

# Phosphate Recycling in the Phosphorus Industry

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## INTRODUCTION

Interest in phosphate recycling is increasing in the industrialized world. There are large amounts of phosphate available in waste streams from e.g. agriculture, sewage treatment and from industrial side streams which pose an increasing problem. To avoid wasting these in e.g. landfills, and to counteract the depletion of natural phosphate sources, routes for re-use are explored.

One possibility is to replace phosphate rock by recycled materials in the production of white phosphorus.

Worldwide, P production is limited to China, Kazakhstan, the USA and The Netherlands. The latter producer, Thermphos International, has decided to replace 40 kt a<sup>-1</sup> of their P<sub>2</sub>O<sub>5</sub> intake (17.5 kt P) by recovered materials.

## LIMITATIONS FOR PHOSPHATE RECYCLING IN THE PHOSPHORUS PROCESS

### The phosphorus process

The phosphorus process consists of two parts. The first part is a wet granulation and sintering of phosphate rock, producing hard pellets of 1-2 cm. This treatment is necessary to prevent blocking of the furnaces further downstream. The rock pellets are then mixed with cokes (reducing agent) and pebbles (SiO<sub>2</sub>, for slag formation) and fed into a furnace. The furnace is heated to 1500 °C by means of electric resistance. At this temperature, phosphate is reduced to P<sub>4</sub> which leaves the furnace as a gas, together with the by-product CO and some dust. This dust is removed in an electrostatic precipitator and recycled into the process. The P<sub>4</sub> is then condensed. The resulting CO gas stream is used as fuel for the sintering plant and other on-site processes. The calcium oxide which is left in the furnace after the phosphate has reacted, combines with the SiO<sub>2</sub> to form a liquid slag. This slag is tapped, cooled, crushed and used for e.g. road construction.

Iron, present as an impurity in the rock, is also reduced in the furnace. These form a separate slag, ferrophosphorus, which contains roughly 75% Fe and 25% P, with small amounts of other metals. It is used as a steel additive.

The usual route for phosphate recycling is to mix the material with the rock before the grinding stage. This implies that it has to fulfil the same set of restrictions imposed on regular phosphates and the impurities it contains.

## Phosphate content

The typical  $P_2O_5$  content of phosphate rock is 30-40% (= 13-17.5% P). The phosphate content of waste streams is usually lower. If the remainder is made up by inorganic compounds, this will lead to more slag per tonne of  $P_4$ . This will affect the energy efficiency of the process negatively, since the heat in slag is lost. The slag takes up a substantial amount, about one-third, of the total electricity consumption of the process; therefore extra slag should be avoided if possible. On the other hand, if the remainder of the secondary stream consists of  $SiO_2$ , this has no effect on the energy balance since the process requires the addition of  $SiO_2$  anyway. Aluminium compounds may replace  $SiO_2$  in slag formation, so that recovered aluminium phosphates would make a good raw material for the process.

## Impurities

Since the phosphorus furnace is a reduction process, it also reduces every (trace) element present which is more easily reduced than phosphorus. The most notable are:

- *Iron*. This forms a separate slag, an Fe-P alloy with 25% P. The removal capacity of this, and the market, are limited. If pure  $FePO_4$  is used, only one-third of the phosphorus is released as  $P_4$ ; the remainder will end up in the ferrophosphorus. Also, the reduction of iron requires additional energy and cokes.
- *Volatile metals*. Sewage sludges and manure often contain considerable amounts of zinc. This is volatilised in the furnace and subsequently precipitated on the furnace dust. Since this is recycled, zinc tends to build up in the system. This makes purges necessary. Similar problems occur for other volatile metals like lead, cadmium and tin. Radioactive isotopes, which are present in the rock as uranium decay products, such as  $^{210}Pb$ , are also accumulated here. This makes this stream lightly radioactive, typically  $800 \text{ Bq g}^{-1}$ , which requires special handling and prevents its use as a Zn source, or landfill. Instead it has to be stored as a radioactive waste. Rock typically contains  $< 300 \text{ mg/kg}$  zinc, higher levels should be avoided.
- *Chloride* causes corrosion damage to the granulation/sintering plant, where metal parts are exposed to the raw materials at high temperatures.
- *Copper* ends up in the ferrophosphorus. Steel producers, the main clients for ferrophosphorus, limit their intake of copper for most high-grade steel types since too much copper weakens the steel. Natural phosphate rock contains very little Cu ( $3\text{-}30 \text{ mg kg}^{-1}$  depending on the source), whereas the Cu content of manure ash or sewage ash is typically about two orders of magnitude higher (see below). This prevents sale of ferrophosphorus, leaving (costly) landfilling as the only alternative.

