

DISSERTATIONES TECHNOLOGIAE CIRCUMIECTORUM  
UNIVERSITATIS TARTUENSIS

**16**



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**MARTIN LIIRA**

Active filtration of phosphorus  
in Ca-rich hydrated oil shale ash:  
precipitation mechanisms and  
recovery



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## LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following published papers, which are referred to in the text by their Roman numerals. The papers are reprinted by kind permission of the publishers.

- I **Liira, M.**, Kõiv, M., Mander, Ü., Mõtlep, R., Vohla, C., Kirsimäe, K. (2009a). Active filtration of phosphorus on Ca-rich hydrated oil shale ash: does longer retention time improve the process? *Environmental Science and Technology* 43, 3809–3814.
- II Kõiv, M., **Liira, M.**, Mander, Ü., Mõtlep, R., Vohla, C., Kirsimäe, K. (2010). Phosphorus removal using Ca-rich hydrated oil shale ash as filter material – the effect of different phosphorus loadings and wastewater compositions. *Water Research*, 44, 5232–5239.
- III Kõiv, M., Ostonen, I., Vohla, C., Mõtlep, R., **Liira, M.**, Lõhmus, K., Kirsimäe, K., Mander, M. (2012). Reuse potential of phosphorus-rich filter materials from subsurface flow wastewater treatment filters for forest soil amendment. *Hydrobiologia* (in press), doi:10.1007/s10750-011-0944-5.

### Author's contribution

Paper I: The author was primarily responsible for planning original research, laboratory experiment and analysis, and interpretation of analytical data, and writing of the manuscript.

Paper II: The author was responsible for planning and running of experiments, collection of mineralogical X-ray diffraction and scanning electron microscopy data, interpretation and synthesis of chemical and mineralogical analysis, and writing of the manuscript (about 50%).

Paper III: The author was responsible for experiment planning and fieldwork, obtaining and interpretation of mineral X-ray diffraction and chemical analysis data, and contributed to the writing of the manuscript (about 25%).

# I. INTRODUCTION

Phosphorus is an important nutrient in the biochemical cycle. However, already slightly elevated concentrations of phosphorus ( $>10 \mu\text{g L}^{-1}$ ) can trigger eutrophication (Vymazal et al., 1998) and for more than 40 years excess phosphorus has been recognized as one of the main nutrients responsible for eutrophication (Schindler, 1971). Phosphorus, mainly in the form of soluble phosphate, is intensively used for agricultural and domestic purposes (fertilizers, detergents etc.) and the run-off from agricultural landscapes and especially the domestic wastewaters are enriched in respect to phosphates. Consequently the effluents from human activities must be treated to remove the surplus P, in order to maintain the good health of natural systems (Conley et al., 2009). The European Union Water Framework Directive (2000/60/EEC) grades ecological status of water bodies as: high, good and poor. Directive aims an objective to achieve status “good” of all water bodies by the year 2015. This emphasises the need to treat wastewater, as a main source of pollutants, in extended areas where both large- and small-scale settlements are involved.

Phosphorus removal from wastewater at large population or industrial sites can be solved in large-scale wastewater treatment facilities (conventional treatment systems) that apply usually P coagulation with Al- and Fe-salts. However, these technological schemes are not feasible for technical and economic reasons at a smaller scale like in single farms/houses and small enterprises/settlements where simple constructed wetlands can be used instead (Vymazal et al., 1998; Leader et al., 2008; Park and Polprasert, 2008; Xiong and Peng, 2008; Kadlec and Wallace, 2009). The use of constructed wetlands has extended rapidly as an alternative choice for waste water purification due to their robustness, relatively low cost, easy operation and maintenance. Although the constructed wetlands have proven to be effective for nitrification and have enhanced the removal of total nitrogen (Cooper et al., 2003), then the capacity of phosphorus removal is not sufficient (Brix et al., 2001; Molle et al., 2005). Therefore, there is an increasing demand for efficient, but cheap filter materials for phosphorus removal in constructed wetland systems.

In recent years worldwide studies have shown effectiveness of active filtration through alkaline media for the removal of phosphorus (Johansson and Gustafsson, 2000; Vohla et al., 2005; Shilton et al., 2005; Drizo et al., 2006; Adam et al., 2007; Gustafsson et al., 2008; Kaasik et al., 2008; Kõiv et al., 2010 – PAPER II). Active filtration technique uses direct precipitation/immobilization of the phosphates into low soluble forms, and it is considered as a promising technique for small-scale wastewater treatment, whereas the nutrient-loaded filter material can be used in agriculture as phosphorous fertilizer and soil conditioner (e.g., Johansson and Hylander, 1998; Hylander et al., 2006; Gustafsson et al., 2008; Kõiv et al., 2012 – PAPER III).

Active filtration relies on simple chemical reactions, the effectiveness of which depends on the ionic strength of the solution, the activity of Ca and other competing ions, and the form and activity of P. Earlier studies (Chen et al.,

2002; Shilton et al., 2005; Adam et al., 2007) have shown that P removal is inhibited in the presence of competitive ions and/or inhibitors such as  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$  and also organic compounds (humic acids), whereas extensive super-saturation of pore-water with respect to  $Ca^{2+}$  and phosphate is required for the precipitation of stable Ca-phosphate phases (House, 1999; Arias et al., 2003; Liira et al., 2009a – PAPER I).

Potential materials for active filtration of phosphorus include metallurgical slags (Johansson and Gustafsson, 2000; Shilton et al., 2006, Pratt et al., 2007) and high Ca content industrial products, where Ca occurs in CaO form (lime) and/or Ca-silicates that have pH >9 (e.g., Zhu et al., 2003; Kvarnström et al., 2004; Adam et al., 2006; Adam et al., 2007). The phosphorus removal by these materials as Polonite®, Filtralite-P®, wollastonite etc. is governed by dissolution of Ca-phases releasing Ca into pore water and precipitation of Ca-phosphates as hydroxyl-apatite or other Ca-phosphate phases (e.g., Johansson and Gustafsson, 2000; Drizo et al., 2006).

Veskimäe et al. (1997), Vohla et al. (2005), Kaasik et al. (2008), Liira et al., 2009a – PAPER I and Kõiv et al., 2010 – PAPER II have recently shown the effectiveness of Ca-rich hydrated oil shale ash as a possible material for P removal in constructed wetland systems. These experiments have shown the P removal effectiveness for fly ash and hydrated ash in the batch experiment to be up to 99.9%, with maximum binding capacity as high as  $65 \text{ mg P g}^{-1}$  (Vohla et al., 2005; Kaasik et al., 2008). Phosphorus retention in this Ca-rich filter material occurs through irreversible reactions of adsorption and precipitation into a solid phase. The remarkably high P-binding capacity of the oil shale ash filter material is influenced by the complex physical-chemical properties of the material, especially its high content of different Ca- and Al-compounds, porosity and high pH.

Ca-rich oil shale ash is derived from burning of low-caloric value solid fuel oil shale (kukersite) in Estonia. The Estonian kukersite oil shale is the largest industrially exploitable oil shale resource in the world (Teedumäe and Raukas, 2006). Current oil shale mining output is at about 14 to 16 Mt and the majority of oil shale (about 80%) is utilized in thermal power plants for electricity and heat production. Oil shale combustion in electric power plants results in generation of large amounts of oil shale ash waste. In electric power plants the amount of ash that remains after combustion is 45–48% of the oil shale dry mass (Bauert and Kattai, 1997). Less than 5% of ash is recycled for construction materials, in agriculture for liming acid soils or in road construction as a stabilizing agent of roadbeds. Majority of ash is still deposited on ash sediment plateaus next to the power plants. The amount of ash deposited in waste plateaus ranges between 5 and 7 Mt each year and the total ash waste volume is close to 300 Mt.

The kukersite oil shale is highly calcareous. As a result of partial-to-complete thermal dissociation of carbonate minerals and subsequent reactions with flue gases and silica the ash remaining after combustion is rich in free lime (CaO), anhydrite ( $CaSO_4$ ) and secondary Ca-silicates (Bitjukova et al., 2010).

Hydration of ash already in transportation system and under open atmospheric storage in plateaus initiates the formation of secondary Ca-phases (e.g., Ca-hydroxide – portlandite, Ca-sulphoaluminate – ettringite) whose dissolution causes high alkalinity (pH 12–13) (Liira et al., 2009b; Mõtlep et al., 2010).

Earlier studies (e.g., Brix et al., 2000; Del Bubba et al., 2003; Molle et al., 2003; Brogowski and Renman, 2004; Adam et al., 2007; Gustafsson et al., 2008) have shown that calcareous materials have efficient phosphorus retention capacities, but with some limitations in sorption kinetics or the chemical stability of the effluent, whereas the retention efficiency on natural calcite is not sufficient, because of its sensitivity to carbonate equilibrium. Oil shale ash, however, behaves in this sense as complex mixtures of several potential P-binding media with several potential substrates for P adsorption not just only calcite surfaces.

The first objective of this thesis is to reveal the principal chemical–mineralogical processes controlling the P binding in hydrated oil shale ash.

Second objective is to test the binding capacity dynamics and mechanisms on oil shale ash sediment substrates at varying phosphorus loadings.

Third objective of the thesis is to assess the potential remobilization and reuse of the P from filter materials. Phosphorus reserves are non-renewable, and it is possible to reuse depleted, but P-enriched filter materials from wastewater treatment soil filters and constructed wetlands as low cost fertilizers, though feasibility of possible applications depends strongly on the concentration and form of bonded phosphorus.

## 2. OIL SHALE ASH

### 2.1. Oil shale

Oil shales are fine-grained sedimentary rocks that contain relatively large amounts (10–65%) of organic matter. Oil shales belong to the group of sapropelic fuels that have been accumulated in marine, lacustrine or terrestrial environments from Cambrian to Neogene age. Estonian oil shale is marine-type calcareous sediment with high organic content (named also as kukersite), occurs in sediments of Lower to Upper Ordovician age in Estonia and north-western Russia (Bauert and Kattai, 1997).

The Estonian kukersite oil shale deposit is the largest industrially exploited oil shale resource in the world today (Bauert and Kattai, 1997). Oil shale reserves in Estonia are found in the area of 2973 km<sup>2</sup>, are in total nearly  $5 \cdot 10^9$  t, including  $1.5 \cdot 10^9$  t of active reserves (Ots, 2006). Since the beginning of the oil shale mining in 1916, about 1 billion tonnes of oil shale has been mined. During the last decade about 14–16 Mt of oil shale has been mined annually in underground mines and open cast quarries (Kattai et al., 2000; Statistical Yearbook of Estonia, 2010). Estonian oil shale is primarily used for electricity production at two large power plants – the Balti Power Plant (established in 1959) and the Eesti Power Plant (established in 1969).

