CALCIUM SILICATE HYDRATE TRIGGERED PHOSPHORUS RECOVERY –
AN EFFICIENT WAY TO TAP THE POTENTIAL OF WASTE- AND PROCESS WATERS
AS KEY RESOURCE

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ABSTRACT

The global economic situation requires the development of sustainable concepts, in order to
provide potential recyclables from waste and to recirculate them to the cycles of matter.
Considering furthermore the increasing limitation of global phosphate rock resources, the
recovery of phosphate from various waste- and process waters is vitally important. Therefore,
research has recently been focused on the development of technologies for an efficient
recovery of phosphorus within the waste- and process water treatment. Approaches are based
on the generation of phosphate minerals as substitutes to be processed in the phosphate
industry or to be straightly applied as fertilisers in agriculture. One approach to achieve this
goal is the use of calcium silicate hydrates (CSH), which are by-products of the building
material industry, in order to recover phosphorus as a potential recyclable by crystallisation.
This was realized with the P-RoC process, the P-recovery from the aqueous phase by
crystallisation. Investigations show that, apart from hydrochemical parameters, the physical
and chemical properties of the applied CSH compounds play a decisive role as trigger
materials for the P-elimination efficiency. Thus, the nature and quality of the generated
products could be specifically optimized.

KEYWORDS

Phosphorus recovery, calcium silicate hydrate, calcium phosphate, ESEM, EDX, mineralogy

INTRODUCTION

Extrapolating the current consumption of fertilisers, the finiteness of low-contaminated
natural resources of phosphorus (P) as an essential and irreplaceable nutrient will become a
severe problem in the next ~100 years (ATV, 2003). These facts imply the necessity to search
for alternative resources of phosphorus. Municipal wastewater treatment plants (WWTP) or
phosphorus-rich industrial process waters are such key resources for the generation of solid
potential recyclables in terms of calcium phosphates. These products could optionally be used
(i) as phosphate rock substitute for the phosphate industry or (ii) as a fertiliser in agriculture,
depending on the product properties. Calcium silicate hydrates (CSH) proved to be suitable
and efficient materials (Berg et al., 2005a) to trigger the kinetically inhibited formation of
calcium phosphate compounds both, in laboratory and semi-technical scale experiments,
carried out in fixed-bed and expanded bed mode. In this way, P was eliminated and recovered
straight from the aqueous phase in one single process – the P-RoC process (Berg et al.,
2005b) - without the addition of further chemicals.
Mineralogical investigations of the generated products showed the formation of different kinds of calcium phosphate compounds. Besides hydroxylapatite (HAP) as the most stable one and the main component of natural phosphate rock, the more soluble brushite (di-calcium phosphate di-hydrate, DCPD) was formed. According to this experimental setup it is possible to specifically control the conditions for the formation of HAP as phosphate rock substitute or the better water-soluble DCPD. The latter is considered to be applied as a fertiliser due to the plant availability of phosphorus.

**METHOLOGY**

**Calcium silicate hydrate compounds (CSH) as trigger materials**

Calcium silicate hydrate compounds (CSH), readily available compounds from the building material industry, were used as trigger and carrier material in order to fix phosphorus straight from the aqueous phase. Some information about the different CSH compounds is listed in Table 1.

<table>
<thead>
<tr>
<th>CSH compound</th>
<th>Grain size [mm]</th>
<th>Specific surface area (SSA) [m²/g]</th>
<th>Mineral composition</th>
<th>Costs [€/Mg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.6-1.3</td>
<td>30</td>
<td>Tobermorite, quartz</td>
<td>240</td>
</tr>
<tr>
<td>B</td>
<td>0.1-1.6</td>
<td>50</td>
<td>Tobermorite, quartz</td>
<td>250-300</td>
</tr>
<tr>
<td>C</td>
<td>0.5-1.0</td>
<td>40</td>
<td>Tobermorite, quartz</td>
<td>800</td>
</tr>
</tbody>
</table>

**Long-term experiments in laboratory- and semi-technical scale**

As a first approach, fixed bed column experiments (0.08 L) were carried out in laboratory scale with CSH compounds A, B and C (Table 1) as filter media, using municipal wastewater, i.e. secondary effluent of a biological wastewater treatment plant (WWTP) spiked by a NaH₂PO₄·H₂O (p.a. Merck) stock solution to a characteristic P concentration of 10 mg/L P (Table 2).

