Phosphate removal by mineral-based sorbents used in filters for small-scale wastewater treatment

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ABSTRACT

The mineral-based sorbents Filtra P, Polonite[®], natural wollastonite and water-cooled blast furnace slag (WCBFS) were studied in terms of their PO_4 removal performance. Results from a long-term column experiment showed that both Filtra P and Polonite[®] removed > 95 % of PO_4 from the applied synthetic solution, and that the used filter materials had accumulated several (1.9-19) g kg^{-1} P. Phosphorus was removed also by natural wollastonite and WCBFS, but these materials were less efficient. Batch experiments on the used materials showed that the solubility PO_4 was considerably larger than the one expected for crystalline Ca phosphates such as hydroxyapatite, and results from investigations with attenuated total reflectance – Fourier-Transform infrared spectroscopy (ATR-FTIR) on the Filtra P material showed that the formed P phase was not crystalline. These evidence suggest that a soluble amorphous tricalcium phosphate (ATCP) was formed in the mineral-based sorbents; the apparent solubility constant on dissolution was estimated to log K_s = -27.94 (±0.31) at 21°C. However, since only up to 18 % of the accumulated PO_4 was readily dissolved in the experiments it cannot be excluded that part of the phosphorus had crystallized to slightly less soluble phases. In conclusion, Filtra P and Polonite are two promising mineral-based sorbents for phosphorus removal, and at least part of the accumulated phosphorus is present in a soluble form, readily available to plants.

1. Introduction

Recent research has identified the use of active filtration through alkaline media for the removal of phosphorus from domestic wastewater (Johansson and Gustafsson, 2000; Drizo et al., 2006; Shilton et al., 2006; Ádám et al., 2007). Active filtration belongs to a family of promising techniques for small-scale wastewater treatment, which can be used in combination

with other treatments such as wetland treatment systems and source separation / collection (Johansson, 1998; Valsami-Jones, 2001; Shilton et al., 2006). An attractive feature of the filter technique is that the nutrient-loaded filter media can be used in agriculture as P fertilizer and soil conditioner (Hylander et al., 2006). This would be of help in rural areas around the world since many houses are devoid of or use private wastewater treatment systems that are not acceptable from sanitary and environmental point of view. However, many aspects of these techniques remain unclear. Most crucial is perhaps the lifetime of the filters and the risk of unacceptable contamination due to metal accumulation in the filters.

Examples of filter materials include metallurgical slags (Johansson and Gustafsson, 2000; Shilton et al., 2006) and various products that contain lime and/or alkaline Ca silicates such as Polonite (Brogowski and Renman, 2004) and Filtralite P (Kvarnström et al., 2004). These filter materials generally have pH values above 9 and they release Ca to the water phase, which causes subsequent removal of P. The formation of Ca phosphates explains the observed P removal. An obvious candidate is precipitation of hydroxyapatite (HAp) (Johansson and Gustafsson, 2000; Drizo et al., 2006).

A large supersaturation is required to form HAp within a short time. In many filter media it is likely that the supersaturation is sufficient and that HAp is formed. Formation of HAp in filter media has recently been shown by some researchers, who identified HAp by use of X-ray diffraction techniques (Khadhraoui et al., 2002; Drizo et al., 2006). Once formed, phosphate bound to HAp would not be easily released in a short time due to the low solubility of HAp. However, other more soluble Ca phosphates may also be formed at least initially (Valsami-Jones, 2001). For example, Kim et al. (2006) were able to identify both ATCP (amorphous tricalcium phosphate, $Ca_3(PO_4)_2$) and DCP (dibasic calcium phosphate, $CaHPO_4$), as well as

HAp, in converter slag used as seed material for phosphorus crystallization. Similarly, by

means of XANES (X-ray absorption near-edge structure) spectroscopy Sato et al. (2005)

found that ATCP and DCP were important phases in poultry manure. No OCP (octacalcium

phosphate, $Ca_4H(PO_4)_3$) or HAp were found although both of these more crystalline phases

are common in soils (Beauchemin et al., 2003). With this evidence in hand it seems likely that

used filter materials from wastewater treatment may contain readily soluble Ca phosphates

such as ATCP and DCP. This is supported by results from plant uptake experiments that

show that the retained P in both slags and Filtralite P is easily accessible (Hylander and

Simán, 2001; Kvarnström et al., 2004; Hylander et al., 2006).

The purpose of this study was to evaluate the performance of four different filter materials for

their ability to remove phosphate by means of a column experiment mimicking a filter system

in the field, and to cast light on the P removal mechanisms by means of solubility experiments

and infrared spectroscopic investigations on the used filter materials. To our knowledge, this

paper is the first to report the solubility of P in used alkaline filter materials.

