Chapter 16
Phosphorus Recovery into Fertilizers and Industrial Products by ICL in Europe

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Abstract Phosphate recycling is an important issue, since phosphate is a finite resource which is essential to food security. The phosphate used in the fertilizer industry, which now solely comes from mining, has to be replaced with so-called secondary phosphates. At ICL Fertilizers, trials have been conducted to investigate the potential implementation of these sources of secondary phosphates into the fertilizer production. Extensive pilot-scale testing and several plant-scale tests have yielded promising results for the use of sewage sludge ash, meat and bone meal ash and struvite. The main issue remaining is the legislation for the use of these sources, as they are currently regarded as waste. Struvite is also suspected to be able to contain contaminants such as pathogens and pharmaceuticals, encapsulated in its crystals. Therefore, further research on this topic is necessary. In the draft of the new Fertilizer Regulations of the European Commission, maximum values for heavy metal content in fertilizer are discussed in greater detail. The first results show that products produced from sewage sludge ash (the big quantity of secondary phosphates) meet some of these demands; however some limits are put (without doing a risk assessment) too low and could block the use of these secondary phosphates in fertilizers. Since heavy metal content in struvite and meat and bone meal ash is low, no problems are expected. The use of secondary phosphate in fertilizer production yields great opportunities; however in parallel ICL is piloting other processes for production of industrial products (elemental phosphorous P_4 and food-grade phosphoric acid). The P_4 route is via the thermal RecoPhos process (inductive heating of ashes and evaporation, cleaning and condensation of the P_4) where no waste what so ever is created, only products with a positive market value. The food-grade phosphoric acid route is via the Tenova process, where ashes are treated with by-product HCl to produce phosphoric acid, which is then purified in several extraction stages. In the coming years, the pilot results will show the economic feasibility of these processes for which ICL has its own captive use in industrial applications. In this way ICL will try to turn the development of a circular economy from a threat into an opportunity.

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16.1 Introduction

For some other finite resources, like oil, it is possible to find alternative sources. For phosphorus this is not the case as this is a chemical element (Heffer et al. 2006). Therefore, usage has to be cut to make the reserves last longer. Still, this will not make phosphorus an infinite resource (Van Vuuren et al. 2010). Closing the phosphorus cycle by recovering and recycling will be required if phosphorus famine is to be prevented (Gilbert 2009).

Phosphorus is disposed of in human excreta, used detergents and food and industrial waste. This stream enters the sewage systems and offers an opportunity to recover it as it accumulates in the sewage sludge at wastewater treatment plants. The sewage sludge can be processed in many different ways to recover the phosphorus (Schick et al. 2009). These can be summarized into three main categories: the watery sludge, dewatered sludge and sewage sludge ash. At wastewater treatment plants, struvite, which is essentially magnesium ammonium phosphate, can also be formed by crystallization and precipitation. This feedstock also contains a high level of phosphorus and can be regarded as a secondary phosphate source (Jaffer et al. 2002).

Next to the wastewater treatment plants, other sources exist (Schipper et al. 2001). Since the ban on the use of meat and bone meal as animal feed due to the outbreak of BSE, it is classified as a waste material (Yamamoto et al. 2006). The meat and bone meal is incinerated, rendering it harmless, but this also renders it useless for its traditional uses. The phosphate content in this is even higher than sewage sludge ash and it contains less contaminants.

The nutrient availability for plants of the phosphate is imperative for it to be used in a fertilizer (Cabeza et al. 2011). The solubility in neutral ammonium citrate and water, which with phosphate rock is realized by acidulating, is important. The processing for this will be discussed later in this chapter. The main issue regarding the use of secondary phosphates is legislation, as the streams currently being tested are regarded as waste. Also, some contaminants are present in selected sources. In sewage sludge ash, for example, a relatively high amount of heavy metals are present. This does not, however, have to be an issue.

