

## **RECOVERY OF PHOSPHATES IN MUNICIPAL WASTE WATER TREATMENT PLANTS**

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### **INTRODUCTION**

The aim of waste water treatment is to clean the waste water to such an extent that it reaches a given quality. Due to the principle of mass conservation, withdrawal of pollutants from waste water, such as heavy metals and organic halogen compounds, as well as elimination of useful material like minerals and nutrients are linked with it.

The major part of the material withdrawn from the waste water during treatment is found in the sewage sludge (in Germany about 2.5 – 3.0 million tons of dry matter per year [1], [2]), that in Germany is still used in agriculture in big amounts. The main interest of this type of reutilisation is to use the nutrients contained in the sludge for fertilisation.

Even after accentuation of standards for indirect discharger during the last decades, from which resulted lower pollutant content in municipal sewage sludge, we can start from the assumption that not all sludge constituents which are toxic for men and/or the environment have already been discovered. During reutilisation of the sludge in agriculture, these substances would be released into the environment and, with this, be an incalculable risk. At present about 1 to 1.4 million tons dry matter per year [1], [2] are recycled in agriculture. In the course of sustainable agriculture, in Germany efforts to eliminate the pollutant potential from sewage sludge by incineration becomes more and more important, compared to the amount of recycled material.

However, complete abdication from sludge reutilisation in agriculture would have for result that the phosphate compounds transferred into the sewage sludge during waste water treatment would no longer be available for plant fertilisation, and thus would have to be substituted by mineral fertilisers. With view to the phosphate deposits with low impurities (particularly in respect of cadmium) being already considerably exhausted (and non-renewable), this represents a conflict for the purposes of sustainable handling of scarce natural resources.

Therefore it has to be examined to what extent it is possible to recycle valuable compounds of the sewage sludge already during waste water treatment and before its disposal.

## **NUTRIENT CONTENTS AND USABLE POTENTIALS IN WASTE WATER AND SEWAGE SLUDGE**

Utilisation of phosphates contained in waste water and sludge is possible just if the nutrient content allows economic and ecologically feasible recovery. On principle the following potentials are available:

In Germany the specific phosphorus load in waste water is about 1.6 – 2.0 g per inhabitant and day [3]. Related to the population connected to sewage treatment plants, the annual amount from municipal waste water is then about 50,000 tons P. Additionally about 20,000 tons P/a from indirect industrial discharges reach the waste water treatment plants. Considering the phosphorus effluent standards for municipal waste water treatment plants (1 mg P/L for plants > 100.000 PT), this corresponds to a quantity of about 64,000 tons of phosphorus per year which can be recovered during the waste water treatment process.

Concerning recovery, the usable potentials from the aqueous and the sludge phases can be differentiated as follows:

Starting from an average phosphorus content in the raw waste water of approx. 1.8 g per inhabitant and day, i.e. 9 mg/L at an average waste water quantity of 200 L per inhabitant and day, about 0.6 g per inhabitant and day or 1/3 of the phosphorus influent load are extracted from the waste water flow together with the sludge by sedimentation and/or incorporation, thus without targeted measures.

In case the legally binding value is fully used, the resulting potential for recovery from the aqueous phase will then be at least 33 % up to maximal 67 % of the average phosphorus influent load.

Without using increased biological phosphorus elimination or a precipitation process it is possible to recover from the sludge about 22 – 33 % of the phosphorus influent load. Using the last-named procedures this part can be increased up to approx. 90 %, related to the influent, so that finally the complete usable phosphorus influent load in the sludge phase will be available for recovery.

In Germany the phosphate quantity recoverable in the field of waste water corresponds to approx. 145,000 tons  $P_2O_5$ . With this quantity it would be possible to substitute about 40 % of the phosphate fertiliser sales of the year 2000/2001 (about 350,000 tons  $P_2O_5$ ). This corresponds to 17 % of the  $P_2O_5$  quantity necessary in the whole Federal Republic of Germany, related to the  $P_2O_5$  demand of agricultural soils/ crops and in accordance with competent fertilising practice – as stated by the Federal Environmental Office [5].

