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Phosphorous removal mechanism in hydrated oil-shale ash

MSc. thesis

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Introduction

Continuing intensive use of phosphates in agricultural and domestic purposes (fertilizers, detergents etc.) has created a situation, where surface waters contain a high level of phosphorous, which subsequently causes eutrophication problems. Phosphorous removal from wastewater is an actual theme in all over the world and is required by European quality objectives (Urban Waste Water Treatment Directive 91/271/EEC and Waste Framework Directive 2000/60/EC).

The problem to phosphorous removal exists, apart from large-scale wastewater treatment facilities at major population or industrial sites, also at a smaller scale in single farms/houses and small enterprises/settlements where conventional treatment plants are economically not feasible. Alternatively, the wastewater treatment at these sites can be done by using constructed wetlands. Constructed wetland systems are widely used in wastewater treatment due of its efficiency for the removal of water pollutants (Vymazal *et al*., 1998). For the treatment of water discharged from single household and small communities, the use of constructed wetlands has extended rapidly as an alternative choice due to their robustness, relatively low cost, easy operation and maintenance. Although the capacity of constructed wetlands to remove pollutants is considered good, the limits for discarded water quality are becoming more stringent and the demand to remove nutrients is rising (Urban Waste Water Treatment Directive 91/271/EEC and Waste Framework Directive 2000/60/EC) and there is an increasing demand for efficient, but cheap filter materials.

The constructed wetlands and the implementation of recycling and recirculation of treated effluents has proven to be effective for nitrification and has enhanced the removal of total nitrogen (Cooper *et al*., 1999; Cooper *et al*., 2003; Marti *et al*., 2003), but its capacity to remove phosphorous is an issue that has not been solved completely (Molle *et al.*, 2005). The potential of constructed wetland systems to remove phosphorous is limited and it is highly dependent on the nature of the materials, which are used for its construction. Other factors that might affect the removal efficiency include the growth of biofilm attached to the media, which reduces the contact and the interaction between the material and the wastewater, and the inhomogeneous nature of

media, which does not guarantee a consistent performance (incl. hydraulic conditions) of the systems.

Suitable and low-cost filter media for phosphorous removal in constructed wetland systems has been a critical issue over a decade (Zhu *et al*., 1997; Grüneberg *et al*., 2000; Arias *et al*., 2001; Drizo *et al*., 2002). Previous worldwide studies have shown, that calcium rich medias can remove effectively phosphorous, organic matter and other substances from wastewater (Brix *et al*., 2000; Del Bubba *et al*., 2003; Molle *et al*., 2003a).

In Estonia, more than 95% of power production is based on burning of low calorific oil-shale – kukersite, which is rich in carbonate minerals. In oil-shale burning large amounts of calcareous fly ash is produced. The annual production of oil-shale treatment wastes (fly-ash, cinder, semicoke) is approximately 5-7 million tons and more than half of it is a chemically unstable fly ash. The ash is removed from boilers by hydrotransport system in water-ash slurry at ratio of 20:1 and stored in large waste heaps next to the power plants, where it continues to react with (atmospheric precipitation) water and CO_2 found in the air (Õispuu *et al.*, 1999). As the result the ash becomes hydrated which is reflected in its mineralogical composition. The main hydration and carbonization products are Ca-rich phases as gypsum, ettringite, portlandite, vaterite, calcite and hydrocalumite etc.

Fly ash and the hydrated sediment at the oil-shale ash plateaus are considered as a possible alternative media for phosphorous removal in constructed wetland systems (Vohla *et al*., 2005). This could also be helpful to reuse some amount of the oil-shale wastes, which has been practically nonexistent during the last 10-15 years. Earlier laboratory batch-experiments have shown phosphorous removal effectiveness for fly ash and hydrated sediment of the oil-shale ash up to 99.9 % (Lokotar, 2002; Karimov, 2003; Vohla, 2004; Vohla *et al*., 2005). The main controlling factors for phosphorous binding mechanism are the pH-value of the solution, porosity of the sample and the content of different calcium minerals such as portlandite $Ca(OH)_2$, ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$ and free CaO.

However, to evaluate the phosphorous removal capability of hydrated oil-shale ash sediment, which use compared to the fly ash is more feasible/easier due to physical and chemical stability of the sediment, needs a more detailed research to examine the mineralogical and structural changes of the media before and after the treatment with phosphorous containing solution and to reveal the P-binding mechanism and removal capacity.

The aim of this research is to study the mineralogical and structural changes of the oil-shale hydrated sediment during the treatment with phosphorous containing solutions and to reveal the P-binding mechanism and the removal capacity of the material.

Phosphorous removal from the wastewater at the constructed wetlands

Phosphorous removal and possible recovery for reuse by the phosphate industry and in agriculture is technically feasible and there are a number of technologies for recovering phosphorous from wastewater originating from various sources (municipal, industrial, run-off). However, the technologies used for removal of phosphorous from wastewater including chemical and biological precipitation, crystallization, and biosorpion need expensive chemicals and/or other consumables (Kadlec *et al*, 1996). Moreover, these processes need complex and strict control of the operating conditions, and some of them produce excess sludge that requires disposal. If wastewater is treated in constructed wetland systems, the main responsibility in phosphorous removal lies usually on plant assimilation and biomass incorporation. During biomass death and mineralization of organic matter the assimilated phosphorous will return again to the mobile phase. Furthermore, assimilation in plants compared to the applied phosphorous load is small (Brix, 1997).

Another way to retain phosphorous from the wastewater in constructed wetland systems is to generate a irreversible reaction by adsorption and precipitation on a solid phase. Sorption and precipitation of phosphorous is influenced by the physical-chemical properties as content of Fe-, Al-, Ca-compounds, porosity, pH, Eh, dissolved ions and hydraulic conditions (load, retention time) of the filter material (Kadlec *et al*., 1996; Faulkner *et al*., 1989; Vymazal *et al*., 2000). The precipitation of phosphorous may be influenced also by the Ca-content of the wastewater (Maurer *et al*., 1999).

The importance of using Al-, Fe- and Ca-rich materials to retain phosphorous is well known thanks to many agricultural studies on the efficiency of different fertilizers in relation to soil characteristics (Barrow, 1987). Phosphorous binding capacity of the filter bed in constructed wetland could be the limiting factor for the lifetime of the wetland due to the fact that phosphorous is the most difficultly removable polluting component from the wastewater (Grüneberg *et al*., 2000). Many studies have explored over a decade this way of retention to demonstrate the advantages of specific

materials for long-term phosphorous retention in order to guarantee the extensive nature of constructed wetland systems (Zhu *et al*., 1997; Brix *et al*., 2000; Drizo *et al*., 2002; Del Bubba *et al*., 2003).

To predict phosphorous retention efficiency according to the characteristics of the influent, the importance of each sorption mechanism (adsorption, precipitation) must be determined for long-term removal. Adsorption will mainly depend on the intrinsic characteristics of the used material and its equilibrium with the solution. Isomorphic substitution of the lattice surface and the proton adsorption and desorption at the functional surface site result in a surface charge that will permit adsorption or not depending on the pH of the solution (Molle *et al*., 2005). Precipitation, on the other hand, requires the formation of stable nuclei, after which crystal growth can take place. In solution some degree of supersaturation is necessary because crystal nuclei can only be formed after an energy barrier has been overcome (Anderson and Rubin, 1981).

Several earlier studies (Brix *et al*., 2000; Del Bubba *et al*., 2003; Molle *et al*., 2003a) have shown that:

1. calcareous materials have efficient retention capacities but with some limitations in sorption kinetics or chemical stability of effluent;
2. retention efficiency on natural calcite was not enough because it is sensitivity to carbonate equilibrium.

Arias and Brix (2005) studied sorption isotherms on different materials including Damoline, Filtralite-P, etc for use in constructed wetlands. Their study shows that equilibrium isotherms are good indicators of the potential capacity of a material to sorb phosphorous and for example the removal capacity for sands were about 2 kg P m^{-3}, which means that the needed amount of media per person per year will be 0.5 m^3 assuming that the annual phosphorous discharge is typically 1 kg per person per year. However, this amount of media is too large to be of any practical usage if an external filter is considered. It is also considered that the removal efficiency will decrease over time and the effluent concentration would eventually exceed the discharge demands (Arias *et al*., 2005).

Molle *et al*., 2005 studied the Ca-phosphate, apatite as a suitable material for phosphorous removal, where apatite would allow a good pH stability of the solution and good kinetic crystallization. The energy barrier is reduced for crystallization and the precipitate seems to be hydroxyapatite, which is the most stable precipitate of calcium phosphate. They found that adsorption is predominant mechanism for phosphorous removal at a low saturation state due to the great chemical affinity between phosphorous and the media even if several mechanism are present. It also showed that the differences in phosphorous retention mechanism are in relation to media saturation. The benefits using apatite in a constructed wetland system is a fact that only a small volume of material is needed for long-term phosphorous removal. Filter containing apatite should be inserted in the last part of horizontal flow constructed wetland to prevent the biomass development on the active media. Limitations can be stated for acidic influent (pH below 6), which can partially dissolve material and release phosphorous into solution.

Also, phosphorous binding capacity will increase with the rise of the content of different metals in the material (Tan, 1993). Due to the small content of metals in conventionally used filter materials such as crushed stones and gravel, this is arguably the reason for non-effective removal of phosphorous. To overcome the limited phosphorous removal capacity of natural media used in constructed wetlands, several alternative solutions have been suggested and tested during the last few years. These include (Arias *et al*., 2005):

1. whole system construction, which is chemically enriched with media (e.g. Filtralite-P) capable of binding phosphorous;
2. chemical precipitation of phosphorous at the pre-treatment stage of the system and;
3. the removal of phosphorous in a separate filter unit, which contains a granular medium with a high phosphorous-removal capacity.

