

# COMBINED PHOSPHORUS REMOVAL AND RECOVERY

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## ABSTRACT

The paper presents directions for a new system technology for municipal wastewater treatment, in order to consider both phosphorus removal and recovery. The system technology is proposed in a way to use as much as possible existing investments for the treatment and focus on modification of the operational mode. The process is based on removal followed by phosphorus recovery as calcium phosphates. In order to secure the biological phosphorus removal internal production of organic acids is necessary as the alternative to use acetic acid is costly. Chemically bound phosphorus may be released by combined thermal and acid treatment followed by phosphorus recovery. Introductory experiments indicate that leaching of phosphates from residues of supercritical water oxidation seem to be more easily dissolved than iron. It seems also to be easier to dissolve phosphate from the residue of supercritical water oxidation compared with leaching of ashes.

## KEYWORDS

Chemical precipitation, phosphorus removal, phosphorus recovery, sludge handling

## INTRODUCTION

Phosphorus removal from municipal wastewater has a long tradition in Sweden to protect receiving waters from eutrophication. In 1961, the first full-scale plant for phosphorus removal was built in Åker municipality, about 100 km south west of Stockholm. Chemical precipitation was the only economically feasible technology known at that time and future implementation of phosphorus removal in Sweden has mainly been based on chemical precipitation with iron salts as dominating precipitation agent.

Recently, Swedish policy requires phosphorus to be recycled and, because agricultural sewage sludge re-use is increasingly limited, this is putting pressure on cities to develop phosphorus recovery systems. In a number of cases, authorisation to construct sludge incinerators includes a condition that phosphorus must be recovered. A national goal has been proposed to the Swedish government that at least 75% of phosphorus from wastewater and other biological wastes should be recovered at latest by 2010 without risks for health and environment. The Swedish Environment Protection Agency (SEPA) has been given a commission from the government to better evaluate possibilities to implement this goal and propose modifications. Phosphorus recovery by spreading sludge on agricultural land has been stopped to a high extent due to resistance from the farmers' organisation (LRF) and food industries. Disposal of organic material to landfill will be forbidden in 2005. Difficulties to use earlier routes of final sludge disposal have led to a great interest in fractionation of sludges followed by recovery of different products and transfer of toxic materials into a small stream.

## PRESENT SOLUTIONS

Phosphorus removal and recovery occur in three steps:

- Transfer of soluble phosphorus into sludge by use of biological and chemical methods
- Solubilisation of sludge by use of physical, mechanical, biological or chemical methods
- Recovery of solubilised phosphate by methods as chemical precipitation, crystallisation or ion exchange

The most common technology is the use of enhanced biological phosphorus removal followed by release of phosphate during anaerobic treatment. Released phosphate may then be recovered as calcium phosphate or magnesium ammonium phosphate. The Scandinavian countries have chemical precipitation as dominating phosphorus removal method. Attention in phosphorus recovery has therefore been given on chemically bound phosphorus and thereby is also biologically phosphorus released and recovered.

Two systems for phosphorus recovery from sludges from biological and chemical treatment have been developed in the Nordic countries, Cambi/Krepro and BioCon. The two systems have in common that thermal treatment is used of the sludge for removal of organic material, dissolution of phosphorus compounds and metals by use of sulphuric acid and a system for recovery of precipitation agents and phosphorus. However, there are also many dissimilarities. Main characteristics of the two processes are shown in Table 1.