2. Materials and methods

2.1. Filter materials

The elemental composition of the four filter materials is shown in Table 1. Polonite® is

manufactured from siliceous sedimentary Opoka rock in Poland that is heated to 900^oC

(Brogowski and Renman, 2004). Samples of Polonite® were supplied by Bioptech AB,

Hallstavik, Sweden. The filter material is available in different fractions and the 2-5.6 mm

particle size was used in our experiment. The material consists mainly of reactive lime and

wollastonite phases, which contribute to the strongly alkaline conditions. This material has earlier proved to be successful for P removal (Hylander et al., 2006). Filtra P is produced after heating a mixture of limestone, gypsum and Fe oxides. The product, which is strongly alkaline because of its content of $Ca(OH)_2$ (about 20 %), is granulated in a particle size of 2-13 mm for use as a filter material in wastewater treatment. Samples of Filtra P were obtained from Nordkalk Oyj Abp, Pargas, Finland. Water-cooled blast furnace slag (WCBFS) is a by-product from the steel industry and contains amorphous glasses and a small amount of crystalline silicates of the åkermanite / gehlenite type. The particular WCBFS sample used in this study was supplied by Merox AB, Oxelösund, Sweden. It had a particle size of 0-4 mm and was pretreated with 1 % CaO to increase its alkaline reaction. Natural wollastonite has been shown to be able to remove ammonium from urine (Lind et al., 2000). Because of its high pH (which can be explained by the dissolution of wollastonite) and because of its mineralogical similarity to Polonite, we decided to investigate also its ability to remove phosphorus. The sample used in this investigation was supplied by Minpro AB, Stråssa, Sweden. It had a particle size of 1-3 mm and contained 27.3 % wollastonite, as revealed by quantitative X-ray diffraction. The remainder consisted mostly of feldspars (39.9 %), diopside (10.8 %) and quartz (10.4 %).

2.2. Column leaching experiment

To provide information on the long-term P removal performance of the filter materials, a column leaching experiment was carried out. Columns were constructed of PVC tubes of 60 cm length and 10 cm inner diameter and filled with a 50 cm layer of the appropriate filter material. However the Polonite was sieved for removal of particles less then 2 mm and its composition was changed by addition of 10 % (w/w) *Sphagnum* peat. The bottom of the

columns was filled with a 2 cm layer of gravel, and with a coarse plastic (HDPE) filter to prevent loss of material from the columns. The experiment was carried out in room temperature (20 ^{o}C) under water-saturated conditions. A synthetic solution with PO_4-P (orthophosphate ions quantified as P) and NH_4-N (ammonium ions quantified as N) concentrations of 5 mg·dm^{-3} and 30 mg·dm^{-3} respectively was prepared by adding KH_2PO_4 and NH_4Cl to 200 dm^{-3} of tap water. These concentrations are within the range normally found in wastewater (see, e.g., Vymazal, 2007). The solution was stored in a container and pumped automatically to the top of each column three times per day (08.00, 13.00, 17.00) throughout the experimental period of 68 weeks. The loading rate was differentiated so that the pumped volumes were roughly proportional to the pore volume of the particular filter material (Table 2). One pore volume (pv) was defined as nV_t, where n is the effective transport porosity and V_t is the total volume of the filled column.

Samples were taken from influent and effluent weekly during the first 40 weeks, thereafter biweekly. The pH was analyzed directly after collection. The samples were then stored in a freezer at -18 ^{o}C until analysis of PO_4-P. Before analysis, the samples were filtered through a 0.45 μm Micropore filter. Inorganic PO_4-P was determined colorimetrically (acid molybdate method) using flow injection analysis (Aquatec-Tecator autoanalyzer). The percentage removal of P was calculated as the difference between influent and effluent concentrations at the same sampling occasion. On the basis of all removal rates for the entire period the mean P removal percentages were determined. Apart from PO_4-P, NH_4-N was also quantified and nitrogen removal rates calculated; however these results will be dealt with in a later publication. However, there was no evidence for precipitation of ammonium-containing phosphates in the experiments; all solutions were consistently undersaturated with respect to struvite (a solubility constant of 10$^{-12.6}$ was used; Doyle and Parsons, 2002).

The synthetic solution and the loading schedule were selected to mimic conditions frequently encountered in onsite wastewater treatment using reactive filter media. The concentrations of P and N represent concentrations typically found in wastewaters.

After termination of the column experiment, the columns were divided into 5-cm sections and sampled. Part of the samples from the uppermost layers (0-5 cm) and from the 15-20 cm layer of the Filtra P columns were air-dried, gently crushed in a mortar, and then examined by a Perkin-Elmer S2000 Fourier Transform infrared (FTIR) spectrometer. The instrument was run in the attenuated total reflectance (ATR) mode using a Golden-Gate diamond cell. The spectra were compared to those recorded for filter material samples that were not used in the column experiment.

Total concentrations of P were determined in three layers (0-5, 5-10, 40-50 cm) of the used filter materials using ICP-OES. Representative samples were dried and melted with $LiBO_2$ and thereafter dissolved in HNO_3 before analysis.

2.3. Solubility studies

To cast light on the mechanisms that control the solubility of PO_4 in the materials, batch experiments were carried out on both unused samples and on samples from the 0-5 cm layer of the used filter materials. Including both unused and used samples in the study provided a means to approach the equilibrium state from both supersaturation and undersaturation. Briefly, 2.00 g material (for wollastonite samples 3.00 g) was suspended in 35 cm^{-3} solutions of variable composition in polypropylene centrifuge tubes and then equilibrated for 5 d in an end-over-end shaker at 21°C and at a background ionic strength of 0.1 mol$\cdot$dm^{-3} (NaNO$_3$ was

used as supporting electrolyte). For the used filter materials wet samples were used, which means that the actual liquid to solid (L:S) ratios were larger; 56.6 for Filtra P, 27.7 for Polonite, 27.3 for WCBFS and 12.0 for wollastonite. To produce a range of pH values and PO_4-P concentrations in the suspensions, various amounts of nitric acid (0-10 mmol·dm^{-3}) were added. To some suspensions with 10 mmol·dm^{-3} nitric acid, an additional 5-20 mmol·dm^{-3} oxalic acid was added, to further increase the variation in pH values and PO_4-P concentrations. After equilibration, the suspensions were centrifuged, their pHs were measured (using a Radiometer combination electrode) and they were filtered with 0.2 μm single-use filters (Acrodisc PF). Directly after filtration, the alkalinity of the samples was measured through addition of 0.02 M HCl to pH 5.4. Samples were analyzed for inorganic PO_4-P with the acid molybdate method. Finally, total dissolved Ca, Mg, and Si were determined by plasma emission spectroscopy using a Jobin-Yvon JY24 ICP instrument.