## Water content

Phosphate rock is usually supplied as a dry material. A considerable number of waste treatment processes generate wet sludges of organic or inorganic phosphates. The P process cannot use wet material on a large scale because it interferes with the wet granulation which is also a binder addition step. Drying materials on-site could solve this problem, but there is no waste (low-grade) heat source available, so that drying would involve energy purchase and consumption and so be costly; more importantly, it is economically and ecologically undesirable to transport materials with a high water content over large distances.

### **Organic material and ammonium, pellet strength**

The presence of significant amounts of organic material lead to a decreased pellet strength after sintering. This will seriously limit the capacity of the plant, which is unacceptable. Therefore, the material should consist of inorganic phosphates only (max. 5% carbon). Other impurities should also be screened for this effect.

### **SEWAGE AS A SOURCE OF SECONDARY PHOSPHATES**

In 1998 the Dutch sewage contained about 14 kilotonne/year phosphorus (as P) [1]. In the wastewater treatment plants about 10 kt P/year was removed by chemical and biological treatment methods, eventually this should become 12 kt/y. Almost all the removed phosphorus is fixed in the primary and secondary sewage sludge. This sludge is treated and disposed of in several ways, but no more than 14% has a useful application as compost (table 1). Roughly half is incinerated. As application in agriculture is no longer accepted, the amount of sludge incinerated will increase.

Wet or dried sludge is not suitable for use in the P process due to the water and organic content. Minor techniques such as wet oxidation also produce unsuitable materials. The ash from sludge incinerators is dry and inorganic, with up to 16%  $P_2O_5$ , but unfortunately the amount of iron is an order of magnitude too high to be useful in the P process. This is due to the use of ferric chloride in many sewage treatment plants to precipitate residual phosphate chemically. Also, the zinc (3000 mg/kg) and copper (1500 mg/kg) content are an order of magnitude too high. Together with the low phosphate content, this makes the material unsuitable for  $P_4$  production.

Replacing iron by calcium or aluminium would make ash processing in the P process much more feasible. At present, the use of aluminium in wastewater treatment is more costly, and calcium use in existing sewage works processes can cause sludge handling problems; it has to be evaluated whether the positive effect on the ash side will compensate for this. The general, government-induced tendency away from landfilling and towards recycling may be helpful here.

### **Bio-P removal**

The problems associated with iron can also be avoided when the ash from sludge from biological phosphate removal treatment plants (bio-P plants) is used. In these plants, all phosphate is removed biologically and no additional phosphate precipitation is needed. Bio-P sludge ash consists of aluminium, calcium, magnesium and sodium phosphates, with a promising 36% of  $P_2O_5$ . However, zinc and copper are still present in the same amounts making the material relatively unattractive for the P process. Also, the separate collection and incineration of bio-P sludge poses logistical problems. Side-stream recovery of phosphate in a WWTP (waste water treatment plant) solves these problems.

### **Side stream recovery**

It is also possible to recover phosphate selectively, at the treatment plant itself, especially at bio-P plants. There are several ways of doing this, such as the Phostrip-process [2] and the BCFS-process [3]. For an overview, see [4].

In the Netherlands the treatment plant of Geestmerambacht uses the Phostrip process. The phosphate is precipitated in a Crystallactor, a sand-seeded precipitation reactor which produces phosphate pellets with less than 20% moisture. The product is a very pure Ca

phosphate with impurity levels well below the limits set for the P process. This material can be used to make  $P_4$  in any amount.

It is estimated that 75% of all phosphate can be recovered in this way. The remainder will stay in the active sludge.