**Table 1.** Comparison of Cambi/Krepro and Bio-Con systems (Hultman et al., 2000).

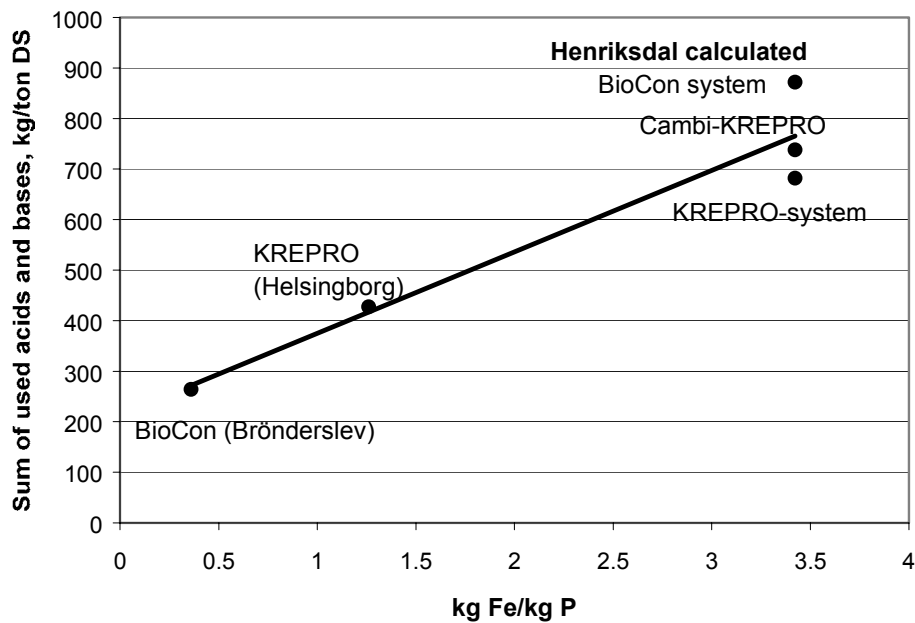
Process function	Cambi/Krepro	BioCon
Removal of organic material	Thermal hydrolysis of dewatered sludge, incineration of rest sludge, biological oxidation of soluble hydrolysed organic material	Heat drying and incineration of dewatered sludge
Dissolution of phosphorus and metals	Use of sulphuric acid treatment of dewatered sludge	Use of sulphuric acid treatment of ashes from incineration
Phosphorus product and recovery technology	Ferric phosphate obtained in chemical precipitation	Phosphoric acid obtained by use of ion exchange
Transfer of heavy metals in a small stream	Precipitation as metal sulphides	Concentration by use of ion exchange
Recovery of precipitation agents	Partial recovery by solution by acids (part of the precipitation agent is used to produce ferric phosphate)	Concentrated and recovered by use of ion exchange

Recently two Swedish companies, Chematur and Feralco, have agreed to co-operate on phosphorus recovery. The system consists of supercritical water oxidation of digested sludge followed by leaching of the residues by acids or bases. The technology is called the AquaReci process and the oxidation process is described by Gidner et al. (2000). The oxidation occurs in water of a supercritical phase at a temperature above 374 °C and a pressure higher than 22 MPa. The reaction time is fast (about 30-90 s). A pilot plant is operating in Karlskoga, Sweden, with a capacity of 250 kg/h.

### CHEMICAL NEEDS FOR PHOSPHORUS RECOVERY

The two systems, Cambi/Krepro and BioCon, and the earlier used process system Krepro have been evaluated concerning the chemical needs in phosphorus recovery. Actual data have been used for Krepro from Helsingborg wastewater treatment plant in Sweden as reported by Hansen et al. (2000) and at Brönderslev treatment plant in Denmark as reported by Svensson (2000). In addition, calculations have been made on the necessary amount of chemicals if Krepro, Cambi/Krepro and BioCon should be applied at Henriksdal treatment plant in Stockholm (Hultman et al., 2001a). Actual and calculated consumptions are shown in Figure 1.

The figure shows that the consumption of chemicals is mainly dependent of the dosage of iron salts calculated as weight ratio of Fe/P and to a much less extent of the choice of process technology. As much as about 800 kg of acids and bases are needed per tonne of dry solids to recover phosphorus at Henriksdal treatment plant if the plant is operated in the way reported in Stockholm Environmental Report for data from 1999. The figure also shows that the chemicals needed could be cut down to about 250 kg/tonne DS if the weight ratio of Fe/P is low and instead main phosphorus removal is performed by use of biological phosphorus removal.



**Figure 1.** Effect of weight ratio Fe/P on total chemical need of acids and bases for the system Krepro, Cambi/Krepro and BioCon (Hultman et al., 2001a).

### LEACHING OF ASHES AND RESIDUES FROM SUPERCRITICAL WATER OXIDATION

Water Resources Engineering, KTH, has performed some leaching experiments with different acid concentrations to find out how leachable phosphorus is from the inorganic phase after supercritical water oxidation.

Leaching experiments was done with hydrochloric acid (HCl) concentrations 0-2 mol/l. The results show that phosphorus is easily leachable, and nearly all phosphorus is leached. The results from iron show that it is partly leachable from the inorganic phase as is shown in Figure 2. B-sludge and K-sludge were obtained from Borlänge and Karlskoga, Sweden, respectively. The iron containing sludges had been treated by anaerobic digestion.