The speciation of leachates from the batch experiments were processed with Visual MINTEQ (Gustafsson, 2006) using equilibrium constants for aqueous complexes (i.e. $CaHCO_3^+$, $CaPO_4^-$, $CaHPO_4^0$, etc.) from the default Visual MINTEQ database, which mostly relies on the NIST Critical Stability constants, version 7.0 (Smith et al., 2003). Calculated ion activity products were compared to solubility constants given in the literature (Table 3). For ATCP, for which few solubility data exists, constants were calculated from raw data given for two amorphous calcium phosphates of varying crystallinity, referred to as ACP1 and ACP2 by the authors (Christoffersen et al., 1990). These thermodynamic data should only be considered as rough estimates, not least because the observed Ca:P ratios in the precipitates were between 1.28 and 1.38, which is slightly less than the ideal ratio of 1.5. The solubility data for OCP were also calculated from experiments conducted by Christoffersen et al. (1990).

3. Results

3.1. Long-term phosphate removal and pH development in columns

The columns received between 1.1 to 1.8 m^3 of synthetic solution during the experiment (Table 2). Technical problems with pumping caused less discharge of solution than that was intended. The column filled with Filtra P clogged after 971 pv and was closed for that reason. Its pore volume decreased and was found to be 0.45 dm^3 less than at the start.

The PO_4-P concentration in the influent was not constant; it averaged 4.5 ($\pm$0.9) $mg \cdot dm^{-3}$. The variation probably resulted from biological activity in the container where the solution was stored.

Clear material-specific differences in PO_4-P removal were observed during the course of the experiment. Wollastonite was the least efficient material in terms of PO_4-P removal; on average 51.1 % of P was removed. This is partly explained by the low pH in these columns; already after 100 pore volumes (134 dm^{-3}), the pH of the effluent was more or less equal to that of the inflow (around pH 8). Water-cooled blast furnace slag (WCBFS) removed more than 95 % P during the first 300 pore volumes (240 dm^{-3}), and afterwards the P retention efficiency decreased steadily; averaged over the whole time period the P removal was 85.6 %. The pH of the column effluent decreased from 11.4 at the start of the experiment to 8.8 at the end.

The two most strongly P-retaining materials were Polonite and Filtra P. Filtra P was slightly more efficient; on average it retained 98.2 % P, whereas Polonite retained 96.7 %. Disintegration of Filtra P was observed, particularly in the beginning of the experiment, as a yellow-brown colour in the effluent. In both cases the pH remained alkaline, particularly so for Filtra P, for which the column effluent pH decreased from 12.9 to 11.6 during the experiment (the corresponding pH values for Polonite was 11.7 and 9.5).

The top layer (0-5 cm) of each material showed the highest concentration of accumulated P (Table 4). The concentration decreased significantly with depth of the columns; this was especially the case in the Filtra P and Polonite materials.

3.3. Characterization of unused and used filter materials with ATR-FTIR

All four unused samples contained peaks at ~1420 and 870 cm^{-1}, characteristic for the carbonate anion in calcite (Fig. 1). Another common constituent was water with characteristic absorption peaks near 3500 and 1640 cm^{-1}. Other peaks in the spectra represent material-specific peaks. For example, the presence of wollastonite (β-CaSiO$_3$) in both Polonite and natural wollastonite was indicated by peaks near 1056, 960, 902 and 680 cm^{-1}(Atalay et al., 2001). The observation that wollastonite was an important constituent of Polonite is in agreement with earlier studies employing chemical dissolution techniques and X-ray diffraction (Eveborn, 2003; Brogowski and Renman, 2004). The unused Filtra P sample was dominated by a number of peaks related to sulphate minerals such as gypsum, *i.e.* the broad sulphate peak near 1100 cm^{-1}. The split of the H$_2$O peak near 1640 cm^{-1} to two peaks is characteristic for gypsum. Furthermore, the OH-stretching peak at 3640 cm^{-1} may indicate the

presence of ettringite. The presence of a small amount of ettringite was supported by the product data sheet supplied by the manufacturer (Nordkalk Oyj Abp, unpublished)

