the solution in a batch reactor.

For both ash types, the concentration curve of SO_3^{2-} ions (Figure 1, d) reached its maximum during a time span of 5-7 minutes and then started to decrease. A presence of S^{2-} ions in small concentrations was detected in the filtrate after 10 minutes of contact time: ≈ 0.2 mg/L for samples PF1 and FBC2, and ≈ 0.5 mg/L for samples PF2 and FBC1. SO_4^{2-} content in the filtrate increased continuously through leachability process (Figure 1, e).

As the environmental impact of ash disposal systems at oil shale combustion facilities is of particular interest nowadays, it is important to know which compounds could be released to the environment. However, data from the literature about the leaching of oil shale ashes are scarce. In order to investigate the mobility of key ions and toxic metals from oil shale ashes after longer periods of contact with water, additional experiments were conducted with several oil shale ashes (PF1, PF3, FBC3) using an ash/water ratio of 1/10. A quantitative estimation of a wide spectrum of ions (incl. Ca , K , Mg , Mn , Fe , Na , Si , Al) and several heavy metals (Cd , Co , Cr , Cu , Ni , Pb , V , Zn) in final fluid was conducted after letting the experiment go to equilibrium in terms of overall oil shale ash leachability (approximately 3 hours).

The results (Table 3) showed that after calcium, K is the second biggest cation present in the filtrate (70-94 mg/L). Other identified ions include Na (2.2-3.4 mg/L), Al (<1 mg/L) and Si (<0.5 mg/L). Ions like Fe , Mg , Mn were not present in the filtrate

Table 3. Concentration of ions in the final fluid after 3-h contact

Ash sample name	Ca	K	Na	Si	Al	Fe, Mg, Mn, Co, Cr, Cu, Ni, Pb, V, Zn, Cd	SO_4^{2-}
						mg/L	
PF1	1523	70.1	3.4	<0.5	<1.0	0	2700
PF3	1716	91.2	2.2	<0.1	<0.1	0	1276
FBC3	1781	93.7	2.5	<0.5	<0.1	0	1251

The main anion found in the filtrate was SO_4^{2-} (1300-2700 mg/L). An important discovery from an environmental point of view is the fact that no trace of heavy metals was detected in any of the studied ash suspension filtrates after 3-hour contact.

3.2 Equilibrium distribution of Ca between phases

By varying ash/millipore water suspensions mass ratios from 1/1250 to 1/10 and letting the experiment in a stirred-batch go to equilibrium in terms of overall oil shale ash leachability (approximately 3 hours), Ca equilibrium concentration in the final liquid-phase c^* was obtained for two ash samples with Ca content of 425 and 215 mg/g of ash, in PF and FBC ash, respectively (Table 4).

The equilibrium leachability curves of the Ca^{2+} ash-water distribution were expressed as the equation:

$$q^* = A + B(c^*) + C(c^*)^2, \quad (1)$$

where coefficients A , B , C are evaluated by equilibrium experiments. To calculate the equilibrium concentration of Ca in ash q^* (unit in mass/mass of ash) (Table 4), the following mass balance was used:

$$W_0 q_0 = V(c^*) + W q^*, \quad (2)$$

where V – volume of liquid; W_0 – mass of ash in the beginning of the experiment; q_0 – initial concentration of Ca in ash, unit mass/mass of ash; c^* – equilibrium concentration of Ca in water, mass/volume of water; W – mass of ash at the end of experiment. It should be pointed out that the mass of ash is considered to be decreasing by the amount of CaO dissolving into water.

Table 4. Ca equilibrium concentration in the final liquid and solid phases

Ash/water ratio	PF ash (PF1)		FBC ash (FBC1)	
	c^* , g/L	q^* , g Ca/g of ash	c^* , g/L	q^* , g Ca/g of ash
1/1250	0.210	0.257	0.066	0.150
1/500	0.440	0.296	0.164	0.150
1/250	0.805	0.312	0.291	0.158
1/100	-	-	0.45	0.163
1/150	1.006	0.348	0.648	0.165
1/50	1.265	0.397	1.085	0.174
1/20	1.350	0.414	1.45	0.194
1/10	1.523	0.419	1.653	0.203

The equilibrium leachability curves of Ca^{2+} ash-water distribution (Figure 2) can be presented by the following equations:

$$q_{PF}^* = 0.2429 + 0.0808(c^*) + 0.0272(c^*)^2 \tag{3}$$

$$q_{FBC}^* = 0.15 + 0.0165(c^*) + 0.0091(c^*)^2 \tag{4}$$

for PF 1 and FBC 1 ashes studied, respectively .

