Phosphorus recovery from wastewater: needs, technologies and costs
P. Cornel and C. Schaum

ABSTRACT
Phosphorus is an essential, yet limited resource, which cannot be replaced by any other element. This is why there are increasing efforts to recycle phosphorus contained in wastewater. It involves the recovery of phosphorus and, normally, the separation of phosphates from harmful substances. Phosphorus can be recovered from wastewater, sewage sludge, and the ash of incinerated sewage sludge, and can be combined with phosphorus removal in most cases. The phosphorus recovery rate from the liquid phase can reach 40 to 50% at the most, while recovery rates from sewage sludge and sewage sludge ash can reach up to 90%. There are various methods which can be applied for phosphorus recovery. Up to now, there is limited experience in industrial-scale implementation. The costs for recovered phosphate exceed the costs for phosphate from rock phosphate by several times. For German conditions, the specific additional costs of wastewater treatment by integrating phosphorus recovery can be estimated at €2–6 per capita and year.

Key words | nutrient recovery, P-recovery costs, P-recovery technologies, phosphorus recovery

INTRODUCTION
Phosphorus: from cycle to finiteness
Phosphorus is an essential element for all organisms. Beside carbon, hydrogen, oxygen, and nitrogen, phosphorus is one of the vital components of the DNA and the key element of the energy supplier ATP (adenosine triphosphate). Phosphorus is an essential nutrient. Already Justus von Liebig (1803–1873) identified phosphorus as the limiting factor for plant growth. As a vital cell component phosphorus cannot be replaced by any other element. This is why phosphorus is different from other resources, such as fossil fuels, where there are potential alternatives, or from nitrogen fertilizers, which can be technically produced from air nitrogen via the Haber-Bosch process.

In nature, phosphorus passes through several interconnected cycles (Figure 1). The inorganic cycle describes the cycle from erosion, transport to the oceans, sedimentation, tectonic uplift and alteration of phosphate-containing rocks into plant-available phosphates in soil (Emsley 1980, 2001; Filipelli 2002). The cycle time of this cycle is several million years, i.e. in human spaces of times, phosphate transported into the oceans can be considered as “lost” for agricultural use.

Beside the inorganic phosphorus cycle there are two organic cycles attached describing phosphorus as part of the food chain. One of the cycles takes place on land (soil–plants–humans/animals–organic waste–soil) the other in water. The cycle time of these cycles is between a few weeks and up to one year (Emsley 1980, 2001; Bennett & Carpenter 2002).

These originally “natural” closed cycles are interrupted when phosphorus compounds in animal and human excrements are not used in fertilization. Then, phosphate contained in wastewater is partly transported to the oceans

doi: 10.2166/wst.2009.045
via the discharge systems, partly fixed in sewage sludge, which is deposited in landfill sites or incinerated; in the latter case phosphorus contained in the ash is deposited in landfill sites or subterranean storage. The procedure can be similar with organic fertilizers (solid and liquid manure) from intensive stock-rearing. The deficit is balanced by “chemical fertilizers”, i.e. the mining of phosphate-rich deposits in the earth’s crust. In Figure 1 the geological and biological cycles are illustrated, including changes due to human impact.

The quality of rock phosphate not only depends on its phosphate concentration but also on its concentration of harmful substances, cadmium and uranium in particular (UBA 2001; Kratz 2004). In order to restrict cadmium concentration in processed ores and, where required, in mineral fertilizers, one has to expect increasing costs for the processing of rock phosphate (ATV-DVWK 2003) in the future.

Based on the assessment of the future consumption of phosphorus fertilizers, the availability of presently payable natural phosphate deposits is forecasted to be approx. 60–240 years (Steen 1998), cf. (IFA 1998). Possible impacts on these estimations are the population development and thus the consumption of fertilizers as well as the activation of those natural phosphate deposits which are not payable under present technical and economic views. Regional phosphate deposits vary distinctively. Presently, approx. two thirds of the phosphate rocks are mined in USA, Morocco, and China. In addition, noteworthy amounts are mined in Russia, Brazil, Israel, Jordan, South Africa, and Tunisia.

**Phosphorus balance for a municipal wastewater treatment plant**

Based on an average phosphorus load of 1.8 g P/(C·d) (ATV-DVWK A 131 2000) in the raw wastewater, with German boundary conditions and a per capita wastewater flow of 200 L/(C·d) the influent concentration is around 9 mg/L. An average of approx. 11% of the incoming phosphorus load is removed with the primary sludge during primary settlement (ATV-DVWK A 131 2000). In biological wastewater treatment approx. 28% of the incoming phosphorus load are incorporated into the biomass and removed with the surplus sludge, even without specific phosphorus removal processes.

