P-RoC - Phosphorus Recovery from Wastewater by Crystallisation of Calcium Phosphate Compounds

U. Berg*[1], G. Knoll**, E. Kaschka**, V. Kreutzer***, D. Donnert*, P.G. Weidler* and R. Nüesch*

* Institute for Technical Chemistry - Water- and Geotechnology Division (ITC-WGT), Forschungszentrum Karlsruhe GmbH, P.O. Box 36 40, D-76021 Karlsruhe, Germany; [1] corresponding author: Dr. Ute Berg (e-mail: *ute.berg@itc-wgt.fzk.de; dietfried.donnert@gmx.de; peter.weidler@itc-wgt.fzk.de; rolf.nueesch@itc-wgt.fzk.de*)
** Posch & Partners, Consulting Engineers, Sebastian-Kneipp-Weg 17, A-6026 Innsbruck, Austria; (e-mail: *knoll@pap.co.at; kaschka@pap.co.at*)
*** Institute of Sanitary Engineering and Water Pollution Control, University of Natural Resources and Applied Life Sciences (BOKU), Muthgasse 18, A-1190 Vienna, Austria; (e-mail: *verena.kreutzer@lycos.at*)

Abstract
The P-RoC process – the phosphorus recovery straight from the aqueous phase by crystallisation of calcium phosphate – was developed in order to simultaneously remove and recover phosphorus from municipal waste- and industrial process waters by applying calcium silicate hydrate (CSH) compounds or synthesised tobermorite pellets as crystallisation seed materials. At first, the experiments were performed in fixed bed reactors in laboratory- and in pilot scale. In continuation stirred reactor technique was developed and optimised in order to reduce operation and maintenance efforts of the process. Apart from the composition and grain size of the seed materials and the hydraulic retention time (HRT) in the reactor, the efficiency and longevity of the P-RoC process was mainly controlled by the initial P concentration of the wastewater. P-RoC proved to be feasible to treat also highly DOC- and P-enriched process waters. Total P (P-tot) contents in the generated crystallisation products of at least 10-11% P-tot were achieved in long-term fixed bed experiments, which was promising for the substitution of natural phosphate rock in the phosphorus industry. Mineralogical investigations (FTIR-ATR, XRD) proved the formation of hydroxy-apatite-(HAP) like coatings onto the surface of the seed materials using municipal wastewater. Using industrial process water, the crystallisation product formed was brushite.

Keywords
Calcium phosphate; crystallisation; phosphorus recovery; Phostrip; process water

INTRODUCTION

Facing the finiteness of the natural resources of phosphorus as an essential nutrient and indispensable fertiliser component in agriculture (ATV, 2003), the declared objective of all industrialised countries should be the sustainable use of available phosphorus sinks. Municipal wastewater treatment plants (WWTP) or phosphorus-rich industrial process waters, serving as major sinks for phosphate, offer highly potential sources for the generation of P-rock substitutes or new fertilisers. Phosphorus recovery straight from the liquid phase offers the noteworthy advantage that phosphate is already dissolved. It just has to be scavenged, either by the precipitation of struvite (Heinzmann, 2001), requiring a constant stoichiometrical ratio of magnesium, ammonium and phosphorus (Ueno and Fuji, 2001), or by the formation of calcium phosphate, e.g. by crystallisation. For that, the properties of the seed material, initiating the kinetically controlled crystallisation process as well as serving as carrier for the generated calcium phosphate compounds, play a decisive role.

Crystallisation has already been realised in full-scale using sand (Giesen, 1999), calcite (Donnert and Salecker, 1999) or synthesised spherical tobermorite pellets (Moriyama *et al.,* 2001, 2003) as seed materials. However, preliminary CO_2-stripping and/or adjustment of the pH-value, prior to the

calcium phosphate precipitation were required. Furthermore, the pH-value had to be re-adjusted prior to discharge.