The implementation of this technology at all WWTP's will be costly. However, it is possible to collect all filter-pressed bio-P sludges separately, transport them to a treatment plant near the central incinerator, and perform the side stream P recovery in one large reactor as described above. The sludge could then be pressed again and incinerated; also, the phosphate would become available at one site which will make transport to the P plant easier.

According to an inquiry [1], about 90 of the 414 Dutch wastewater treatment plants have included biological P removal in their process (Figure 2). The total amount of phosphate that can theoretically be recovered in this way is about 18 kton  $P_2O_5$ /year (8 kt P/year).

### **MANURE AS A SOURCE OF SECONDARY PHOSPHATES**

In countries with intensive livestock farming, manure can pose a problem since its spread on arable land is often limited by regulations. Much as with WWTP sludge, manure can be treated in an incinerator, or treated in a dedicated plant. The first category is currently being developed in the UK and the Netherlands, where incinerators for poultry manure are operational or under construction. Unfortunately, this ash has also too much zinc (1500 mg/kg) and copper (600 mg/kg). Ash from pig manure typically contains double the amount of zinc. This and the low phosphate content (15-20%  $P_2O_5$ ) make these materials unattractive for the P process.

An interesting opportunity is the dedicated treatment of liquid calf manure to recover potassium struvite. This type of material is very pure and in theory suitable for  $P_4$  production. A plant test using this struvite was concluded successfully and the material will be used as feedstock for the phosphorus process on a regular basis.

### **BONE MEAL ASH AND DICALCIUM PHOSPHATE**

The recent developments in the livestock industry (BSE, foot-mouth disease) have led to a change in the market for bone meal ash and DCP from gelatin producers. Both materials are technically suitable for use in the P process, provided that the chloride content is not too high. However, the issues associated with these diseases and the consequences for their re-use make it difficult to use them as raw materials for other applications.

### **INDUSTRIAL AND FOOD INDUSTRY WASTE STREAMS**

Many industries produce phosphate waste streams, for example food and dairy processing, metal treatment and etching, electronics manufacturing and other processes that use phosphorus, phosphoric acid or phosphates. A large variety of phosphate-containing wet and dry materials result from the treatment of these waste streams. In The Netherlands, these contain at least 5 kt/y (as P). A large part of these materials is suitable for processing in the P process, depending on the nature of the material.

A large problem in obtaining secondary phosphates from other countries is the waste legislation. It is usually not permitted to transport waste across the border, and many secondary phosphates are currently classified as waste. There is need for less rigid legislation

and regulation on national and European scale, especially regarding the difference between waste materials and recyclable raw materials. This should prevent landfill of valuable materials. The current legislation creates barriers which discourage or prevent recycling.

## REFERENCES

1. **Centraal Bureau voor Statistiek (2000)** Waterkwaliteitsbeheer. Zuivering van afvalwater, 1998, CBS, Voorburg/Heerlen, The Netherlands, 59 pp.
2. **Levin, G.V. and Shapiro, J. (1965)** Metabolic uptake of phosphorus by wastewater organisms. *J. Water Pollut. Control Fed.* **37**, 800-821
3. **Loosdrecht, M.C.M. van, Brandse, F.A. and Vries, A.C. de (1998)** Upgrading of waste water treatment processes for integrated nutrient removal- The BCFS® process. *Water Sci. Technol.* **37**, 209-217.
4. **Brett, S, Guy, J., Morse, G.K., and Lester, J.N.** Phosphorus removal and recovery technologies, Selper Ltd, London, UK 1997.
5. **Van Soest, J.P., Sas, H. and Wit, G. de (1997)** *Apples and Oranges*, Centrum voor Energiebesparing en Schone Technologieën, Delft, The Netherlands
6. **Potjer, B., Vermeulen, J., Weerd, G. de, Bergsma, G. en Croezen, H (2000)** *Fosforkringloop voor Thermphos*, Centrum voor Energiebesparing en Schone Technologieën, Delft, The Netherlands
7. **de Wit G., Davidson, M.D., and Bleijenberg, A.M.**, Economisch-Sociale Berichten 4159 (1998), 516-518