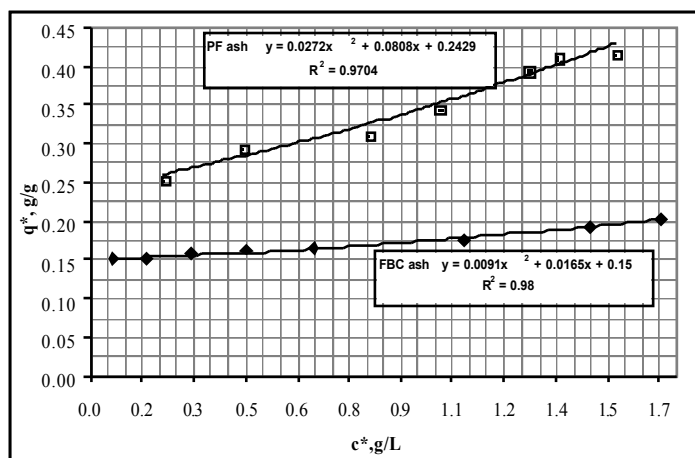


Figure 2. Equilibrium leachability curves of Ca^{2+} ash-water distribution for PF (PF1) and FBC (FBC1) ashes

In leaching of Ca out from ash, the concentration q_{ins} (intersection of equilibrium line with q^* -axes) corresponds to the insoluble part of Ca in the ash (from eq. (3) and (4) 0.2429 and 0.15 g/g of ash for PF1 and FBC1 ashes respectively), the corresponding value of CaO is $q_{ins} * 56/40$, by molar masses of Ca and CaO . In addition, equation:

$$CaO_{free}, \% = (q_0 - q_{ins}) * 56/40 \tag{5}$$

should correspond to free CaO in ash. Therefore, for FBC1 ash eq. (5) gives a result of 0.091 g CaO_{free} /g of ash or 9.1 wt-%, while the corresponding analytically measured value is about 8% (Table 1).

It can be concluded that the above described approach works quite well and collected data can be used for simulation of processes of leaching/dissociation of Ca^{2+} - ions.

3.3 The effect of temperature on the Ca^{2+} equilibrium concentration

A PF bottom ash (PF1) was selected as the initial material in the temperature effect studies on the Ca^{2+} equilibrium concentration (after 3h-contact), because of its higher CaO_{free} content ($\approx 30\%$). The ash suspension temperature variation range was from 15 to 45 °C.

As expected, leachability is greater at higher temperature, as conductivity increases with temperature increase (Table 5). In terms of Ca , however, increasing temperature causes a decline in the Ca equilibrium concentration,

which is in good correlation with theoretical knowledge, as the highest levels of calcium hydroxide solubility are reached at the lowest temperatures [9].

Table 5. Effect of temperature on the Ca^{2+} equilibrium concentration and suspension conductivity value

ash/water ratio $T, ^\circ C$	$c^*, mg/L$				Conductivity, mS/cm		
	1/500	1/250	1/20	1/10	1/250	1/20	1/10
15	460	822	1371	1530	6.96	9.59	9.70
23	440	805	1350	1523	7.27	10.40	10.72
30	439	784	1291	1447	8.34	11.00	11.35
45	437	743	1124	1248	9.56	11.41	12.00
Theoretical max	429	857	10714	21429			

Based on the results (Table 5) there was no significant temperature effect on the Ca content when the ash suspension ratios 1/500 and 1/250 were used. However, use of more concentrated ash suspensions (1/20 and 1/10) showed a noticeable temperature effect. In the last case, conducting Ca dissolution below or at room temperature (15-23 $^\circ C$) had practically no effect on the Ca equilibrium concentration value in the final solution (about 1360 and 1525 mg Ca/L for ratios 1/20 and 1/10, respectively), increasing the suspension temperature from 30 to 45 $^\circ C$ resulted, however, in a Ca content decline by 170-200 mg/L. At 30 $^\circ C$ the Ca equilibrium concentration was only about 60-80 mg/L lower than that at room temperature. Therefore, favorable conditions for batch dissolution of ash could be achieved at room temperature, which simplifies the first stage of PCC production process.