The use of enriched media as an example Filtralite-P (lightweight ceramic particle aggregate with high porosity, which contains in addition to clay particles also some amount of Ca-compounds for phosphorous precipitation) in constructed wetland systems for phosphorous removal is an effective way. In addition Filtralite-P shows

also good capability to remove organic matter, but there are also some obstructions, which prevent the wider use of Filtralite-P:

a) Filtralite-P is a comparatively expensive material with a price of 650-700 EEK/m³ (42-45 €/m³);
b) Wastewater treated with Filtralite-P could result in very high pH-value (pH = 10 – 12) due to high concentration of calcium compounds in the Filtralite-P material (Jenssen *et al*., 2005), which could adversely affect the natural conditions of treated water.

Different products and also industrial wastes are investigated as a possible material for phosphorous removal from the wastewater. At this point it is important, that the used material will not contain heavy metals or other toxic substances. For example the iron slag from the metal industry will effectively bind phosphorous (Shilton *et al*., 2006) and the bounded phosphorous in the slag is available for the plants, but the problem is a content of heavy metals, which will prevent the use of iron slag in wastewater treatment.

Oil-shale ash as a potential filter material

Kerogenous oil-shale used at the Estonian Thermal Power Plants (TPP) is a solid fuel of low energetic value, which leaves after combustion large amounts (45-48%) of ash. The Estonian oil-shale is highly calcareous (calcite/dolomite content of 40-60%) and the ash remaining after combustion is due to thermal decomposition of carbonate minerals rich in free lime (CaO) and anhydrite ($CaSO_4$). The ash removed from boilers is transported to plateaus through a pipe system in water slurry at ash-water ratio of 1:20. The lime and anhydrite start to react with water already in ash removal system and the hydration processes continue in open plateaus forming different secondary Ca-minerals. The mineral composition of fresh ash from power plants is dominated by free lime (CaO), anhydrite ($CaSO_4$), quartz (SiO_2), C2S belite (b-Ca_2SiO_4), merwinite ($Ca_3Mg(SiO_4)_2$), orthoclase ($KAlSi_3O_8$), melilite and periclase (MgO). The ash contains also minor amounts of calcite ($CaCO_3$) and tricalcium-silicate C3S, tricalcium-aluminate C3S, pseudowollastonite ($CaO*SiO_2$) (Table 1; Kuusik *et al*., 2005). The hydration of the ash results in rapid formation of different hydrated Ca-phases as portlandite, ettringite and hydrocalumite (Table 1; Kespre, 2004).

Portlandite results from the hydration of quicklime (CaO):
$CaO + H_2O \rightarrow Ca(OH)_2$ [portlandite]

Portlandite is under atmospheric conditions an unstable phase and evolves by reaction with the atmospheric CO_2 into a stable calcium carbonate phase (calcite, vaterite and/or aragonite).
$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Second important phase in hydrated ash sediment is the ettringite, which results from the reaction of calcium oxide, Al-oxide and gypsum/anhydrite. The limiting factor of this reaction is the amount of $CaSO_4$ in the ash (Myneni *et al*., 1998).
$3CaO + Al_2O_3 + 3CaSO_4 + 32H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$ [ettringite]

Third secondary Ca-phase is the hydrocalumite, which forms by the reaction between calcium oxide and aluminium oxide. This reaction is limited by the content of Al_2O_3, which remained unused during the formation of ettringite.

$4CaO + Al_2O_3 + 13H_2O \rightarrow 2Ca_2Al(OH)_7*6H_2O$ [hydrocalumite]

Table 1. The average mineral composition of (wt%) of oil-shale ash and hydrated plateau sediments (after Kuusik *et al*., 2005; Kespre, 2004).

Mineral	average fresh ash	average ash-plateau sediment
Quartz	6.4	6.0
Orthoclase	6.3	6.9
Clay minerals	3.4	3.1
Ca/Mg-silicates	24.1	9.5
Periclase	3.0	2.0
Melilite	10.3	5.3
Anhydrite	11.0	
Lime	28.0	
Calcite	4.5	26.0
Portlandite	2.1	6.8
Ettringite		20.9
Hydrocalumite		11.1
Gypsum		2.3

The composition of the ash-plateau sediments is considerably variable depending on the advancement of diagenetic processes, specifically the carbonization, which is the most well developed in the surface layer of the plateau sediments (Kespre, 2004).

The oil-shale fly ash and the hydrated ash plateau sediment, as an alternative filter media for phosphorous removal, has been earlier studied by Lokotar (2002), Karimov (2003) and specifically by Vohla (2004) and Vohla et al. (2005). These previous experiments have provided promising results, and good capacities to remove phosphorous under laboratory conditions. In experiments all these materials showed phosphorous removal capacity of around 25 kg P m^{-3} and up to 99% compared to the initial ratio, whereas the hydrated calcium phosphate $Ca(PO_4)_2*nH_2O$ was forming in

the treated sediments. However, field studies (Vohla *et al*., 2005) indicated that the actual binding capacity was only about 7,4 %. The reasons of this phenomenon are quite unclear and it has not been thoroughly studied yet. One of the possible reasons for observed differences is a possibility that the contact time between wastewater and phosphorous removing material was not long enough (Vohla, 2004; Vohla *et al*., 2005).

Materials and methods

The purpose of the experimental work was to (1) determine the physical, chemical and mineralogical properties of the ash sediment and (2) the phosphorous removal mechanism and binding capacity in the ash plateau sediment.

Phosphorous binding capacities of the ash sediment were studied in open containers using various amounts of hydrated oil-shale ash sediment with different particle size and contact surface. The ash-sediment used in experiments was sampled from ash-plateau at the Balti Thermal Power Plant and represents partially carbonized surface layer of the plateau sediments. Together with the phosphorous content in the solution treated with ash sediment, also mineralogical and electron microscope analyzes of the material were performed.

The phosphorous was measured by author 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 analyzes. The principle of the method is that the phosphates present in organic and condensed inorganic forms (meta-, pyro- or other polyphosphates) must be converted to reactive orthophosphate before analyses. Pre-treatment of the sample with acid and heat provides the conditions for hydrolysis of the condensed inorganic forms. Organic phosphates are converted to orthophosphates by heating with acid and persulfate. Orthophosphate reacts with molybdate in an acid medium to produce a mixed phosphate/molybdate complex. Ascorbic acid then reduces the complex, giving an intense molybdenum blue colour. Test results are measured at 880 nm and the given results are in mg/l PO_4^{-3}.

The mineralogical composition of the samples was 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 difractometer using Ni-filtered Cu*K*a radiation in 2 – 50 °2θ region, with scan step of 0.03 °2θ and count time of 5 sec per

step. The quantitative mineral composition was found by full-profile Rietveld analysis using Siroquant^{TM} code (Taylor, 1991; Colin *et al.*, 1999).

Scanning electron-microscopy and microanalyses (SEM and SEM-EDS) of ash-sediments was carried out on Zeiss DSM940 (micromorphology observations) and JEOL 845 (SEM-EDS analyses, Institute of Physics, University of Tartu). The samples were coated with gold (SEM) or chromium (SEM-EDS) prior analyses.

Isotherms and kinetic batch experiments were carried out in an opened glass containers with KH_2PO_4 solution, which were regularly agitated to guarantee proper contact between solution and the media. The slightly acidic (pH ~5) KH_2PO_4 solution was buffered to neutral pH before the experiment.

Batch experiments to evaluate phosphorous removal capacities and to observe the mineralogical and structural changes of the media were carried out in three phases:
(1) Adsorption/precipitation kinetics measurements from the solutions containing of 4 mg/l of PO_4^{-3}, which was treated with different amounts of hydrated ash sediment (0.1 g, 0.5 g and 1 g of ash sediment per 100 ml of phosphate solution) and periodically sampled over a period.
(2) Structural and mineralogical changes of the hydrated sediments before and after the treatment with KH_2PO_4 using SEM, SEM-EDS and XRD analyses. For mineralogical and SEM analyses solution containing of 4 mg/l of PO_4 was used. For SEM-EDS analyses samples treated with 4 mg/l of PO_4^{-3} and 1000 mg/l of PO_4^{-3} were used to reveal the form and composition of Ca-phosphate precipitates.
(3) Phosphorous binding capacity measurements from the solution containing KH_2PO_4 with concentrations ranging from 5 to 300 mg/l (calculated as PO_4^{-3}) and treated with different amounts of hydrated ash sediment. Two parallel experiments with 1 g and 5 g of pulverized ash sediment in 100 ml of solution were carried out. Data of P-removal and equilibrium P-concentration obtained from the experiment were fitted with Langmuir and Freundlich isotherm equations.

The Langmuir equation is valid for single-layer adsorption and assumes maximum adsorption corresponding to a saturated monolayer of adsorbate molecules on the

surface of the adsorbents where the energy of adsorption is considered to be constant. Mathematical expression for the Langmuir equation is in terms of solute concentration in solution is

$$q_e = (Q * bC_e) / (1 + bC_e)$$

where C_e is the equilibrium adsorbate concentration (mg/l), q_e the mass of adsorbate per mass unit of adsorbent at equilibrium (mg/g), Q the maximum mass adsorbed at saturation conditions per mass unit of adsorbent (mg/g), b the empirical constant with units of inverse of concentration C_e (l/mg). The Langmuir equation allows estimating both the maximum adsorption, Q, and the constant, b, which represents the inverse of the equilibrium concentration of adsorbate at one-half saturation and gives, therefore, a measure of the affinity of the adsorbate for the adsorbent.

Freundlich equation often represents an initial surface adsorption followed by a condensation effect resulting from extremely strong solute-solute interaction and it also incorporates the heterogeneous surface energy in which the energy term, b, in the previous Langmuir equation varies as a function of surface coverage due to the heat of adsorption (Barrer, 1978). The Freundlich equation is the form of:

$$q_e = K_F C_e^{1/n}$$

where q_e and C_e have the same meaning as in Langmuir equation and K_F and n are constants, whereas index 1/n is adsorption intensity and K_F can be related to the surface energy of the adsorbent.