The organic matter of kukersite is composed of kerogen with few percent of bitumen (Koel, 1999). Organic matter is derived from extinct colonial microorganisms *Gloeocapsomorpha prisca* (Koel, 1999; Lille, 2002). The calorific value of oil shale burned at power plants is rather low (8–10 MJ/kg) compared with coal (in average 22.5 MJ/kg) and natural gas (33.5 MJ/m<sup>3</sup>) (Ots, 2006; Valdma et al., 2009).

Estonian oil shale contains high amount of mineral matter (30–90%) composed of terrigenous-silicate and carbonate mineral phases (Ots, 2006). The content of carbonate mineral phases (calcite and dolomite) varies between 20–70%. The terrigenous-silicate mineral fraction is dominated by quartz, K-feldspar and clay minerals (15–60%) (Table 1, compiled after Saether et al., 2004; Kuusik et al., 2005).

The Estonian oil shale is characterized by generally low micro- and heavy element concentrations (Table 2, compiled after Ots, 2006; Kaasik et al., 2008).

**Table 1.** Mineral composition of Estonian oil shale and residual ash, average values in wt% (after Saether et al., 2004 and Kuusik et al., 2005).

Mineral	Kukersite oil shale	Fresh ash	Ash-plateau sediment
Calcite /vaterite	58.2	4.5	28
Dolomite	12.6		
Quartz	11.8	6.4	9.6
Feldspar/Orthoclase	4	6.3	6.9
Pyrite	3.4		
Clay minerals /Illite	10	3.4	3.1
Ca/Mg-silicates		24.1	16.6
Periclase		3	2.1
Melilite		10.3	5.3
Anhydrite		11	
Lime		28	
Portlandite		2.1	6.8
Ettringite			15.2
Hydrocalumite			4.1
Gypsum			2.3

**Table 2.** Average chemical composition of major oxides (wt%) and selected trace elements (ppm) in hydrated plateau sediments compared with Earth's crust average trace elements concentrations (after Ots, 2006 and Kaasik et al., 2008).

	Ash-plateau sediment	Earth's crust
In ppm		
Ni	27	60
Mo	3.7	1.5
Cu	8.6	47
Pb	42.1	16
Cd	<0.1	0.5
As	15.1	50
Sc	6	
Zn	50.3	
In wt%		
SiO <sub>2</sub>	25.96	
Al <sub>2</sub> O <sub>3</sub>	6.25	
Fe <sub>2</sub> O <sub>3</sub>	3.56	
MgO	3.42	
CaO	29.22	
Na <sub>2</sub> O	0.11	
K <sub>2</sub> O	2.97	
TiO <sub>2</sub>	0.36	
P <sub>2</sub> O <sub>5</sub>	0.13	
MnO	0.04	
Cr <sub>2</sub> O <sub>3</sub>	<0.01	
LOI	27.98	
TOT/C	2.22	
TOT/S	1.63	

LOI – loss on ignition, TOT/C – total C, TOT/S – total S.

## 2.2. Oil shale ash

The ash content of the shale after burning is ~45% in the dry state, and ~6–8 million tonnes of waste is produced annually at the power plants. The ash removal at electric power plants is managed by hydraulic transportation system, and the ash-water slurry is mixed at ratio of 1:20. The ash plateaus near power plants cover an area of about 20 km<sup>2</sup> and contain ~300 million tonnes of hydrated ash sediment.

The secondary use of oil shale ash is limited and more than 95% of the ash produced in oil shale combustion is deposited in large ash fields (hereafter named ash plateaus). On previous decades only a small fraction of the total ash produced has been reused: in road construction, production of construction materials (including as an additive to portland cement), and for soil liming in agriculture (Pets et al, 1985; Kikas, 1988; Turbas, 1992; Hanni, 1996; Paat, 2002).

Due to high content of initial carbonate mineral phases in raw oil shale the ash remaining after combustion is rich in free lime (CaO), anhydrite (CaSO<sub>4</sub>) and belite ( $\beta$ -Ca<sub>2</sub>SiO<sub>3</sub>), on average 17%, 10% and 11%, respectively (Bitjukova et al., 2010), which are unstable phases upon hydration. Beginning at ash transportation and continuing at plateaus several secondary hydrous Ca-phases as portlandite, Ca-sulphoaluminate (ettringite) and hydrocalumite are formed. Slow dissolution of portlandite and ettringite causes high alkalinity (pH 12–13) of the transportation and leachate water in contact with ash sediment (Liira et al., 2009b).

Hydration process is completed at ash plateaus and subsequently followed by carbonation reactions (Liira et al., 2009b; Mötlet et al., 2010). The hydration experiments of oil shale ash show rapid and almost complete slacking of lime during the first 24 hours, and dissolution of anhydrite and precipitation of gypsum and ettringite/hydrocalumite in two weeks (Liira et al., 2009b). Laboratory experiment shows also that the carbonation of metastable portlandite is completed in few weeks or months (Kuusik et al., 2004; Liira et al., 2009b). In ash plateaus the carbonation reactions are inhibited by slow, diffusion controlled, transport of CO<sub>2</sub> into the ash sediment, therefore portlandite and ettringite are often well preserved in deeper parts of the ash deposits (Mötlet et al., 2010).

Kaasik et al. (2008) has shown that hydrated oil shale ash is composed of several Ca-phases including calcite and vaterite as Ca-carbonate phases – CaCO<sub>3</sub> and  $\gamma$ -CaCO<sub>3</sub>, respectively; ettringite Ca<sub>6</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>(OH)<sub>12</sub>\*26H<sub>2</sub>O, hydrocalumite Ca<sub>2</sub>Al(OH)<sub>7</sub>\*6H<sub>2</sub>O, portlandite Ca(OH)<sub>2</sub>, C2S belite  $\beta$ -Ca<sub>2</sub>SiO<sub>4</sub>, merwinite Ca<sub>3</sub>Mg(SiO<sub>4</sub>)<sub>2</sub>, melilite (Ca,Na)<sub>2</sub>(Al,Mg,Fe)(Si,Al)<sub>2</sub>O<sub>7</sub> and wollastonite CaO\*SiO<sub>2</sub>. About 10–20% (maximum 40%) of the ash consist of amorphous glass-like aggregates of (alumino-) silicate composition (Mötlet et al., 2010). These phases are dissolved at different rates (a) providing Ca favoring phosphate precipitation and (b) increasing the pH to alkaline (>9.0), which promotes P speciation towards PO<sub>4</sub><sup>3-</sup> (Berg et al., 2005b).

Similarly to raw oil shale, the content of trace/heavy elements in oil shale ash is low and does not exceed their average concentration in Earth's crust, except for Mo and Pb (Table 2, after Ots, 2006 and Kaasik et al. 2008).

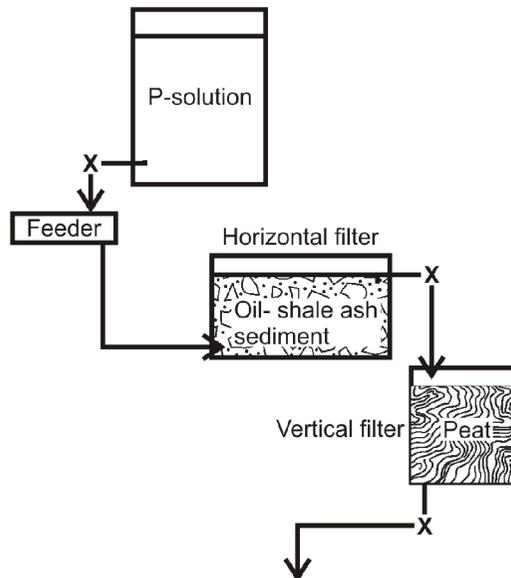
Veskimäe et al. (1997) showed that fresh unhydrated oil shale ash from the Baltic Power plant cyclone unit is suitable material for phosphorus removal, but the hydrated ash material from ash plateaus has not had any use until recently when Vohla et al. (2005), Kaasik et al. (2008) and Kõiv et al., 2010 – PAPER II showed that hydrated ash sediment can be used as an effective filter material for wastewater treatment.

## 3. MATERIAL AND METHODS

### 3.1. Filter experiments

#### 3.1.1. Lab-scale experiment

Three parallel column experiments were established to study the phosphorus binding capacity of hydrated oil shale ash at different residence times (Liira et al., 2009a – PAPER I). The experiment was carried out under water-saturated conditions in horizontal flow filters (H1, H2, H3) filled with 11 kg of crushed (fraction 6 – 16 mm) hydrated oil shale ash sediment with ~45% porosity. The surface area of the water-saturated horizontal flow filters was 840 cm<sup>2</sup> and the volume 12.6 L. Because of the high pH value (>9) of the output water from the ash-sediment filled saturated-flow filters, the vertical flow filters (V1, V2, V3), filled with highly decomposed peat were added to neutralize the pH of the output water (Figure 1).



**Figure 1.** The principal scheme of the column experiment. The arrows show the flow path from P-solution container through saturated horizontal and vertical filters to the discharge. X – sampling places.

The columns were loaded with feeder pumps with an artificial P-solution made of dissolved disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) in tap water. Through the experiment period, the concentration of phosphorus in the stock solution was changed from 8 to 15 mg L<sup>-1</sup> to simulate expected variation in the wastewater treatment systems. To assure the maximal contact of P-solution and filter

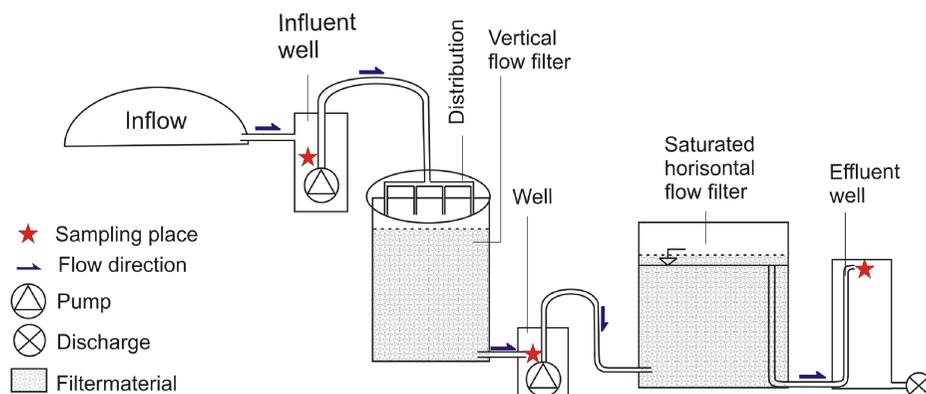
media in the horizontal filter, the inlet tube of the solution was installed to bottom part of the filter wall and outlet tube to the upper part of the opposite wall. The vertical flow filter was filled with about 5 kg of highly decomposed peat. The first column system (H1/V1) was loaded at a hydraulic loading rate of  $12 \text{ L d}^{-1}$ , which is equal to  $923 \text{ L}\cdot\text{m}^{-3}$  per day. The second column system (H2/V2) was loaded at a rate of  $18 \text{ L d}^{-1}$ , which is equal to  $1385 \text{ L m}^{-3}$  per day, and the third at a rate of  $24 \text{ L d}^{-1}$ , which is equal to  $1846 \text{ L m}^{-3}$  per day (H3/V3). The respective residence times were 12, 8 and 6 h. All filters were covered with plastic membrane to prevent evaporation.