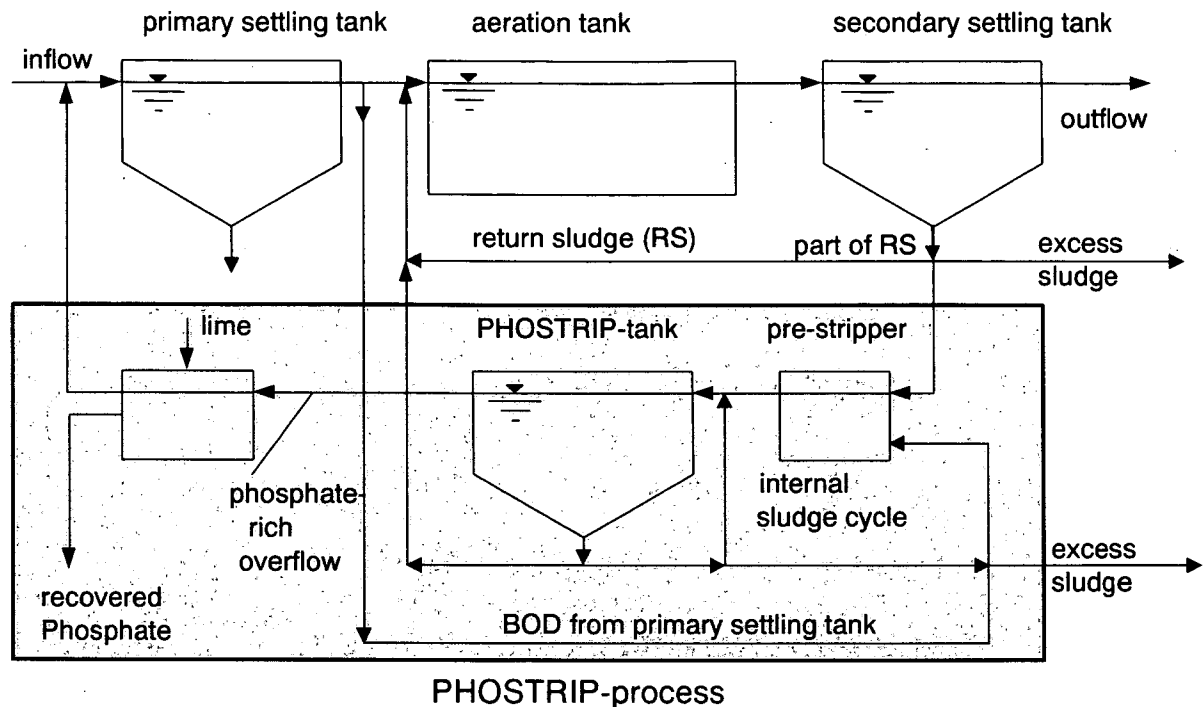
## **STATE OF RECOVERY OF PHOSPHATES IN WASTE WATER AND SLUDGE TREATMENT**

Several years ago far-reaching removal of phosphates from waste water has been realised at all big waste water treatment plants in Germany, in order to avoid excessive nutrient immission into water bodies. For this purpose simultaneous precipitation with metal salts in the activated sludge stage is mainly used. Due to the circumstances described above, it becomes actually more and more important to prepare the ground for phosphorus recovery instead of phosphorus removal. Here especially the experiences from European countries as well as from Japan are used as basis for considerations which take into account the circumstances in Germany. A few pilot plants as well as a couple of plants within the framework of research projects are already run.

In the following both well-known and rather new technologies with different approaches for the recovery of phosphates on wwtp's are described. This list is not exhaustive.

## THE PHOSTRIP PROCESS

The Phostrip process (Figure 1) [9] is a biological-chemical process for the recovery of phosphates from the secondary sludge of municipal waste water treatment plants. Premise for increased phosphorus uptake of the activated sludge is that anaerobic and aerobic zones are flown through. The Phostrip process is able to meet the legally binding value of 1 mg P/L without using iron or aluminium salts [10].