The objective of this study was to develop a simple technology for phosphorus recovery from municipal waste- and industrial process waters, by which the above mentioned complex pre-treatment steps could be avoided. This was realised in the P-RoC process (phosphorus recovery from waste water by crystallisation of calcium phosphate compounds), using readily available tobermorite-rich calcium silicate hydrate (CSH) compounds (Berg *et al.* 2005, Berg *et al.*, in press) or alternatively synthesised spherical tobermorite as seed material.

Two technical process application variants – fixed bed- and stirred reactor – were developed and optimised in laboratory- and pilot scale concerning both, the efficiency in P-elimination and the P-recovery. The generated crystallisation products from the P-RoC process were analysed regarding their applicability as a P-rock substitute for the phosphate industry and/or as a new fertiliser.

EXPERIMENTAL SECTION

Long-term experiments were carried out in continuous-upflow fixed bed- and in stirred reactor experiments. Upscaling from laboratory to pilot scale was undertaken for both technologies (Table 1).

Fixed bed column experiments in laboratory scale (0.08 - 0.24 L) were performed with municipal wastewater from the biological WWTP of the Forschungszentrum Karlsruhe (secondary effluent), spiked to a P-concentration of 10 mg/L P by a $NaH_2PO_4.H_2O$ (p.a. Merck) stock solution and with municipal wastewater (supernatant) from a WWTP side-stream Phostrip process (Kaschka and Donnert, 2002) in Austria with a P concentration of 25 mg/L P (Table 2). Furthermore, the crystallisation process was tested with two industrial process waters 1 and 2 (Table 2) with P concentrations of 90 mg/L P and 400 mg/L P, respectively, and considerable concentrations of dissolved organic carbon (DOC; 70 mg/L, 2000 mg/L). Continuous-flow stirred reactor experiments in laboratory scale were also performed with the spiked secondary effluent from the WWTP of the Forschungszentrum Karlsruhe (10 mg/L P). A hydraulic retention time (HRT) of 1 h (2 h, process water 1) was applied in the fixed bed reactors and of 1 h and 2 h, respectively, in the stirred reactors.

Table 1. Experimental setup of fixed bed- and stirred reactor device in laboratory and pilot scale. HRT: hydraulic retention time; n.s.: not specified; SSR: solid solution ratio

	fixed bed						stirred reactor		
	laboratory					pilot	laboratory	pilot	
Volume (L)	0.16	0.24	0.08	0.08	0.08	24	2.5	60	60
Seed	B	B	B	B	C	B	B	B	B
SSR (wt-%)	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	5	5	5
HRT (h)	1	1	2	1	1	1	1, 2	1,2,~4[a]	2
P concentration (mg/L)	10[b]	25[c]	90[d]	400[e]	10[b]	25[c]	10[b]	25[c]	25[c]
Pre-treatment (electro-flotation)	-	-	-	-	-	x	-	x	-

[a] long-term discontinuous batch experiment: feeding period 25 min, stirring period 120 min, sedimentation period 30 min and a draining period 45 min per batch cycle
[b] spiked secondary effluent from WWTP of the Forschungszentrum Karlsruhe (DOC: 10 mg/L)
[c] Phostrip supernatant from a WWTP in Austria (DOC: 50 mg/L)
[d] industrial process water 1 (DOC: 70 mg/L)

Pilot-scale fixed bed- (24 L) and stirred reactor experiments (60 L) were carried out with the side-stream Phostrip supernatant (25 mg/L P) at a municipal WWTP in Austria (Table 1, Table 2). The influent was preliminary treated by means of an electro-flotation device, in order to reduce the concentration of suspended solids (SS) to < 0.02 g/L. In the fixed bed reactor experiment, an HRT of 1 h was applied. The efficiency of continuous-flow experiments in the stirred reactor (HRT: 1 h, 2 h) – with and without preliminary treatment – was compared to a long-term discontinuous batch experiment. One batch cycle consisted of: a feeding period of 25 min, a stirring period of 120 min, a sedimentation period of 30 min and a draining period of 45 min (Table 1).