Results and discussion

Mineralogical composition

The results of XRD analyses indicate significant changes in the mineral composition of the ash sediment during the treatment with phosphorous solution. The content of the most reactive Ca-phases – ettringite and portlandite decreases drastically and after prolonged treatment (10 days) these minerals disappear from the sediment (detection limit by XRD method is usually 1%). At the same time the content of calcium carbonates (calcite and vaterite) increases, which suggest both carbonization of the portlandite and the precipitation using the Ca released from the dissolution of ettringite (Table 2 and Figures 1-3). Also the periclase (MgO) and bassanite ($CaSO_4*0.5H_2O$) are missing after the treatment. The content of other minerals (gypsum, quartz, melilite, etc) is practically unchanged.

Table 2. Mineralogical composition of hydrated ash sediment before and the after treatment with phosphorous containing solution (~4 mg/l of PO_4^{-3}) during 10 days.

	Portlandite	Periclase	Merwinite	Melilite	Bassanite	Wollastonite	Hydrocalumite	Afwillite	Gypsum	C2S	Diopside	Adularia	Calcite	Ettringite	Quartz	Vaterite
Content before the treatment with PO_4^{-3}, %	1.0	1.3	2.2	2.2	2.7	2.9	2.9	3.0	3.1	4.9	5.6	8.9	13.0	13.8	14.6	17.9
Content after the treatment with PO_4^{-3}, %			2.1	2.6		3.2	2.4	3.3	2.5	4.8	6.3	9.7	22.5		17.5	23.0

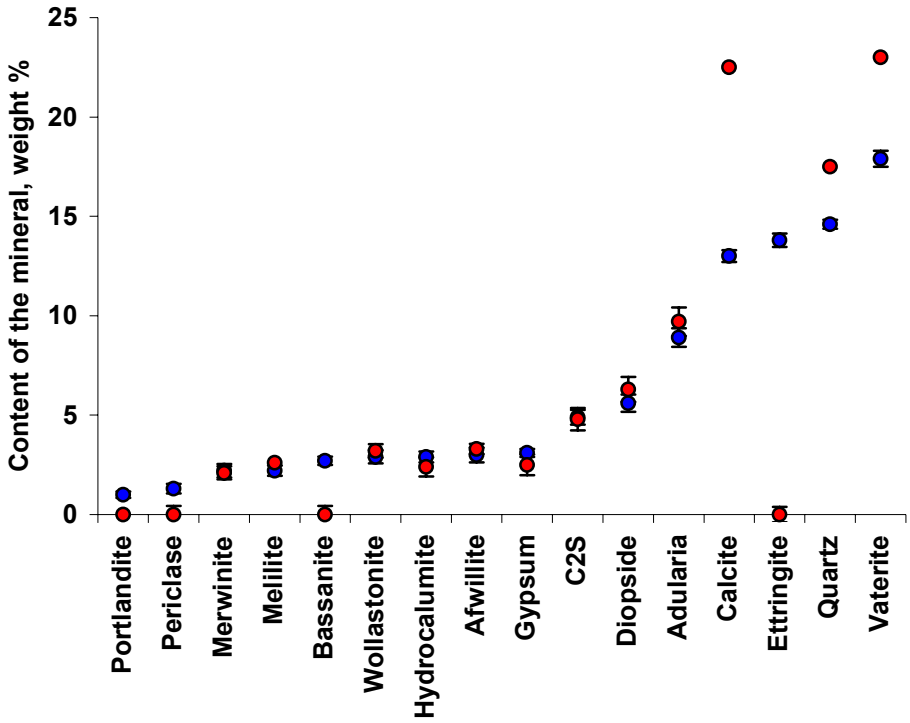

Figure 1. Changes in mineralogical composition of hydrated ash sediment before and the after treatment with phosphorous containing solution (~4 mg/l of PO_4^{-3}) during 10 days.

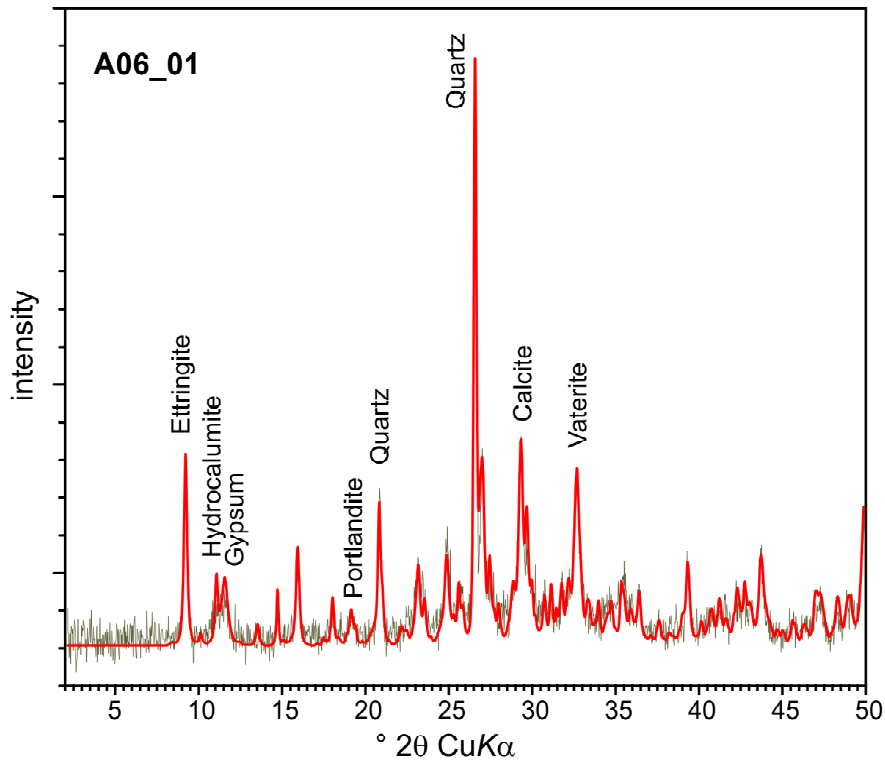

Figure 2. XRD pattern of hydrated fly ash sediment before the treatment with phosphorous containing solution.

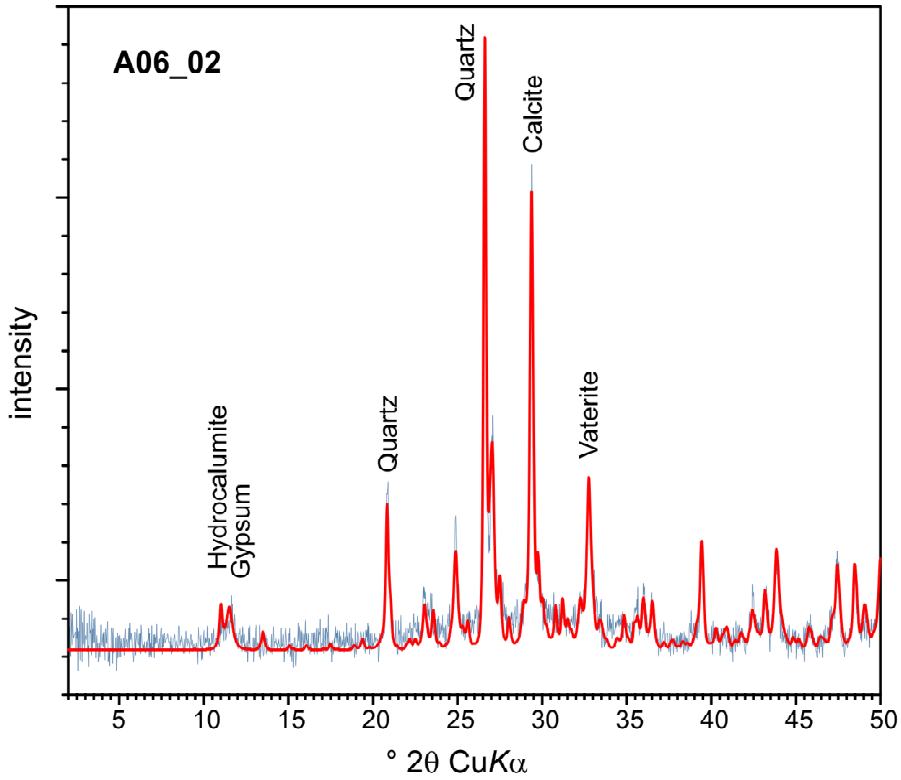

Figure 3. XRD pattern of hydrated fly ash sediment after the treatment with phosphorous containing solution.

The observed changes suggest that the unstable calcium-rich minerals such as ettringite and portlandite (probably also hydrocalumite) in the hydrated ash sediment control the removal of phosphorous providing Ca^{2+} as the source of stable nuclei where the crystals of phosphate can form.

Previous experiments (Karimov, 2003) have shown that the phosphorous is bonded in the oil-shale ash sediment as a hydrated calcium phosphate $Ca_3(PO_4)_2*nH_2O$ or as a β-form of calcium phosphate $Ca_3(PO_4)_2$. Assuming that phosphorous is a dominant phosphate ion in wastewater, the reaction will be as follows:

$$2PO_4^{3-} + 3Ca^{2+} + nH_2O = Ca_3(PO_4)_2*nH_2O,$$

where the activity of Ca^{+} in the pores is controlled by the solubility/dissociation of reactive Ca–phases – most importantly ettringite or portlandite and less calcite:

$Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O = 6Ca^{2+} + 2Al(OH)_3 + 3SO_4^{-2} + 29H_2O$

$Ca(OH)_2 = Ca^{2+} + 2OH^-$,

$CaCO_3 = Ca^{2+} + CO_3^{2-}$,

The rise of content of calcium carbonates (calcite, vaterite) is explained with the single reaction between portlandite $Ca(OH)_2$ and dissolved carbon dioxide in the solution or by precipitation of the Ca^{2+} released from ettringite.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Other minerals do not have any important role in this process.