The experiments were repeated with higher initial P concentration of 25 mg/L P using CSH material B. Furthermore, industrial process water with a P-concentration of ~ 400 mg/L P (Table 2) was also treated with CSH material B in laboratory scale.

Fixed bed experiments were scaled up (24 L) with side-stream supernatant of the Phostrip process (Kaschka and Weyrer, 1999) with a P-concentration of about 25 mg/L using CSH compound B (Table 1, 2).
In order to avoid the deficiencies of fixed bed technology in semi-technical scale (Berg et al., 2005c), further experiments were carried out in expanded bed mode (40 L reactor) with secondary effluent spiked to 25 mg/L P using CSH compounds A, B and C for comparison.

Table 2 - Composition of waste- and process waters as key resource for phosphorus recovery by means of CSH compounds; DIC (dissolved inorganic carbon), DOC (dissolved organic carbon)

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>P [mg/L]</th>
<th>Ca [mg/L]</th>
<th>DIC [mg/L]</th>
<th>DOC [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-spiked secondary effluent</td>
<td>7.0±0.3</td>
<td>10, 25</td>
<td>100</td>
<td>60</td>
<td>5-10</td>
</tr>
<tr>
<td>Phostrip supernatant</td>
<td>7.4±0.2</td>
<td>25</td>
<td>60</td>
<td>60</td>
<td>10-50</td>
</tr>
<tr>
<td>Industrial process water</td>
<td>6.2</td>
<td>400</td>
<td>700</td>
<td>20</td>
<td>2000</td>
</tr>
</tbody>
</table>

Analysis

Analysis of the water samples

The pH value, P- and Ca-concentration of in- and effluents were monitored according to relevant EU-DIN norms. DIC and DOC of the original waste- and process waters used were measured with a DIMA-TOC 100 Analyzer (DIMATEC Analysentechnik GmbH, Germany).

Analysis of the original CSH compounds and the generated products

Pore size distribution and bulk porosity of the original CSH compounds A, B and C were determined by mercury intrusion porosimetry by a Porotec Pascal 140 (up to 3,5 bar) and Pascal 440 (up to 2000 bar) system. The calculation of the pore size distribution and the porosity were performed by the Porotec Software.

The generated products were analyzed with respect to the yield of total P (Ptot) by hot nitric acid (65 %) digestion (AL-SOP AH 301 W).

Preparation of thin sections (30 µm, sample material was embedded in blue epoxy resin) and microscopic investigations of the original CSH compounds gave information about the morphology and location of newly formed crystals and the potential occurrence of amorphous compounds. Cross sections of single particles were prepared by fixation in epoxy resin and polishing. They were investigated by ESEM (Environmental Scanning Electron Microscope, XL 30 FEG, Philips). The chemical composition was semi-quantitatively analyzed by ESEM-coupled EDX (Energy dispersive X-Ray Analysis). Detailed qualitative and quantitative chemical composition was detected by XRF analysis (X-Ray Fluorescence Analysis, Rh tube, 50 kV voltage, Spectrace 5000, Tracor). The mineralogical composition of the original CSH
compounds and the generated products, i.e. the nature of calcium phosphate formed, was investigated by XRD (X-Ray Diffraction, D5000, Siemens, CuKα radiation). In addition, specific surface area (SSA) and microporosity of the CSH compounds was investigated by nitrogen adsorption according to multi-point BET (Brunauer et al., 1931) using the Quantachrome Autosorb 1-MP.

Regarding the potential of plant availability of P, elution experiments were carried out with desalinated water according to VDLUFA (1999).

RESULTS

Characterization of the original CSH trigger materials A, B and C

Chemical composition

All investigated calcium silicate hydrate compounds (CSH) showed an SiO₂ content of 40 – 56 % and a CaO content of ~ 30 % as main components (Table 3). Material B obviously exhibited comparatively the lowest Fe₂O₃ concentration as well as significant low heavy metal concentrations. In contrast, CSH material C was more enriched in Fe₂O₃, Al₂O₃ and heavy metals.