16.1.1 ICL Fertilizers' Position

ICL Fertilizers runs several fertilizer production units in different parts of the world with two in Europe (the Netherlands and Germany) with a combined capacity of 800,000 t/a product and a use of 250,000 t/a rock phosphate. All of them are based

Fig. 16.1 ICL Fertilizers' production plant in Amsterdam

on the attack of phosphate rock with sulphuric acid, phosphoric acid or combinations of the two (secondary attack) after which potassium chloride (MOP) or potassium sulphate (SOP) or trace elements (Cu, Mg, Mn, Mo, Zn, etc.) can be added to make different forms of PKs and on top of that ammonium sulphate to produce NPKs. These processes are very suitable for the recycling of secondary phosphates (contrary to other NPK processes) without any safety issue.

At ICL Fertilizers in Amsterdam (Fig. 16.1), a lot of research and testing has been done regarding the use of secondary phosphates in the fertilizer production. Extensive pilot-plant scale tests (Ten Wolde 2012) have been done regarding the use of struvite as well as that of sewage sludge ash and meat and bone meal ash on plant-scale tests.

As a phosphate fertilizer producer with an own supply of phosphate in the Israeli desert and a mine in China, it could be perceived as odd to be researching the use of secondary phosphates. The vision of ICL Fertilizers is that sustainability is important and the environment is to be taken care of. 'Closing the loop' on phosphorus could elongate the use of the phosphate mines and improve the distribution of phosphorus on a worldwide scale. The fact that ICL's European plants are in countries with excess phosphate adds to this philosophy: 'Using a part of all recycled phosphate in factories that export a major part of their products to countries with a deficit on phosphate helps solving the existing phosphate surplus in The Netherlands and Germany'.

16.1.2 Value Chain Agreement

In the Netherlands, ICL Fertilizers Europe is taking part in the so-called value chain agreement (covenant), initiated by the Nutrient Platform in 2011. Together with 19 other parties, the ambition is to create a sustainable market where reusable phosphate streams will be returned to the cycle in an environmentally friendly way. ICL Fertilizers Dutch ambition is to base its entire fertilizer production in the Netherlands on secondary phosphates by 2025 (Dutch Nutrient Platform 2011). Since the phosphate issue is not merely a Dutch issue but a European one, the expansion to a European Union-based platform was desirable. In 2013, at the 1st European Sustainable Phosphate Conference in Brussels, the European Phosphorus Platform was launched, with over 150 participants. This is an important development to move forward and could improve Europe's competitive position and avoid potential geopolitical tensions (European Phosphorus Platform 2013).

16.2 Secondary Phosphate Sources

Different sources are available within the European Union. These can be categorized in three main categories. These are manure and litter, phosphate-rich ashes and struvite. The main differences between these sources are the solubility of phosphate and the contaminants it can contain. Also the physical form is an important factor that differs. These facts impact the way the secondary phosphates can be employed in the fertilizer value chain. In this section, the properties of the sources will be discussed.

16.2.1 Manure and Litter

Several countries, such as the Netherlands, with intensive livestock agriculture have a surplus of animal manure and poultry litter. Since these contain phosphates, research is being done to be able to use these as a raw material for fertilizer production. Untreated manure contains organic components and water and is of a low nutrient content. For industrial applications it therefore needs to be dewatered and incinerated (Schipper et al. 2001). These ashes could be employed as raw material for the fertilizer production in secondary attack units in the same way as sewage sludge ashes.

Other techniques currently being researched is the pyrolysis of manure (Azuara et al. 2013) and the gasification of chicken litter (Kaikake et al. 2009). The products from these processes could also be implemented in the production of phosphate fertilizer. Since incineration of manure destroys the organic material and the nitrogen, an alternative route for treatment of manure by digestion (energy production), taking out the N as ammonium sulphate and the P as calcium phosphate (both products to be used as secondary raw materials in industrial NPK production), the remaining organic fraction has a good value for the farmer to be used on his fields without over-fertilization with N and P. One of the projects researching this option is the SYSTEMIC project led by Wageningen University in which ICL is a partner.