The used filter materials resembled the original samples except that the intensity and position of the carbonate peaks changed somewhat, and that a new peak appeared near 1025 cm^{-1}, which likely corresponds to the ν_3 band of the phosphate anion (Fig. 1). This peak was seen most clearly in the Filtra P and Polonite samples. In the Filtra P 0-5 sample, the peak position was slightly lower probably because of overlap with a silicate peak near 980 cm^{-1}, which is visible as a shoulder in the original Filtra P sample and also in the Filtra P 10-25 cm sample. Gypsum, which was present in large amounts in the unused sample, had disappeared completely. In the wollastonite sample the phosphate peak was visible as a weak shoulder, whereas in the WCBFS sample there was no clear evidence at all for a phosphate peak, probably because of overlap with neighbouring silicate peaks. In the Filtra P 0-5 cm sample, where the phosphate peak was a dominant one, there was no indication of a second high-wave-number ν_3 component at around 1050-1070 cm^{-1}, which would be typical for crystalline hydroxyapatite (Soejoko and Tjia, 2003). Similarly, OCP and dibasic calcium phosphates (DCP and DCPD) are not very likely candidates since these compounds are expected to possess two or more well resolved peaks in the ν_3 region (Fowler et al., 1993; Sivakumar et al., 1998). Hence the results for the Filtra P sample indicate that the formed phosphate phase was poorly crystalline in nature. The presence of a single peak near 1025-1030 cm^{-1} is in general agreement with amorphous tricalcium phosphate (Gee and Deitz, 1954), but the peak can also be attributed to the presence of other poorly crystalline phosphate minerals (e.g., Al and Fe phosphates) as well as to adsorbed phosphate.

3.3. Solubility of phosphate in the filter materials

All PO_4-P that was added to unused WCBFS, Filtra P and Polonite was removed by 100 % in batch experiments. This can be explained by the very high initial pH (= 11-13) and dissolved Ca in these samples, which caused PO_4 to precipitate quantitatively as calcium phosphates. Addition of PO_4-P as NaH_2PO_4 did not cause a sufficiently high pH reduction to increase PO_4-P to detectable levels. By contrast, no added PO_4-P was bound to natural wollastonite, for which pH and dissolved Ca was lower. Therefore the batch experiments on unused filter materials provided little useful information about solubility-controlling mechanisms.

Batch experiments performed on the surface layer (0-5 cm) of the spent filter materials revealed that the pH had decreased considerably as a result of the column experiment. For example in the Filtra P sample, the pH was only 7.8 compared to 12.6 before the experiment. The release of PO_4-P from the samples was also rather high. On further acidification of the sample, the soluble PO_4-P concentration of the Filtra P sample increased further, which would be expected if a Ca phosphate controls the P solubility (Fig. 2). At the lowest pH almost 2 mM PO_4-P was dissolved, which was equivalent to 3.5 g P kg^{-1} dry matter, or 18 % of the total amount of accumulated P (see Table 4). The same trend, although much weaker, was observed for wollastonite. For WCBFS the dissolved PO_4-P concentration increased with increasing acid additions until pH 6.9, at which point 5.6 % of the total accumulated P had dissolved. Further pH reduction caused decreasing PO_4-P concentrations. A possible explanation is adsorption of PO_4-P to an oxide phase (Fe or Al oxide) at low pH in the slag. Interestingly, Pratt et al. (2007) showed that most of the retained P in a melter slag filter was associated with Fe and Al after 5 years of operation; the pH in their filter was reported to range from 6.7 to 7.4. For Polonite, the results are less clear because pH could not be

decreased below 7.6, when not more than 3.5 % of the accumulated P was dissolved. Results from ICP measurements indicate that the wollastonite matrix is dissolved near this pH (data not shown), which would prevent Ca phosphates from dissolving.

In an earlier study with other filter materials in which equilibrium was obtained only from supersaturation, it was hypothesized that hydroxyapatite (HAp) was formed (Johansson and Gustafsson, 2000); this was based on the observed slope between pH and $5\log\{Ca^{2+}\}+3\log\{PO_4^{3-}\}$. However, the data we present here are not in agreement with this hypothesis, because PO_4-P in the used filter materials was more soluble than would be expected from this equilibrium. Most of the samples were supersaturated with respect to HAp (Fig. 3). Two other candidates to control PO_4 solubility are DCPD (dibasic calcium phosphate dihydrate; $CaHPO_4\times2H_2O$) and DCP. However, most samples were undersaturated with respect to these phases, although the most acid Filtra P samples seemed to be in equilibrium with DCP or DCPD. At high pH however, the samples were far from equilibrium indicating that the results could not be resolved easily in terms of equilibrium with respect to DCP or DCPD. Many of the samples were relatively close to the solubility line of OCP (Fig. 3), indicating that OCP might be involved in determining PO_4-P solubility.

Finally ATCP, with the stoichiometric composition $Ca_3(PO_4)_2$, may also control PO_4-P solubility. As shown in Fig. 3, many samples were close to equilibrium with the less non-crystalline ATCP termed ACP2 (Christoffersen et al., 1990). Moreover, the pH dependence of the ion activity products were in better agreement with ACP2 than with OCP, which suggested that solubility control by ACP2 (or ATCP) was slightly more likely although a prominent role for OCP could not be ruled out from these observations only.

4. Discussion

Both Filtra P and Polonite had a remarkable potential to remove PO_4-P from solution, as evidenced by the results shown in Table 4. This suggests that they can be applied for a relatively long time in the field before saturation of phosphate occurs; this would be attractive from a sustainability perspective. In practice however, the lifetime of these materials is likely to be limited by their technical performance (*i.e.,* clogging). In the column experiment it was noted that severe clogging occurred for the Filtra P column and it was consequently shut down after 971 pore volumes. This seemed to be related to structural degradation of the material because of matrix dissolution and subsequent precipitation of secondary phases. In the field with real wastewater the lifetime is likely to be shorter for both materials because of inflow of particulate and colloidal matter.

