A New Thermo-Chemical Approach for the Recovery of Phosphorus from Sewage Sludge

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Abstract

In order to utilise sewage sludge as phosphorus resource, several wet-chemical and thermo-chemical techniques have been developed so far, yet only few seem promising for large-scale implementation. In the EU-funded research project *RecoPhos* starting in March 2012, the Montanuniversitaet Leoben, the University of Stuttgart and eight partners from the industry will develop a new P-recovery process that produces phosphoric acid, a calcium-silicate slag and an iron alloy, all resources for the industry. The chemical principle, the Woehler reaction, will be realised on the chemically reacting packed bed of the so-called InduCarb retort. The ashes can be pre-purified in a reductive melt reactor connected upstream, using alternative heat sources like dried sludge.

1. Introduction

In the discussion about the sustainable use of natural resources the element phosphorus is gaining importance quickly. One of the most promising secondary phosphorus resources is sewage sludge, which has led many countries in and outside the EU to commit their near-future sludge strategy to phosphorus recycling instead of mere disposal.

The goal of most previous research works was to recover phosphorus directly either from a wastewater side stream or from liquid and dewatered sludge by wet-chemical processes. Many of them are combined with the removal of nitrogen from the wastewater, producing the ready-to-use N-P fertiliser MAP. Others precipitate the phosphorus as metal phosphates for the industry.

However, there is a general trend in Europe towards thermal treatment of sewage sludge, being the only way to destroy organic pollutants adsorbed at the sludge. Additionally, in the sludge disposal chain the highest concentration of phosphorus is found in the ashes from mono-incineration. With roughly 15 mass-% of P_2O_5 they can be considered as low concentrated rock phosphates. Hence both common ways of rock phosphate processing, the chemical digestion with sulphuric acid, as well as the thermo-chemical reduction, have in the past been considered appropriate to separate phosphorus from its mineral matrix.

Several other thermo-chemical approaches using dried sludge or ash attempt to leave the phosphorus in a purified mineral matrix, which shall serve as fertiliser directly or after further treatment.

Since up to now the development of efficient and competitive P-recovery techniques has had limited success, the EU as well as national and regional authorities in Europe are encouraging and funding further research in this field.

Currently, the Montanuniversitaet Leoben is working together with the University of Stuttgart and eight partners from the industry on the EU-funded research project *RecoPhos*. The goal of the project is to develop a new thermo-chemical process, in which sewage sludge ash will be separated on a reductively reacting packed bed into different fractions, mainly thermal phosphoric acid, a calcium silicate slag and an iron alloy. The chemical principle of *RecoPhos* is the Woehler reaction also used in the commercial process to produce elemental phosphorus or thermal phosphoric acid. However, due to the *RecoPhos* reactor design, the side reactions, mainly concerning iron and heavy metals, are expected to be crucially different to the ones taking place in the electric arc furnace, opening new possibilities to obtain pure products without restrictions by the used input material.

2. Phosphorus elimination from sewage

In most mechanical biological sewage treatment plants (STP) phosphorus is removed from the wastewater by chemical precipitation with iron salts as hardly soluble $FePO_4$. Alternatively aluminium salts can be used. Because of disturbances by iron in nearly all phosphorus recovery processes, aluminium salts are the more favourable precipitation agents in this regard in spite of their higher price. However it is not to expect that a significant renunciation from iron salts will take place in near and mid future [1].

A theoretically additive-free P-removal technique is the Bio-P process, in which a net amount of phosphorus is removed biologically from the wastewater. In an anaerobic stress situation in presence of easily degradable organics, microorganisms first release phosphate. In the following activated sludge tank they take up more phosphate than released before (*luxury uptake*).

Regarding phosphorus recovery, Bio-P can be interesting in two ways: Firstly, pure Bio-P-sludges contain a reduced amount of metals, mainly iron, and are therefore a preferred secondary P-source. Secondly, the first step of Bio-P can be used to enrich the water phase in phosphates, which can then be recovered more efficiently, e.g. by crystallisation or precipitation as described in the following chapter.

However, because of the elaborate control and unsteady efficiency of Bio-P due to seasonal temperature changes and its dependence on an easily digestible carbon source [2], only few STP remove phosphorus biologically. Also the phosphates remaining after Bio-P, which under unfavourable conditions represent the main load, usually need to be precipitated chemically.

3. Wet chemical P-recovery processes

Wet-chemical processes can be divided into two main groups: The first one transfers phosphates dissolved in wastewater or sludge water into a solid phase by crystallisation or precipitation with suitable salt solutions. The second group chemically digests liquid or dewatered sludge with various chemicals to re-dissolve the precipitated inorganic phosphates, which are then separated from disturbing substances (organics, re-dissolved metals) and finally crystallized or precipitated again.

The products of both process types are fertilisers (magnesium ammonium phosphate MAP) or raw materials for the industry (other metal phosphates).