The formation of supposed phosphates such as apatite - $Ca_5(PO_4)_3(OH, F, Cl)$, whitlockite - $Ca_9(Mg,Fe)(PO_4)_6PO_3OH$ or hydrated calcium phosphate - $Ca_3(PO_4)_2$ or its β-form was not detected due the low concentration of phosphorous in the solution (about 1 mg/l of phosphorous).

Scanning electron microscopy

The structural and compositional changes of treated hydrated ash sediments observed with SEM (scanning electron microscope) and SEM-EDS (scanning electron microscope with energy dispersive detector) show that the structure (especially on the surface) of the hydrated ash was significantly modified during the treatment. The untreated sediment contains abundant needle-like prismatic ettringite crystallites, which form irregular and/or spherulitic aggregates in the pore space (Figures 4, 5). After the treatment with solution the ettringite has disappeared or is partly dissolved and overgrown with secondary precipitates. In short experiments (less than 4 days) the ettringite was dissolved from the sediment surface and the needle-like crystals were found only in the deep pores of the ash sediment (Figures 6, 7). The treated samples reveal also secondary calcium carbonate precipitates in the sediment, which occurs in a form of euhedral crystallite aggregates (Figures 8, 9).

The SEM-EDS analyses on material treated with KH_2PO_4 solution are showing a formation of Ca-phosphate mineral, which is most probably the hydrated calcium phosphate - $Ca_3(PO_4)_2*nH_2O$ (Figure 10). The formation and precipitation of Ca-phosphates is confirmed by the SEM-EDS spectra (Figure 11) of these precipitates. This is clear evidence of phosphorous precipitation on ash material. At low concentration of phosphorous the precipitate occurs in the form of small crystal spherulitic aggregates (Figure 10), whereas during the experiment in solution containing 1000 mg/l of PO_4 the phosphate aggregates were growing directly on the ettringite (Figure 12) or replaced ettringite crystallites by retaining its crystal shape (Figures 13). These results confirm the primary importance of the ettringite on the phosphorous removal capacity of the ash sediment.

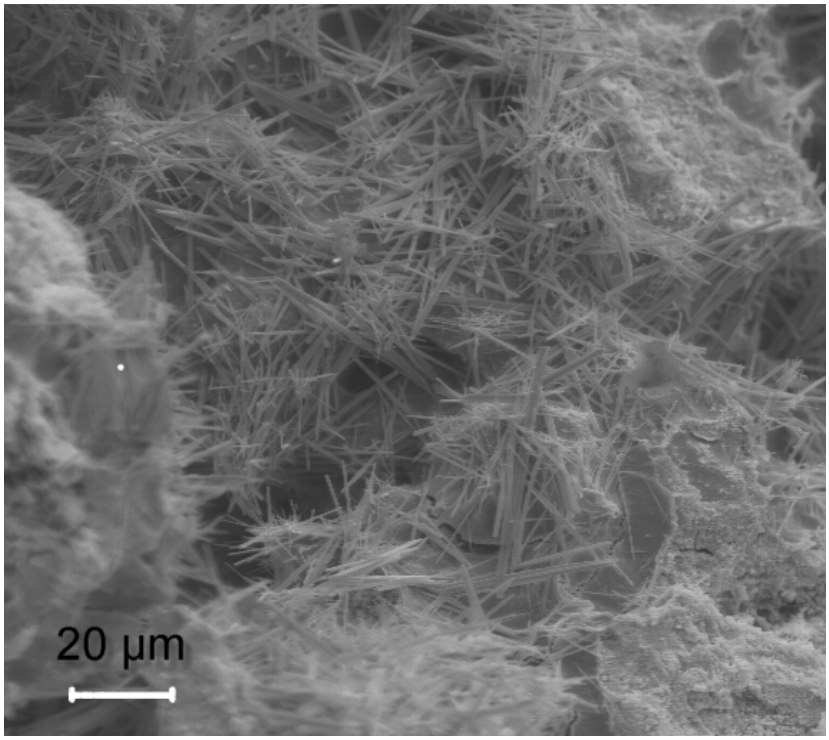

Figure 4. Structure of needle-like ettringite minerals on untreated hydrated ash sediment.

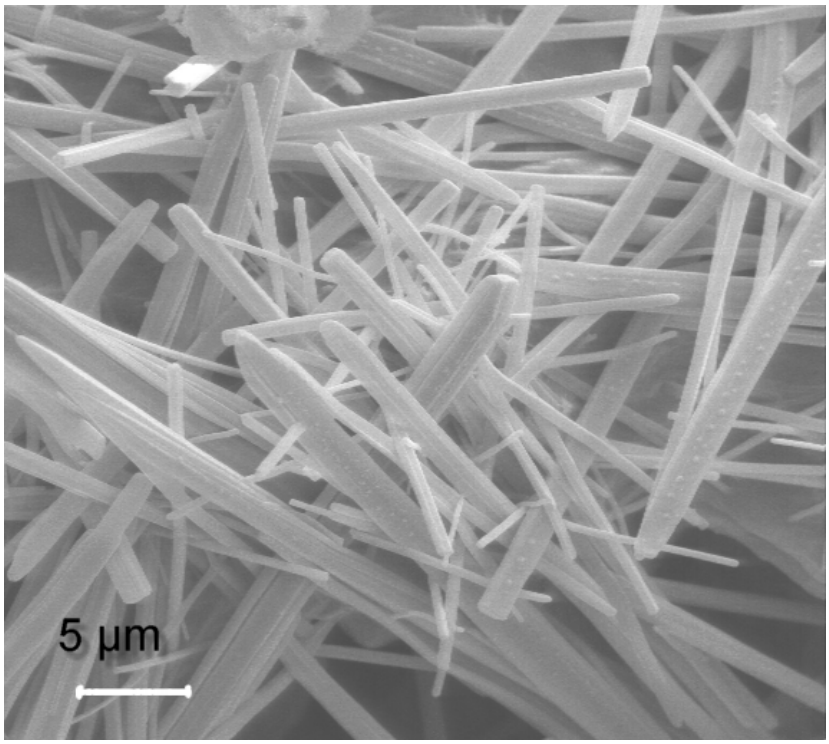

Figure 5. Needle-like prismatic crystallites of ettringite in untreated hydrated ash sediment.

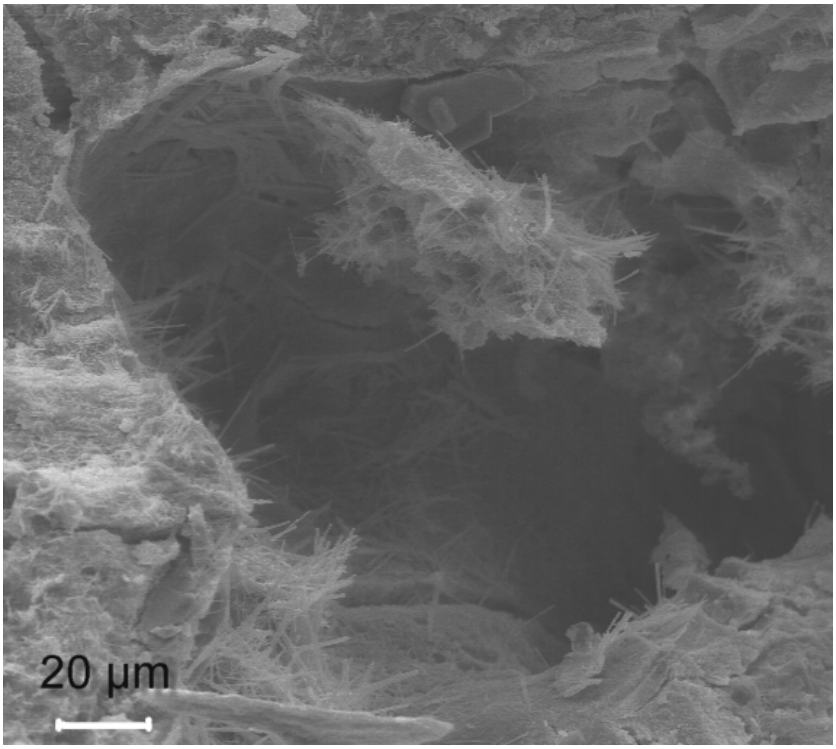

Figure 6. Deep pores of hydrated ash sediment after the treatment with phosphorous containing solution (4 mg/l of PO_4^{-3}) where the ettringite has partially preserved.

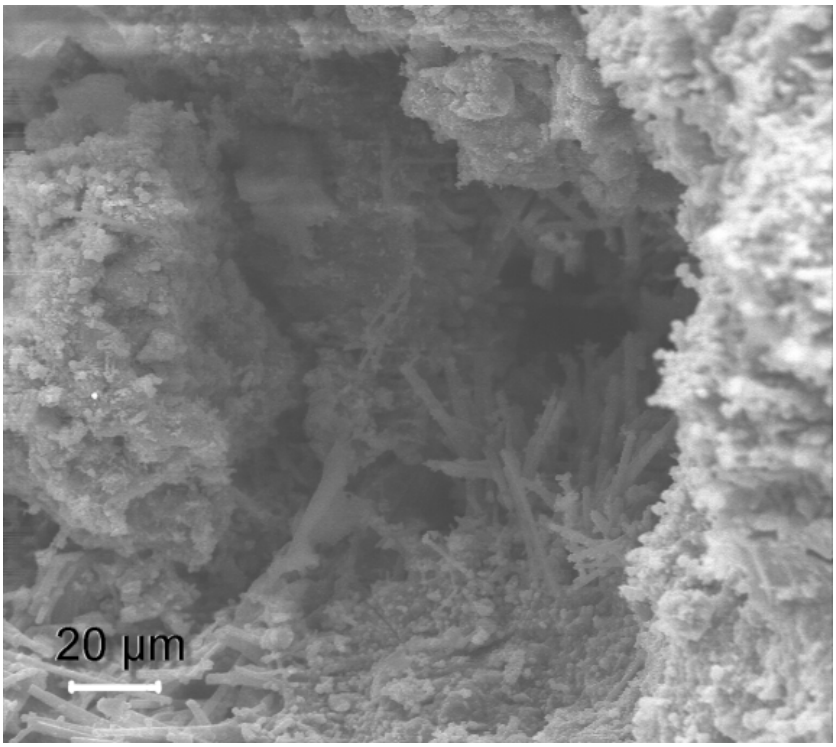

Figure 7. Deep pores of hydrated ash sediment after the treatment with phosphorous containing solution. Note the dissolved and overgrown (Ca-phosphate? and calcite?) ettringite crystallites (4 mg/l of PO_4^{-3}).