Table 2. Composition of waste- and process waters applied in fixed bed- and stirred reactor experiments

water		pH	P	Ca	Mg	DIC	DOC
			mg L^{-1}				
WWTP	sec. effl.	7.5	10[a]	100	13	60	10
WWTP	Phostrip	7.2	25	60	20	60	50
process water	1[b]	7.8	90	40	40	200	70
process water	2	6.2	400	550	70	20	2000

[a] spiked with a $NaH_2PO_4.H_2O$ (p.a. Merck) stock solution
[b] according to Song et al., 2004

In addition, two tobermorite-rich seed materials B and C were compared in laboratory fixed bed experiments, whereas only seed material B was used in the stirred reactor- and pilot scale experiments. Seed material B (calcium silicate hydrate / CSH; grain size: 0.5 - 1.5 mm, specific surface area (SSA) of 40-50 m^2/g) was characterised by significantly lower background concentrations of heavy metals such as Fe, Cu, Zn, Cd and Pb compared to seed material C (synthesised spherical tobermorite pellets, Moriyama *et al.*, 2003, 2001; grain size: 0.5 - 1 mm, SSA of 30-40 m^2/g), and was therefore considered to be more favourable for an application in a recycling process (Table 3).

The soluble reactive phosphorus (P) content and the pH value of the in- and outflow of all reactors were analysed. Additionally, analysis of the dissolved Ca concentration was performed for in- and outflow of the fixed bed reactor experiments according to relevant EU-DIN norms.

The total phosphorus concentration (P-tot) of all crystallisation products obtained was measured at the end of the experiments. In addition, the original seed materials as well as the products from the fixed bed experiments were analysed for their semi-quantitative chemical composition by XRF (Spectrace 500, Tracor) and for their mineralogical composition by infrared spectroscopy (FTIR-ATR, Bruker IFS 66) and XRD (powder diffractometry, Siemens D 5000).

RESULTS AND DISCUSSION
Fixed bed column reactor experiments
In the laboratory scale experiments conducted with secondary effluent (input concentration of 10 mg/L P) using seed material B, a constant P-elimination rate between 80 and 100% could be maintained over a wastewater throughput of about 2600 bed volumes (BV) prior to a steady decrease (Figure 1). In contrast, P-elimination efficiency of seed material C continuously degraded under analogous conditions. However, after a water throughput of about 800 BV, a steady state of

30% P-elimination was obtained prior to an increase to more than 70% P-elimination. An explanation for this behaviour of seed material C is a slower Ca release for the formation of HAP compared to seed material B due to a kinetic hindrance, and therefore a decelerated HAP-crystal growth.

Applying seed material B and Phostrip supernatant with an initial P concentration of 25 mg/L P, a P-elimination efficiency between 80 and 100% was maintained over a water throughput of 800 BV prior to a continuous decrease. The upscaled pilot experiments showed nearly identical results (Figure 1).
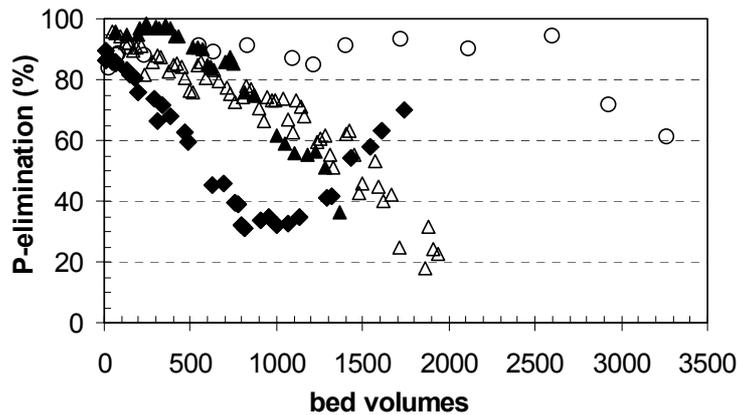