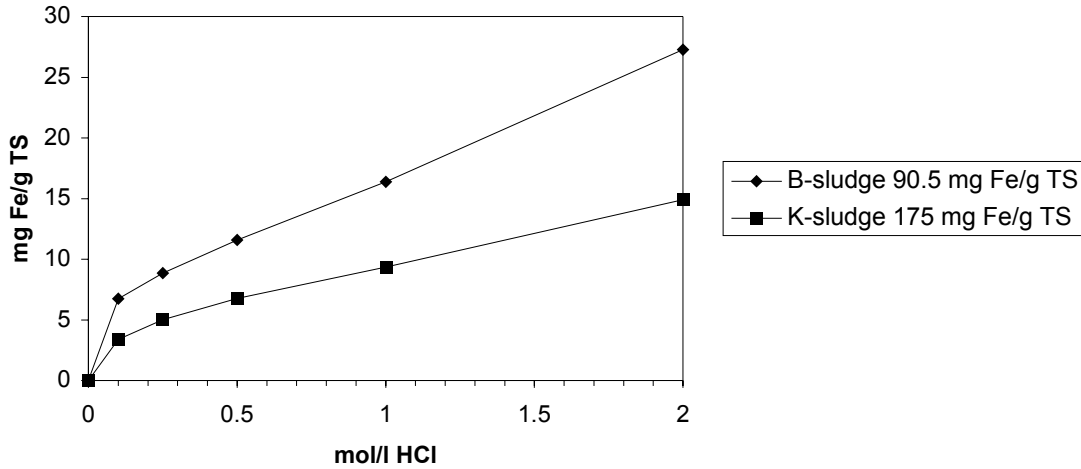


Figure 2. Iron leaching by HCl from supercritical water oxidation.

After the supercritical water oxidation the metal ions are not so tight bound as by incineration, where crystallisation and glassification may occur. Comparison of the results from supercritical water oxidation of waste water treatment sludge and from co-incineration of waste water treatment sludge together with household waste or re-cycled wood, are shown in (Figure 3) for the leaching of phosphorus. Phosphorus is easier to leach than iron from residues from supercritical water oxidation (Figure 2 and 3).

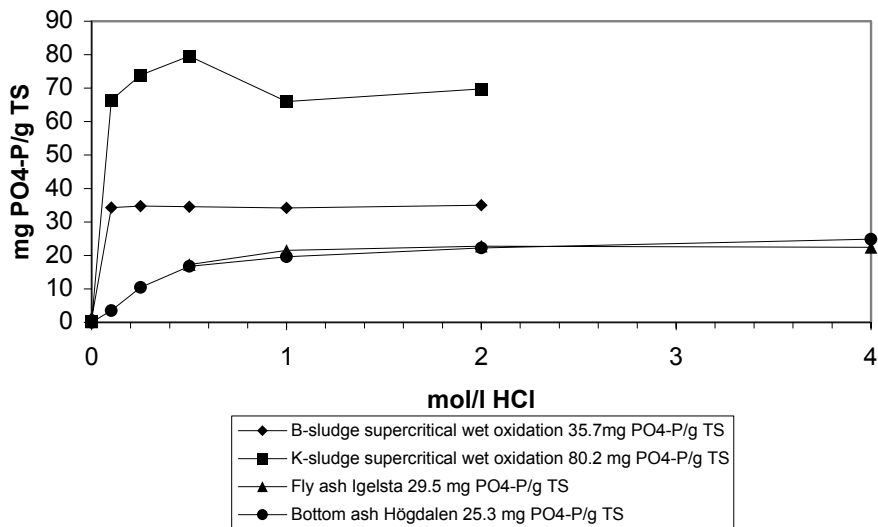


Figure 3. Phosphorus leaching by HCl.

## **CHANGED OPERATION FROM CHEMICAL TO BIOLOGICAL PHOSPHORUS REMOVAL**

Biological phosphorus removal was developed from about 1965 in USA and South Africa and has gained a wide application in many countries (Rybicki, 1997, Fujii, 2000). In Sweden there are about 15 plants in operation (mainly smaller plants). The combined requirement from authorities of both efficient phosphorus removal and recovery makes it important to evaluate if present operational methods (as for instance at the treatment plants in the Stockholm region) can be modified in such a way that chemical demands for phosphorus recovery can be significantly diminished without increasing the phosphorus concentration in the effluent and without the need for expensive new investments.

Suggested modification is illustrated by process schemes 1, 2 and 3 in figure 4 of operational modes in an existing plant with main removal of phosphorus by use of chemical precipitation.