The average phosphorus loading in the first column system (H1/V1) was  $1.66 \text{ gP m}^{-2} \text{ d}^{-1}$  and  $2.49 \text{ gP m}^{-2} \text{ d}^{-1}$  in the second column system (H2/V2). In the third column system the average phosphorus loading was  $3.32 \text{ gP m}^{-2} \text{ d}^{-1}$ .

### 3.1.2. Field-scale experiments

Pilot-scale experiments were conducted simultaneously at two sites: at the municipal wastewater treatment plant in the small town of Tapa and at Väätsa waste landfill in Estonia (Kõiv et al., 2010 – PAPER II). Small, insulated buildings were erected for both experiments in order to avoid freezing of filters during the winter period. The Tapa experiment lasted from September 2006 to March 2007 (6 months) and Väätsa experiment from September 2006 to September 2007 (one year).

In both onsite experiments, two sequential systems, which consisted of vertical flow (VF) filters filled with mineralized peat (VV1 in Väätsa and TV1 in Tapa) and hydrated oil shale ash (VV2 in Väätsa and TV2 in Tapa), followed by horizontal flow (HF) hydraulically saturated hydrated oil shale ash filters (VH1, VH2 and TH1, TH2, in Väätsa and Tapa respectively), were used (Figure 2). The experimental design is described in detail in Kõiv et al. (2009). The hydraulically unsaturated VF mineralized peat filters (VV1, TV1) were primarily designed for removal of organic materials and different forms of nitrogen. In this thesis only the phosphorus removal processes in oil shale ash filters are discussed. The performance of peat filters is discussed in detail in Kõiv et al. (2009). In order to test the higher inflow P load on horizontal flow hydrated ash filters (VH2 and TH2), the vertical flow filters (VV2 and TV2) were, after almost 5 months in operation, removed from the system.



**Figure 2.** Experimental design of the pilot systems in Tapa and Väätsa.

The VF filters had a volume of  $0.86 \text{ m}^3$ , and HF filters  $1.24 \text{ m}^3$ . Both the VF filters ( $D=1.0 \text{ m}$ ,  $h=1.5 \text{ m}$ ) and the HF filters ( $D=1.2 \text{ m}$ ,  $h=1.5 \text{ m}$ ) were made of PVC pipe. The filter systems were periodically loaded using timer-adjusted pumping every 2 hours, i.e. 12 times per day. The water amount in one dose was  $\sim 5 \text{ L}$ . The loading rate was  $76 \text{ mm d}^{-1}$  for VF filters, and  $53 \text{ mm d}^{-1}$  for HF filters. The average flow rate for all filters was  $60 \text{ L d}^{-1}$ . The total phosphorus loading at Väätsa landfill leachate was stable, varying from  $2.5$  to  $5.2 \text{ mg L}^{-1}$  (median  $3.5 \text{ mg L}^{-1}$ ). However, the median  $P_{\text{total}}$  content in Tapa wastewater was higher ( $5.25 \text{ mg L}^{-1}$ ) and highly variable ( $0.14 - 17.0 \text{ mg L}^{-1}$ ). The P in both sites was mostly in the form of soluble reactive P, analyzed as orthophosphate phosphorus ( $\text{PO}_4\text{-P}$ ; median 80% and 94% of total P in Väätsa and Tapa respectively).

For the identification of spatial variability of P inside the filters at Tapa (filter TH1) and Väätsa (filter VH1) site, subsamples were taken from three different height of the container (indicated as 1 to 3 from top to bottom). While four samples were taken from each level. In Tapa site samples were taken from central axis of the tank, and three samples radially on edge of the container (indicated as A, B, C, and D). In Väätsa site average samples in the central area were taken from upper and middle levels, and three samples at the bottom level as indicated in Figure 3.

The ash sediment used both in lab-scale and field-scale experiments was taken from the Baltic Thermal Power Plant ash-plateau No.2 and represents the partially carbonized surface layer of the plateau sediments. Uppermost layer ( $\sim 20 \text{ cm}$ ) of friable material was removed before collecting the ash sediment for the experiment, and the bulky ash sediment chunks were crushed and sieved to the fraction  $\text{Ø } 5\text{--}20 \text{ mm}$ .

### 3.2. Phosphorus recovery experiment

The phosphorus recovery experiment (Kõiv et al., 2012 – PAPER III) was carried out using silver birch (*Betula pendula* Roth.) seedlings, which were planted on wastewater-treated filter materials from Tapa and Väätsa experiments (Kõiv et al., 2010 – PAPER II). The experiment lasted for one vegetation period (from May to the end of September 2007). Silver birch was selected because it is a pioneer species in nature (Grime, 1979), and it has already proven to resist inhospitable conditions such as growth in recultivated opencast oil shale mining areas and on semi-coke waste deposits (Ostonen et al., 2006; Lõhmus et al., 2007; Rosenvald et al., 2011). No extra soil was mixed with filter materials. Each pot (with a volume of 1.8 L) held one seedling. 70 pots with seedlings planted on hydrated ash, 50 pots on peat and 50 pots on a peat/ash mixture, plus an extra five pots of each material without seedlings were prepared and placed under a transparent plastic roof in order to rule out the impact of uncontrolled precipitation. Seedlings were watered daily (or every other day during periods of elevated air humidity) with tap water (pH 6.8).

When the foliar mass achieved its maximum (in the middle of September), the samples of the seedlings and the growth substrate materials were collected: 15 pots from each treatment were chosen randomly. Additionally a composite sample was prepared for each substrate type by mixing material from five different pots together. Also 45 plant samples were taken using the same mixing technique as with the substrate materials.

### 3.3. Analytical methods

In lab-scale experiment (Liira et al., 2009a – PAPER I) the phosphorus in water samples was measured with Hach Lange portable spectrometer DR/2400 according to the method 8190 “PhosVer® 3 with Acid Persulfate Digestion Method”, which is accepted by USEPA (The United States Environmental Protection Agency) for reporting wastewater analyses. Test results were measured at 890 nm wavelength and the results were obtained as  $\text{mg L}^{-1} \text{PO}_4^{3-}$ . The results in tables and figures are recalculated to  $\text{mgP} \cdot \text{L}^{-1}$ . From every water sample the temperature and pH were measured with portable METTLER TOLEDO SevenGo pro™ pH/Ion meter during sampling.

The water samples from the field-scale experiment (PAPAER II) were analysed at Tartu Environmental Research Ltd. laboratory using standard methods (APHA, 1989). In both experiments, BOD<sub>7</sub>, COD, TN, NH<sub>4</sub>-N, NO<sub>3</sub>-N, NO<sub>2</sub>-N, TP, PO<sub>4</sub><sup>3-</sup>, Ca, Mg, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, K and pH were measured.

The mineralogical composition of the initial hydrated ash and the hydrated ash after the experimental periods were studied by means of powder X-ray diffraction (XRD). The samples were prepared in the agate mortar to the maximum particle size of about 5 µm and unoriented preparations were made. The powdered preparations were measured on Dron 3M diffractometer using Ni-filtered CuKα radiation in 2–55 °2θ region, with scan step of 0.03 °2θ and count

time of 5 sec per step, and on Bruker D8 diffractometer using Ni-filtered CuK $\alpha$  radiation over 2–70 °2 $\theta$  region, with a scan step of 0.02 °2 $\theta$  and a count time of 2 s per step. The semi-quantitative mineral composition was found by full-profile Rietveld analysis using Siroquant<sup>TM</sup> code (Taylor et al., 1991). The chemical composition of the filter materials in field-scale experiment was determined using standard inductively coupled plasma spectroscopy (ICP-ES, ICP-MS) techniques at ACME Analytical Laboratories Ltd., Vancouver, Canada (ISO 90001).

Micromorphology and spatial relationships of secondary mineralization were carried out using scanning electron microscope (SEM) Zeiss DSM 940 equipped with Idfix Si-drift technology energy-dispersive analyzer (EDS). SEM preparations were coated with conductive gold or carbon coating during preparation. The composition of amorphous precipitates was additionally studied by means of Fourier transformed infrared spectroscopy (FTIR) at Institute of Chemistry, University of Tartu.

The composition of ash sediment (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, MnO, and Cr<sub>2</sub>O<sub>3</sub> – all in wt %; and micronutrients trace metals in mg kg<sup>-1</sup>) used in phosphorous recovery experiment as a substrate was analysed using the ICP-ES and ICP-MS techniques at ACME Analytical Laboratories Ltd. In the laboratory at Tartu Environmental Research Ltd, the pH value, P, Ca and N concentration (%), organic matter (%), loss on ignition (LOI; %), and plant available phosphorus were measured using the ammonium lactate (AL) method (APHA et al., 1989). Major and trace element concentrations in plant samples (except N) were determined by Inductively Coupled Plasma Mass Spectrometry (ICP) in the laboratory of the Finnish Forest Research Institute.

The normality of variables was checked using the Lilliefors and Shapiro-Wilk tests; for normally distributed variables the inflow and outflow values in different peat filters and the efficiency of different filter materials were compared using the pairwise *t*-test. When the distributions were skewed, the non-parametric Wilcoxon pairwise test was used. The STATISTICA 7.0 software was used and the level of significance of  $\alpha = 0.05$  was accepted in all cases. In the following thesis, numeric values of wastewater parameters (e.g. in mg L<sup>-1</sup>) and purification efficiency (in %); chemical composition of materials (e.g., in mg kg<sup>-1</sup>) and different parameters describing changes in birch seedlings are the mean values, unless specified otherwise.

## 4. RESULTS AND DISCUSSION

### 4.1. Phosphorus removal in hydrated oil shale ash filter material

Vohla et al. (2005) and Kaasik et al. (2008) have shown in batch experiments the effectiveness of Ca-rich hydrated oil shale ash as a possible material for P removal in constructed wetland systems. In these laboratory batch experiments the P removal effectiveness for fly ash and the hydrated ash was up to 99.9%, whereas the maximum binding capacity was estimated as high as 65 mg P g<sup>-1</sup>.

However, the batch experiments tend to overestimate the binding capacity of the filter media. The actual efficiency in real or large-scale laboratory flow systems where the retention times limit the filter-water reactions is usually considerably lower (e.g., Adam et al., 2007). This is even more crucial in active filters, where large super-saturation of pore-water is required for precipitation of stable Ca-phosphate phases (Gustafsson et al., 2008). Batch tests can be used only as a pre-test to estimate roughly the affinity between P and filter material, and eventually to compare samples behaviour using the same protocol. Maximum sorption capacities estimated through batch tests should not be used to design full scale units as they might result to misleading data.