16.2.2 Ashes from Mono-incineration

The phosphate-rich ashes are a product of mono-incineration of a phosphate-rich stream, such as from wastewater treatment plants or meat and bone meal from rendering factories. Due to the incineration of phosphate-rich streams separately from phosphate-poor streams, relatively high phosphorus content can be achieved in the ash.

16.2.2.1 Sewage Sludge Ash

At wastewater treatment plants, surface water-polluting phosphate is precipitated using iron or aluminium compounds forming sludge. The Dutch sewage system contained about 32 kt P_2O_5 per year in 1998 (Schipper et al. 2001). Recovery can be done directly from the sludge, from dewatered sludge or incinerated sewage sludge ash. Wet or dewatered sludge is not suitable for the traditional industrial processing, as these streams contain water and could contain organic compounds, viruses, medicine and other contaminants. These can be rendered harmless by incinerating the sludge.

This yields sewage sludge ash. Dewatered sewage sludge is incinerated in dedicated furnaces in order to prevent more contaminants from other streams such as industrial waste to contaminate the sludge, further diluting the phosphate content (European Commission 2000). As this is the form from which over 90% can be recovered, this is the most interesting, and it could be possible to integrate it into existing infrastructure (Cornel and Schaum 2009). Another advantage of incineration of the sewage sludge is that it has a caloric value, so it yields energy on incineration.

The main problem with sewage sludge ash (SSA) is the content of heavy metals, iron and aluminium. These hinder the regular processing, which will be discussed later. Since the flocculants for sewage sludge vary, several different analyses are shown in Tables 16.1 and 16.2. A sewage sludge ash sample is depicted in Fig. 16.2.

16.2.2.2 Meat and Bone Meal Ash

Prior to 2001, meat and bone meal (MBM) was primarily used in animal feed, but in 2001 this was banned in Europe due to the fact that MBM was suspected to be the cause of the mad cow disease outbreak (Yamamoto et al. 2006). This caused large-scale waste problems which were solved by incinerating the MBM and thus creating meat and bone meal ash (MBMA) (Cascarosa et al. 2012). This meat and bone meal ash is very similar to regular phosphate rock in terms of chemical composition. Also

Table 16.1 Analyses of the main components of sewage sludge ash (SSA), meat and bone meal ash (MBMA) and phosphate rock

Total wt%	SSA 1	SSA 2	SSA 3	SSA 4	MBMA	Wood ash	Phosphate rock
P_2O_5	15,20	20,44	18,90	17,80	25,50	4,8	30,96
CaO	18,80	20,59	11,50	18,60	37,40	13,5	47,50
SO_4	5,30	4,50	1,60	3,00	6,40	6,2	2,70
K_2O	1,30	1,66	0,80	1,20	2,20	14,8	0,70
MgO	2,30	2,74	1,19	2,90	0,99	8,1	0,40
Al_2O_3	6,28	9,39	9,44	9,20	1,74	12,9	0,11
Fe_2O_3	12,08	5,82	3,05	5,60	0,99	9,5	0,17

Table 16.2 Heavy metal content analyses of sewage sludge ash (SSA), meat and bone meal ash (MBMA) and phosphate rock

ppm	SSA 1	SSA 2	SSA 3	SSA 4	MBMA	Wood ash	Phosphate rock
As	20,1	19,9	9,4	9,0	8,1	0,4	17,8
Cd	2,1	1,0	2,2	<0,1	1,7	<0,2	25,9
Cr	115,5	124,5	25,0	79,5	18,1	1,0	53,0
Cu	760,3	1146,0	404,0	749,6	365,0	1,5	13,5
Ni	44,6	49,6	17,8	37,7	7,8	1,1	30,7
Mn	871,6	825,5	3070,0	719,4	207,0	11,7	6,7
Pb	273,0	254,0	157,6	84,4	82,4	2,2	< 0,1
Zn	3053,0	2139,0	876,0	1624,0	209,0	–	260,2

Fig. 16.2 Sewage sludge ash

the content of contaminants is very low, as can be seen in Tables 16.1 and 16.2. The product received at ICL Fertilizers for testing can be seen in Fig. 16.3.