Figure 1. P-elimination in fixed bed reactor experiments in laboratory- and pilot scale: seed materials B and C; spiked secondary effluent, Phostrip supernatant; HRT: 1 h; (▲) laboratory scale, seed B, Phostrip supernatant (25 mg/L P); (△) pilot scale, seed B, Phostrip supernatant (25 mg/L P); (○) laboratory scale, seed B, secondary effluent (10 mg/L P); (◆) laboratory scale, seed C, secondary effluent (10 mg/L P).

Figure 2 shows the P-elimination of seed material B using two different industrial process waters, varying mainly in the P- and DOC concentration. The results reveal the feasibility to recover phosphorus successfully also from higher P concentrated organic rich process waters. Whereas the efficiency of almost 100% decreased spontaneously after a water throughput of only about 70 BV applying process water 2 (400 mg/L P), an 80 to 100% P-elimination was maintained over a water throughput (process water 1) of at least 180 BV, admittedly with the double HRT of 2 h.
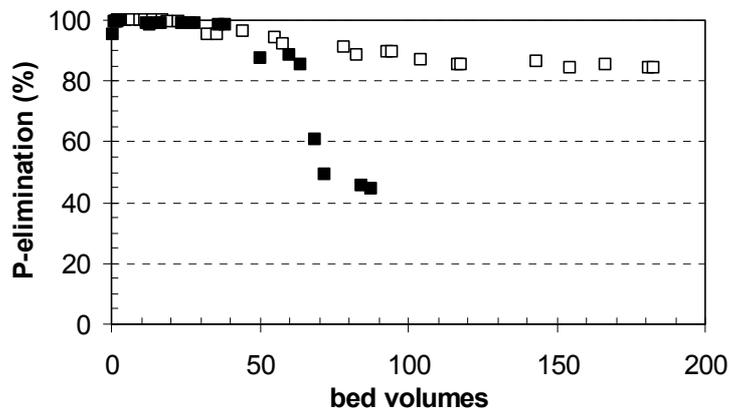

Figure 2. P-elimination in laboratory fixed bed reactor experiments: seed material B, industrial process waters 1 and 2. (□) Process water 1 (90 mg/L P), HRT: 2 h; (■) Process water 2 (400 mg/L P), HRT: 1 h.

Thus, mainly the initial P concentration controlled the longevity of the fixed bed columns, i.e. the higher the initial P-concentrations (10, 25, 90, 400 mg/L P), the lower the number of bed volumes for a P-elimination better than 80% (2600, 900, >200, 70 BV) corresponding to a hyperbolical function correlation (not shown). Therefore, the life-cycle of the P-recovery process could be forecasted for the fixed bed technology in dependence of the P concentration, whereas the effects of HRT ($\geq$1 h) and the DOC concentration were less decisive using seed material B. This correlation could be explained by the faster depletion of Ca ions in the reactor - partly released from the CSH seed - with higher P concentration (Berg *et al.*, in press).