Table 3. Chemical composition of the original seed materials A, B and C

<table>
<thead>
<tr>
<th></th>
<th>SiO₂ (%)</th>
<th>Fe₂O₃ (mg/kg)</th>
<th>Al₂O₃ (mg/kg)</th>
<th>P₂O₅ (mg/kg)</th>
<th>CaO (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>U (mg/kg)</th>
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</thead>
<tbody>
<tr>
<td>material A (original)</td>
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<td>1.1</td>
<td>2.5</td>
<td>0.1</td>
<td>27</td>
<td>85</td>
<td>22</td>
<td>70</td>
<td>&lt;5</td>
<td>&lt;0.3</td>
<td>&lt;10</td>
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<tr>
<td>material B (original)</td>
<td>56</td>
<td>0.2</td>
<td>0.1</td>
<td>0.03</td>
<td>30</td>
<td>9</td>
<td>8</td>
<td>20</td>
<td>&lt;5</td>
<td>&lt;0.3</td>
<td>&lt;10</td>
</tr>
<tr>
<td>material C (original)</td>
<td>40</td>
<td>1.8</td>
<td>3.2</td>
<td>0.1</td>
<td>34</td>
<td>152</td>
<td>62</td>
<td>107</td>
<td>11</td>
<td>2</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

Porosity

In Figure 1 the results of the analysis of the pore size distribution and total porosity of the original CSH materials A, B and C by mercury intrusion are presented. The investigated materials showed significant differences in the pore size distribution as well as in the total porosity: CSH material C had lowest total porosity with about 46 %, whereas the total porosity of CSH materials A and B was higher with 61 % and 71 %, respectively.
CSH material C did not show any pores in the pore diameter range of micro capillary pores (~ 0.05 – 2 µm; Gerdes, 2002, Setzer, 1991, IUPAC, 1971), which play a decisive role for transport processes in cement-based materials. Material C exhibited its maximum pore size distribution between 0.01 and 0.02 µm. The maximum pore size distribution of CSH materials A and B was in the range from 0.01 and 0.2 µm and was comparatively shifted to larger pore diameters.

Figure 1 - Pore size distribution and total porosity of the original CSH compounds A, B and C

P-elimination efficiency of the CSH materials in waste- and process waters

Figure 2 shows the P-elimination efficiency of laboratory fixed bed experiments, performed in municipal wastewater spiked to a P concentration of 10 mg/L P and treated with CSH materials A, B and C. The P-elimination efficiency of the three materials differed significantly. Materials A and B show rather similar behaviour and achieved an 80 % - 100 % P-elimination during a time period of about 2500 bed volumes. In contrast, the efficiency using material C dropped continuously to 30 % until a water throughput of ~ 1000 bed volumes. However, during the following 1000 bed volumes the efficiency increased to ~ 90 % P-elimination. A comparable behaviour – however, significantly less distinct - was observed for CSH material A during the water throughput of 500 and 1000 bed volumes, respectively.

P-elimination induced by CSH material B proved to be efficient both, from waste- and process waters in laboratory scale (Figure 3). However, the life-cycles of the experiments differed significantly: Whereas an 80 to 100 % P-elimination could be maintained for about 3000 bed volumes in fixed bed columns in laboratory scale with an initial P-concentration of 25 mg/L (only shown up to 100 bed volumes), the capacity of CSH was already exhausted after about 70 bed volumes using industrial process water (Berg et al. 2005b) with significant higher P- and DOC-concentration (Table 2).
Figure 2 – P-elimination from wastewater in laboratory fixed bed experiments by the application of CSH materials (♦) A, (▲) B and (●) C. The secondary effluent was spiked to 10 mg/L P.

Figure 3 - P-elimination from waste- and process waters in laboratory fixed bed experiments by the application of CSH material B; (▲) secondary effluent spiked to 25 mg/L P; (●) process water of 400 mg/L P.