**Figure 1: Flow sheet of the Phostrip process [9], modified**

A split-stream of the secondary sludge is piped together with part of the pre-cleaned waste water into the pre-stripper, where the nitrate still present in the sludge water is denitrified and where organic acids develop which accelerate dissolution of phosphate in the succeeding Phostrip tank. In the Phostrip tank the micro-organisms emit the stored phosphate reserves again by their cell metabolism. The sludge, now poor in phosphates, settles under anaerobic conditions and is partly fed back into the aeration tank, where it accumulates phosphate again. The overflow of the Phostrip tank, which is rich in phosphate is fed to the precipitation reactor.

The phosphates released in the water phase of the settled sludge in the Phostrip tank are kept back by the internal sludge cycle and thus get into the clear water part of the stripper. Therewith it is avoided that too much dissolved phosphate is fed back into the biological stage of the waste water treatment plant. In the precipitation reactor, phosphate precipitates by the use of lime milk at pH values of more than 8.5 as calcium phosphate and then is separated. The precipitation product contains about 33 % up to 41 %  $P_2O_5$  in the dry mass and is free of interfering substances [9]. So the precipitation product meets the demands for raw material of the Thermphos process for phosphate production [6]. It is also possible to use sodium aluminate instead of calcium; in this case, however, the utilisation of the product is strongly limited [4]. Since the supernatant liquor of the precipitation is fed back into the influent of the waste water treatment plant, no limit values have to be observed, i.e. it is not necessary to carry out phosphate precipitation to a residual concentration below 1 mg P/L. If

necessary, a sludge separator can be used which separates the precipitated phosphate from the liquor. [4], [9], [10], [11]

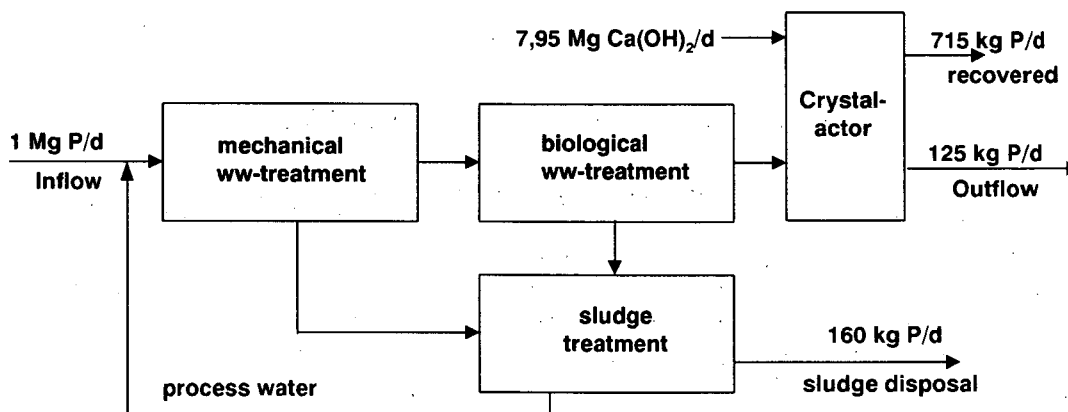
About 45 % of the phosphorus can be recovered at best. Various operational problems had for result that both plants at Darmstadt (Germany) had to be closed down, so that in Germany there is no Phostrip plant in operation by now [4]. Some plants in the USA and in Austria are still working.

## CRYSTALLISATION PROCESSES

Crystallisation processes for phosphorus recovery can easily be integrated into the processes in municipal waste water treatment. They can be divided into main-stream and split-stream processes. In both variations phosphate precipitates using chemicals, e.g. calcium, and is recovered that way; the pH has to be set at approx. 9. Using calcium hydroxide, iron or aluminium salts are saved, that normally are used for chemical phosphorus elimination.