Stirred reactor experiments
Although the upscaling in fixed bed experiments did not show significant differences in the P-elimination efficiency, the maintenance of the pilot scale experiments seriously interfered with bio-clogging of the seed crystals causing short-circuits and a considerable increase of the head loss. Even backflushing could not improve the P-recovery process. Therefore, stirred reactor experiments were performed, as the continuous movement of the seed crystals was assumed to (i) impede the formation of biofilms, (ii) to facilitate the interaction of P-containing crystals and water and thus, (iii) to prolong the life-cycle of the seed material. In preliminary batch experiments, a solid/solution ratio (SSR) of 5 wt-% proved to be the optimum.
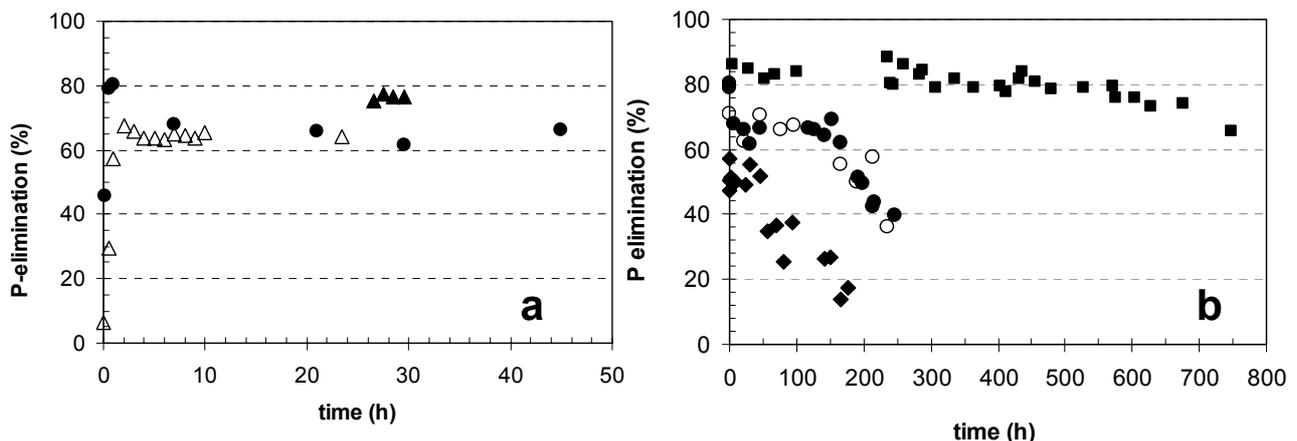

Figure 3. P-elimination in stirred reactors (seed B, 5 wt-% SSR); **a)** ($\triangle$, $\blacktriangle$) laboratory- (secondary effluent, 10 mg/L P) and ($\bullet$) pilot scale continuous-flow experiments (Phostrip supernatant, 25 mg/L P), HRT: ($\triangle$) 1 h and ($\blacktriangle$, $\bullet$) 2 h. **b)** Pilot scale continuous-flow experiments, Phostrip supernatant (25 mg/L P); HRT: ($\blacklozenge$) 1 h (with preliminary flotation), ($\bullet$) 2 h (with preliminary flotation), ($\bigcirc$) 2 h (without preliminary flotation). ($\blacksquare$) Discontinuous batch experiment (HRT ~ 4 h, Table 1).

In continuous-flow laboratory scale experiments (10 mg/L P) a constant P-elimination efficiency of about 60-70% (HRT = 1 h) or ~ 80% (HRT = 2 h) was observed over at least 24 h (Figure 3a) applying 5 wt-% of seed material B. In analogous pilot-scale experiments using Phostrip supernatant with 25 mg/L P, 50 to 60% of P was eliminated over a period of about 48 h with an HRT of 1 h, followed by a continuous decrease in P-elimination efficiency (Figure 3b). Doubling the HRT to 2 h led again to an improvement of about 10%. However, the efficiency was 10% lower compared to the laboratory scale (Figure 3a), but a rather constant P-elimination of 60 to 70% could be maintained over a period of about 180 h (Figure 3b). Even without any preliminary treatment such as flotation nearly identical results were obtained. The following significant declines were probably caused by wash-out of the smallest (and therefore most reactive) CSH grains generated by mechanical abrasion due to the stirring process. This loss of seed material amounted up to ~ 70% within 240 h, but was significantly reduced by applying a discontinuous long-term batch