3.4 Determination of effective diffusion coefficient in solid phase D_s

The dynamics of leaching (dissolving) of calcium from ash involves a rate controlling step of mass transfer inside an ash spherical particle. The equation describing homogeneous diffusion in a sphere, assuming a constant effective diffusivity, D_s , at all coordinates r in the particle, is (Figure 3):

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right) \quad (6)$$

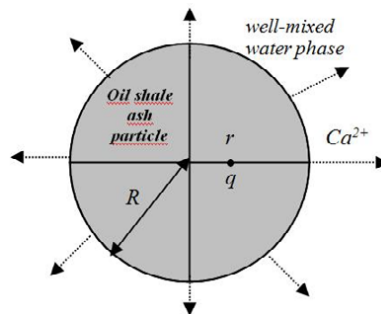


Figure 3. Leaching of Ca from an oil shale ash particle

For ash leaching, the Ca concentration in ash q in eq. (6) and later q is in grams per volume of ash.

As a solution of eq. (6), Crank [11] developed the following analytical equation for the average concentration in the solid at any given time $\bar{q}(t)$, relative to the average concentration in the solid at infinite time q_∞ :

$$\frac{\bar{q}(t)}{q_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_s n^2 \pi^2 t}{R^2}\right) \quad (7)$$

For small times (beginning of the experiment), this equation may be written as:

$$\frac{\bar{q}(t)}{q_\infty} = 6 \left(\frac{D_s t}{R^2} \right)^{1/2} \left[\pi^{1/2} + L \right] \quad (8)$$

Thus, a plot of $\bar{q}(t) / q_{\infty}^*$ vs. the square root of time should give a straight line of slope (k):

$$k = 6(D_s / \pi R^2)^{1/2}, \tag{9}$$

from which D_s can be determined.

Based on the above theoretical considerations and calculations, the values of the solute Ca concentration $c(t)$ in the liquid vs. time in stirred -batch leaching experiments with ash/water mass ratio of 1/500 and 1/250 for PF ($PF1: 0.425 \text{ g Ca/g of ash}; \rho_s=2.83\text{g/cm}^3$) as well as 1/100 and 1/50 for FBC ($FBC1: 0.215 \text{ g Ca/g of ash}; \rho_s=2.73\text{g/cm}^3$) ash were determined.

From the mass balance, $\bar{q}(t)$ values can be calculated:

$$\bar{q}(t) = \frac{W_0 q_0 - V c(t)}{V_s}, \tag{10}$$

where q_0 is the initial solid-phase concentration; $c(t)$ and $\bar{q}(t)$ are the values of the liquid and solid phase concentrations at any later time; V is the liquid volume; W_0 is the mass of solid material; V_s is the volume of solid material. The last volume is calculated by mass of solid: W_0/ρ_s , where ρ_s is the density of ash. The value of q_{∞}^* is obtained from the same mass balance by letting the experiment go to equilibrium and measuring the final liquid - phase solute concentration. Equilibrium time was found to be about 10800 seconds (3h).

Although one must run a batch leaching experiment for a long time, in order to obtain q_{∞}^* only short -time values are needed when plotting $\bar{q}(t) / q_{\infty}^*$ values vs. $t^{1/2}$ (Figure 4). Over such short times, the assumption of a constant surface concentration (on which the above equations are based) is reasonably good, and thus this approach works well.

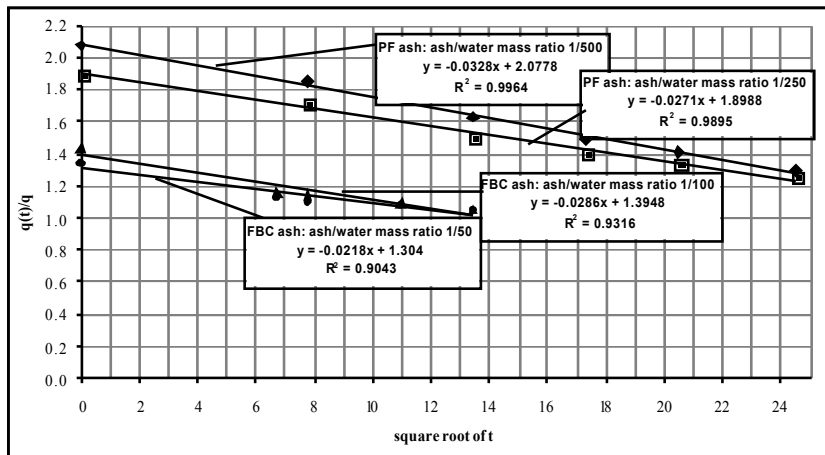


Figure 4. Plot of $\bar{q}(t) / q_{\infty}^*$ vs. the square root of time for different ashes

A plot of $\bar{q}(t) / q_{\infty}^*$ vs. the square root of time (Figure 4) for ash PF 1 (ash/water ratio 1/500) gives a straight line:

$$\frac{\bar{q}(t)}{q_{\infty}^*} = -0.0328\sqrt{t} + 2.0778 \tag{11}$$

of slope k eq. (9), from which D_s can be determined:

$$-0.0328 = 6(D_s / \pi R^2)^{1/2} \Leftrightarrow D_s = 2.988 * 10^{-5} \pi R^2, \tag{12}$$

where R is the particle average radius from size distribution measurement.