#### 4.1.1 Phosphorus immobilization in ash sediment filter in field experiments at Tapa and Väätsa

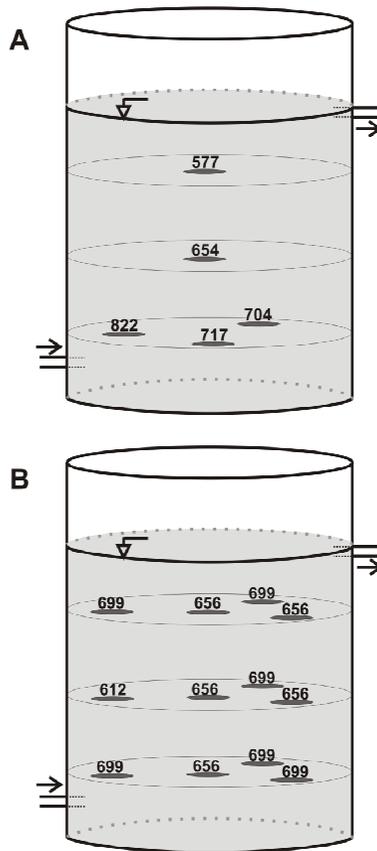
Despite to this known discrepancy between batch and field experiments the oil shale hydrated sediment filter experiments at Väätsa and Tapa sites fed with real wastewater did show good P removal efficiency in hydrated ash filters (Kõiv et al., 2010 – PAPER II). The median removal efficiency of total P in the vertical flow hydrated ash filters of Väätsa and Tapa experiments was 58% and 89%, respectively. During the operation of the vertical flow hydrated ash filters, the subsequent saturated horizontal filters removed 68.9% and 82.4% of remaining total P from the outflow of the vertical filters. After the vertical filters were switched off, the median removal efficiency of total P in horizontal hydrated ash filters increased to 85.4% and 99.2% in the Väätsa and Tapa experiment respectively. The median total P concentrations of the outflow from Väätsa and Tapa horizontal flow filters were 0.50 and 0.14 mg L<sup>-1</sup> respectively. The median removal efficiency in the horizontal flow hydrated ash filters followed after vertical flow mineralized peat filters show of 88.6% in Väätsa and 86.1% in Tapa. The median outflow of P<sub>total</sub> from Väätsa filter was 0.27 mg L<sup>-1</sup> and 0.05 mg L<sup>-1</sup> from Tapa filter (Kõiv et al., 2010 – PAPER II). The somewhat higher removal rate in the Tapa filter system was because of lower content of non-phosphate P (polyphosphates, organic phosphorus etc.) than in Väätsa, whereas the PO<sub>4</sub>-P removal rate in both systems was the same (Kõiv et al., 2010 – PAPER II).

Hydrated oil shale ash show increased P concentration from all filter systems. Väätsa experiment showed almost complete  $P_{\text{total}}$  removal by horizontal flow ash sediment filter from the inflow leachate, ( $R^2=0.99$ , see figure 8B in Kõiv et al., 2010 – PAPER II) and the removal efficiency was high throughout the test period (Kõiv et al., 2010 – PAPER II). The chemical composition of the filter materials tested after the experiment period confirms its P retention capacity. Initial P concentration in hydrated ash was  $490 \text{ mg kg}^{-1}$  and raised to  $706 \text{ mg kg}^{-1}$  in vertical flow filter and to  $665 \text{ mg kg}^{-1}$  in horizontal flow filters at Väätsa site by the end of the experiment. At Tapa site the P concentration raised to  $693 \text{ mg kg}^{-1}$  in vertical flow filter and to  $612 \text{ mg kg}^{-1}$  in horizontal flow filters by the end of the experiments. The data show that the vertical flow ash filters at Väätsa and Tapa were removing most of the P from the influent during the 5 months they were in operation. More importantly, the P accumulation in all of the horizontal filters did not show any signs of saturation (see figure 8B in Kõiv et al., 2010 – PAPER II) which is evidently due to a short period of operation (6 and 12 months at Tapa and Väätsa, respectively) and at least an order of magnitude higher phosphorus concentrations in a completely saturated filter material can be expected.

At the end of the experiment at Väätsa and Tapa site (12 and 6 months respectively) the distribution of P concentrations inside the filter bodies (Table 3 and Figure 3) showed relatively even P distribution in the Tapa experiment. Although somewhat higher P content ( $\text{mg P kg}^{-1}$ ) was determined close to the inlet at Väätsa site (Figure 3). This could be explained by the different duration of the experiments.

**Table 3.** Distribution of P ( $\text{mg P kg}^{-1}$ ) inside the filter at Väätsa (VH1) and Tapa (TH1) site after the experiment.

<b>Sample</b>	<b>mg P kg</b>	<b>Sample</b>	<b>mg P kg</b>
VH1 initial	612	TH1 initial	568
VH1-1	577	TH1-1A	699
VH1-2	654	TH1-1B	656
VH1-3A	822	TH1-1C	699
VH1-3B	704	TH1-1D	656
VH1-3C	717	TH1-2A	612
		TH1-2B	656
		TH1-2C	699
		TH1-2D	656
		TH1-3A	699
		TH1-3B	699
		TH1-3C	699
		TH1-3D	656



**Figure 3.** Distribution of P (mg P kg<sup>-1</sup>) inside horizontal filters at Väätsa (A) and Tapa (B) site after the experiment. Samples were taken at three levels and exact sampling places are indicated with dark circles. Water flow directions are indicated with arrows.

Kaasik et al. (2008) and Liira et al., 2009a – PAPER I suggest that the phosphorus retention in hydrated oil shale ash occurs through irreversible reactions of adsorption and precipitation on a solid phase. Several earlier studies (e.g., Brix et al., 2000; Del Bubba et al., 2003; Molle et al., 2003) have shown that calcareous materials have efficient retention capacities, but with some limitations in sorption kinetics or the chemical stability of the effluent, whereas the retention efficiency on natural calcite and dolomite is not sufficient because of its sensitivity to carbonate equilibrium. In this sense hydrated oil shale ash behaves as a complex mixture of several potential P-binding media. Kaasik et al. (2008) and Liira et al. (2009a – PAPER I) show that hydrated oil shale ash contains several potential Ca sources with different solubilities. The fastest and most efficient Ca release into solution and highest phosphorus removal rate was suggested to occur due to reactions between reactive Ca-(sulphoaluminate)-sulphate-hydroxide phases (ettringite, probably Ca-aluminate and portlandite),

whereas in later stages of the reaction, the existing and/or authigenic calcite and/or vaterite ( $\gamma$ -CaCO<sub>3</sub>) precipitates controlled P-binding processes.

Other potential substrates for P adsorption are surfaces of authigenic clay phases replacing devitrified aluminosilicate glass phases, which share and importance for phosphorous removal will grow with time. The geochemical behaviour of ettringite can be compared to natural Ca-phosphate – apatite, which phosphorus removal capacity was studied by Molle et al. (2005). Similarly to apatite ettringite creates suitably high and stable pH of the solution and good kinetics for secondary Ca-phosphate crystallization, by providing a high number of nucleation sites on its needle like crystallites (Kaasik et al., 2008; Liira et al., 2009a – PAPER I).

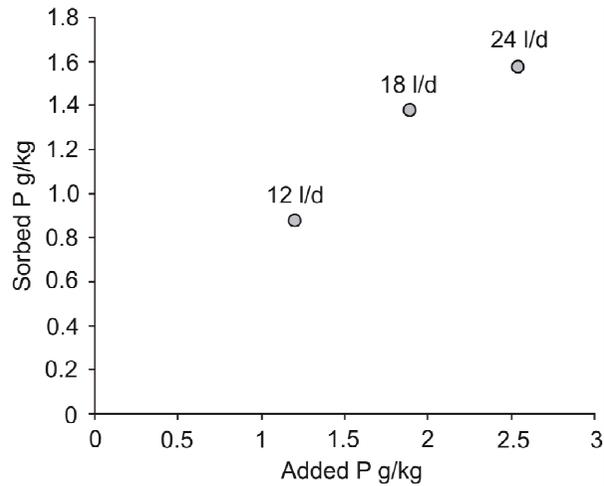
Typically, poorly-crystallized or amorphous octa-calcium phosphate (OCP), di-calcium phosphate di-hydrate (DCPD) and tri-calcium phosphate (TCP) form as precursor phases in solutions containing Ca and P, and are only then re-crystallized into thermo-dynamically stable hydroxyl-apatite (HAP) over time (Valsami-Jones, 2001). This suggests that the P removal in hydrated ash occurs through precipitation of the discrete amorphous Ca-phosphate phases by either homogenous precipitation or heterogeneous nucleation on the suitable crystal surfaces. The P removal efficiency of the ash then depends on the availability of the dissolved Ca at the expense of dissolution of Ca-rich filter materials, whereas the removal efficiency does not depend on the Ca concentration in inflow and the Ca is significantly removed from effluent during filtration as it was seen in pilot-scale field experiments (Kõiv et al., 2010 – PAPER II).

Field experiment also shows that, probably due to solid phase precipitation through a variety of potential binding media, the removal efficiency of phosphorus in the hydrated ash filter is not (at least significantly) affected by competing ions in wastewater, although the concentrations of several known inhibitors of phosphate adsorption such as magnesium, sulphate and chloride (e.g., Salimi et al., 1985; Chen et al., 2002; Shilton et al., 2005) were present at considerably high concentrations, specifically in landfill leachate at Väätsa compared to municipal wastewater at the Tapa site. Typically, the ionic and organic inhibitors are strongly affecting phosphorus removal through adsorption mechanism when competing ions or organic carbon compounds block the adsorption sites on suitable crystal surfaces such as calcite (e.g., Vdović and Kralj, 2000; Berg et al., 2005a). Homogenous precipitation of Ca-phosphate, however, is not as much influenced by the inhibitors. Although magnesium is known to inhibit the growth of the most stable Ca-phosphate crystalline form, which is hydroxyl-apatite (HAP), the other phases such as octa-calcium phosphate (OCP) and di-calcium phosphate di-hydrate (DCPD) are less affected by elevated magnesium concentrations (House, 1999). This means that even high Mg concentration does not slow down the P precipitation in ash sediment as far as P is bound in the form of amorphous and/or poorly-crystallized DCPD, OCP and tri-calcium phosphate (TCP) phases, both in batch and small-scale flow experiments (Kaasik et al., 2008; Liira et al., 2009a – PAPER I).