16.2.2.3 Wood Ashes

Several initiatives are taking place to incinerate clean waste wood as a biofuel. The ashes coming from this incineration are fairly pure and contain phosphates and potash as valuable nutrient, however in a not-available form for plants. They can, however, be transformed by secondary attack into soluble fertilizers. The results of component analysis can be seen in Tables 16.1 and 16.2. It should be remarked that nutrient content varies a lot over different types of wood.

Fig. 16.3 Meat and bone meal ash

16.2.3 Struvite

At wastewater treatment plants, struvite crystallization is a widely used technique to remove phosphorus, ammonium from digested sludge liquors (Martí et al. 2010) by adding a source of soluble Mg in the proper stoichiometric ratio. The main driver for this is not the nutrient recovery, but the improvement of process conditions (less scaling, better filterability) (Jaffer et al. 2002). Struvite is sometimes also referred to as MAP (magnesium ammonium phosphate) and consists of these ions in a molar ratio of 1:1:1. The reaction that takes place is shown in Eq. (16.1):

$$Mg^{2+} + NH_4^{\ +} + PO_4^{\ 3+} + 6\,H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad (16.1)$$

Since struvite is not incinerated, a certain fear exists that it could contain pathogens, pharmaceuticals, hormones and other contaminants encapsulated in the crystals (Decrey et al. 2011). Research on struvite precipitated from urine has shown that 98% of the hormones and pharmaceuticals remained in the filtrate and only a small fraction of the heavy metals remained in the struvite. Drying has shown to be effective to inactivate viruses that could be present in the struvite. Heating struvite to a temperature higher than 40–55 °C causes it to decompose, releasing gaseous ammonia (Bhuiyan et al. 2008). Therefore, drying should be done in a controlled fashion, and further research is needed in this field.

Struvite can be obtained from several different processes. The struvite samples that have been tested at ICL Fertilizers for the use in fertilizer production were obtained from the Anphos and Airprex processes (Figs. 16.4 and 16.5). Analyses from these struvite are shown in Tables 16.3 and 16.4, with a phosphate rock analysis for comparison.

16.3 Processing in Mineral Phosphate Fertilizer Production

The main two types of secondary phosphates which can be used in the production of phosphate fertilizer are ashes (from mono-incineration such as meat and bone meal ash, wood ash, sewage sludge ash) and struvite. At ICL Fertilizers, these have been extensively tested on a pilot scale, and some have also been tested on plant scale. The results of these tests will be discussed in this section, as well as the technical implications it has on the current infrastructure at the production location in Amsterdam.

16.3.1 Ashes from Mono-incineration

As well in sewage sludge ash as in wood and meat and bone meal ash, the phosphate is not soluble in water or neutral ammonium citrate (NAC) and thus not plant-available. With phosphate rock, acidulating the rock with either sulphuric or

Fig. 16.4 Struvite from the Anphos process as received in bulk

Fig. 16.5 Struvite crystals from the Airprex process (STOWA 2012)

Table 16.3 Analyses of the main components of Airprex and Anphos struvite and phosphate rock

wt% (TQL)	Struvite Airprex	Struvite Anphos	Phosphate rock
Total P_2O_5	19,8	14,7	30,96
NH_4	3,8	2,6	0,00
CaO	0,8	2,3	47,50
SO_4	0,1	0,5	2,70
MgO	10,2	7,6	0,40
Al_2O_3	0,1	< 0,1	0,11
Fe_2O_3	1,5	0,3	0,17
Moisture	14,9	21,9	1,8