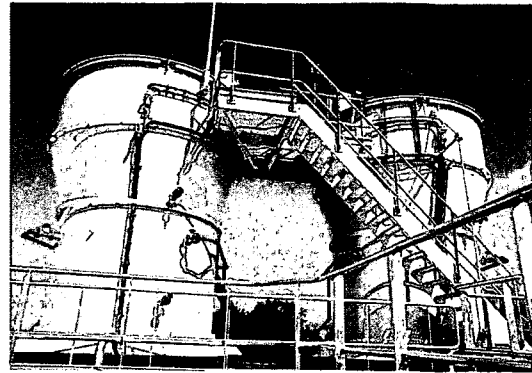
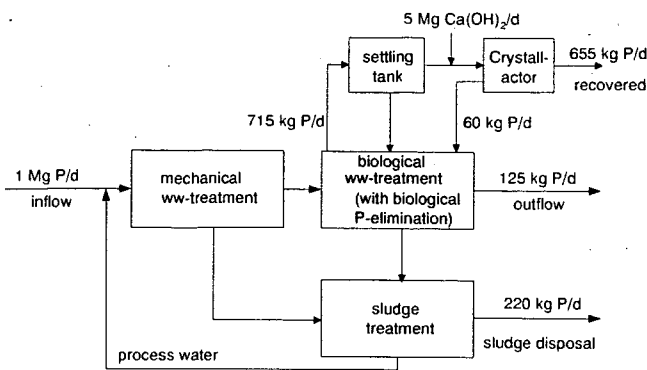
Crystallisation processes have been tested in the Netherlands (e.g. Westerbork, Heemstede), England, Japan and Australia and put in operation in Geestmerambacht (Netherlands) in 1994 for 230.000 PT [8], [13].

Especially the mainstream crystallisation (Figure 6) can easily be integrated in existing municipal waste water treatment plants. After biological waste water treatment phosphate elimination is done by adding  $\text{Ca}(\text{OH})_2$  in a crystallisation unit. Under favourable conditions it is possible to recover about 70 % of the phosphorus load contained in the influent of the waste water treatment plant. It has to be taken into account that the crystalliser operated in the mainstream has to be designed for all hydraulic peaks.



**Figure 2: Flow sheet of the mainstream crystallisation**

In split-stream crystallisation, used in combination with increased biological phosphorus elimination (Figure 3), part of the sludge rich in phosphorus from the biological process is treated in a settling tank and a succeeding crystalliser. Studies carried out in Geestmerambacht have shown that under local conditions up to 65 % of the phosphorus load in the plant influent could be recovered. Based upon usual German approaches, this value seems to be very high.



**Figure 3: Flow sheet of a Bio-P plant with split-stream crystallisation and view of the crystalliser**

As a consequence of the crystallisation processes there is the risk that the operation of the wwtp is soon disturbed by the formation of incrustations in aggregates and pipes. Moreover, after crystallisation the pH value has possibly to be adjusted to discharge conditions by adding acids (e.g. carbonic acid).

There are several possibilities in process engineering to implement crystallisation [16]:

- DHV crystalliser,
- RIM-NUT,
- Unitika PHOSNIX,
- Kurita fixed bed,
- CSIR fluidised-bed reactor.