As can be seen in Fig. 3, PO_4-P was slightly more soluble in the Polonite samples than in the Filtra P samples. The reason seems to be connected to the different response to the acid additions. For Filtra P increasing acid additions led to decreasing ion activity products for ATCP (Fig. 4), probably because dissolved PO_4-P reached equilibrium with respect to DCP or DCPD. For Polonite, the ion activity products for ATCP increased with increasing acid additions (Fig. 4). A possible explanation is that the acid addition initially released PO_4-P, which was then re-precipitated as ATCP during the batch experiment when pH was increased because of wollastonite dissolution. At the same time equilibrium with DCP/DCPD was not reached, allowing the ion activity products for ATCP to rise. Thus in many of the Polonite samples equilibrium may have been approached from supersaturation rather than from undersaturation.

It is of interest to compare the batch experiment results on PO_4-P solubility with those from the previous study (Johansson and Gustafsson, 2000), in which equilibrium was approached from supersaturation for a series of blast furnace slags (similar to WCBFS of the present study). Not surprisingly, the PO_4 solubility of these slag samples was slightly larger (Fig. 5). Below pH 10.5 the deviation between the two series of data was comparably large, which may suggest that equilibration from supersaturation is slow at low pH. At higher pH the ion activity products were in better agreement. These observations, together with the ATR-FTIR evidence, provide support for the formation of ATCP as a reactive surface phase on the filter materials. An estimate of the apparent solubility constant for ATCP was made by averaging the logarithms of the ion activity products for samples for which no acid additions had been made. This resulted in log K_s = -27.94 ± 0.31(1σ, n = 7) As is seen in Fig. 5, the solubility line is close to the observed values for many samples, particularly at pH 6.6 and higher.

The observation that a soluble Ca-P phase, probably ATCP, had accumulated in the filter materials suggests that at least part of the PO_4-P is easily available to plants. However, only between 3.5 and 18 % of the accumulated PO_4-P was readily dissolved from the used filter materials in the batch experiments. There may be several reasons for this, partial crystallization to slightly less soluble phases (such as HAp) or adsorption of PO_4-P to Fe / Al oxide components are two possibilities. Thus more detailed spectroscopic studies need to be performed to fully elucidate the solid-phase speciation and reactivity of the accumulated phosphates.

5. Conclusions

Polonite$^{®}$ and Filtra P$^{®}$ are two promising filter materials for removal of PO$_4$-P from households. In column experiments using synthetic solutions these materials were able to accumulate between 1.9 and 19 g kg^{-1} PO$_4$-P, maintaining a PO$_4$-P removal efficiency of > 95 %. However, Filtra P is susceptible to clogging because of structural degradation; this will limit its practical lifetime in field applications. Water-cooled blast furnace slag and natural wollastonite were also able to remove PO$_4$-P, although less efficiently. Batch experiments on used filter materials indicated that amorphous tricalcium phosphate (ATCP) had formed. This means that at least part of the accumulated PO$_4$-P is readily available to plants.

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Table 1. Original elemental composition of the four filter materials

	Filtra P	Polonite	WCBFS	Wollastonite
Si	14.6	241	155	276
Al	11.1	27	69.7	54.6
Ca	312	245	216	151
Fe	41.3	16.5	3.11	21.5
K	4.89	9.15	6.18	26.2
Mg	4.68	4.4	97.6	13.3
Mn	0.317	0.121	4.69	0.894
Na	1.46	1.46	4.28	12.3
P	1.44	0.34	<0.1	<0.1
LOI (% TS)	20.9	5.1	0.8	1

The unit is g kg^{-1} dry matter, unless otherwise stated

Table 2. Pore volumes of the columns and daily load of NP (nitrogen-phosphorus) solution

Material	Pore volume (dm^3)	Pore volume (% of bulk material)	Daily load (dm^3 m^{-2})	No. of pore volumes of water applied during 68 weeks
Filtra P	1.39	34.4	710	971[a]
Polonite	1.40	35.6	530	1410
WCBFS	0.80	20.8	340	1590
Wollastonite	1.34	35.0	610	1700

[a]The Filtra P column was shut down after 35 weeks because of clogging

Table 3 - Solubility constants and heats of reaction for Ca phosphates used in the calculations

Reaction	log K_s (25°C)[a]	ΔH_r (kJ/mol)[a]
HAp: $Ca_5(PO_4)_3OH(s) + H^+ \Leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + H_2O$	-44.3[b]	0
OCP: $Ca_4H(PO_4)_3(s) \Leftrightarrow 4Ca^{2+} + 3PO_4^{3-} + H^+$	-47.95[c]	-105[c]
DCP: $CaHPO_4(s) \Leftrightarrow Ca^{2+} + PO_4^{3-} + H^+$	-19.28	31
DCPD: $CaHPO_4 \times 2H_2O(s) \Leftrightarrow Ca^{2+} + PO_4^{3-} + H^+ + 2H_2O$	-19.00	23
ACP2: $Ca_3(PO_4)_2(s) \Leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	-28.25[c]	-87[c]
ACP1: $Ca_3(PO_4)_2(s) \Leftrightarrow 3Ca^{2+} + 2PO_4^{3-}$	-25.5[c]	-94[c]

[a]Unless otherwise stated, the values are from Smith et al. (2003).