Table 16.4 Analyses of the heavy metal content of Airprex and Anphos struvite and phosphate rock

ppm	Struvite Airprex	Struvite Anphos	Phosphate rock
As	<0,1	0,0	17,8
Cd	<0,1	0,0	25,9
Cr	11,1	0,0	53,0
Cu	31,6	2,0	13,5
Hg	<0,1	0,0	< 0,1
Ni	3,6	0,0	30,7
Mn	<0,1	12,0	6,7
Pb	652	0,0	0,0
Zn	85,9	11,0	260,2

phosphoric acid will yield single or triple superphosphate, respectively. These fertilizers have a typical water and water + NAC solubility of 90–92% and 95–97%. The reaction equations of the acidulation to single and triple superphosphate are shown in Eqs. (16.2) and (16.3) (Kongshaug et al. 2000):

$$2Ca_5(PO_4)_3F + 7H_2SO_4 \leftrightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF \qquad (16.2)$$

$$2Ca_5(PO_4)_3F + 7H_3PO_4 \leftrightarrow 5Ca(H_2PO_4)_2 + 2HF \qquad (16.3)$$

Phosphate from ashes is not present in the form of apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), but in complexes with iron, calcium or aluminium. Due to this different form and the presence of other contaminants such as heavy metals which could react with the acid, a regular acidulation mixture does not yield the physical and chemical results required. Another important difference between the apatite and these ashes is that the apatite contains fluorides, chlorides, hydroxides and carbonates. During acidulation, these are released into gaseous form such as HF, SiF_4, HCl and CO_2. In order to create sufficient surface area during the acidulation process, which delivers a product that is softer and better processable, some additives have to be mixed with the ash prior to acidulation. These ashes are much finer than regular phosphate rock.

Therefore, milling is not necessary. This does impact the handling and storage. Therefore, storage in silos and direct input in the mixers are desirable.

16.3.1.1 Meat and Bone Meal Ash

Meat and bone meal ash shows most similarities with apatite; the phosphate is mainly present as calcium phosphate. This reacts with acid in a similar way as apatite, as can be seen by comparing Eqs. (16.2) and (16.3) with (16.4) and (16.5):

$$Ca_3(PO_4)_2 + 3H_2SO_4 \leftrightarrow 3CaSO_4 + 2H_3PO_4 \tag{16.4}$$

$$Ca_3(PO_4)_2 + 4H_3PO_4 \leftrightarrow 3Ca(H_2PO_4)_2 \tag{16.5}$$

This suggests that regular acidulation with a slightly different acid concentration would be possible. Also, since the meat and bone meal ashes have a phosphate content that almost reaches the concentration found in phosphate rock, it can be mixed with phosphate rock to achieve regular products. During extensive tests on pilot scale at ICL Fertilizers, it has shown that this is the case. Mixing with regular phosphate rock was possible, achieving a high water solubility and neutral ammonium citrate solubility yield. The physical properties of the produced superphosphate are also similar to that of phosphate rock.

Besides a mixed acidulation with phosphate rock, acidulation of pure MBMA was also possible and yielded good results with regard to the chemical properties. The physical properties of the acidulated MBMA did impact the processability, and at this moment, a mixture with phosphate rock is preferred.

16.3.1.2 Sewage Sludge Ash

As shown in Tables 16.1 and 16.2, the levels of aluminium, iron and heavy metals are much higher than that in phosphate rock or meat and bone meal ash. Next to the fact that it is possible for the phosphate to be present in complexes with the iron and aluminium, it is also possible for the acid to react with these:

$$2Ca_5(PO_4)_3F + 7H_2SO_4 \leftrightarrow 3Ca(H_2PO_4)_2 + 7CaSO_4 + 2HF \tag{16.6}$$

$$2Ca_5(PO_4)_3F + 7H_3PO_4 \leftrightarrow 5Ca(H_2PO_4)_2 + 2HF \tag{16.7}$$

Acidulation of different sewage sludge ashes has been tested at ICL Fertilizers. This resulted in a large spread in the resulting products. Since the contaminant levels are high in the sewage sludge ash, mixtures with phosphate rock showed only negative effect. Acidulation using phosphoric acid also did not yield good results, as the product did not coagulate fully, which was not processable. Therefore, only acidulation using sulphuric acid was further tested.