technology, i.e. cycles of reactor feeding, stirring, settling of the generated product and reactor draining periods (Table 1). Thus, a constant P-elimination of 80% was maintained over a time period of at least 600 h (Figure 3b). Furthermore, an optimised reactor geometry, i.e. a clear water sedimentation zone above the suspension zone (Figure 4) should help to minimise this loss of finest grains. Thus, neither a preliminary flotation nor a sedimentation tank would be necessary for the stirred reactor technology (optional units, Figure 4).
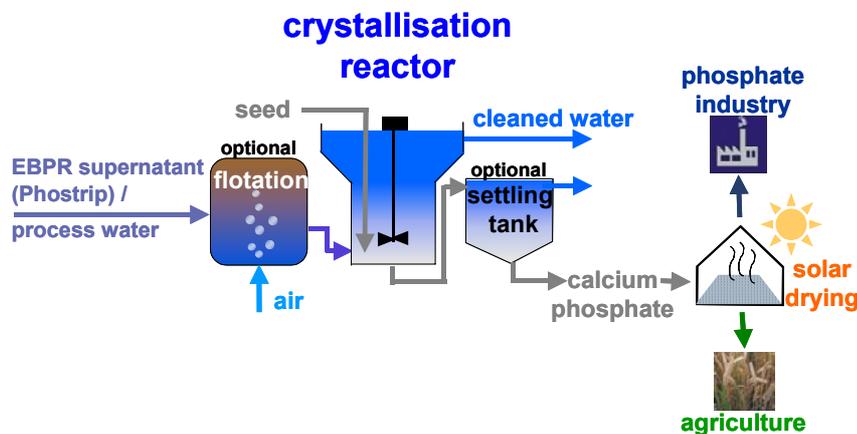

Figure 4. Flow-chart of the P-RoC process (modified according to Berg and Schaum, 2005)

Quality of the generated products, marketing potentials and strategies

All crystallisation products generated in the fixed bed experiments exhibited a P-tot content of 10-11% (seed material B), which was comparable to natural phosphate rock (10-14% P-tot content). The formation of hydroxy-apatite (HAP, $Ca_5(PO_4)_3OH$)-like compounds was proven by FTIR-ATR (not shown) and XRD investigations (Figure 5a), whereas XRD analysis revealed also the formation of brushite ($CaHPO_4*2H_2O$) in case process water 2 was applied (Figure 5b). This water had the lowest initial pH-value and the highest P- and Ca concentrations. Therefore, an accelerated dissolution of CSH causing high local supersaturation with respect to calcium phosphate minerals, triggering the formation of more soluble calcium phosphate compounds as a precursor compound of HAP (Wu and Nancollas, 1999) was expected within the rather short reaction time of only 90 BV. With longer duration of the experiments, HAP formation was favoured.

Up to now, the duration of the stirred reactor experiments was too short to obtain a relevant yield of Ca-P compounds (< 5% P-tot). Therefore, the optimisation of this process will be focus of further studies.