Most of the phosphorus organically bound in the sludge microorganisms (about 50 % of the P-influent to the sewage treatment plant) is not accessible this way. Therefore some approaches try to release some of the organic phosphorus by biological pre-treatment („interrupted Bio-P“, e.g. *Phostrip, Ostara Pearl* process).

Next to *Ostara* in Canada and USA, several other wet chemical P-recovery processes are currently tried out in pilot or industrial plants, e.g. the modified *Seaborne* process in Gifhorn, *P-Roc* in Neuburg, *AirPrex* in Berlin, the *Stuttgarter* process in Offenburg, all Germany, and *Unitika* in Japan. The main target of the operation of these and other processes is to reduce the operating costs in order to reach marketability of their processes and products.

Wet-chemical approaches re-dissolving P from sludge mono-incineration ashes following the classical phosphoric acid production from rock phosphate, have mostly been given up because of relatively low efficiencies due to large mass flows and elaborate purifying steps (iron, heavy metals).

The company *RecoPhos*, which is *not related* to the EU-project with the same name presented later in this article, claims to produce 1,000 t/mon of a marketable P-fertiliser complying with the limits of the German fertiliser ordinance from ash by treatment with phosphoric acid, similar to the production of double- and triple-superphosphate, without further purifying [3].

4. Thermo-chemical P-recovery processes

The absence of disturbing organic material, the small masses to be treated and a P-recovery potential relating to the STP-influent of around 90 % make the thermo-chemical processing of sludge ashes a promising alternative. However, like in conventional phosphate processing, wet-chemical techniques seem much easier to realise. Also the implementation of processes depending on prior thermal treatment of the sludge is limited to regions that can and do afford this way of sludge disposal. Hence compared to the wet chemical approaches only few thermo-chemical P-recovery processes have been developed in the past years. Large scale experiments have been carried out by *AshDec (today Outotec), Mephrec*[1] and *ATZ*.

Even if the principles of these processes are completely different, they do have as one significant commonality their main products – phosphorus-containing mineral phases reduced in heavy metals, which they intend to use as fertilizer. Because of the relatively low phosphorus concentrations in some products, it can either be necessary to add phosphorus-rich material like animal meal (ash) to the input, or to mix the product with additional nutrients [4, 5].

[1] The Mephrec process works with dried sewage sludge; however, the process can be seen as a combination of thermal treatment (gasification) and conversion of the mineral residue to a fertiliser substitute.

After successful initial technical scale experiments in own plants, Ash Dec/Outotec [6] and Mephrec [7] are currently planning the erection of pilot plants in the near future to gather information about the economical feasibility of their respective processes under market conditions.

The phosphorus producer Thermphos (NL) is able to process rather big amounts of low iron sewage sludge ash in their electric arc furnaces. The incineration plant SNB is able to provide such ash by treating sludges with different iron contents separately. Iron, which is present in sludge ashes in average concentrations of 10 mass-%, is disturbing the process significantly as it is also reduced and captures phosphorus to form a ferrophosphorus alloy of rather low value. SNB claim on their website [8] that the planned amount of ash delivered to Thermphos in 2013 will be 18,000 tons, which corresponds to about 1.3 % of the annual phosphorus production of the plant[2].

5. A new thermo-chemical approach

The phosphorus recovery process to be developed in the recently started EU-project *Reco-Phos* is in its core using the same chemical principle as the classical phosphorus production in the electric arc furnace. The following equation shows the Woehler reaction for calcium phosphate:

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \rightarrow 3\,CaSiO_3 + 5\,CO + P_2$$

The phosphates in the ashes are reduced to white phosphorus, which is, after combustion of the off-gas, retrieved as phosphoric acid. This reaction takes place on the surface of an inductively heated carbon packed bed in the so-called InduCarb retort. While the phosphates and the flux SiO_2 are main constituents of the ash (see Table 1), the carbon can either be supplied by the bed material or by addition of a carbon carrier to the input.

Oxides	Mass-%	Heavy Metals	mg/kg dry matter
SiO_2	37	Zn	2,800
Al_2O_3	15	Cu	900
CaO	14	Pb	270
Fe_2O_3	13	Cr	200
P_2O_5	13	Ni	140
MgO	2.0	Cd	5
K_2O	1.4	Hg	not detectable
Na_2O	0.7	Remark: The Fe and Al contents may vary strongly with the P-precipitation and sludge conditioning process.	
TiO_2	0.7		
MnO	0.2		

Table 1:

Orientating composition of sewage sludge ash and heavy metal contents

Source: ISWA – University of Stuttgart

Next to the P_2-CO gas, the main products will be a Ca-Si slag as well as an alloy consisting mainly of iron. The slag is expected to be usable as binder in the cement industry, avoiding the release of fossil CO_2 by calcination of natural carbonates; the iron alloy will be offered to the steel industry.

2 assuming an annually processed rock phosphate amount of 700,000 tons [9] at double the P_2O_5-content of sludge ash.