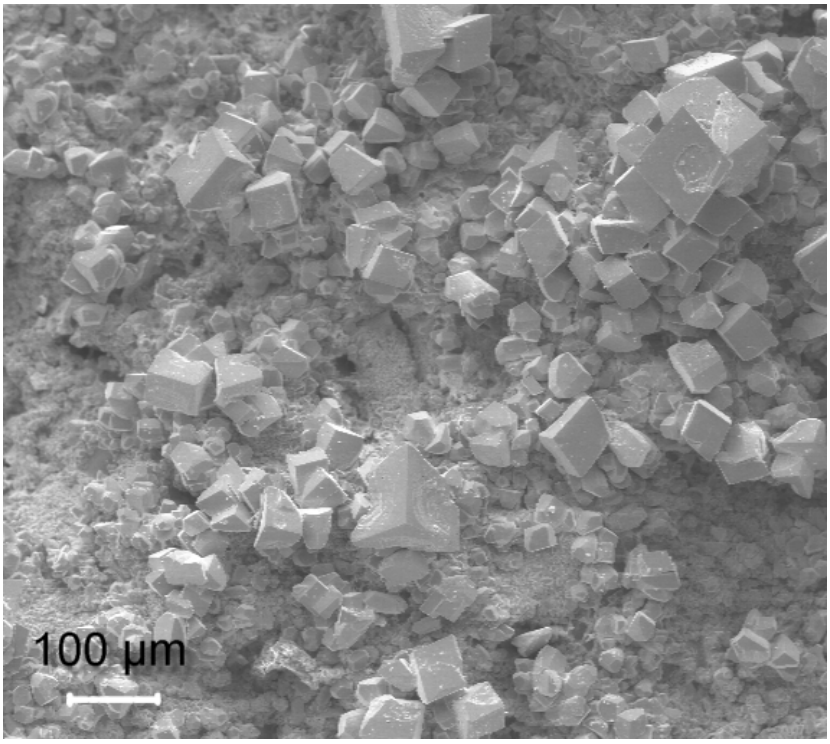

Figure 8. Calcium carbonate crystals on the hydrated ash sediment after the treatment.

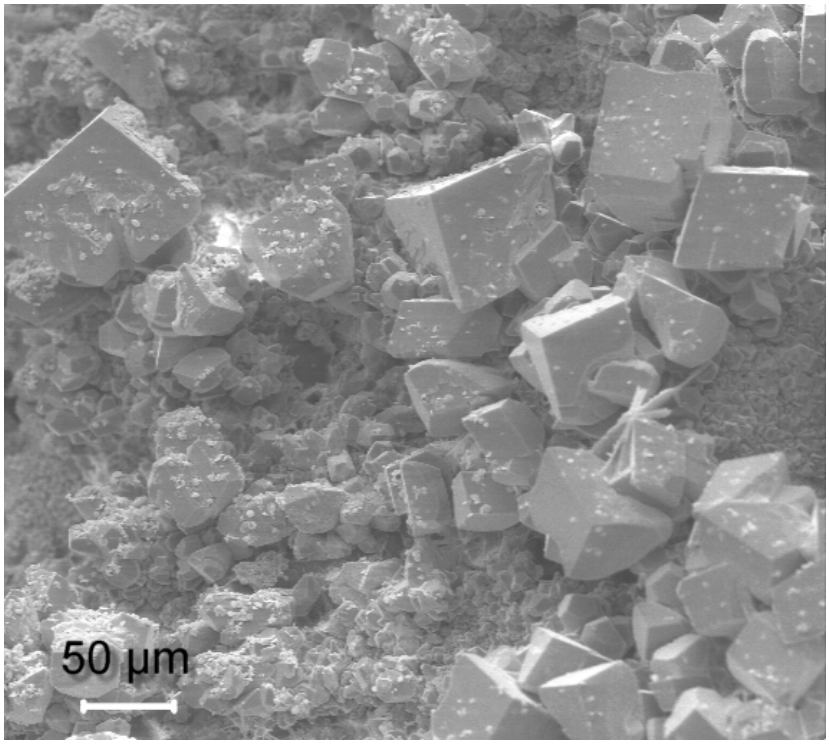

Figure 9. Calcium carbonate crystals on the hydrated ash sediment after the treatment.

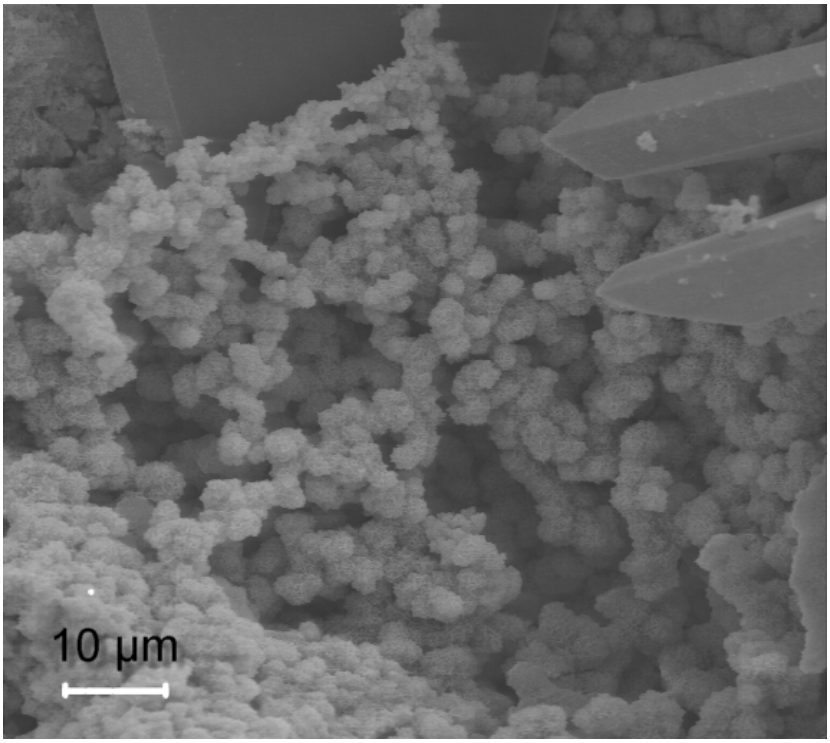

Figure 10. Calcium phosphate aggregates on the hydrated ash sediment after the treatment with phosphorous containing solution.

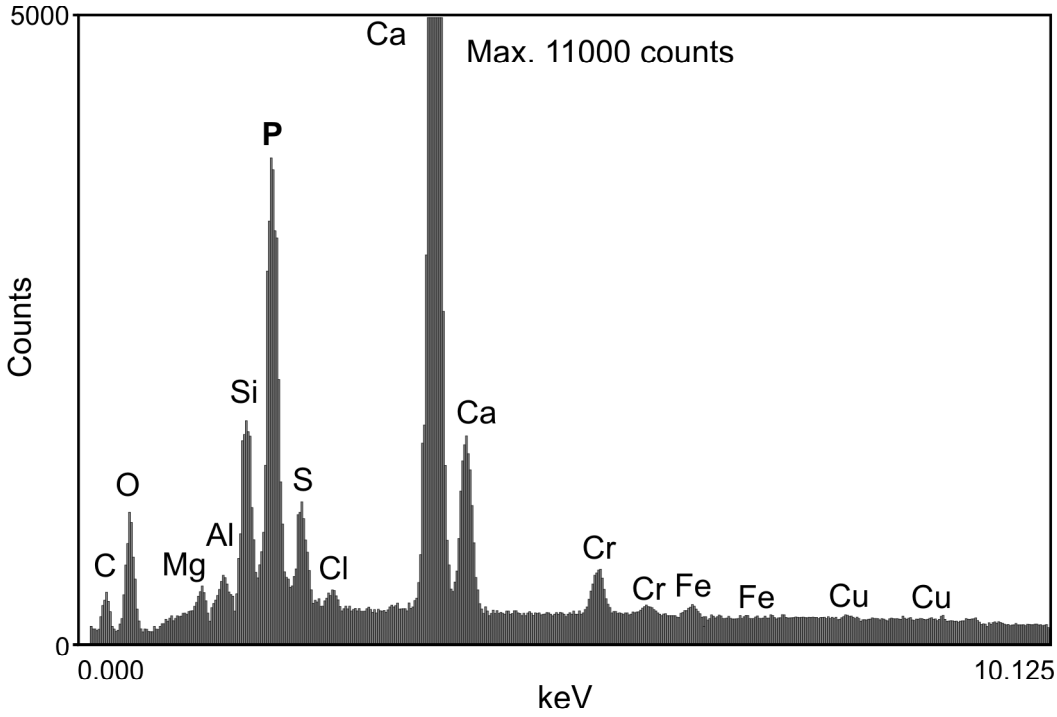

Figure 11. SEM-EDS analyse spectrum of the hydrated ash sediment surface after the treatment with phosphorous containing solution.