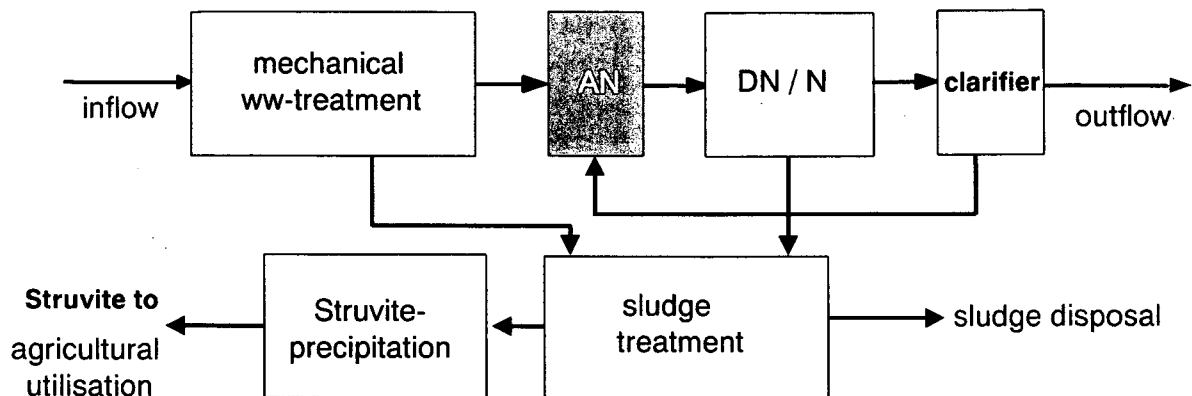
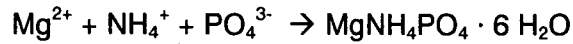
The nutrients recovered by means of the crystallisation process as calciumphosphate, magnesium-ammonia-phosphate (MAP, only in the split-stream) or hydroxylapatite (HAP) can be used directly for fertilising in agriculture or after processing in the phosphate industry.

#### PRISA-PROCESS, CONSIDERING THE EXISTING WASTE WATER TREATMENT TECHNOLOGY

Within the scope of several research and development projects carried out at present at the Institute of Environmental Engineering of RWTH Aachen University (ISA), processes are studied which allow simple phosphate recycling based on the process technology installed, but increased biological phosphorus removal presumed. A process being tested in the field of anaerobic sludge and process water treatment is described more precisely in the following.

The first step of the PRISA process is increased acidification of the raw sludge (Bio P) with phosphate dissolution in a dissolution reactor (e.g. pre-thickener) (Figure 4). Then the raw sludge is separated from the supernatant which contains the major part of the phosphate which had been biologically bound before as well as a smaller part of dissolved phosphate from the hydrolysis of biomass. Thus it is possible to concentrate more than 40 % of the phosphorus load from the raw waste water in this split-stream. It is particularly important to gain the phosphorus before the sludge digestion, where parts of dissolved phosphates are fixed again to sludge particles.

Sludge digestion follows, where increased incrustations of tanks, aggregates and pipes are no longer expected, as a result of preceding phosphate separation. Now the sludge is dewatered again. The centrate produced is rich in ammonia and finally will be mixed with the process water from pre-thickening. By adding magnesium oxide, phosphate as well as ammonia finally precipitates as struvite in the precipitation reactor:



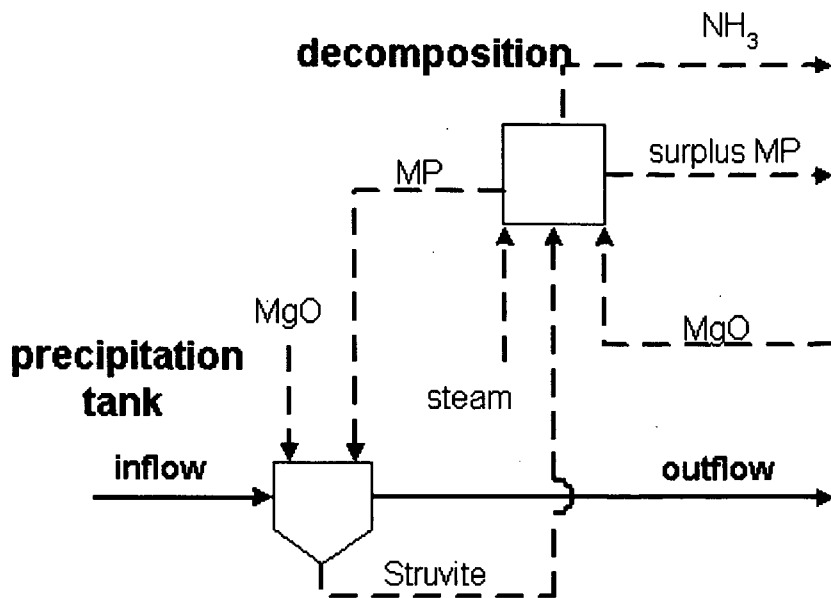
**Figure 4: Acidification of the raw sludge and phosphate precipitation from the split-stream-flows as Struvite**

As positive side effect, the nitrogen content in the centrate of approx. 0.45 kg N/kg P is reduced, which is linked with phosphate precipitation. Pilot-scale experiments in this connection are being carried out at the test plant of ISA.