In general, the products obtained met the requirements of the P-industry (Schipper, 2001, Lijmbach, 2004). In particular the use of seed material B was promising, since its heavy metal contents were significantly lower compared to those of seed material C (Table 3). Restrictions remained regarding the enrichment of Zn onto the seed materials during the crystallisation process. 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 3). 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 crystallisation with the P-RoC process.
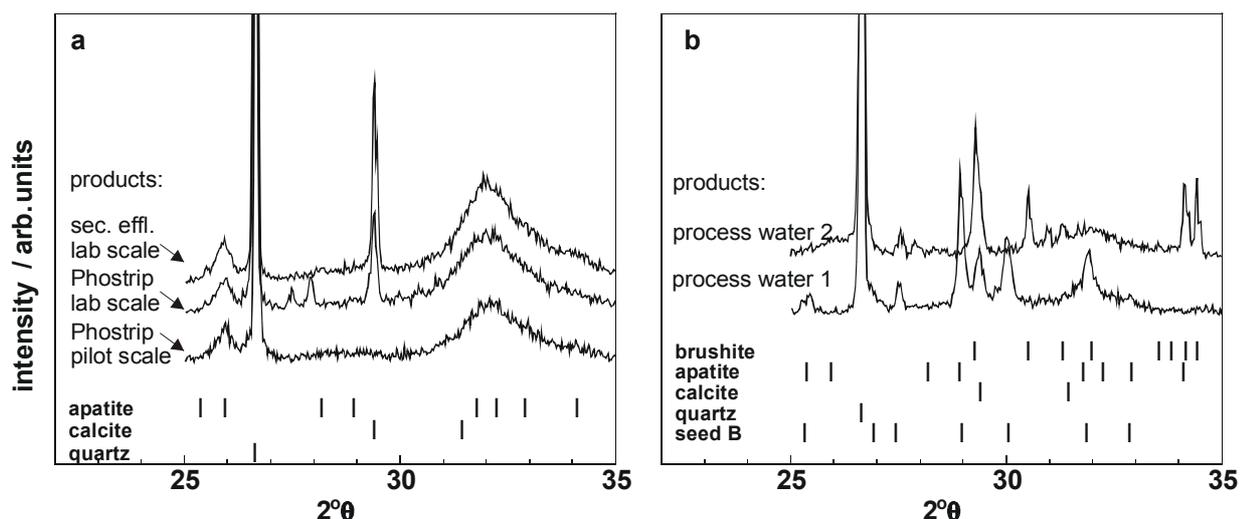
Figure 5. XRD analysis of the products generated **a)** in laboratory- and pilot scale fixed bed reactor experiments using municipal wastewater (Phostrip, secondary effluent) as well as **b)** in laboratory scale using industrial process waters 1 and 2. Brushite, apatite, calcite, quartz and seed B were used as references.

Furthermore, due to the high silica content, which favours the supply of trace metals, the direct use of the generated products as a fertiliser in ecological agriculture seemed to be promising. The low water solubility confirmed the formation of HAP-like compounds. Therefore, the application of the crystallisation products to low acid soils seemed to be favourable regarding the plant availability of phosphorus, which will be investigated in future elution- (VDLUFA, 1999) as well as greenhouse- and field experiments

Table 3. Chemical properties of the original seed materials B and C, natural P-rock (apatite ref.) and the generated recycling products from the half-scale fixed bed reactor experiments compared to the requirements for its reuse as a substitute for natural P-rock in the phosphate industry. n.a.: not analysed; n.s.: not specified

	SiO_2	Fe_2O_3	Al_2O_3	P_2O_5	CaO	Zn	Cu	Cr	Pb	Cd	U
			(%)					(mg/kg)			
seed B (original)	56	0.15	0.1	0.03	30	9	8	20	<5	<0.3	<10
product (seed B)	34	0.30	0.5	25	35	142	15	23	<5	<0.3	<10
seed C (original)	40	1.80	3.3	0.10	34	152	62	107	11	2	<10
P-rock (apatite ref.)	4.0	0.30	0.5	30	53	240	30	270	n.a.	17	72
Requirements of P-industry (NL)	supply	0.4-<1.0	n.s.	≥23	n.s.	50-100	50-100	n.s.	n.s.	n.s.	n.s.

CONCLUSIONS

Two different process engineering technologies in laboratory and pilot scale have been applied within the frame of the development of the P-RoC process. This process proved to be feasible not only to recover P from municipal- but also from highly P-enriched industrial process waters using fixed bed technology. Furthermore, neither calcium addition nor pH adjustment turned out to be necessary. The efficiency and longevity was mainly controlled by the initial P concentration due to the velocity in the depletion of Ca ions and could therefore be forecasted. Upscaling revealed some difficulties in maintenance, but showed a comparable efficiency and longevity. With the

circumvention of a loss of the finest fraction of the seed material, the stirred reactor seemed to represent the optimal method from the technological point of view. The optimisation of the stirred reactor process will be the focus of further investigations.