Based on the permitted discharge concentrations of 1 or 2 mg/L, respectively, approx. another 50% of the incoming phosphorus load has to be removed specifically, either by biological or chemical-physical P-removal processes or their combination. In summary, this means approx. 90% of the incoming phosphorus load is incorporated into the sewage sludge. In Figure 2 the phosphorus balance for a typical German municipal wastewater treatment plant with phosphorus removal is illustrated schematically.

**Applications of phosphorus recovery in wastewater technology**

In Figure 3 different applications of potential phosphorus recovery processes are illustrated via the scheme of a model

"Figure 1 | Geological (inorganic) and organic (land) phosphorus cycles (Pinnekamp 2002, modified), cf. Bennett & Carpenter (2002), including human impacts (phosphorus cycle in water not included)."

"Figure 2 | Phosphorus balance for a typical municipal wastewater treatment plant in Germany with biological phosphorus removal and/or precipitation (PS: primary sludge, SS: surplus sludge, EBPR: enhanced biological phosphorus removal)."
wastewater treatment plant. The letters A–C indicate potential locations of phosphorus recovery from the liquid phase, i.e. the effluent of the wastewater treatment plant (A), the supernatant liquor from side-stream treatment (B), and the sludge liquor (C). As with all these processes the phosphorus removed with the sewage sludge is “lost”, the theoretical recovery potential from liquid phase in common activated sludge plants is limited to 50–60%.

The numbers 1 to 6 indicate potential applications of phosphorus recovery from sewage sludge, i.e. primary (1), excess (2) and raw sludge (3), stabilized sludge before and after dewatering (4 and 5) and sewage sludge ash (6). As in wastewater treatment plants without phosphorus removal 90–95% of the incoming phosphorus load is contained in the sewage sludge, the theoretical recovery potential is significantly higher than with separation processes from the aqueous phase.

**FUNDAMENTAL TECHNOLOGIES IN PHOSPHORUS RECOVERY**

**Phosphorus recovery during wastewater treatment**

The implementation of phosphorus recovery during wastewater treatment allows for the separation of already dissolved phosphorus applying relatively basic technologies. Thereby, phosphorus-rich side streams or process water with phosphorus concentrations > 50 mg/L are economically rewarding. One big advantage of phosphorus recovery during wastewater treatment is the possibility of combining it with phosphorus removal.

Investigations of recent years showed that phosphorus recovery is particularly successful in combination with biological phosphorus removal in side streams (supernatant liquor of the anaerobic stripper) or from process water during sludge treatment. The phosphorus-rich water is fed into a precipitation/crystallization tank, where by adding calcium or magnesium salts and, where need be, seed crystals, phosphorus is removed as calcium phosphate or magnesium ammonium phosphate, cf. Figure 4.

**Phosphorus recovery from sewage sludge: wet chemical technology**

The wet chemical treatment of sewage sludge involves that in a first step phosphorus, bound in sewage sludge is dissolved by adding acid or base, in combination with temperature if necessary. Thereby, in most cases (heavy) metals are re-dissolved as well. After the insoluble compounds have been removed, phosphates can be separated from the phosphorus-rich water, e.g. via precipitation, ion exchange, nanofiltration, or reactive liquid–liquid extraction, cf. Figure 5.

The same technologies can be applied to recover phosphorus from sewage sludge ash. The advantage here is that by disintegrating the organic matter – including all organic pollutants–there is an enrichment of phosphorus. In contrast to sewage sludge, solid-liquid separation after alkaline or acidic treatment is significantly easier to realize due to the exclusively inorganic formation of the sewage sludge ash (Schaum 2007).
Phosphorus recovery from sewage sludge: thermochemical technologies

Via specific thermochemical treatment of sewage sludge ash it is possible to remove heavy metals and, at the same time, improve the plant availability of phosphorus, cf. Rhenania process. Based on the thermochemical approach, ashes are exposed—under suitable conditions—to chlorine containing substances, potassium chloride or magnesium chloride, and treated thermally. With temperatures $>1,000\, ^\circ C$, a large (%) of the heavy metals is turned into heavy metal chlorides which vaporize, thus removing them from the ashes (Kley et al. 2005). The heavy metals are captured at flue gas treatment.