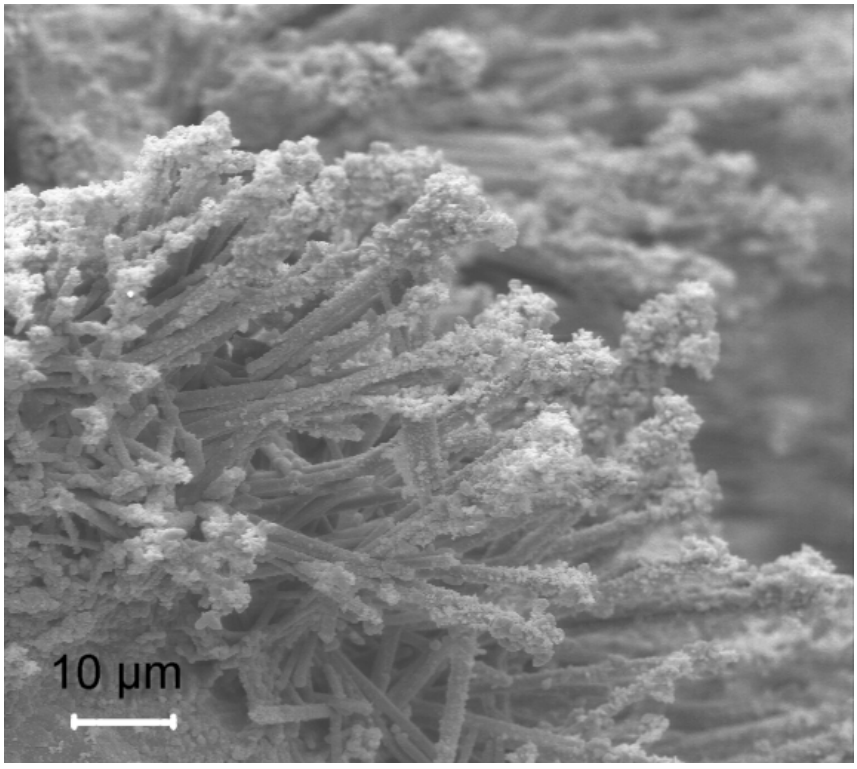

Figure 12. Calcium-phosphate aggregates on the ettringite needles after the treatment with phosphorous containing solution.

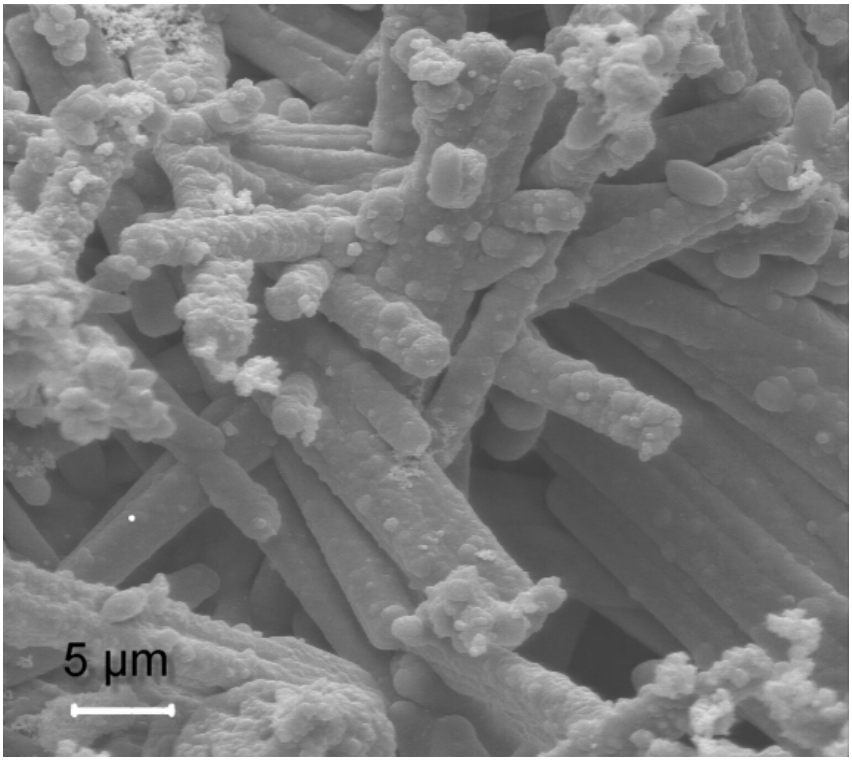

Figure 13. Calcium-phosphate overgrowths on ettringite after the treatment with phosphorous solution. Note the difference in crystallite shape (e.g. Figure 5).

Phosphorous removal experiment

The results of the phosphorous removal experiments are show in Tables 3-6 and Figures 14-16. The batch experiments to evaluate the phosphorous binding kinetics and capacities in hydrated fly ash sediment show that the initial ratio of phosphorous drops very quickly in the beginning of the treatment (Figures 14, 15, 16). This is due to rapid dissolution of ettringite and subsequent Ca-phosphate precipitation, which was observed by XRD and SEM-EDS analyses. The decrease of phosphorous content takes place during the first two days and it stabilizes over three to four days at the level, which most likely depends on the equilibrium solubility of the precipitated Ca-phosphate phase. The small rise of phosphorous content at the end of the cycle (Figure 14) is probably due the vaporization effect. In real conditions the content of phosphorous will remain unchanged.

Table 3. Phosphorous removal and pH analyzes with ash sediment 1 g and 0.1 g per 100 ml of solution containing 4 mg/l of PO_4^{3-}.

	1 g / 100 ml			0.1 g / 100 ml		
	PO_4^{-3}	P	pH	PO_4^{-3}	P	pH
31/01/2006	4.00	**1.31**		4.00	**1.31**	
31/01/2006	2.97	**0.97**	8.8	3.70	**1.21**	9.0
01/02/2006	1.32	**0.43**	9.0	3.39	**1.11**	9.0
02/02/2006						
03/02/2006	1.20	**0.39**	8.7	2.97	**0.97**	7.8
04/02/2006						
05/02/2006						
06/02/2006	0.81	**0.26**	7.9	2.67	**0.87**	7.9
07/02/2006						
08/02/2006						
09/02/2006	0.83	**0.27**	7.8	2.68	**0.87**	8.0
10/02/2006						
11/02/2006						
12/02/2006						
13/02/2006						
14/02/2006						
15/02/2006	1.01	**0.33**	7.8	2.92	**0.95**	8.0

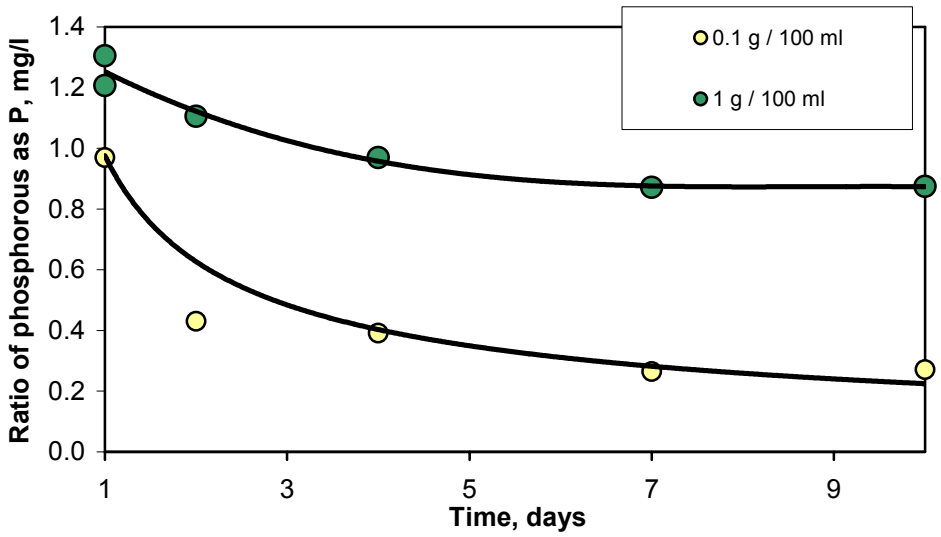

Figure 14. Phosphorous removal with ash sediment 1 g and 0.1 g per 100 ml of solution containing 4 mg/l of PO_4^{3-}.

Also, if to compare the removal of phosphorous with similar amounts of hydrated ash sediment (1 g and 0.5 g of sediment per 100 ml of solution), then the differences are very small and the final result (phosphorous remaining in the solution) is practically the same (Figure 15). In both cases the main decrease in phosphorous content occurs during the first days and in particular the falloff is the most remarkable already in the first few hours of the experiment.

Table 4. Phosphorous removal and pH analyzes with ash sediment amounts of 1 g and 0.5 g in 100 ml of solution containing about 4 mg/l of PO_4^{3-}.

	1 g / 100 ml			0.5 g / 100 ml		
	PO_4^{-3}	P	pH	PO_4^{-3}	P	pH
21/02/2006	3.99	**1.30**	8.8	3.74	**1.22**	8.9
21/02/2006	3.76	**1.23**	8.67	3.25	**1.06**	8.98
21/02/2006	2.61	**0.85**	9.38	2.68	**0.87**	9.32
22/02/2006	2.02	**0.66**	9.05	2.12	**0.69**	8.89
23/02/2006						
24/02/2006	1.00	**0.33**		1.20	**0.39**	

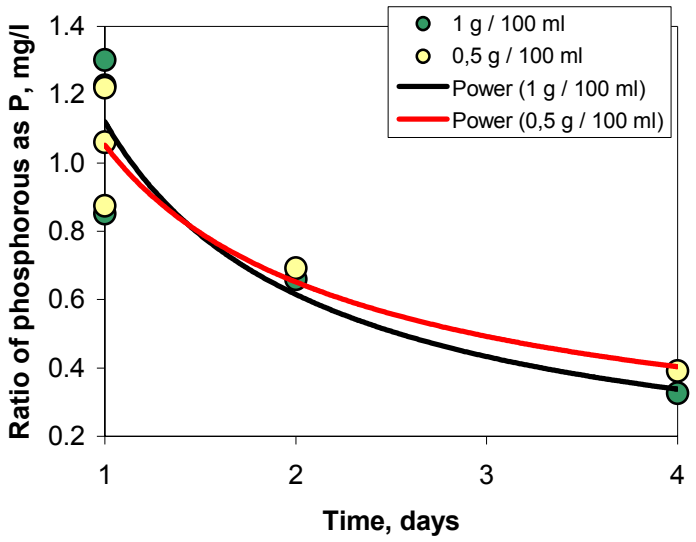

Figure 15. Phosphorous removal with ash sediment amounts of 1 g and 0.5 g in 100 ml of solution containing about 4 mg/l of PO_4^{3-}.