A sketch of the reactor with the principle mass flows is shown in the following picture.

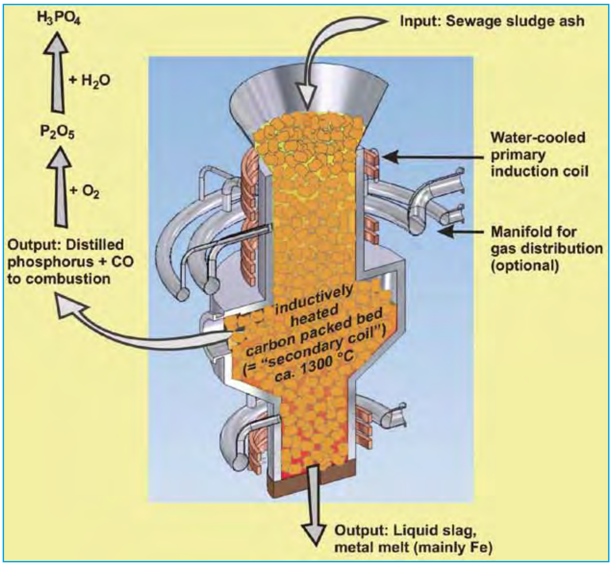

Figure 1:

Principle of the phosphorus recovery from sewage sludge ash in the InduCarb retort

In order to explain possible side reactions of the process, table 1 shows an orientating composition of sewage sludge ash including average heavy metal contents.

Next to phosphorus also other ash elements reducible by carbon will be reduced. While high-boiling heavy metals (e.g. Cu, Pb) will predominantly alloy with the iron, others like Zn and Cd will rather evaporate together with the phosphorus. Less noble lighter metals will mainly be found in the Ca-Si slag.

The ash's phosphorus compounds, e.g. calcium and iron phosphates, are theoretically all accessible for the Woehler reaction. Unlike the large dimensions of the melt in the electric arc furnace, the thin reacting layer of molten ash on the InduCarb's packed bed particles allows the gaseous product to escape easily without reacting significantly with the other constituents. The loss of phosphorus to the alloy will therefore supposedly be very low.

In the planned laboratory plant, the product gas will be incinerated and subsequently scrubbed to produce phosphoric acid. Depending on the heavy metal concentration of the ash input, the phosphoric acid as well as the solid products may be also contaminated. To reduce this effect, it is possible to pre-treat the ash by a melt step in the so-called Flash reactor, which has already been used successfully for the recovery of zinc from steel dust in the RecoDust process [10, 11, 12].

In this two-stage RecoPhos process, the heat necessary for the melting of the sludge ash can be generated from alternative heat sources such as dried sewage sludge mixed with the ash input. The reduced and evaporated heavy metals are removed from the waste gas stream of the first stage (Flash reactor); the purified melt is further reduced on the InduCarb. Electricity is hence only needed as energy source for the endothermic reduction.

6. The EU-project RecoPhos

The EU-project RecoPhos has officially started in March 2012 and is funded by the European Commission via the FP7 programme *Eco-Innovation*. Coordinating party is the

Montanuniversitaet Leoben, Austria, who is supported by nine partners from academia and industry: the University of Stuttgart (D), SGL Carbon GmbH (D), INERCO Ingenería S.A. (E), INSPYRO N.V. (B), H-CPE Hariri Chemical Process Engineering (CH), JELOGA Engineering (F), M.I.T. Metallurgy & Inorganic Technology (A), GCTU mbH Chemical and Environmental Engineering (D) and MAL GmbH Metal Construction – Plant Engineering (A).

Tasks to be solved during the three years' project duration are design, construction and operation of a continuous lab scale plant, process modelling and simulation, optimisation of output quality, operational safety as well as environmental and economical aspects. The behaviour and paths of heavy metals will require particular attention.

7. Outlook

The thermal treatment of sludge mono-incineration ashes is a promising approach to recover a maximum share of the phosphorus contained in sewage sludge. The advantage of thermal recovery is that minimal mass flows have to be processed. Approaches recovering P as element or as thermal P-acid like *Thermphos* and the new *thermal RecoPhos* process offer high flexibility in the use of their products. To establish these techniques, further research and testing is necessary in the coming years.

The use of sludge mono-incineration ashes as secondary P-resource also makes it necessary to stop their material utilisation or co-disposal with other wastes, and to provide facilities for the intermediate storage of the ashes instead. As this change means a rearrangement of parts of the waste economy, political steps are going to be inevitable in the near future.

Most wet chemical processes are not depending on this issue as they are processing sludge or sludge water. Some of them seem to be relatively easy to realise in near future. In spite of their rather low efficiencies, their decentralised application would replace a certain amount of the P-imports to their respective countries where thermal sludge treatment and thermal P-recovery is not available or not affordable. However, also the wet-chemical approach requires some years of further research and development.

8. References

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