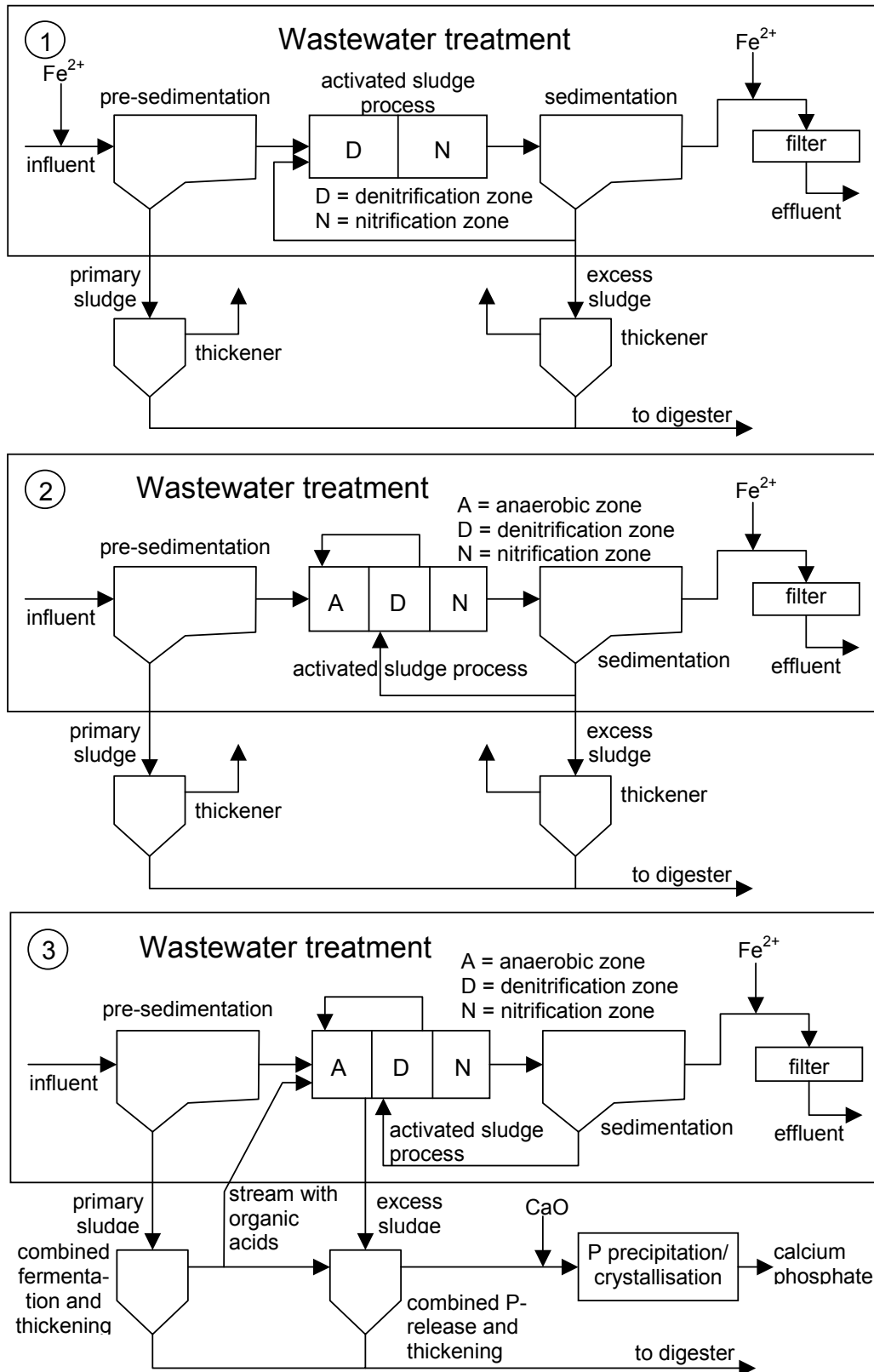
System 1 illustrates approximately the used process technology at the Bromma, Henriksdal and Käppala treatment plants and the process technology is similar at many other Swedish treatment plants. The technology permits a very efficient removal of phosphorus (effluent values below about 0.2 mg total-P/l). The chemical need for phosphorus is, however, very high as illustrated in Fig. 1 (corresponding to about 25 kg acids and bases per kg recovered phosphorus).