Products from phosphorus recovery processes

With few exceptions, most of the processes include phosphorus separation by precipitation/crystallization of calcium phosphate or magnesium ammonium phosphate (MAP, struvite):

Calcium phosphate, e.g. hydroxyl apatite, is a product directly comparable to rock phosphate. Thereby, one has to keep in mind that in practice the kinetics of calcium phosphate precipitation plays a major role than thermodynamic equilibrium considerations. Thus, in most cases, spontaneous precipitation of calcium phosphate from the solution does not occur at all or only with very high oversaturation. However, the separation of calcium phosphate can be achieved by adding seed crystals, such as sand (Giesen et al. 2005) or calcium silicate hydrate (Berg 2005), which are able to initiate the precipitation/crystallization process of calcium phosphate.

To produce MAP is it necessary to provide a stoichiometric ratio of magnesium, ammonium and phosphate of 1:1:1. Filtrates from sludge dewatering are particularly suitable for MAP precipitation as only “magnesium” has to be added, cf. ATV-DVWK (2003, 2005). Due to thermodynamics, the separation of calcium phosphate and MAP only takes place in alkaline pH medium (pH-value approx. 8–10), cf. Stumm & Morgan (1996), Wu & Bishop (2004). Resulting from the ammonium contents, the utilization of MAP in the phosphate industry is limited. However, direct use as fertilizer seems to be possible. Laboratory-scale tests showed that the uptake of phosphorus from MAP on acidic and neutral soils is comparable to the uptake of triple superphosphate (Richards & Johnston 2001; Römer 2006).

EXEMPLARY APPLICATIONS OF PHOSPHORUS RECOVERY

Wastewater: crystallization of calcium phosphate: CRYSTALACTOR® (The Netherlands)

DHV Water (The Netherlands) developed a crystallization process for the recovery of phosphorus. Thereby, a so-called CRYSTALACTOR® is used, a cylindrical fluidized-bed reactor with e.g. sand as seed material. Originally, the reactor was used for water softening. There have also been investigations on the separation of further compounds, e.g. heavy metals. By adding calcium, phosphorus crystallizes on the seed material (quartz sand) in a fluidized bed at pH-values of approx. 9, thus forming calcium phosphate. Due to the crystallization, the pellets grow, and separation is possible (Giesen et al. 2005).

In 1993, the process was realized in side streams of the wastewater treatment plants Geestmerambacht (230,000 C) and Heemstede (35,000 C), Germany, in combination with biological phosphorus removal. With a concentration of 60–80 mg/L the phosphorus-rich supernatant liquor from the stripping tank of the biological phosphorus removal unit is fed into the CRYSTALACTOR®. Here, 70–80% of phosphorus is eliminated and separated. In order to minimize precipitation of calcium carbonate, the pH-value is decreased in the inflow area, thus inducing the stripping...
of carbon dioxide. The separated phosphorus-rich pellets are utilized as a substitute for rock phosphate in the phosphate industry (Giesen et al. 2005).

**Wastewater: crystallization of calcium phosphate: P-ROC (Germany)**

Via the application of suitable seed crystals, such as calcium silicate hydrate, a by-product from the building materials industry, a process was developed in the Forschungszentrum Karlsruhe (Germany) which allows the separation of phosphorus without the dosage of further chemicals. Within the frame of several research projects the process was investigated in pilot-plant scale.

Phosphorus-rich water, e.g. from strippers of sidestream phosphorus removal, is fed into a crystallization reactor, which can be designed as fixed-bed reactor, stirred reactor or floating-bed reactor. By adding seed crystals, calcium phosphate is formed which can then be separated. The phosphorus removal rate is approx. 80%, almost independent of the water’s DOC as investigations have shown. The phosphorus-rich product can be used in agriculture as well as in the phosphate industry.

**Process water from sewage sludge treatment: crystallization of MAP (Japan, Canada, Germany)**

Repeatedly, there have been reports about incrustations of pipes following the digestion step, in particular in those wastewater treatment plants with biological phosphorus removal. Due the formation of ammonium during digestion in combination with dissolved phosphorus and magnesium, slight changes in the pH-value can induce spontaneous precipitation of magnesium ammonium phosphate (MAP), which can lead to the incrustation of pipes, cf. Heinzmann & Engel (2005). In this context, processes have been developed, e.g. in Japan, Canada, and Germany, which focus on the formation and separation of MAP.