[b]Solubility of HAp at 21°C (McDowell et al., 1977).

[c]Calculated from raw data given by Christoffersen et al. (1990)

Table 4 - Total concentration of P (g kg^{-1} dry matter) in selected layers of the filter materials after termination of the column experiment

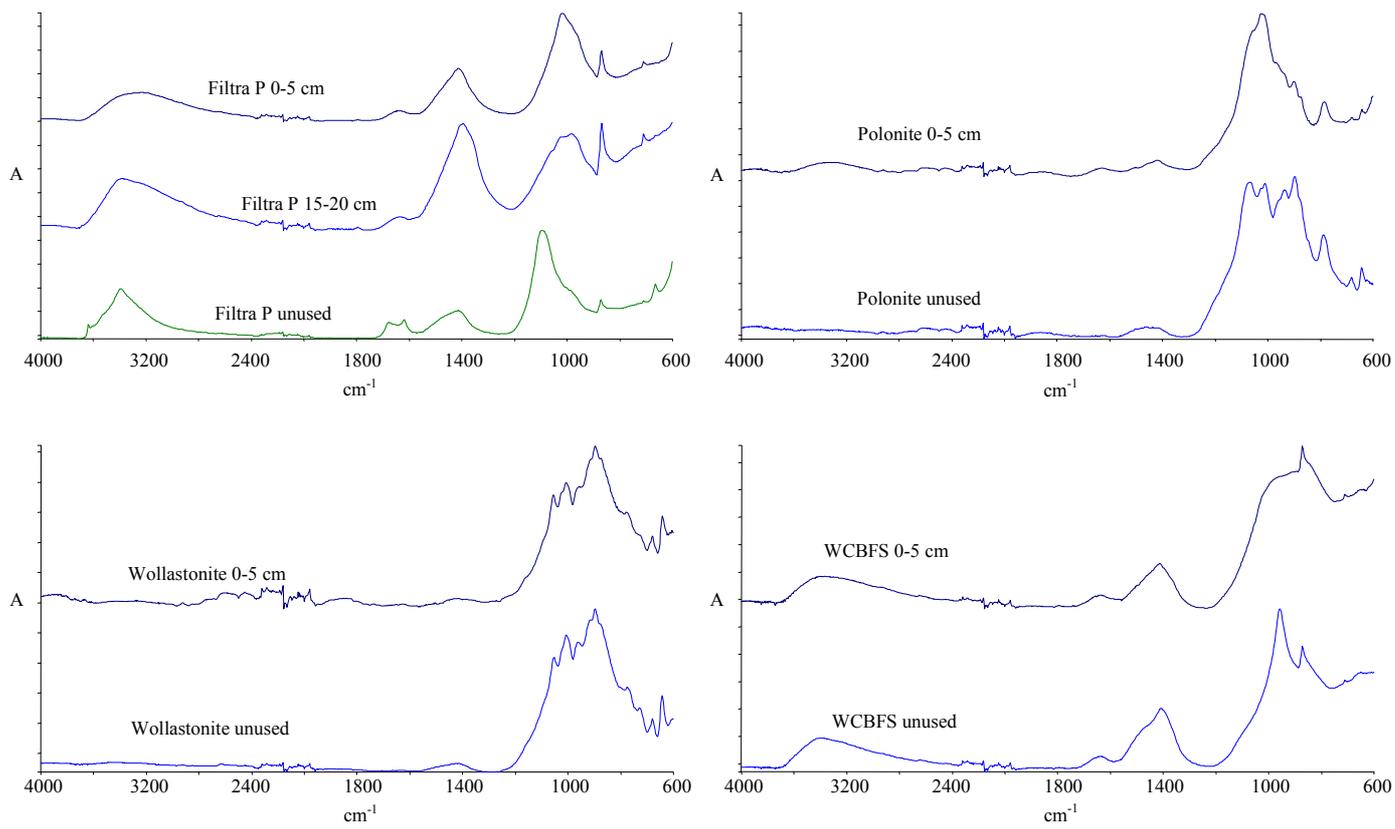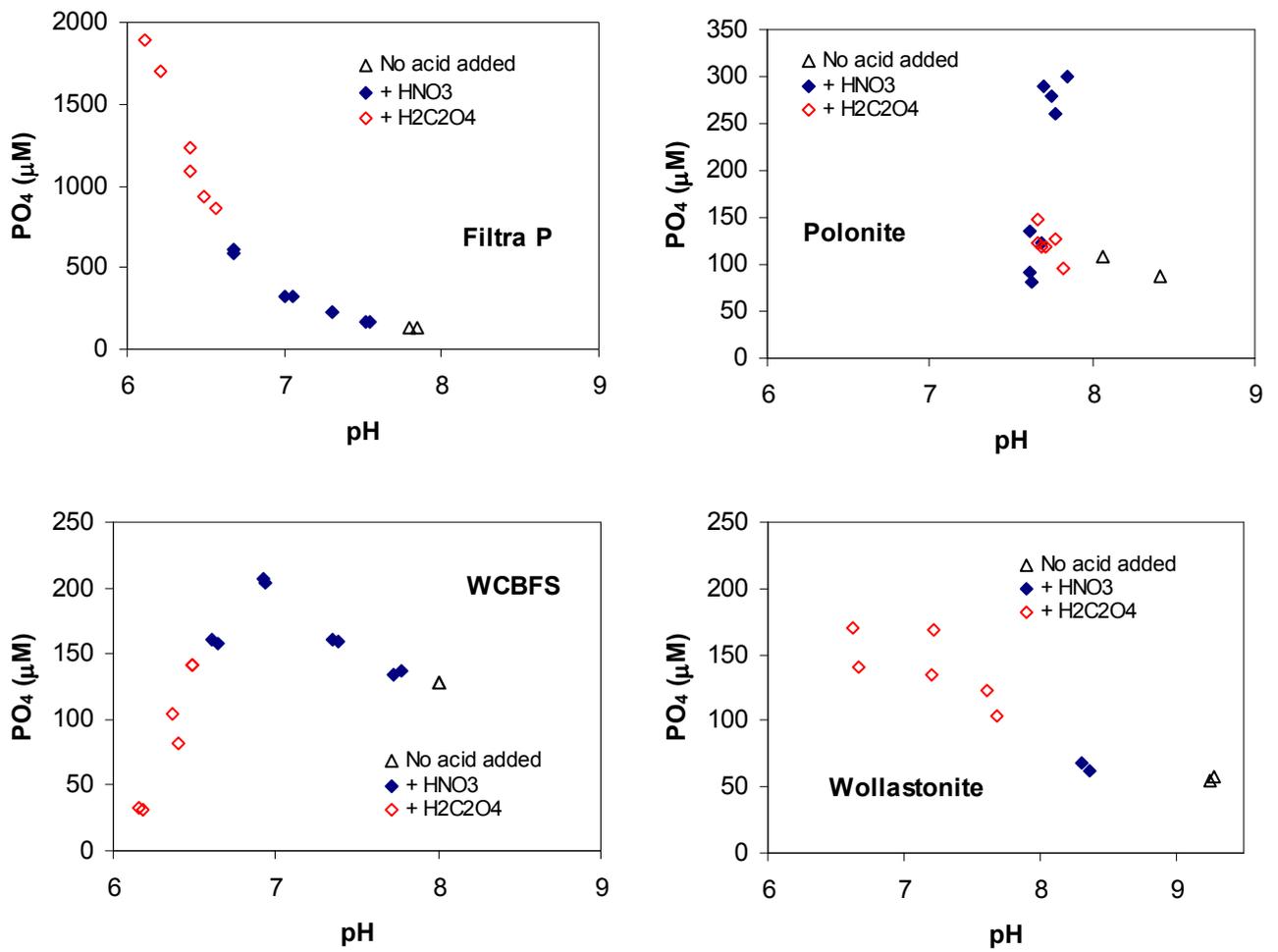| Layer (cm)	Filtra P	Polonite	WCBFS	Wollastonite
0-5	19.4	7.39	3.11	0.467
5-10	13.7	5.31	2.25	1.80
40-50	2.47	1.87	1.00	0.589