The results from laboratory scale treating wastewater of a P-concentration of 25 mg/L P with CSH material B in fixed bed mode (Figure 2) were transferable to semi-technical scale experiments with Phostrip supernatant of a municipal wastewater treatment plant with the same initial P concentration of 25 mg/L P. Expanded bed experiments using simulated Phostrip water (25 mg/L P) showed rather similar results (Figure 4). However, the efficiency dropped continuously in both experimental set-ups.
Figure 4 - P-elimination from wastewater in semi-technical scale experiments using CSH material B (Δ) in fixed bed mode; Phostrip supernatant, 25 mg/L P (▲) in expanded bed mode, secondary effluent spiked to 25 mg/L P

Figure 5 shows the P-elimination efficiency of all three CSH materials A, B and C in expanded bed experiments treating wastewater of a P-concentration of 25 mg/L P. All materials behaved comparable and showed a better than 80% P-elimination up to 1300 bed volumes apart from a decrease in the first 300 bed volumes, comparable to the laboratory experiments already mentioned.

Figure 5 - P-elimination from wastewater in semi-technical scale experiments in expanded bed mode by the application of CSH materials (♦) A, (▲) B and (●) C. The secondary effluent was spiked to 25 mg/L P
Characterization of the generated products

P yield

All crystallisation products generated in the fixed bed experiments, both in laboratory and semi-technical scale, exhibited a total P concentration (P-tot) content of 10 – 11 % w/w (23 – 25 % P2O5 w/w) except CSH material C with only 7.2 % w/w P-tot (16.5 % w/w P2O5) in maximum. In semi-technical expanded bed experiments a P-tot yield of only 5 - 7 % w/w (11.5 – 16 % w/w P2O5) was achieved for CSH materials A and C, whereas the product generated from CSH material B showed a P-tot content of 12.6 % w/w (29 % P2O5).

Mineralogy

The formation of hydroxylapatite-like compounds (HAP, Ca5(PO4)3OH) was proven by XRD investigations (Figure 6) for all products generated in wastewater, whereas XRD analysis revealed also the formation of brushite or DCPD (Bs, CaHPO4*2H2O, di-calcium-phosphate-di-hydrate), respectively, apart from HAP-like compounds, in case process water was applied (Figure 3).

Figure 6 - Formation of a) hydroxylapatite (HAP) in wastewater and b) brushite (Bs) / di-calcium-di-hydrogenphosphate (DCPD) in process water (XRD)

Microstructure of the original CSH materials and the generated products – ESEM investigations

Figure 7 shows the surface microstructure of a CSH A particle and a close-up of the surface before the treatment with wastewater (Figure 7a). The once porous and rough surface became rather smooth by the mechanical abrasion and/or the formation of a calcium phosphate coating during the treatment in wastewater in expanded bed mode (Figure 7b). In the close-up micro-cracks in the surface HAP-coating could be observed, which were also shown by Liu.
et al. (2001). The treatment of process water with CSH material B in fixed bed mode led to the formation of platy rosulate crystals (Figure. 7c) which proved to be DCPD according to XRD analysis. But, also granules were detected, which are characteristic for the formation of HAP, in accordance to XRD analysis and to Liu et al. (2001). However, EDX analysis revealed a Ca:P ratio of 1, which is characteristic for DCPD. In contrast, the product generated in wastewater showed a Ca:P ratio of about 1.7, characteristic for pure HAP.

Figure 7: Microstructures of CSH compounds, investigated by ESEM (environmental scanning electron microscopy); a) CSH particle A before and b) after treatment with wastewater (expanded bed); c) CSH particle B after treatment with process water (fixed bed)
Microscopic investigation of thin section samples

Figure 8 shows light-optical micrographs (LM-micrographs) of the original CSH particles from material B (Figure 8a) as well as of two generated products from CSH material B (Figures 8b and 8c). Dark parts of the original material B particles represent CSH compounds, whereas bright regions belong to quartz minerals. The blue epoxy resin poured into the pores of the CSH particles.

Figures 8b and c show thin sections of the products generated under different hydrochemical conditions. Obviously, the original structure of the CSH particle had completely transformed. The dark parts had disappeared. However, quartz remained as residual mineral. Applying process water (Figure 8c), the particles were coated with needle-like rosulate crystals, which proved to be DCPD crystals in accordance to ESEM and XRD investigations (Figures 6 and 7c). Regarding the CSH particles used for wastewater treatment (Figure 8b), a distinct coating was not observed.