In the case of the PHOSNIX process developed by Unitika (Japan), phosphorus- and ammonium-rich process water is fed into a fluidized-bed reactor. The pH-value is adjusted to approx. 8.5–9 by adding sodium hydroxide solution and by adding magnesium MAP crystals are formed which can then be separated. By applying this process, phosphorus removal rates of approx. 90% can be achieved. The generated product can be used in agriculture. Since 1987, an industrial scale plant is operating in Japan (Ueno 2004).

Similar technologies have been investigated in Canada, OSTARA process (Prasad et al. 2007) operated in industrial scale since 2007, and in Germany, PRISA process—which is so far not realized in industrial scale (Pinnekamp & Montag 2005).

**Digested sludge: wet chemical re-dissolution and crystallization of MAP: SEABORNE process (Germany)**

In winter 2006, the Seaborne process was put into operation at the wastewater treatment plant Gifhorn (Germany), a municipal treatment plant with approx. 50,000 C. Following anaerobic stabilization, sulphuric acid is added to acidify the digested sludge achieving a pH-value of approx. 3. In order to improve dewaterability, hydrogen peroxide is added and the sludge is dewatered. The dewatered sludge is thermally recycled via a mono-sewage sludge incineration plant.

Precipitation of heavy metals is initiated by adding sodium sulphide. One can also feed biogas, by which sulphur is removed from the biogas at the same time. The separation of the heavy metals is carried out by means of a belt filter. Following the removal of the heavy metals, magnesium hydroxide is added and the pH-value is increased by adding sodium hydroxide solution. This procedure results in MAP precipitation, which can be separated by centrifuges and used in nutrient recycle. The residual water passes an ammonium/ammoniac stripping with subsequent acidic wash, thus producing diammonium sulphate. The water from which the nutrients have been removed is fed into the inflow of the wastewater treatment plant (Müller et al. 2005; Wittig 2007), cf. Figure 6. So far, there are no updated data about operational costs and mass balances.

**Sewage sludge ash: wet chemical re-dissolution and sequential precipitation–SEPHOS process (Germany)**

In case of the SEPHOS process (Sequential Precipitation of Phosphorus), the first step is the elution of the sewage
sludge ash with sulphuric acid. After removing undissolved residuals, the pH-value in the filtrate is increased stepwise, whereas at pH \( \sim 3.5 \) aluminium phosphates precipitate. The heavy metals like copper and zinc remain dissolved and precipitate at pH-values \( > 3.5 \). The heavy metal poor aluminium phosphate can be used in the electrothermal phosphate industry. By an alkaline treatment of aluminium phosphate (advanced SEPHOS process) phosphorus as well as aluminium is dissolved. By adding calcium, precipitation of calcium phosphate can be achieved. Aluminium stays in solution and can be recycled as coagulant. Respective investigations have been carried out at Institute WAR of Technische Universität Darmstadt (Schaum 2007).

**Sewage sludge ash: thermochemical treatment (Germany)**

Based on the thermochemical approach, ashes are exposed—under suitable conditions—to chlorine containing substances, potassium chloride or magnesium chloride, and treated thermally. With temperatures \( > 1,000^\circ C \), a large (%) of the heavy metals are turned into heavy metal chlorides which vaporize, thus removing them from the ashes (Kley et al. 2005; Prinzhorn 2005). The thermochemical treatment of the sewage sludge ash/chloride mixtures is performed in quasi-closed systems, e.g. rotary furnaces. The chlorides are discharged via the gas phase with subsequent precipitation during flue gas cleaning. By applying the mentioned chlorides, potassium and/or magnesium phosphates are formed which can then be used in agriculture. By subsequent specific dosage of nitrogen and/or potassium—following the removal of heavy metals—various multi-nutrient fertilizers can be produced. After pellets forming they can be used as granulates (Prinzhorn 2005). Respective investigations are carried out within the frame of the EU research project ”SUSAN–Sustainable and Safe Re-use of Municipal sewage Sludge for Nutrient Recovery” (SUSAN 2008). The start-up of a pilot plant in Leoben (Austria) with a load of 4,000 Mg/a ash is projected for Spring 2008.