Final phosphorous removal efficiency does not depend on the mechanical state (different contact surface) of the sediment. The results from the experiment with crushed (grain size 1-2 mm) and pulverized (grain size <10 μm) material at a ratio of 1 g of sediment in 100 ml of solution show that with larger contact surface the removal will take place much faster and the equilibrium state is reached already in 24 hours. The crushed material reaches the same removal efficiency, but in ten days (Figure 16), which suggests that the phosphorous removal is governed only by the chemical precipitation mechanism that depends on the content of soluble Ca-phases, in this case the ettringite. If the removal would be controlled by surface sorption then we would expect higher removal efficiency in pulverized sediment.

Table 5. Phosphorous removal analyzes with 1 g of crushed and pulverized ash sediment in 100 ml of solution containing 4 mg/l of PO_4^{3-}.

	1 g of crushed ash / 100 ml		1 g of pulverized ash / 100 ml	
	PO_4^{-3}	P	PO_4^{-3}	P
07/03/2006	4.10	**1.34**	4.10	**1.34**
07/03/2006	4.03	**1.31**	1.33	**0.43**
07/03/2006	3.40	**1.11**	0.89	**0.29**
08/03/2006	2.21	**0.72**	0.67	**0.22**
09/03/2006				
10/03/2006				
11/03/2006				
12/03/2006				
13/03/2006				
14/03/2006	0.81	**0.26**	0.60	**0.20**

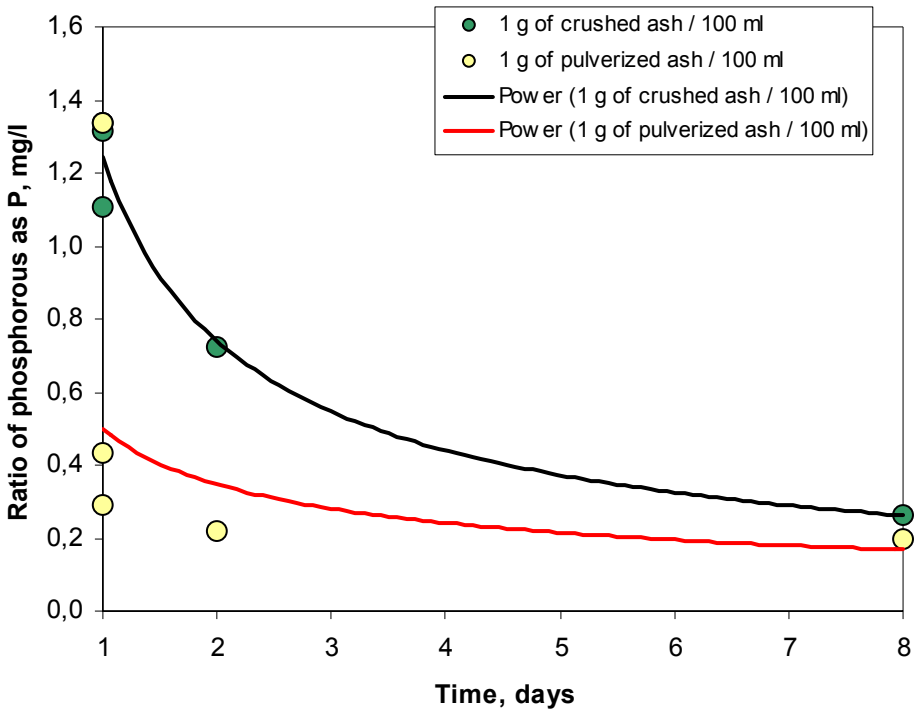

Figure 16. Phosphorous removal with 1 g of crushed and pulverized ash sediment in 100 ml of solution containing 4 mg/l of PO_4^{3-}.

The binding capacity of pulverized hydrated ash sediment at different phosphorous loadings ranging from 5 to 300 mg/l (calculated as PO_4^{-3}) further confirms the precipitation mechanism of the phosphorous removal in the ash sediment and the total binding capacity is not dependent on the amount of material as far as even five times larger amount of ash sediment does not show better capability to remove phosphorous also at higher initial concentrations of phosphorous. And so, if to estimate the binding capacity of the sediment in mg P g^{-1}, then the effectiveness of 1 g of pulverized ash sediment will be simply five times higher (Figure 18). The highest removal capacity was detected with solution containing 300 mg/l of PO_4^{-3} where the phosphorous binding capacity was calculated to 65 mg P g^{-1} (Figure 17). The capacity will rise with rise of phosphorous content and the effectiveness was in range 67-85 % which was not dependent on the initial load of phosphorous.

Table 6. Total phosphorous binding capacity results of 1 g and 5 g of pulverized ash sediment in 100 ml of solution containing 5 – 300 mg/l of PO_4^{-3}.

	1 g / 100 ml		5 g / 100 ml	
	PO_4^{-3}	P	PO_4^{-3}	P
5	4.04	**1.32**	4.46	**1.46**
10	7.64	**2.49**	8.64	**2.82**
25	21.25	**6.93**	22.50	**7.34**
50	42.00	**13.70**	31.80	**10.38**
100	84.20	**27.47**	62.00	**20.23**
200	151.00	**49.27**	156.00	**50.90**
300	201.00	**65.59**	198.00	**64.61**

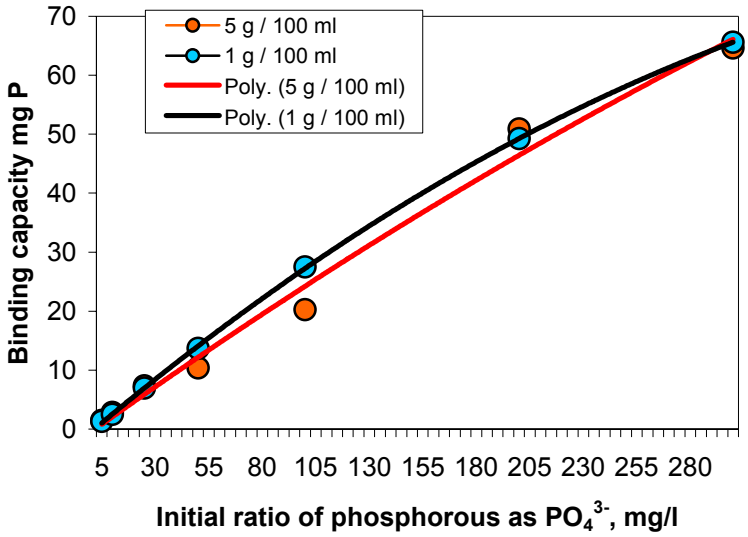

Figure 17. Total phosphorous binding capacity of 1 g and 5 g of pulverized ash sediment in 100 ml of solution containing 5 – 300 mg/l of PO_4^{-3}.

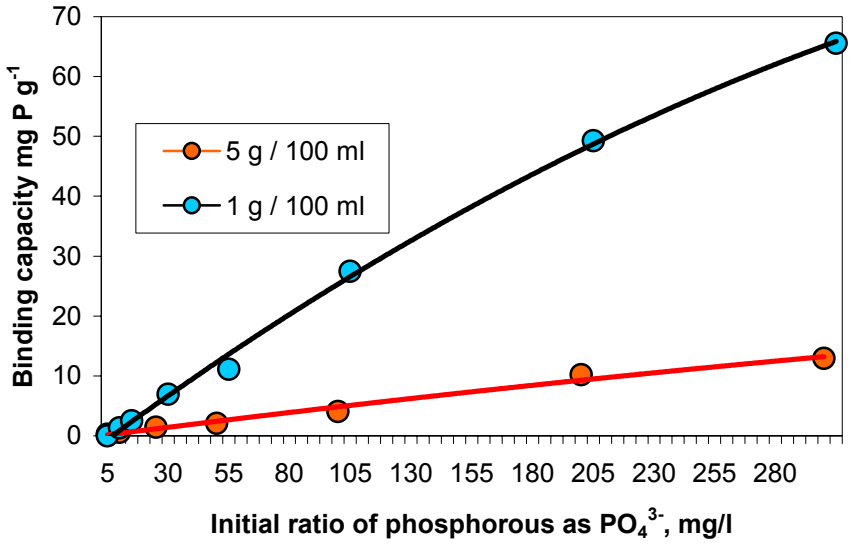

Figure 18. Phosphorous binding capacity calculated as mg P g^{-1} of 1 g and 5 g of pulverized ash sediment in 100 ml of solution containing 5 – 300 mg/l of PO_4^{-3}.

Phosphorous adsorption isotherms

Isotherms of possible phosphorous adsorption on the surface of hydrated ash sediment are shown in Figures 19 and 20.

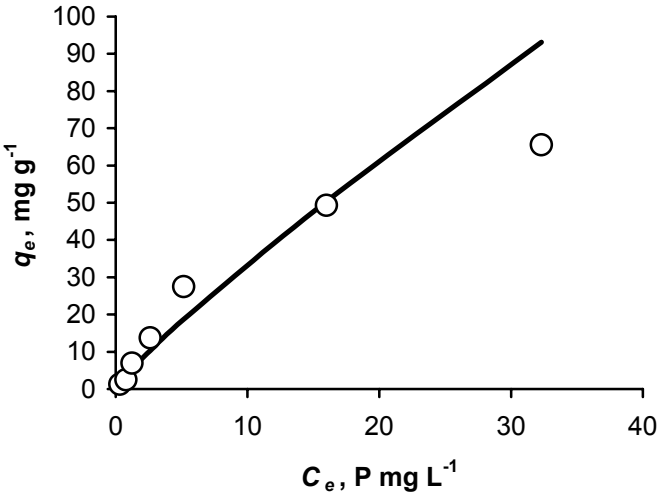

Figure 19. Freundlich P-sorption isotherm of experiment with 1 g sediment in 100 ml solution.