Promising P-tot yields of 10-11% were obtained for the products using seed material B, generated in fixed bed reactors, being similar to natural P-rock. The formation of Ca-P compounds and minerals was proven. The products generated met the requirements of the P-industry as a phosphate rock substitute and were less Cd and U contaminated than natural phosphate rock itself. The fertilising properties will be subject of further studies.

REFERENCES

ATV (2003). ATV-DVWK-Arbeitsgruppe AK-1.1 Phosphorrückgewinnung (ed.). *Korrespondenz Abwasser: Wasserwirtschaft, Abwasser, Abfall*, **50**, 805-814.

Berg, U. and Schaum, C. (2005). Recovery of Phosphorus from Sewage Sludge and Sludge Ashes – Applications in Germany and Northern Europe. Proceedings, *1st National Sludge Symposium, Izmir, Turkey,* March, 23rd – 25th, 2005

Berg, U., Donnert, D., Ehbrecht, A., Weidler, P.G., Bumiller, W., Kusche, I. and Nüesch, R. (in press). "Active filtration" for the elimination and recovery of phosphorus from waste water. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Special Issue.

Berg, U., Donnert, D., Ehbrecht, A., Weidler, P.G., Kusche, I., Bumiller, W. and Nüesch, R. (2005): Phosphate elimination and recovery from waste water by active filtration using crushed gas concrete. *Env. Technol.,* **26**(2), 219-229.

Donnert, D. and Salecker, M. (1999). Elimination of Phosphorus from Waste Water by Crystallisation. *Env. Technol*., **20**(7), 735-742.

Giesen, A. (1999). Crystallisation process enables environmental friendly phosphate removal at low costs. *Env. Technol.*, **20**(7), 769-776.

Heinzmann, B. (2001). Options for P-recovery from Waßmannsdorf Bio-P wwtp, Berlin. Implications for wwtp operation and phosphorus recovery potential at different locations in the Bio-P and sludge treatment process. *2nd international Conference on Recovery of phosphates, Noordwijkerhout, NL,* 12.-13th March, 2001.

Kaschka, E., and Donnert, D (2002). Das Phostrip-Verfahren in Verbindung mit „Aktivfiltration", ein wirtschaftlicher Weg zur P-Rückgewinnung. *Schriftenreihe WAR* **147** (ISBN 3-932518-43-8), 101-128

Lijmbach, D. (2004). Phosphorus recycling in the phosphorus industry, *Workshop of ATV-AK 1.1 "Phosphorrückgewinnung"*, 28.10. Weimar.

Moriyama, K., Kojima, T., Minawa, Y., Matsumoto, S. and Nakamachi, K. (2001). Development of artificial seed crystal for crystallization of calcium phosphate. *Env. Technol*., **22**(11), 1245-1252.

Moriyama, K., Kojima, T., Koga, K., Takino, S. and Minawa, Y. (2003). Crystallisation process using calcium silicate hydrate for phosphorus removal. *Env. Engineering Res*., **40**, 389-394.

Schipper, W.M. (2001). Phosphate recycling in the phosphorus industry. *2nd Int. Conference on Recovery of Phosphates, Noordwijkerhout, NL*, March 12-13, 2001.

Song. Y., Berg, U., Weidler, P.G., Donnert, D., Beuchle, G. and Nüesch, R. (2004). Tobermorite-seedes crystallization of calcium phosphate for phosphorus recovery from wastewater. *Proceedings of the 11th Gothenburg Symposium*, November, 8.-10th, Orlando, Florida, USA, IWA Publishing.

Ueno, Y. and Fujii, M. (2001). Three years experience of operating and selling recovered struvite from full-scale plant, *Env. Technol*., **22**(11), 1373-1381.

VDLUFA (1999): Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten. *Die Untersuchung von Düngemitteln,* Methodenbuch Band II.1, VDLUFA-Verlag Darmstadt.

Wu, W. and Nancollas, G.H. (1999). Determination of interfacial tension from crystallization and dissolution data: a comparison with other methods. *Adv. Colloid Interface Sci.* **79**, 229-279.