The MAP crystals recovered can easily be dewatered and might be used in a decentralised way in agriculture [17], [12] or in the production of fertilisers.

The MAP process intended for nutrient recycling had already been studied in the 1980s at ISA. At that time, however, with the aim to remove ammonia nitrogen from the process water. Several pilot plants had been installed and operated at different places in Germany. At the end all the plants were closed down because at that time there was seen neither the necessity for nutrient recovery, nor an economical way of operation. The CAFR process (chemical ammonia precipitation with recycling, Figure 5) represents a follow-up development of the MAP "one-way" precipitation. In the CAFR process ammonia is stripped by means of steam from the precipitated MAP by alkalisation (MgO) at temperatures of about 70 °C, so that magnesium phosphate (MP) can be used again for MAP precipitation.

The crude ammonia liquor can be used for flue gas denitrogenation or serve as nitrogen source in fertiliser production. Recycling is five to eight times possible, afterwards secondary constituents, enclosed in the magnesium phosphate, concentrate and disturb the process [20].



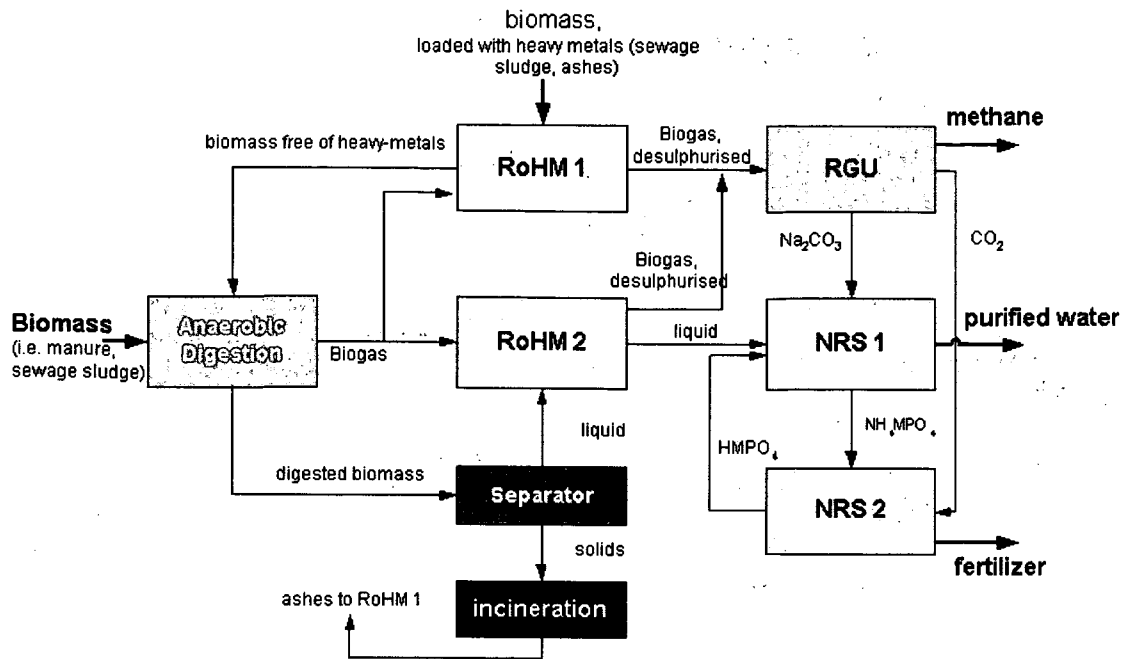
**Figure 5: CAFR process for P recycling with increased NH<sub>4</sub>-N withdrawal**

**SEABORNE PROCESS**

The Seaborne process [14], [15] for processing of organic residues was developed by the Seaborne Environmental Research Laboratory (Figure 6); a pilot plant is in operation since February 2000 in Owschlag (Germany).