Although competing ions are not affecting overall P removal, the removal rate of phosphorus in hydrated ash filters is significantly depending on the inflow phosphorus concentration. Our results show that the removal efficiency is low (<50%) at low P concentrations (<0.2 mg L<sup>-1</sup>), and efficiency increases abruptly if the phosphorus concentrations are higher than 0.5 mg L<sup>-1</sup>. This suggests different removal mechanisms upon P loading. Hinedi et al. (1999) and Plant and House (2002) show that at low P concentrations (<20 μmol L<sup>-1</sup> = 0.62 mg L<sup>-1</sup>) phosphorus in the calcite seeded system is co-precipitated with calcite by incorporating P ions into calcite crystal surfaces. At P concentrations exceeding 20 μmol L<sup>-1</sup>, however, the calcite precipitation ceases and homogeneous nucleation of Ca-phosphate phases occur at high oversaturation with respect to the stable HAP phase (Plant and House, 2002). Similar switch between two prevailing removal mechanisms depending on inflow of P concentrations can be suggested in hydrated oil shale ash sediment filter material.

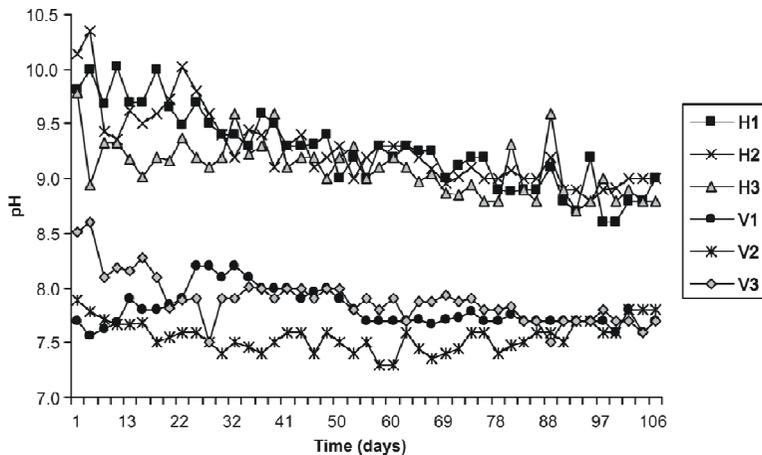
#### **4.1.2 Phosphorus removal efficiency and precipitated solid phases at different retention times**

Lab-scale experiment results show that the initial phosphorus removal efficiency in the first column (H1) was in the range of 75–80% and 0.87 g P kg<sup>-1</sup> out of 1.2 g P kg<sup>-1</sup> phosphorus added was adsorbed (Figure 4). During the first weeks the removal efficiency increased to a maximum of 91%. The maximum removal rate was attained for ~3 weeks and then the removal efficiency began to decrease rapidly. By the end of the experiment, i.e. after 5 months (equals to the 321 bed volumes), P removal efficiency decreased to ~49%. In the second column (H2), which had a residence time of 8 hours, the initial removal of phosphorus was, as expected, somewhat lower, i.e. 60–65%, which improved to ~85% over 3 weeks. After that removal efficiency dropped gradually to ~65% of the total phosphorus loaded. By the end of the experiment 429 bed volumes of influent were treated in the H2 experimental setup and 1.38 g P kg<sup>-1</sup> of 1.89 g P kg<sup>-1</sup> added phosphorus was adsorbed. In the third column (H3), with a residence time of 6 h, the average P-removal efficiency increased from the initial 49% to the maximum of ~80% during the first five weeks of operation. Over the rest of the period (equals to 642 bed volumes), the efficiency slowly decreased to 55%, and 1.57 g P kg<sup>-1</sup> out of 2.54 g P kg<sup>-1</sup> of added phosphorus was adsorbed (Figure 4).



**Figure 4.** The removal efficiency as ratio of added and sorbed phosphorus. Legend: experiment with hydraulic loading 12 L d<sup>-1</sup> – H1; experiment with 18 L d<sup>-1</sup> – H2; experiment with 24 L d<sup>-1</sup> – H3.

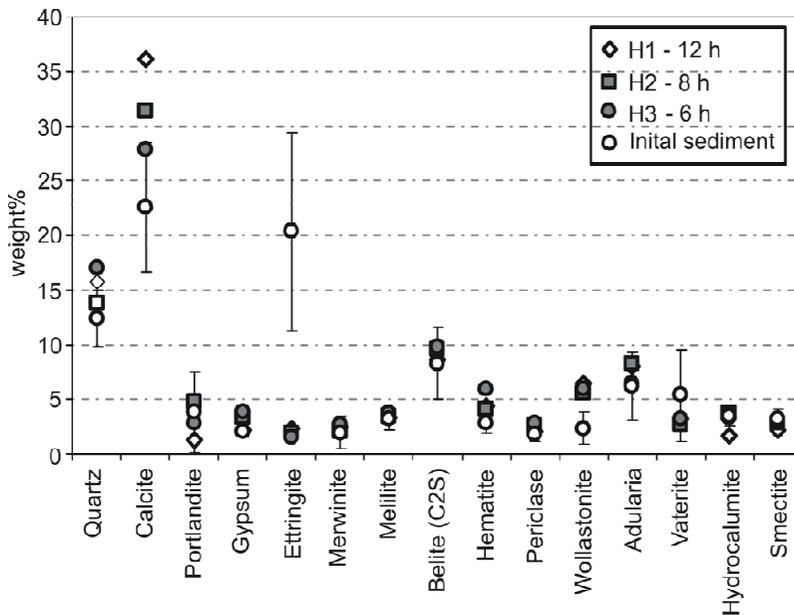
Effluent from all horizontal filters showed high pH (initially ~11), which decreased slowly during the experiment, to pH ~9 (Figure 5). Vertical flow peat filters installed after horizontal oil shale ash filters reduced effluent pH down to ~7.8 in all experiments.



**Figure 5.** The pH changes in the laboratory experiment at hydraulic loadings 12 L d<sup>-1</sup> (H1/V1), 18 L d<sup>-1</sup> (H2/V2) and 24 L d<sup>-1</sup> (H3/V3). H – horizontal filter, V – vertical filter.

After the treatment with P-solution mineralogical composition of the initial hydrated oil shale ash sediment (Kõiv et al., 2010 – PAPER II) changed significantly (Figure 6). The proportion of ettringite in all three filter beds decreased

drastically, from ~20% to ~2.0%. At the same time, the content of calcium carbonate (calcite) increased from about 23% in initial ash to up to 36% in the H1 filter. The increase of calcite was highest in the filter bed with the longest retention time. The amount of other phases did not change significantly. The slight increase in the content of quartz and other less soluble phases after the experiment is most probably due to the enrichment effect caused by almost complete dissolution of ettringite in the treated material. The chemical composition of hydrated oil shale ash sediment corresponds to its mineral composition – the major oxides are CaO (in average 31%), SiO<sub>2</sub> (in average 24%) and Al<sub>2</sub>O<sub>3</sub> (in average 6%).



**Figure 6.** Mineral composition of filter material before and after the experiment. Legend – H1, experiment with hydraulic loading 12 L d<sup>-1</sup>; H2, experiment with 18 L d<sup>-1</sup>; H3, experiment with 24 L d<sup>-1</sup>. Bars show the variation of initial ash sediment composition.

Chemical and mineralogical analyses of initial and treated materials indicate noticeable mass-transfer through the filter bed, of which the most important is the dissolution of ettringite and the precipitation of additional calcite, which has evidently also used up additional Ca from the artificial wastewater solution. More importantly, chemical analyses indicate an increase in phosphorus content in filter material after the experiment, from 0.13% of P<sub>2</sub>O<sub>5</sub> in the initial ash to 0.37%, 0.44% and 0.46% of P<sub>2</sub>O<sub>5</sub> in the H1, H2 and H3 experiments respectively. The relative phosphorus accumulation in respect to the added

phosphorus is lowest in the experiment with the highest hydraulic loading. After 5 months of the experiment, when the removal efficiency of the filters decreased to 40–55%, the amount of phosphorus adsorbed in filters was 0.4, 1.4 and 1.6 gP kg<sup>-1</sup> in the H1, H2 and H3 experiment respectively.

The results show a significant dependence of phosphorus-binding capacity in the saturated hydrated oil shale ash filter system on hydraulic loading. As expected, the peak removal rate (90.6% of loading 1.66 gP m<sup>-2</sup> d<sup>-1</sup>) was observed in the experiment with the longest residence time (12 h). Unexpectedly, however, the overall performance of the filter did not improve with increased retention time, and the loss of binding capacity was most rapid (41% decrease) in the same experiment with the retention time of 12 h.

In all filter beds, a white precipitate formed on the surface of sediment particles. The isolated precipitate was analysed by means of XRD after drying at 70 °C and heating at 500 °C and 1000 °C for 2 hours. The phase remained X-ray amorphous after heating at 500 °C, but after heating at 1000°C the typical hydroxyl-apatite peaks were identified (see Figure 2a in Liira et al., 2009a – PAPER I). The composition of thin precipitate layers covering the ash sediment particles was also studied using FTIR, indicating the presence of CaCO<sub>3</sub> (calcite) and Ca-phosphate by specific adsorption maxima at 1400 cm<sup>-1</sup> and 550/1000 cm<sup>-1</sup> respectively.

The SEM and SEM-EDS analyses show that the untreated sediment is a porous aggregate that contains abundant needle-like prismatic ettringite crystallites that form irregular and/or spherulitic aggregates in the pore space. After the experiment, ettringite disappeared, and the sediment particles are overgrown and/or have been replaced with abundant secondary precipitates of calcite and Ca-phosphate.

The SEM observation of the precipitates on ash particles indicates that in the experiment with the longest residence time (H1), the authigenic calcite and Ca-phosphate aggregates form a dense and tightly packed layer with a large number of acicular (>10 µm) calcite crystallites. In experiments with higher hydraulic loading, the precipitate forms a more porous framework of considerably larger scalenohedral to rombohedral calcite crystallites that vary from 10–20 µm in H2, and in the H3 experiment the calcite precipitates show mixed scalenohedral and rombohedral aggregates. In all experiments, confirmed by EDS analyses, Ca-phosphate forms spheroidal aggregates that are composed of flake/plate like crystallites, which are visible at higher magnification. The Ca-phosphate masses fill the space and/or are intergrown with a calcite matrix, indicating co-precipitation.