To estimate the reliability of the calculated effective diffusion coefficient value the experiments were performed with different ash/water ratios and results are given in Table 6 for both ashes studied.

Table 6. Values of effective diffusion coefficient for PF and FBC ashes

Ash sample name	D_{eff} , m ² /s			
	Ash/water ratio			
	1/500	1/250	1/100	1/50
PF1 ash	$1.46 \cdot 10^{-12}$	$1.0 \cdot 10^{-12}$		
FBC1 ash			$1.25 \cdot 10^{-14}$	$0.73 \cdot 10^{-14}$

4. Conclusions

The main characteristics of Ca^{2+} -ion leachability process in oil shale ash-water suspensions as of the first step of process utilizing oil shale for PCC production have been established. Mobility of different accompanying elements existing in ash was investigated and quantitative estimation of the solubility of a wide spectrum of ions (Ca , K , Na , Al , Si , Fe , Mg , Mn , S^{2-} , SO_3^{2-} and SO_4^{2-}) including several heavy metals (Co , Cr , Cu , Ni , Pb , V , Zn , Cd) was made. The low leachability of heavy metals in these conditions has been proved.

The leaching equilibrium equations of Ca for both types of oil shale ashes were obtained on the basis of the experiments. The single sphere diffusion model was used with determination of the effective diffusion coefficient characterizing the leaching process dynamics of Ca . This was the first step in modeling of the whole process, starting with Ca leaching, taking into account CO_2 mass transfer and finishing with calcium carbonate formation.

Acknowledgments

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References

- [1] A. Ots, *Oil Shale Fuel Combustion*. Tallinn University of Technology, Tallinn, 2006.
- [2] Environmental Issues Associated with Narva Power Plants: Executive Summary. Narva Power, Estonia, 2001. [WWW] <http://www.ebrd.com/projects/eias/narva.pdf> (Retrieved on 10.10.2008)
- [3] R. Kuusik, M. Uibu, K. Kirsimäe. Characterization of oil shale ashes formed at industrial-scale CFBC boilers. *Oil Shale* 22(4S) (2005) 407-420.
- [4] I. Roos, O. Gavrilova. Greenhouse gas emissions in Estonia 1990–2005. National Inventory Report to the UNFCCC Secretariat, 2007. [WWW] <http://www.envir.ee/kliima/files/c/0/0/1/85.pdf> (Retrieved on 10.10.2008)
- [5] M. Kaasik, T. Alliksaar, J. Ivask, J. Loosaar. Spherical fly ash particles from oil shale fired power plants in atmospheric precipitations: Possibilities of quantitative tracing. *Oil Shale* 22(4S) (2005) 547-562.
- [6] J. M. Punning, A. Karindi. Composition of Estonian atmosphere: Estonia in the System of Global Climate Change. *Institute of Ecology: Publications* No. 4 (1996) 26-34.
- [7] R. Kuusik, H. Veskimäe, T. Kaljuvee, O. Parts. Carbon dioxide binding in the heterogeneous systems formed by combustion of oil shale: 1. Carbon dioxide binding at oil shale ash deposits. *Oil Shale* 18(2) (2001) 109-122.
- [8] R. Kuusik, H. Veskimäe, M. Uibu. Carbon dioxide binding in the heterogeneous systems formed by combustion of oil shale: 3. Transformations in the system suspension of ash – flue gases. *Oil Shale* 19(3) (2002) 277-288.
- [9] J. A. H. Oates, *Lime and Limestone: Chemistry and Technology, Production and Use*. Weinheim etc., Wiley - VCH, USA, 1998.
- [10] M. Uibu, M. - L. Muulmann, R. Kuusik. CO_2 wet mineralization by oil shale ash and model compounds. Poster presented at the 4th Minisymposium on Carbon Dioxide Capture and Storage, Finland, Espoo, 2005. [WWW] www.eny.tkk.fi/minisymposium/proceedings/Uibu-poster.pdf (Retrieved on 10.10.2008)
- [11] D. Cooney, *Adsorption design in wastewater treatment*. Lewis publishers, Boca Raton, USA, 1998.