Figure 8 – LM-micrographs of thin sections of CSH material B and its generated products by treatment of waste- and process waters
Energy dispersive X-ray (EDX) analysis

Figure 9 shows EDX-mappings of cross sections of CSH particles, which were used for the treatment of process- and wastewaters, regarding the elements P and Ca. The spatial distribution of P and Ca within the various particles from the generated products differed significantly: The distribution of Ca and P of material A was rather similar (Figure 9a). Comparable results were detected for product particles of material B (Figure 9b). However, these particles were covered with mineral compounds. Within these mineral compounds increased contents of Ca and P at the particle surface were detected.

Figure 9c shows a mapping of a product particle of material C. P was mainly detected on the surface area, which interacted with the wastewater.

**Figure 9 - EDX-mapping of the elements Ca and P of cross sections of a) CSH particle A treated in wastewater; b) CSH particle B treated in process water; c) CSH particle C treated in wastewater**
Figures 10 – 12 show the results of an electron microscopic investigation of cross sections of the generated products from materials A, B and C. Along the marked white line, EDX line scans were performed with respect to the elements P, Ca and Si.

An EDX line scan across a particle of the generated product A showed a significant correlation of the elements P and Ca (Figure 10). Regarding the results for Si a clearly complementary distribution compared to Ca and P was detected, indicating quartz minerals within the CSH compounds (Figures 6 and 8).

**Figure 10 – Cross section of the generated product from CSH material A including an EDX line scan across the particle considering the element distribution of P, Ca and Si**
The results of an EDX line scan of the generated product from material B are presented in Figure 11. The highest contents of P and Ca occurred within the first 75 µm of the scan line. This part belongs to the brushite or DCPD coating formed during the interaction of CSH and highly P- and Ca-enriched process water. The sharp boundary between the DCPD coating and the residues of the CSH particle is characterized by a distinct increase of the Si content up from 75 µm onwards. However, Ca and P content decreased only steadily and remained constant from 125 µm.

Figure 11 – Cross section of the generated product from CSH material B including an EDX line scan across the particle considering the element distribution of P, Ca and Si
Figure 12 shows an EDX line scan across a particle of the generated product from material C. Distinct P peaks indicate the formation of a calcium phosphate coating onto the CSH surface of about 40 µm thickness. Also Ca showed its maximum at the surface, whereas in contrast, highest Si contents were detected in the residual CSH core.

Figure 12 – Cross section of the generated product from CSH material B including an EDX line scan across the particle considering the element distribution of P, Ca and Si.
DISCUSSION

Technical and chemical aspects

The results have shown that CSH compounds are suitable materials to recover phosphorus efficiently from waste- and process waters. It was feasible both, from the mineralogical and chemical but also from the engineering process point of view to generate reusable P-enriched products.

Considering the efficiency of the CSH compounds (A, B and C) and concerning the P-elimination and the mineralogical and chemical properties of the generated products, the P-recovery process was mainly controlled (i) by the hydrochemical conditions but also (ii) by the properties of the CSH materials.

The CSH materials A, B and C showed a very similar behaviour in wastewater – independent of the engineering process performed (Figures 2, 4 and 5). However, the generated products from materials A, B and C differed significantly in the mineralogical structure.

As the mineralogical and chemical composition of the original porous CSH compounds was in general comparable, the reaction mechanisms were expected to be also comparable. This was confirmed by the P-elimination efficiency in expanded bed mode (Figure 5) and less significant in laboratory fixed bed experiments (Figure 2). A kind of “initial” reaction mechanism was observed in laboratory scale for CSH material A within the first 1000 bed volumes and more distinct for CSH material C within the first 2000 bed volumes (Figure 2). However, in expanded bed experiments (Figure 5), this change of de- and increase in P-elimination efficiency was comparable for all CSH compounds within the first 500 bed volumes. This effect seemed to be influenced by dynamic kinetics and sensitive equilibration reactions and will be focus of further investigations.