Generally, for the efficient functioning of sorption process, a contact time/residence time is critical, and thus it is necessary to keep hydraulic conductivity and loading on the level that allows the sorption mechanism to function (Faulkner et al., 1989). Longer residence times would significantly improve the contact between the substrate and the wastewater. In active filtration, the removal of phosphorus from water is controlled by the crystallisation of Ca-phosphate phases (e.g., Valsami-Jones, 2001). Typical (domestic)

wastewater contains calcium and phosphate in concentrations ( $>50 \text{ mg L}^{-1} \text{ Ca}$ ;  $>2 \text{ mg L}^{-1} \text{ P}$ ) that are oversaturated with respect to calcium-phosphate phases. Phosphate precipitation in wastewater can occur spontaneously by homogenous nucleation (e.g., Williams, 1999), that has been explained as being triggered by  $\text{CO}_2$  degassing and an increase in pH (Valsami-Jones, 2001). Heterogeneous nucleation, however, is less energetically demanding, and can utilize different surfaces available in filter material (calcite, ettringite, gypsum, Ca-Al phases, suspended particles etc.) for Ca-phosphate seedling, and is therefore preferred for wastewater reactions. In either case, extensive supersaturation is required in wastewater for the precipitation of solid Ca-phases (Valsami-Jones, 2001; Gustafsson et al., 2008), whereas if the activity of Ca exceeds the equilibrium with respect to the phosphate then the excess of Ca may precipitate as another solid phase(s) that is most probably Ca-carbonate(s).

The SEM observation of the dense and tightly packed layer of acicular calcite crystallites suggests that a considerably higher supersaturation in respect to calcite was attained in the slowest experiment, which resulted in rapid nucleation at a large number of sites and the formation of acicular crystallites that progressively cover the entire surface of the ash sediment particles. As a result, the dissolution of Ca-bearing phases in ash sediment is inhibited, and the input of additional Ca for phosphate precipitation decreases. Consequently, the ash sediment particles become chemically clogged by phosphate and carbonate precipitates and the phosphorus removal capacity of the filter decreases rapidly. On the other hand, at higher flow rates/shorter residence times, saturation with respect to Ca-carbonate is lower, and nucleation occurs in lesser sites, thus allowing the continuation of crystal growth and the formation of coarse-grained and porous aggregates. As a result, Ca input from the dissolution of ash particles remains unhindered, and the ions are readily transported to crystallization sites for a longer period.

The increase in phosphorus removal at the beginning of the experiment could be explained by the additional seeding effect at numerous new nucleation sites created by the formation of Ca-phosphate and probably authigenic calcite crystallites.

## 4.2. Phosphorus recovery experiment

Chemical analysis of the filter materials from the Väätsa and Tapa site (Kõiv et al., 2010 – PAPER II) showed that hydrated oil shale ash contained after the wastewater experiment (6 months period) an average  $651 \text{ mg P kg}^{-1}$ . Mineralized peat contained an average  $451 \text{ mg P kg}^{-1}$  after the wastewater treatment experiment. Kõiv et al., (2009) have shown that P retention in mineralized peat filters occurs by sorption phenomena, which is limited by suitable sorption sites on peat fibres, and removal efficiency falls when the sorption sites become saturated. Consequently, the content of plant-available P in peat was an average  $115 \text{ mg kg}^{-1}$  after wastewater treatment. Contrary to the

peat filter, alkaline oil shale ash filter immobilised most of the P in the form of  $\text{Ca}_3(\text{PO}_4)_2$ , which is a stable phosphate phase with low solubility (Liira et al., 2009a – PAPER I), and is, therefore, difficult for plants to use. As a result the content of lactate-soluble (plant-available) P in ash sediment was only  $25.4 \text{ mg kg}^{-1}$  after the wastewater experiment, and prior to the recovery experiment (Kõiv et al., 2010 – PAPER II).

During the recovery or pot experiment the pH value of the hydrated ash decreased from 12.5 to 10.7, which suggests significant leaching of its alkaline components in mineral composition. In comparison, there was no change in the pH value of the planted peat (7.0 before and after the experiment) (Kõiv et al., 2012 – PAPER III). Importantly, strong acidification occurred in plant root rhizosphere growing in hydrated ash and ash/peat mixture where pH decreased up to 5.5 and 3.9 units compared to bulk soil, respectively. In the unplanted pots the changes in the pH value were small, and in the end of the experiment the materials had slightly higher pH values compared to the same material in the pots with plants (hydrated ash: unplanted – 11.2, planted – 10.7; peat: unplanted – 7.2, planted – 7.0; ash/peat: unplanted – 10.7, planted – 10.3).

The content of plant-available P in hydrated ash sediment was  $25.4 \text{ mg kg}^{-1}$  before the pot experiment, and  $40.2 \text{ mg kg}^{-1}$  and  $34.6 \text{ mg kg}^{-1}$  after the pot experiment in unplanted and planted pots, respectively, which indicates that during the experiment the share of easily dissolved P in hydrated ash increased (Kõiv et al., 2012 – PAPER III). On contrary, in the planted peat and in the mixture of hydrated ash and peat substrates the content of plant-available P decreased significantly (from  $115.0 \text{ mg kg}^{-1}$  to  $95.4 \text{ mg kg}^{-1}$  in peat, before and after the pot experiment, respectively), while the content of insoluble P in peat increased from 451 to  $520 \text{ mg kg}^{-1}$  after the pot experiment, which can be explained by the mineralization of the material.

Hydrated oil shale ash contains also elevated amounts of K (average  $\text{K}_2\text{O}$  content  $\sim 3.00\%$ ), (Liira et al., 2009a – PAPER I; Kõiv et al., 2010 – PAPER II), which is easily dissolved ( $2000\text{--}2300 \text{ mg L}^{-1}$  of K in ash water; Kirsimäe et al., unpublished data). Before the pot experiment the potassium concentration was  $7.7 \text{ g kg}^{-1}$  in hydrated ash filter material, but after the pot experiment the K concentration in the hydrated ash decreased more than 60% and was only  $4.8 \text{ g kg}^{-1}$  after the pot experiment. However, there were no significant differences between planted and unplanted pots, which suggest that the potassium was leached only by watering without any significant effect from rhizosphere processes. As expected, Ca and Mg concentrations changed only slightly during the pot experiments.

Phosphorus and nitrogen accumulation in silver birch seedlings on hydrated oil shale ash was remarkably lower compared to ash/peat mixtures and mineralized peat as a substrate, 3.9, 4.8 and  $6.2 \text{ mg P g}^{-1}$ , respectively. However, the mean N and P intake efficiency of seedlings was twice as high in hydrated ash compared to the peat and peat/ash mixture and is in average  $1013 \text{ kg kg}^{-1} \text{ yr}^{-1}$ . The efficiency value shows net production of seedlings produced per unit of accumulated N or P.

Important parameter for characterising mineral nutrition of seedlings is the N:P:K ratio; the optimum according to Ingestad (1987) is 100:13:65. The N:P:K ratio of leaves (ratio 100:15:36 before the experiment) of the seedlings grown on hydrated ash had excessive K (ratio 100:14:198), whereas the ratio was closest to the optimum in the leaves of the seedlings grown on the peat/ash mixture (100:16:84) (Kõiv et al., 2012 – PAPER III). The strong potassium misbalance probably affected the foliar P concentrations in seedlings grown on hydrated ash, and for that reason seedlings grown on hydrated ash had 2–3 times lower P concentrations than the peat/ash mixture and peat.

Lower P accumulation in silver birch seedlings grown on hydrated ash filter material correspond to lowest initial biologically available P concentration, whereas twice as high P consumption efficiency in ash treatment indicates decreased P uptake and hindered transport of P to the leaves. However, elevated K concentration in a hydrated ash may preclude P transport in the xylem (Marchner, 2002), and this could have led to the low plant-available P concentration within hydrated ash. Moreover, plants fine root contact with the substrate was also poorest in hydrated ash due to the physical properties of the substrate. Nevertheless, the mean P use efficiency of birch seedlings in different treatments (505 – 1013 kg kg<sup>-1</sup> yr<sup>-1</sup>) was similar to the result obtained by Vares et al. (2004) for black alder grown on reclaimed oil shale mining detritus in Estonia (737 – 1941 kg kg<sup>-1</sup> yr<sup>-1</sup>).

The optimal P content in birch leaves is 1.8–2.5 mg g<sup>-1</sup> (ICP Forest Manual, 2001). The pot experiment shows that the P content was optimal in the leaves of the seedlings grown on ash/peat mixture and on peat, and the seedlings grown on hydrated ash had an insufficient amount of P in their leaves. In all cases, and especially valid with hydrated ash, the limiting factor for plant growth is low nitrogen concentration. However, when hydrated ash is used scattered and mixed in the correct proportions with natural soils, it is also suitable as a P and K fertilizer (forested land in Estonia is short of P and K nutrients (ICP Forest Manual, 2001)).

During the pot experiment the content of insoluble P in hydrated ash decreased about 2–5% that suggest some reuse of stabilised P by plants. This may indicate that the silver birch roots in hydrated ash and in peat/ash mixtures are capable of acidifying the rhizosphere through root exudates, and the phosphorus in Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is made more available for plant usage. This is also confirmed by chemical analyses that show the increase in the concentration of plant-available P in hydrated ash after the pot experiment. The organic acids produced by the soil micro-organisms and root exudates are strong enough to dissolve less soluble phosphorous forms such as calcium phosphate or hydroxyl-apatite and struvite (all obtained from wastewater treatment systems) (de-Bashan and Bashan, 2010). Also, Hylander and Simán (2001) indicate in their study with crystalline blast furnace slag (similar process of P precipitation with Ca as in hydrated ash) that phosphorus bound to Ca is more available to plants than P sorbed with Al or Fe. The utilization of filter materials from wastewater treatment as fertilizers for plants is based on the principle that

moderate concentrations of environmentally harmful elements (e.g., trace elements) are a part of the nutrient cycle and do not increase in net concentrations in soils.

The analysis of major, minor or trace elements in filter materials and in different compartments of seedlings shows low content of all potentially harmful trace elements in seedlings grown on hydrated ash (Kõiv et al., 2012 – PAPER III). Only Zn concentration in leaves was close to the toxic threshold of birch seedlings grown in peat and peat/ash mixture, although there was no visible damage of leaves. The excess of Zn could be one reason for the equivalent growth (or production) of birch seedlings in peat and the peat/ash mixture compared to hydrated ash, while higher N content, and the presence of all other macro- and micronutrients in peat and peat/ash as well as the optimal N:P:K ratio in the leaves of the seedlings grown in those substrates would have predicted higher biomass of plants.

The low concentration of toxic or trace elements in birch seedlings can be explained by low content of trace elements in hydrated oil shale ash that is close to the earth's crust concentrations for most of the trace elements (Saether et al., 2004; Ots, 2006; Table 2). Moreover, high alkalinity of hydrated oil shale ash inhibits the mobility of trace elements. On contrast, trace elements had higher mobility in peat due to lower pH (Kõiv et al., 2012 – PAPER III).

Several authors have mentioned the slow release of P from P-saturated filter materials (Dobbie et al., 2005; Cucarella et al., 2007; Cucarella et al., 2008; Dobbie et al., 2009). That means that less frequent applications would be required when using conventional P fertilizer. Regarding economic and environmental advantages, it is possible to develop a wide range of fertilizers, including very slow-release fertilizers for pasture and forest, a combination of slow- and fast-release fertilizers for most agricultural practices, and fast-release fertilizers combining recovered phosphate with strong phosphate-solubilising micro-organisms for crops needing rapid start up (de-Bashan and Bashan, 2010).