**COSTS AND PRICES OF PHOSPHORUS**

The prices of phosphate are a matter of quality, demand and the capacity of the phosphate industries. They depend as well on politics and speculation at the stock market. As for example the price of phosphate rock from Morocco remained below 50 US $/Mg up to 2006, it went up to more than 300 US $/Mg by 2008 with peaks around 1,000 US $/Mg (Pickett 2008).

Even more difficult is the estimation of an unsubsidized price for recovered phosphate. Mass balances as well as cost evaluations for an industrialized scale phosphorus recovery plant are not published in detail. Balmér (2003) calculated costs of about €3,600/(Mg·P) for a phosphorus recovery from waste waster in combination with a phosphorus elimination. For a phosphorus recovery from sewage sludge, Balmér calculated about €8,800/(Mg·P). Off course this costs and prices are not directly to compare as phosphate rock has to be processed before use and the recovered phosphorus is of different quality. Anyhow, up to today, the recovered phosphorus seems more expensive as mined phosphorus.

With a daily phosphorus load of approx. 1.8 g P/(C·d) the annual load is approx. 660 g P/(C·a). Based on production costs for phosphorus recovery of 3,600 to €8,800/(Mg·P) the annual costs for the implementation of phosphorus recovery processes are approx. €2 to 6/(C·a). In Germany, these costs equal approx. 2 to 5% of the specific annual costs of approx. €124/(C·a) for wastewater treatment and disposal (BGW/ATV-DVWK 2003).
CONCLUSIONS

Through human excrements, dishwashing agents, and other unspecific sources, approx. 1.8 g phosphorus per capita and day reach the wastewater treatment plants. Owing to the eutrophication effect in water bodies the discharge of phosphorus is limited by laws.

The removal of phosphorus in wastewater treatment plants involves that dissolved phosphorus is turned into insoluble forms. One possibility is incorporation into biomass (biological phosphorus removal), another chemical-physical treatment by adding precipitants. With common processes, phosphorus removed from the liquid phase goes into the sewage sludge 100%. Since many years, there are controversial discussions about the use of sewage sludge in agriculture, on the one hand because sewage sludge can be seen as nutrient storage as well as a sink for harmful substances, and on the other hand because the plant availability of the precipitated phosphorus products is at least debatable.

Phosphorus is an essential, yet limited resource, which cannot be replaced by any other element. This is why there are increasing efforts to recycle phosphorus contained in wastewater. Thereby it is necessary to separate the nutrients from harmful substances.

Phosphorus recovery is possible from the liquid phase (wastewater) as well as from sewage sludge and sewage sludge ash, respectively. Recovery from the liquid phase is particularly interesting for phosphorus-rich process water, e.g. from sludge dewatering. However, the recovery potential, based on the incoming load, is limited to approx. 10 – 40%.

Phosphorus recovery from sewage sludge and sewage sludge ash first involves the re-dissolution of the bound phosphorus. Subsequently, the separation of the phosphorus, e.g. by precipitation processes, can be accomplished. The advantage of treating sewage sludge ashes is their exclusively inorganic formation, a fact which–in contrast to sewage sludge–facilitates phosphorus recovery. Furthermore, the incineration of organic matter causes the enrichment of phosphorus in the ashes. However, phosphorus recovery from sewage sludge ashes is only possible in those cases when sewage sludge is incinerated in mono-sewage sludge incineration plants. Co-incineration in cement furnaces and coal-burning power plants should not be accepted with regard to phosphorus recovery.

Based on a load of 660 g P/(C·a) and recovery costs of 3,600 to €8,800/(Mg P) the annual costs for the implementation of phosphorus recovery processes within the waste water treatment process would be approx. €2 to 6/(C·a) at German boundary conditions.

In view of unlasting phosphorus resources, the development and enhancement of phosphorus recovery processes, which allow for phosphorus reuse without potential health risks and meet ecological criteria, should be followed. The objective should be the production of phosphorus compounds which provide minimum contamination, easy handling and storage. They should allow for either direct use as fertilizer or further use in the fertilizer industry.

REFERENCES


ATV-DVWK 2005 Bericht der ATV-DVWK Arbeitsgruppe Ak-1.1 Phosphorrückgewinnung. Korrespondenz Abwasser, Nr. 6, Hennef, Germany.

ATV-DVWK 2005 Rückbelastung aus der Schlammbehandlung – Verfahren zur Schlammwasserbehandlung. DWA-Arbeitsgruppe AK-1.3 Rückbelastung aus der Schlammbehandlung, Hennef, Germany.