The efficiency of P-recovery was improved by the treatment of P-rich solutions, as shown in Figure 3 compared to the results presented in Figure 2, as a P-elimination of nearly 100 % could be achieved. However, the life-cycle was significantly shortened with the increase of the initial P-concentration. But finally, the product achieved a comparable P yield in a shorter reaction time, i.e. the P-fixation capacity of the various CSH compounds was comparable, but its service life was limited. Thus, kinetics was controlled by the initial P-concentration.

Although the efficiency of all tested CSH materials with respect to P-removal and P-recovery were comparable, the generated products differed significantly in the kind of minerals formed and furthermore in the distribution of newly formed calcium phosphate compounds.

The results reveal a clear correlation of the pore structure of the CSH materials and their reaction behaviour: Regarding the much more porous CSH materials A and B, precipitation processes occurred also in the pores of the particles as the elements Ca and P were detected within the whole particles (Figures 9 - 11). Furthermore, as the EDX line scans and mappings through the cross sections showed a constant Ca/P ratio, an apparent homogeneous transformation of the original CSH compounds was assumed to occur. The complete transformation of the porous CSH materials A and B due to the interaction with an aqueous phase was exemplarily also shown for material B by the LM-micrographs (Figure 8). In contrast, regarding the product generated from less porous CSH material C, lacking in micro capillary pores, only an approximately 40 µm thick surface coating at the surface had formed.
(Figures 9 and 12). The expected crystallisation process was impeded, as the pore diameters were too small for a continuous and sufficiently fast transport of the solution into the particle. Vice versa, also the release of Ca from the CSH compound was inhibited which would be necessary for the maintenance of the crystallisation of calcium phosphate compounds.

The CSH-triggered P-binding mechanism could be explained by hydrolysis of the CSH compounds, exemplarily confirmed by LM-micrographs (Figure 8), i.e. by the disappearance of the black regions indicating amorphous CSH compounds and the substitution by calcium phosphate compounds. The connected release of Ca ions initiated an increase of the pH value (Berg et al., 2005a) and thus, supersaturation with respect to calcium phosphate compounds, favouring surface complexation and/or heterogeneous precipitation (Wu and Nancollas, 1999, Lützenkirchen and Behra, 1996), i.e. crystallisation. As long as the supply of Ca ions persisted, the precipitation of calcium phosphates continued. The formation of the calcium phosphate coating more and more inhibited further Ca-release from the CSH compound and led to a loss in P-elimination efficiency (Berg et al., 2005c).

Thus, the pore size distribution of the CSH compounds, i.e. the volume of micro capillary pores responsible for transport processes, mainly controlled whether only a surface coating was formed or whether the whole CSH compound was transformed into calcium phosphate compounds.

The generation of different calcium phosphate compounds could be explained by the impact of the hydrochemical conditions: DCPD coating (Figures 7c, 8b, 9b and 11) formed onto porous CSH material B in process water. This water had the lowest initial pH-value and the highest P- and Ca concentrations, thus favouring the formation of more soluble calcium phosphate compounds as a precursor compound of HAP (Wu and Nancollas, 1999, Tung, 1998) – according to Ostwald rule. In accordance to Arifuzzaman and Rohani (2004) brushite nucleates more easily than HAP at low pH value, as nucleation is in general easier for high soluble crystalline species. The crystallisation rate of DCPD is about 1000 times higher than for HAP at low temperature (Elliot 1994). However, HAP formation was also observed inside the particles due to the significant porosity. It is still unknown, which mineral compound formed first and which area of the porous CSH particle was transformed first. Only a detailed study and modelling of the surface phenomena and the pore water chemistry can bridge this gap. By now, however, it is obvious that the process can be controlled technically via the factors already identified.

The more alkaline initial pH value of municipal wastewater with comparably low Ca- and P concentrations favoured the formation of HAP-like compounds, as proven by mineralogical analysis (Figure 6). This could also be explained by the pH dependent equilibrium and thus, species distribution of orthophosphate favouring a shift to PO$_4^{3-}$ ions. The location of the HAP formation (Figures 8 - 12) again depended mainly on the pore size distribution regarding the products generated from CSH materials A and B.