## 5. CONCLUSIONS

1. Alkaline hydrated oil shale ash filters showed good P-removal efficiency using different real wastewater compositions and P loadings. The median removal efficiency of total P in horizontal flow filters reached 85.4% and 99.2% in the experiments with landfill leachate and municipal wastewater respectively. The P-removal capacity of the Ca-rich hydrated ash-sediment is not influenced by presence of known inhibitor ions (chlorine, magnesium, sulphate etc.), and the filter material retains high removal rate for prolonged periods. However, our results show that the P-removal efficiency using active filtration, which means precipitation of discrete Ca-phosphate phases, depends significantly on the P-concentration in the inflow. The precipitation mechanism is effective only at P-concentrations exceeding  $0.5 \text{ mg L}^{-1}$  and at lower concentrations the P-removal is probably governed only by adsorption. Further research is needed to identify the P-removal capacity of the hydrated ash filters in the presence of high organic concentrations and different phosphorous forms.
2. Three column experiments for phosphorus removal in hydrated oil shale sediment filters at different retention times showed good maximum removal efficiency (up to 91%) in the experiment with the longest retention time. The overall performance of the filters does not, however, improve with increasing retention time, and the loss of binding capacity is most rapid in the experiment with the longest retention time. Mineralogical and microscopical observations suggest that at longer retention times, supersaturation in respect to Ca-carbonate in filter material containing several soluble Ca-rich mineral phases is attained. As a result, a rapid nucleation at the large number of sites is initiated, and numerous densely spaced small acicular calcite crystallites are formed on the surface of ash sediment particles. Chemical clogging by carbonate precipitates probably reduces the availability of Ca from the dissolution of unstable mineral phases of ash sediment, and phosphate removal capacity decreases rapidly. On the other hand, at shorter residence times/higher flow rates, the crystal growth of calcite particles is slower, and a more porous precipitate structure forms, thus allowing Ca dissolution and transport to suitable crystallization sites for a longer period, although maximum performance is less than in the experiment with the lowest loading rate.
3. The carbonate balance has significant control on Ca-phosphate active filtration in Ca-rich media such as oil shale ash, Filtralite-P, Polonite, etc. Although the prolonged contact time of P in the wastewater and the filter would facilitate P removal, in the case of long residence time it would cause high supersaturation ratios ( $>2-3$ ) with respect to Ca-carbonate and the rapid precipitation of solid phase carbonates would occur. The supersaturation of Ca-carbonate (either calcite or vaterite) is further amplified by the high pH of the solution, as the supersaturation ratio of Ca-phases increases with pH. Regardless of residence time (that is super-

saturation level), the solid phosphate is precipitated in an amorphous Ca-phosphate form. Thermodynamically, the most stable Ca-phosphate phase in neutral and alkaline conditions is hydroxyl-apatite (HAP). The HAP is the less soluble phase, and at equilibrium state its solubility product would suggest phosphorus concentration in water of less than  $0.005 \text{ mg L}^{-1}$ . However Ca-phosphate is likely precipitated firstly as amorphous tri-Ca phosphate (ATCP,  $\text{Ca}_3(\text{PO}_4)_2$ ) and dibasic Ca-phosphate (DCP,  $\text{CaHPO}_4$ ), as a precursor phase, and will eventually crystallize to hydroxyl-apatite form.

4. Phosphorus in alkaline oil shale ash sediment filter material is immobilised in the form of low soluble  $\text{Ca}_3(\text{PO}_4)_2$  type phase, and despite the initially enriched content (in average  $651 \text{ mg P kg}^{-1}$ ) of the immobilized phosphorus, the lactate-soluble (plant-available) P in ash sediment was only  $25.4 \text{ mg kg}^{-1}$ .
5. The organic acids produced by the soil micro-organisms and root exudates are strong enough to dissolve less soluble phosphorous forms such as calcium phosphate or hydroxyl-apatite, and the content of lactate-soluble P in ash sediment increased two-fold at the end of the pot experiments, indicating that oil shale ash sediment that is saturated with P could be regarded as slow-release fertilizers for pasture and forest. Oil shale ash sediment can be also considered as a soil liming agent and potential source for easily dissolved potassium. Alternatively, the phosphorus recovery could be enhanced by use of phosphate-solubilising micro-organisms for plants needing rapid start up.

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## SUMMARY IN ESTONIAN

### Fosfori aktiivfiltratsioon kaltsiumirikka hüdratiseeritud põlevkivituhasetega: sadestusmehhanismid ja taaskasutus

Käesolev doktoritöö uurib esiteks fosfori ärastusmehhanisme ja neid kontrollivaid keemilis-mineraloogilisi protsesse põlevkivituhasette filtermaterjalides. Teiseks selgitab uurimistöö küllastunud filtermaterjalide potentsiaalset taaskasutuse võimalust täiendava fosforväetisena põllumajanduses.

Fosfor on üks tähtsamaid biokeemilise tsükli toitaineid, mistõttu juba natuke kõrgeenenud fosfori kontsentratsioonid ( $> 10 \mu\text{g L}^{-1}$ ) võivad vallandada veekogude eutrofeerumise (Vymazal et al., 1998). Enam kui neljakümne aasta vältel on veekogudesse sattunud liigne fosfor tunnistatud koos lämmastikuga üheks peamiseks eutrofeerumist põhjustavaks toitaineks (Schindler, 1971). Fosforiühendid on põllumajanduses väetistena intensiivses kasutuses, seda peamiselt lahustuva ortofosfaadina. Fosforit kasutatakse ka tööstuses ja olmevaldkonnas mitmesugustes detergentides. Seetõttu on põllumajandusmaastikelt äravool ja eriti majapidamiste heitvesi rikastatud fosfaatidega. Siit tuleneb otsene ja tungiv vajadus puhastada inimtegevusega seotud heitveed liigest fosforist sellisel määral, et säiliks looduslike süsteemide ökoloogiline tasakaal (Conley et al., 2009).

Eelneva puhastuseta või puudulikult puhastatud reovesi (eriti olme- ja toiduainetetööstuse reovesi) on üks antropogeense reostuse põhjustajaid kõigis pinnaveekogudes. Kui veekogudesse suunatavates heitvete väljavooludes sisalduvat fosforit (P) ei eemaldata küllaldasel hulgal, on tulemuseks intensiivne veekogude eutrofeerumine. Eesti veekaitse teravaks põhiprobleemiks on jätkuvalt kõrge fosfori üldtase Soome lahe vesikonna jõgedes ja Väinamere piirkonna madalates merelahtedes (nt. Matsalu, Haapsalu). Eesti Keskkonnaministeeriumi andmetel on Eestimaal ligikaudu 800 reoveepuhastit. Neist poolte puhastusvõime fosfori osas on ebapiisav.

Euroopa Liidu Vee raamdirektiivis [2000/60/EEC] hinnatakse veekogude ökoloogiline seisund kolme kategooriasse: kõrge, hea ja halb/ebapiisav. Direktiiv seab eesmärgiks saavutada seisund "hea" kõigis Euroopa Liidu veekogudes aastaks 2015. Positiivse tulemuseni jõudmiseks Eestis ei piisa reovee puhastamisest ainult (suur-)asulates, rakendama peab ka täiendavaid meetmeid väikesemõõduliste tööstuste, väikeasulate ja isegi üksikmajapidamiste/väikefarmide heitvee puhastamiseks. Seega on loodusesse juhivate heitvete puhastamine muutunud aktuaalseks mitte ainult asulate kogumites vaid ka Eestile tüüpilise hajaasustuse majapidamistes ja suvekodudes ning põllumajandusmaastikel, kus ei ole võimalik ja majanduslikult põhjendatud liitumine tsentraalsete reoveepuhastussüsteemidega. Seal on põhjendatud eraldiseisvate konventsionaalpuhastite rajamine ja käigushoidmine.

Fosfori eemaldamine heitveest asulates või tööstuspiirkondades on piisavalt hea puhastusefektiivsuse ning mõistliku majandusliku tasuvusega konventsionaalsetes reoveepuhastites, kus fosfori eemaldamine tagatakse tavaliselt

Al- ja/või Fe-koagulantidega. Paraku ei ole need tehnoloogilised skeemid tehnilistel ja majanduslikel põhjustel mõistlikud väikesüsteemides s o üksik-majapidamistes, hajaasulates või (väike-)farmides, kus on otstarbekam kasutada tehismärgalade tüüpi puhastussüsteeme (Vymazal et al., 1998; Leader et al., 2008; Park ja Polprasert, 2008; Xiong ja Peng, 2008; Kadlec ja Wallace, 2009). Tehismärgalade kasutamine heitvee puhastuseks on viimastel kümnenditel kiiresti laienenud tänu nende töökindlusele, suhteliselt odavale ehitusmaksu-musele ja lihtsale kasutamisele ning hooldusele. Tehismärgalade efektiivsust saasteainete eemaldamiseks peetakse üldiselt heaks, kuid keskkonnanorma-tiividega sätestatud piirnormid saastekomponentidele ja üldisele vee kvaliteedile on muutumas järjest rangemaks ning seega kasvab nõudlus tõhusate, kuid ühtlasi ka odavate filtermaterjalide järgi. Seda enam, et kuigi tehismärgalad on osutunud tõhusaks keskkonnaks nitrifikatsioonile ja töötavad hästi üldlām-mastiku eemaldamisel (Cooper et al., 2003), ei ole nende süsteemide fosfori sidumisvõime seniajani olnud piisav (Brix et al., 2001; Molle et al., 2005).

Viimaste aastate tehismärgalade (filtermaterjalide) uuringud kogu maailmas on esile tõstnud nn aktiivfiltratsiooni tehnoloogia edukuse fosfori eemaldamisel heitveest (Johansson ja Gustafsson, 2000; Vohla et al., 2005; Shilton et al., 2005; Drizo et al., 2006; Adam et al., 2007; Gustafsson et al., 2008; Kaasik et al., 2008; Publikatsioon II). Aktiivfiltratsiooni toimeks on lahustunud fosfaatide sidumine/sadestamine madala lahustuvusega mineraalsetesse vormidesse. Seda peetakse praegusel hetkel üheks lootustandvamaks fosfori eemaldamise meetodiks väikesemõdulistes reoveepuhastites ja biogeenide kontrollimiseks põllumajandusmaastike äravooludes. Seejuures saab sellise filtri sidumisvõime amendumisel tekkinud toitainetest küllastunud filtermaterjali kasutada järgnevalt põllumajanduses fosforväetise kandjana ja mullaomaduste paran-dajana (nt Johansson, 1998; Hylander et al., 2006; Gustafsson et al., 2008; Publikatsioon III).