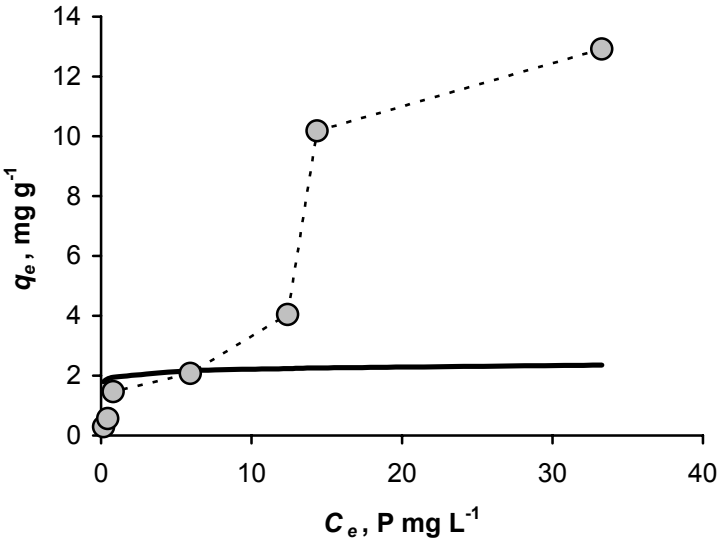

Figure 20. Freundlich P-sorption isotherm of the experiment with 5 g sediment in 100 ml solution.

Equilibrium data for phosphorous suggests that the adsorption mechanism does not control the P binding in ash sediment and the removal occurs mainly by precipitation of Ca-phosphate phases. The assumed Langmuir isotherm did not give any acceptable result for equation coefficients (Figure 21) and the Langmuir model was discarded in further study.

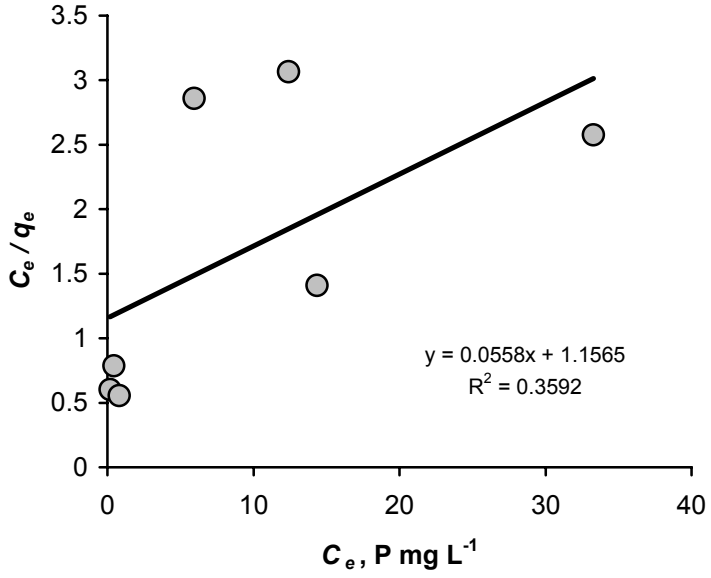

Figure 21. Langmuir P-sorption isotherm coefficient plot for the experiment using 5 g sediment in 100 ml solution.

However, the P-removal obtained in experiment with 1 g sediment in 100 ml solution was described using the Freundlich equation (Figure 19), which suggest that at least at high solution/sediment ratios part of the material is adsorbed on ash material (K_F = 4.46, 1/n = 0.8743). Potential mineral(surfaces) are partially devitrified alumosilicate glass phases and neoformed clay minerals (illite-smectite and smectite) or calcite surfaces. At lower water/sediment ratios (experiment with 5 g of sediment in 100 ml solution) the slope of the sorption isotherm changed dramatically when the initial P concentration reached already about 20 mg P ml^{-1} (Figure 20). The abrupt change in slope of the sorption isotherm suggests that P precipitation began clearly to dominate the process as concentrations increased beyond that of the point of inflection.

Summary and conclusions

The quest for suitable media for phosphorous removal implies the selection of materials, which simultaneously must have good hydraulic characteristics, consistent and sustained elimination of phosphorous from wastewater. The initial determination of the mentioned properties of the materials includes typically the characterization of the physical and chemical features. Once these parameters are considered acceptable for wetland construction, the phosphorous removal capacity of the materials can be tested at larger scale.

Fly ash and the hydrated sediment at the oil-shale ash plateaus are considered as a possible alternative media for phosphorous removal in constructed wetland systems (Vohla *et al*., 2005). The results from this research confirm that hydrated fly ash sediment is a good alternative media for phosphorous removal in constructed wetland systems. The high phosphorous sorption potential of hydrated oil-shale ash is considered due to the high ratio of reactive calcium minerals of which portlandite $Ca(OH)_2$, ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$ are the most important. Ettringite can form up to 25 % of the hydrated ash sediment and it is clearly the most reactive mineral in the hydrated ash sediment. The equilibrium dissolution of ettringite provides free calcium ions that act as stable nuclei for phosphate precipitation. The precipitation mechanism of phosphorous removal in hydrated ash plateau sediment is suggested by Ca-phosphate formation in batch-experiments at different P-loadings. The treatment with phosphorous containing solution causes partial-to-complete dissolution of ettringite and portlandite, and precipitation of Ca-carbonates and Ca-phosphate phases which was confirmed by XRD and SEM (SEM-EDS) studies.

Batch experiments indicate that the capability of hydrated oil-shale ash sediment to remove phosphorous is relatively good (up to 65 mg P g^{-1}) and the effectiveness is in range of 67-85 %. The effectiveness is not as high as showed by previous experiments made by Lokotar (2002) and Vohla (2004) but the binding capacity of 65 mg P g^{-1} is almost three times higher than with any other similar media studied before. The dominant dissolution-precipitation mechanism of phosphorous removal is also suggested from adsorption isotherms. However, the P-removal obtained in experiment

with high solution/sediment ratio was described using the Freundlich equation that suggest that at these conditions at least part of the phosphorous is bind by surface adsorption.

Results of this study also show that due to the rapid dissolution of ettringite the hydrated fly ash sediment could cause problems in long-term use. If the efficient phosphorous removal is controlled by ettringite only, then the sediment could lose its binding capacity rapidly. This question needs further studies. However, hydrated ash sediment can be used for efficient phosphorous removal from wastewaters with high phosphorous concentration by periodical replacement of the filter beds or in combined use with other filter materials.

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Eesti Vabariigi Jäätemeseadus (Waste law), 2004

Kokkuvõte

Hüdratiseeritud põlevkivituha fosfori sidumismehhanism

Ago Kaasik

Põlevkivi lendtuhka ja tuhaplatoode hüdratiseeritud setet on peetud võimalikuks alternatiivseks filtermaterjaliks fosfori eemaldamiseks heitveepuhastus-tehismärgalades. Antud uurimustöö tulemused kinnitavad, et hüdratiseeritud põlevkivituhk sobib tehismärgalades fosfori eemaldamiseks. Hüdratiseeritud põlevkivituha hea fosfori sidumisvõime põhjuseks peetakse kõrge reaktsioonivõimega kaltsiumit sisaldavate mineraalide (portlandiit $Ca(OH)_2$, ettringiit $Ca_6Al_2(SO_4)_3(OH)_{12}*26H_2O$) sisaldust.

Ettringiit võib hüdratiseeritud tuhasettest moodustada kuni 25% ning on seal sisalduvatest mineraalidest kõige reaktsioonivõimelisem. Ettringiidi tasakaaluline lahustumine viib lahusesse vabasid kaltsium-ioone, mis fosfaadi sadenemisel käituvad püsuvate tuumadena. Fosfori eemaldamisel hüdratiseeritud põlevkivituha abil toimuvale fosfaatide välja sadenemisele viitab kaltsiumfosfaadi moodustumine katsete käigus erinevatel fosfori kontsentratsoonidel. Tuhasette töötlemine fosforit sisaldava lahusega põhjustab ettringiidi ja portlandiidi osalise või täieliku lahustumise ning toob endaga kaasa kaltsiumkarbonaatide ja kaltsiumfosfaatide sademise. Need protsessid on tõestatud XRD ja SEM(SEM-EDS) analüüsidega.

Katsed näitavad, et hüdratiseeritud tuhasette fosfori sidumisvõime on suhteliselt hea (kuni 65 mg P g^{-1}) ning sidumisefektiivsus oli vahemikus 67-85 %. Sidumisefektiivsus ei ole võrreldes varasemate töödega (Lokotar (2002) ja Vohla (2004)) küll nii kõrge, kuid sidumisvõime 65 mg P g^{-1} on pea kolm korda kõrgem kui mistahes teisel uuritud materjalil. Fosfori eemaldamisel domineeriva lahustumise-sadenemise mehhanismi olemasolu võib kinnitada ka adsorptsiooni isotermide põhjal. Kõrge lahus/sete suhte puhul kasutati fosfori eemaldamise kirjeldamiseks Freundlich`i võrrandit, mille tulemuste põhjal võib oletada, et teatud tingimustel seotakse mingi osa fosforist adsorptsiooni teel sette pinnale.

Antud töö tulemused näitavad, et ettringiidi kiire lahustumine võib takistada hüdratiseeritud tuhasette pikaajalist kasutamist. Kui fosfori eemaldamist kontrollib üksnes ettringiit, kaotab tuhasete väga kiiresti oma sidumisvõime. See küsimus vajab edasist põhjalikumat uurimist. Sellest hoolimata võib hüdratiseerunud tuhasetet kasutada reoveest fosfori eemaldamiseks kõrge fosforisisalduse puhul, kui filtermaterjali perioodiliselt vahetatakse või kasutatakse tuhasetet koos muude materjalidega.