Fig. 1 - ATR-FTIR spectra of used and unused filter materials.

Fig. 2 – Dissolved PO$_4$ (µmol·dm^{-3}) from the 0-5 cm layers of the used filter materials as a function of pH, as recorded in batch experiments with varying amounts of acid.
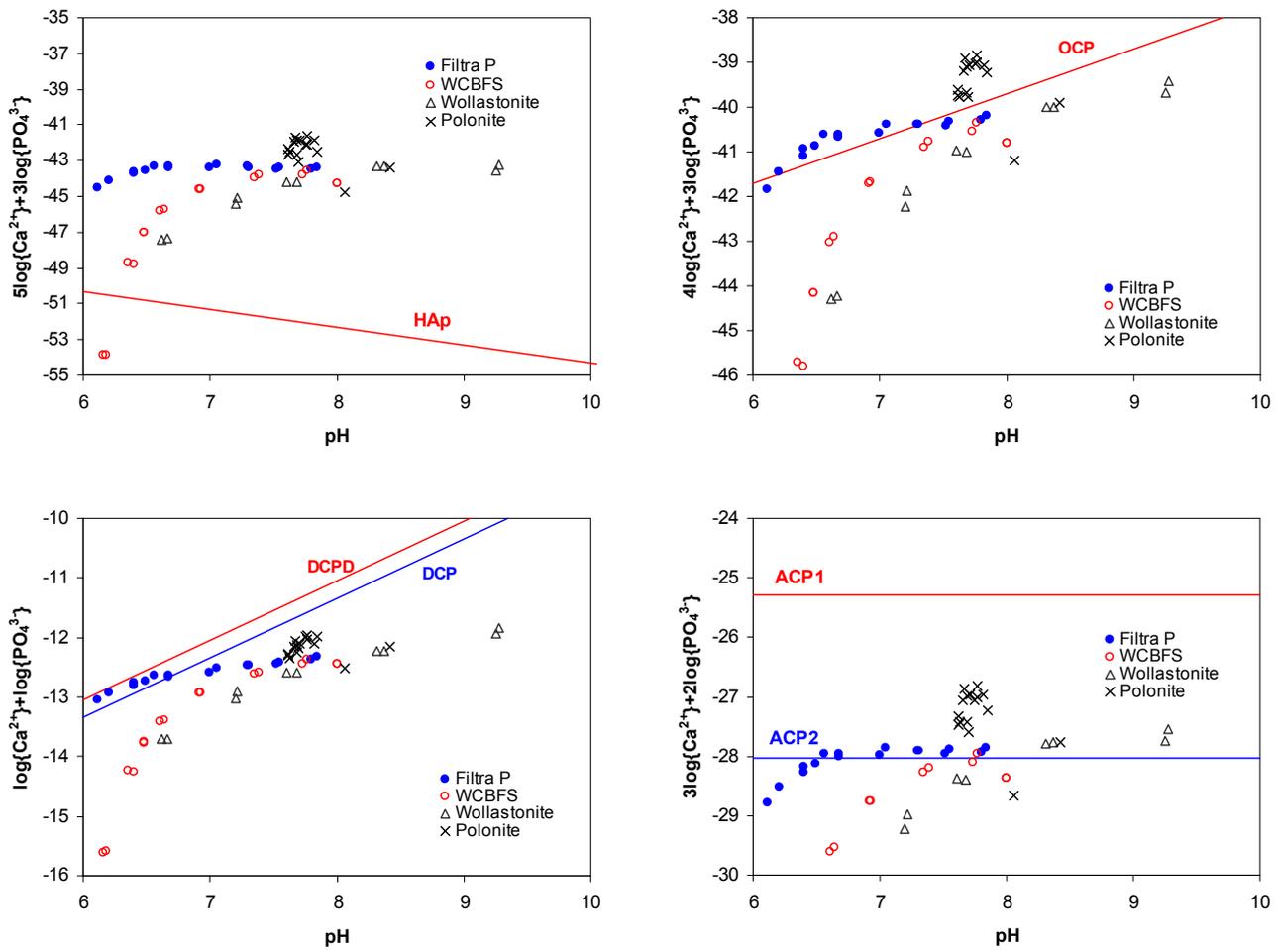
Fig. 3 - Solubility diagrams for the 0-5 cm layer of the used filter materials. The points represent the calculated solution activities in the batch experiment extracts. The solubility lines are calculated from the data given in Table 3. Data points above the lines indicate supersaturation.
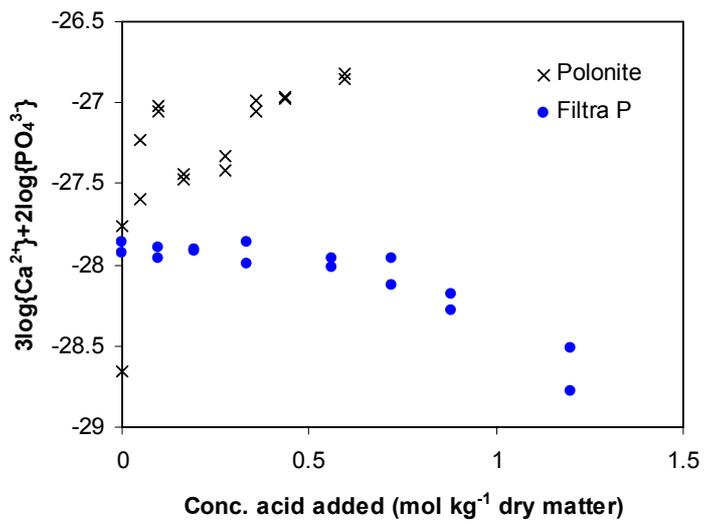
Fig. 4 - The logarithm of the ion activity product of ATCP, $3\log\{Ca^{2+}\} + 2\log\{PO_4^{3-}\}$, as a function of the concentration of added acid for the 0-5 cm layers of Filtra P and Polonite.
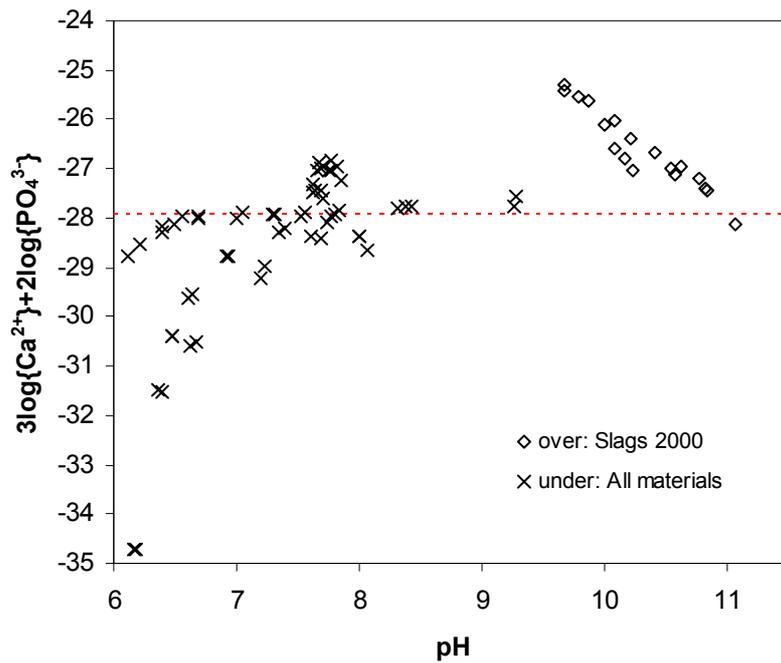
Fig. 5 – Solubility diagram for a) slag samples in which equilibrium was approached from supersaturation (Johansson and Gustafsson, 2000), and b) the materials from the present study, in which equilibrium was approached from undersaturation. The dotted line indicates the suggested solubility constant (= $10^{-27.94}$ at 21°C) for the ATCP phase formed.