Aktiivfiltratsioon tugineb keemilistele reaktsioonidele, mille tõhusus sõltub reovee üldisest ioontugevusest, Ca aktiivsusest ja teiste konkureerivate ionide sisaldusest ning samuti lahustunud fosfori vormidest ja aktiivsusest. Varasemad uuringud (Chen et al., 2002; Shilton et al., 2005; Adam et al., 2007) on näidanud, et P eemaldamine on pärsitud mitmete konkureerivate ionide ja/või inhibiitorite, nagu  $Mg^{2+}$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$  -ioonide, kuid ka orgaaniliste ühen-dite (nt humiinhapped), juuresolekul. Samas on stabiilse Ca-fosfaadi sades-tamiseks vajalik poorivee ulatuslik üleküllastatus  $Ca^{2+}$  ja fosfaatide suhtes (House, 1999; Arias et al., 2003; Publikatsioon I). Potentsiaalsed materjalid aktiivfiltratsiooniks on mitmesugused tööstusjäätmed nagu metallurgiatööstuse räbu (Johansson ja Gustafsson, 2000; Shilton et al., 2006, Pratt et al., 2007), samuti kõrge Ca (ka Fe/Al) sisaldusega lubjatööstusjäätmed või siis tööstus-likult suurendatud Ca sisaldusega tööstuslikud filtermaterjalid, kus Ca esineb  $CaO/Ca(OH)_2$  ja/või Ca-silikaatide vormis, mis tagab efektiivselt fosfori sadestamiseks vajaliku poorivee  $pH > 9$  (nt Zhu et al., 2003; Kvarnström et al., 2004; Adam et al., 2006; Adam et al., 2007). Fosfori eemaldamine nende mater-jalidega (nt Polonite ®, Filtralite-P ®, vollaioniit jne) toimub läbi primaarsete

Ca-faaside aeglase lahustumise ja Ca-fosfaatide sadenemise (nt hüdroksüülapatiidina) (nt Johansson ja Gustafsson, 2000; Drizo et al., 2006).

Viimaste aastate intensiivsed uuringud (Veskimäe et al., 1997; Vohla et al., 2005; Kaasik et al. 2008; Publikatsioon I; Publikatsioon II) on näidanud Ca-rikkast hüdratiseeritud põlevkivituhast valmistatud filtersüsteemide häid omadusi P eemaldamiseks tehismärgalasüsteemides. Need katsed on näidanud, et P eemaldamise efektiivsus lendtuha ja hüdratiseeritud tuhasette katsetes küünib kuni 99,9%, kusjuures materjali maksimaalne sidumisvõime ulatub kuni 65 mg P g<sup>-1</sup> (Vohla et al., 2005; Kaasik et al., 2008) ning fosfor seotakse selles Ca-rikkas heitmaterjalis läbi sadenemise tahkesse faasi.

Hüdratiseeritud põlevkivituha kasutamine keskkonna parandamise eesmärkidel omab märgilist tähendust. Eesti põlevkivi baasil töötavates elektri-jaamadades tekib 5 kuni 7 Mt põlevkivituhka aastas, millel peaaegu täielikult puudub taaskasutus, ning kokku on põlevkivituhaplatodele ladestatud umbes 300 Mt hüdratiseerunud põlevkivituhka. Põlevkivitööstuse tahkete jäätmete taaskasutus on tänaseni, vaatamata mitmete uurimisasutuste aastatepikkustele pingutustele, olnud äärmiselt piiratud, ulatudes kuni 5%-ni tekkiva tuha kogumahust. Seejuures leiab praeguste tehnoloogiate juures kasutust ainult värske tuhk ning tuhaplatodele ladestatud materjalil puudub igasugune sisuline kasutus. Kuigi on ilmne, et ka filtermaterjalina rakendamisel ei ole mõeldav hüdratiseeritud põlevkivituha ressursi jääkideta kasutamine ning tehismärgalades leiaks rakendust vaid väike osa kogu 300 miljonist tonnist ladestatud tuhast, oleks see üheks esimeseks reaalseks jääktuha suuremahulise kasutamise perspektiiviks, milleks uuringute tulemused loovad võimaluse. Lisaks veepuhastustehnoloogiate edendamisele põlevkivi kasutamisel tekkivate tahkete jäätmete taaskasutamiseks tuleneb sellest ka keskkonda kahjustavate mõjude oluline vähenemine.

Põlevkivituha kui odava filtermaterjali märkimisväärselt kõrget P-sidumisvõimet põhjustavad ja mõjutavad selle materjali koostis ja füüsikalise-keemilised omadused: Ca-faaside lahustuvustasakaalust tingitud poorivee kõrge pH, erineva lahustuvusega mineraalsed Ca- ja Al-ühendid, poorsus jt omadused. Siiski on ilmne, et kuigi meie varasemad eksperimendid näitavad P eemaldamisvõimet kuni 91% varieeruvatel fosfori koormustel ja kuni 8–15 mg P L<sup>-1</sup> viibejaga 12 tundi, siis nõnda üledimensioneeritud voolusüsteemides kaotatakse kiiresti tuhafiltermaterjali sidumisvõime tänu filtermaterjali pindade nn. keemilisele ummistumisele läbi sekundaarse Ca-karbonaatide sadestumise (Publikatsioon I). Lisaks näitavad meie varasemad uuringutulemused (Publikatsioon II), et hüdratiseeritud põlevkivituha filtrite sidumisvõime sõltub oluliselt P kontsentratsioonist lahuses ning madalatel sisendkoormustel võib tuhasette sidumisvõime olla ebapiisav rangeimate piirväärtuste tagamiseks. Ei saa välistada, et see nähtus on omane kõigile maailmas uuritud Ca-rikastele aktiivfiltratsiooni filtermaterjalidele (nt. C-tüüpi kivisöe tuhk, purustatud gaasbetoon ja Filtralite-P<sup>®</sup> tüüpi kergtäitematerjalid jne.).

Käesoleva doktoritöö põhitulemused näitavad, et:

1. Hüdratiseeritud põlevkivituhasette fosfori sidumiseefektiivsus erineva reovee koostise ja fosfori koormuste juures on kõrge ning fosfori sidumiseefektiivsus horisontaalvoolulistes filtrites oli 85,4% prügila nõrgvee korral ja 99,2% olmereovee puhul. Fosfori sidumiseefektiivsus ei ole pärsitud konkureerivate ionide (kloriid, sulfaat, jne.) poolt ning filtermaterjal säilitab kõrge efektiivsuse pika aja jooksul. Kuid fosfori ärastus sõltub suuresti fosfori sissevoolu kontsentratsioonist ning madalamatel sisendkontsentratsioonidel, kui  $0,5 \text{ mg L}^{-1}$ , Ca-fosfaate faasi sadenemine lõpeb, ning peamiseks ärastusmeetodiks on tõenäoliselt väheefektiivsem adsorptsioon.
2. Põlevkivituhasette filtrite fosfori sidumisvõimet läbivoolulises laborikatses erinevatel viibeagadel näitasid sidumiseefektiivsuse olulist sõltuvust hüdraulilistest koormustest. Oodatult olid kõige suuremad sidumiseefektiivsused (91%) katsesüsteemis, millele rakendati kõige väiksemat hüdraulilist koormust, aga hoolimata esimese katsesüsteemi suuremast viibeajast ja paremast fosfori sidumisvõimest oli selle filtri sidumiseefektiivsuse vähenemine kõige kiirem ning üldine sidumisvõime materjali ühiku kohta kõige väiksem. Filtermaterjali mineraloogilised ja mikroskoopilised uuringud näitavad, et katsesüsteemide sidumiseefektiivsuse muutlikkust kontrollib pooriruumi üleküllastus kaltsiidi suhtes. Esimeses katsesüsteemis, mille viibeag oli pikim, saavutati kõrge üleküllastus, mille tulemusena tekkis kiiresti suur hulk kristallisatsioonitsentreid ja tuha osakeste pinnale moodustus arvukalt väikseid ( $<10 \text{ }\mu\text{m}$ ) ja tihedalt pakitud nõeljaid kaltsiidi kristalliite. Kiire kaltsiidi väljasettimise tulemusena kaeti tuhasette osakeste pind autigeense kaltsiidi massidega ning seetõttu aeglustub põlevkivituhasette ebastabiilsete kaltsiumirikaste mineraalsete faaside lahustumine ning väheneb lahustunud Ca ionide osakaal lahuses. Samal ajal ei saavutata lühemate viibeagade korral nii suurt kaltsiidi üleküllastust ning karbonaatide kristallisatsiooni kiirus on väiksem. See omakorda tagab moodustunud sademe poorsema struktuuri ning Ca lahustumine ning transport tuhasetteosakesest pooriruumi on võimalik pikema aja jooksul.
3. Karbonaatide tasakaal omab suurt kontrolli Ca-fosfaadi sadestamisele aktiivfiltratsioonil kaltsiumirikaste materjalide korral. Kuigi pikem viibeag reovee ja filtermaterjali vahel tagab parema fosfori ärastuse, põhjustab see samuti suure üleküllastuse Ca-karbonaatide suhtes. Üleküllastus Ca-karbonaatide suhtes on veelgi võimendatud lahuse kõrge pH tõttu. Katsete andmed näitavad ühtlasi, et sõltumatult viibeajast (ehk üleküllastuse tasemest) settib lahusest tahke fosfaadi faas amorfse Ca-fosfaadi kujul. Termodünaamiliselt kõige stabiilsem Ca-fosfaadi faas on hüdroksüül-apatiit (HAP), mis tasakaalulises süsteemis annaks fosfori kontsentratsiooniks vees alla  $0.005 \text{ mg L}^{-1}$ . Kuigi Ca-fosfaat settib esialgselt amorfasel kujul, siis kristalliseerub see hiljem ümber stabiilseks hüdroksüül-apatiidiks.
4. Fosfor on hüdratiseeritud põlevkivituhasettes seotud raskesti lahustuva Ca-fosfaadi vormina ning hoolimata kasutatud filtermaterjali suurtest seotud fosfori

sisaldustest (keskmiselt 651 mg P kg<sup>-1</sup>) oli laktaat-lahustuva ehk taimedele kättesaadava fosfori hulk põlevkivituhasettes kõigest 25.4 mg kg<sup>-1</sup>.

5. Taime juurte ja pinnase mikroorganismide poolt produtseeritavad orgaanilised happed on piisavalt tugevad lahustamaks rasklahustuvaid Ca-fosfaadi vorme. Taimedele kättesaadava fosfori sisaldus põlevkivituhasettes kasvas taaskasutuskatse lõpuks kaks korda. Seega on fosforiga küllastatud põlevkivituhasete sobilik kasutamiseks aeglase toimega väetisena näiteks karjamaadel ja metsades. Põlevkivituhasete on samuti sobilik materjal põldude lupjamiseks ja kiiresti kättesaadava kaaliumi allikaks.

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