**Reuse options for the generated products**

A P-yield of about 5 - 13 % P-tot w/w (12 - 29 % P$_2$O$_5$ w/w) was achieved for all CSH induced products. This P-load is quite comparable to the natural P-content of apatite of ~ 14 % P-tot w/w (32 % P$_2$O$_5$ w/w), the main component of phosphate rock; and thus, required as a minimum by the European P-industry Thermphos International B.V. (Schipper et al., 2005) for a potential reuse as a P-rock substitute.
In general, the products obtained in the P-RoC process met the requirements of the P-industry (Table 4). In particular the use of seed material B was promising, since its heavy metal contents were significantly lower compared to those of the original CSH material C (Table 3). Restrictions remained regarding the enrichment of Zn onto the CSH materials during the CSH/water interaction (Berg et al., 2005b). Even though limit values set by the phosphorus industry on the maximum tolerable Zn content were always exceeded, the content was still lower than the one normally found in natural phosphate rock (P-rock, Table 4). Taking the natural content of P-rock regarding Cd and/or U into consideration, it was feasible to generate purer substitutes for P-rock by the CSH-triggered P-recovery P-Roc process.

Table 4 – Chemical composition of the generated products from CSH materials A and B in expanded bed and fixed bed; n.a.: not analysed; n.s.: not specified

<table>
<thead>
<tr>
<th></th>
<th>SiO₂ (%)</th>
<th>Fe₂O₃ (mg/kg)</th>
<th>Al₂O₃ (mg/kg)</th>
<th>P₂O₅ (mg/kg)</th>
<th>CaO (mg/kg)</th>
<th>Zn (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Cd (mg/kg)</th>
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<td></td>
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</tr>
<tr>
<td>P-rock (apatite ref.)</td>
<td>4.0</td>
<td>0.3</td>
<td>0.5</td>
<td>30</td>
<td>53</td>
<td>240</td>
<td>30</td>
<td>270</td>
<td>n.a.</td>
<td>17</td>
<td>72</td>
</tr>
<tr>
<td>Requirements of P-industry (NL)¹,²</td>
<td>supply 0.4-&lt;1.0</td>
<td>n.s. ≥23</td>
<td>n.s.</td>
<td>50-100</td>
<td>50-100</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
<td>n.s.</td>
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</tbody>
</table>

¹ Schipper (2001)  
² Lijmbach (2004)

The about 20 times higher water solubility of the generated DCPD-rich but also HAP-containing product from process water compared to HAP-like compounds formed during the treatment of wastewater (VDLUFA, 1999), is rather promising for a reuse as a fertiliser with respect to the plant availability of phosphorus. The latter will be investigated in future elution- as well as greenhouse- and field experiments. However, the weak mechanical stability and high porosity were expected to further favour the plant availability compared to the product generated from CSH material C. Furthermore, the direct use of the generated products as a fertiliser seemed to be promising due to the high silica content, which favoured the supply of trace metals for plants.
CONCLUSIONS
The calcium silicate hydrate triggered phosphorus recovery is an efficient way to tap the potential of waste- and process waters as key resource. CSH compounds proved to be suitable carrier materials, as in all experiments P-rich calcium phosphate compounds were generated and a P$_2$O$_5$ content of up to 29 % was achieved.

Independent of the process engineering, the P-RoC technology was mainly controlled by the hydrochemical conditions but also by the properties of the CSH materials. Especially the pH value determined the kind of calcium phosphate formed apart from the P- and Ca concentration of the waste- and process waters, whereas the initial P concentration controlled the life cycle of the process.

In addition, the degree of mineral transformation, i.e. the dissolution of CSH compounds connected with the formation of calcium phosphates, is influenced by the pore structure of the CSH compounds, i.e. the existence of mainly capillary pores. These pores control the transport processes such as the release of Ca ions as well as the penetration of P-rich solution into the particles. However, without any detailed investigations and complex modelling of the physico-chemical conditions in the near-surface of the particles and of the pore water chemistry it is not feasible to predict the reaction behaviour.

The influencing factors such as porosity and hydrochemistry are identified, but not yet quantified. Therefore, it is feasible to control the type and composition of the calcium phosphate products by systematically varying the process parameters. As far as their chemical purity and mineralogical composition is concerned, the products can be used as P resource in various industrial domains.

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