Within the Seaborne process, nutrients are recycled, and heavy metals contained in the raw substrate are removed from the nutrient circuit. Not only sewage sludge, but also co-ferments such as manure can be used as raw substrates. Besides a fertiliser and water which meets the discharge standards, electricity and thermal energy are produced in the end of the process; the heavy metals separated probably will have to be disposed.

The process consists of two blocs which are closely connected: A fermentation reactor together with a combined heating plant (CHP) serves to recover and to produce energy; process steps of biogas cleaning (**R**egenerative **G**as **U**pgrading and **R**emoval of **H**eamy **M**etals) are integrated. Anaerobic treatment is completed by removal of heavy metals (**R**o**H**M) and nutrient separation (**N**itrogen **R**ecycling **S**ystem). An incineration plant is installed in order to treat the solids separated from the fermented biomass. Ashes should be fed back into the treatment process.



**Figure 6: Flow sheet of the Seaborne process [14]**

Some questions concerning this interesting and in this kind of configuration new type of process technology remain still open, especially with regard to the removal of heavy metals and the anticipated costs. Moreover, the plant safety of the complex technology has to be examined. Non-specialised personnel must be able to run the plant, so that this process can be spread widely. Only in that case relevant amounts of phosphorus can be recovered and therewith save the phosphate rock deposits.

## CONCLUSIONS

A large number of technologies already do exist for the recovery of phosphates at municipal waste water treatment plants, which in Japan or in some European countries are partly already applied in industrial scale and more and more studied in Germany, too. Moreover, in Germany there is a great deal of discussion about the implementation of a recycling imperative combined with possibilities in refinancing the recovery plant.

However, the processes for phosphate recovery from sewage sludge cannot be seen separately from those for waste water treatment. The latter determine the usable potentials as well as costs of recovery. Based on the waste water treatment technology installed in Germany, the following three possibilities can be implemented in medium-term:

- Post-precipitation/ main-stream crystallisation of phosphate with precipitating agents which allow recycling in agriculture (e.g. lime [7] or MAP) or processing as raw material in the fertiliser industry (recovery rate about 75 %).
- Increased biological P elimination with downstream mono-incineration of the sludge and dissolution of phosphate from the ash ("Bio-Con process"; recovery rate about 85 %).
- Increased biological P elimination and recovery from the process water of the sludge treatment (e.g. PRISA process, recovery rate about 50 %).



The economic efficiency of the processes is determined especially by the phosphate content in the raw waste water and the logistics in reutilisation of the precipitated nutrients, and less by the process for phosphate recovery itself. This is due to the fact that the costs for necessary process changes at the waste water treatment plant are compensated by savings of precipitation agents.

Seen exclusively from the economic point of view (phosphate price), phosphorus recovery from waste water at the moment is not profitable. The costs are twice up to ten-times the price of imported phosphates. This is due to the fact that decentralised phosphorus recovery at more than 10,000 municipal waste water treatment plants in Germany cannot be competitive, compared to the production of mineral fertilisers in a few big chemical plants.

For struvite precipitation of one kilogram phosphorus, for example, about 2 kg of magnesium oxide (MgO) must be dosed ( $\beta = 1.5$ ). The chemical costs are about 0.6 EUR/kg P, so they are in the lower range of the prices for the substituted iron or aluminium precipitants, which must no longer be used in advanced waste water treatment for the phosphate amount regained.

It depends on the market price of the phosphates extracted from deposits, to what extent processes for phosphorus recovery will become important in future. In the beginning of 2002, 28 US\$ had to be paid for one ton of phosphate ore ( $P_2O_5$  content about 26 – 34 %) [18]. This corresponds to a price of 0.24 to 0.32 EUR/kg P. The price for phosphate fertiliser in wholesale trade is approx. 1.0 EUR/kg P [19].

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