System 2 is the most studied technology for phosphorus recovery from sludges. The activated sludge process is modified to biological phosphorus removal (a small amount of coagulants is added before the filter to ensure a low effluent value of phosphorus). Phosphate is released in the digester and the obtained supernatant after dewatering of digested sludge is treated by chemical precipitation or crystallisation in order to obtain calcium phosphates or magnesium ammonium phosphate (Morse et al., 1998). The system has, however, some disadvantages:

- (1) Operational problems due to precipitation of magnesium ammonium phosphate during the digestion process
- (2) Too little presence of readily biodegradable organic material in the influent to ensure an efficient biological phosphorus removal process (this is actually the case for Henriksdal and Käppala treatment plants; Hultman et al., 2001a, Fujii, 2000).
- (3) The released phosphate in the digester may be adsorbed by metal precipitates and zeolites or be precipitated for instance as magnesium ammonium phosphate and thereby significantly diminish the degree of phosphorus recovery to values below 50% (cf Jardin and Pöpel, 2001).

The disadvantages of system 1 and 2 may be solved by use of system 3 and the objective of this process scheme is to provide:

- (1) Sludge is withdrawn from the anaerobic zone and thickened separately and complementary release of phosphate is obtained in the thickener, especially, if organic acids are supplied (cf Klapwijk et al., 2001). The ammonium concentration is much less than in a digester and therefore risks for precipitation of magnesium ammonium phosphate is reduced.
- (2) The use of combined thickening and fermentation of pre-sedimentated sludge for production of organic acids which can be used to improve the biological phosphorus removal efficiency.
- (3) Adsorbing materials as zeolites or post-precipitated sludges are removed in the pre-sedimentation process and will not cause refixation of released phosphates during the anaerobic treatment of activated sludge. Data by Klapwijk et al. (2001) indicate a release of up to 75% of phosphate in a system with removal of excess sludge from the anaerobic zone.



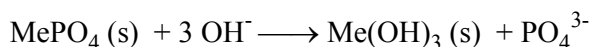
**Figure 4.** Different operational modes of an existing municipal wastewater treatment plant. System 3 is partly based on Hultman et al. (2001b) and Klapwijk et al. (2001).

System 3 seems to fulfil in a better way than system 1 and 2 the combined requirement of efficient phosphorus removal and recovery. The costs for new investments seem to be rather low and some costs may be regained due to use of only a small amount of chemical precipitation agents, product recovery and especially in further sludge handling. The obtained product has probably a high purity as most of the pollutants (heavy metals and organic micro pollutants) are bound to the sludge and not in the liquid phase. Many possibilities exist to further improve the overall process performance as the production of organic acids also from excess and digested sludge (for instance treatment with heat or sodium hydroxide) and to recover part of the phosphorus in the digested sludge.

### **TWO-STAGE PHOSPHORUS RECOVERY**

System 3 in figure 4 shows a way to recover phosphorus as calcium phosphate. The system will not recover phosphorus in primary sludge, sludge and filter sludge that is supplied to the digester. Additional phosphorus recovery may be obtained by thermal treatment of the digested sludge by methods developed by Cambi/KREPRO, BioCon or Chematur/Feralco. Special attention should be given to use of leaching methods that mainly dissolve phosphorus and not other materials in the sludge. Such methods include:

- Use of sulphides that react with iron phosphates to iron sulphide and thereby phosphates are released (Ripl et al., 1988)
- At a high pH-value aluminium and iron may be converted to metal hydroxide and phosphates are dissolved (Stumm and Morgan, 1981):



- In leaching of residues from supercritical water oxidation phosphates seem to be more easily dissolved than iron (cf figure 2 and 3)

### **CONCLUSIONS**

Combined requirements of phosphorus removal and recovery may lead to substantial changes in operation of municipal wastewater treatment plants. For treatment plants with chemical precipitation high amounts of chemicals are needed for phosphorus recovery by use of systems as Cambi/KREPRO and BioCon. Changes from chemical precipitation to biological phosphorus removal will reduce the necessary amounts. Efficient phosphorus recovery seems possible by use of two stages, one mainly for recovery of biologically bound and one mainly for chemically bounded phosphorus. Supercritical water oxidation gives a residue that makes it easier to dissolve phosphate compared with leaching of ashes.

### **ACKNOWLEDGEMENT**

This study has been supported by Stockholm Water Co. The authors thank Erik Levlin, Elzbieta Plaza and Kristina Stark for valuable comments on the paper.

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