Three sewage sludge ashes with a different iron content were acidulated and monitored in time, since the water solubility in acidulated phosphate rock normally increases in time as the reaction continues. This increase in time was not noticed with the sewage sludge ashes. The water solubility of the reaction product is a clear function of the iron and aluminium content of the ash. The solubility in neutral ammonium citrate of these products shows the same dependency, be it that in general Al-based ashes are reducing recoveries less than Fe-based ashes.

Another important factor for employing sewage sludge ash in the production of phosphate fertilizer is its physical properties. Regular acidulation mixtures showed a sticky product, which was not processable. Removing part of the water and thus increasing the acid concentration showed positive effect on this. The iron-based sewage sludge ashes delivered less processable products, regardless of the used acid concentration. The acidulation has also been tested at ICL Fertilizers on plant scale, which resulted in good acidulation of 10–14 tons sewage sludge ash (7 wt% Fe_2O_3) per hour. No optimized acidulation mixture has been found yet for the acidulation on plant scale, since tests need to be continued. The resulting product did show good physical and chemical properties.

To check the granulation properties, several different recipes were used. Six PK- and four P-fertilizer granulations were executed in the initial trials. The conclusion found from these results is that the optimum for using sewage sludge ashes is making a specific mixture of acidulated high reactive Israeli rock phosphate with acidulated sewage sludge ash in the granulator. This caused the granulation to yield a good granule size distribution and a proper nutrient content.

During the granulation, the temperature was over 10 °C higher than regular phosphate rock granulation. In the PK granulation, this could be attributed to the exothermic reaction taking place between the free acid and potash as shown in Eq. (16.8). During granulation some hydrochloric acid fumes were noticeable. However, this temperature rise is also present in the P-only fertilizer, of which the temperature rise cannot be ascribed to this reaction (Schultz et al. 2000). In the used setup, it was impossible to determine the cause of this:

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl \tag{16.8}$$

Besides this difference in temperature, the granulation process itself is more sensitive. More water is needed for the granulation to start, and the granulation is more prone to spontaneous over-granulation than is the case with comparable non-SSA containing fertilizers. When granulating the mixtures, the P_2O_5 water-soluble yield was not proportional to the yield in both components. This suggests that there could be a reaction taking place during granulation, which could also attribute to the temperature increase.

Fig. 16.6 PK 8-27+7MgO from plant-scale test with Airprex struvite

16.3.2 Struvite

Unlike the ashes from mono-incineration, the phosphate in struvite is readily neutral ammonium citrate soluble. Therefore, the acidulation step does not have to be carried out on this feedstock which simplifies the processing of it. Several plant-scale tests have been carried out with struvite as a secondary phosphate. Struvite obtained by the Airprex process from a wastewater treatment plant was very well usable and could be added to a maximum of 20% of the total granulation input. The moisture content of the used struvite appeared to be the limiting factor. As the struvite used in the plant-scale test contained between 15% and 20% total moisture (so including crystal water), water and steam addition to the granulation drum had to be limited, and smearing occurred on several points.

The main differences in the obtained products using struvite are a decrease in heavy metal content and water-soluble phosphate and an increase in pH. Emission measurements for fluorine, phosphorus and chloride were also performed during the granulation of a PK 8-27+7MgO, which indicated lower emissions when struvite was added. Phosphate and fluorine emissions to wastewater decreased, indicating a positive impact on the environment. The granules produced during the plant-scale test are shown in Fig. 16.6.

16.4 Future Perspective

16.4.1 Implementation in ICL Fertilizers

A proposal for a Euro 2 million investment has been approved (supported by a local Dutch subsidy of Euro 0.5 million) at ICL Fertilizers in Amsterdam in order to store and process sewage sludge and meat and bone meal ashes in a more professional way and to enable us to reach the target of 100% replacement by 2025.

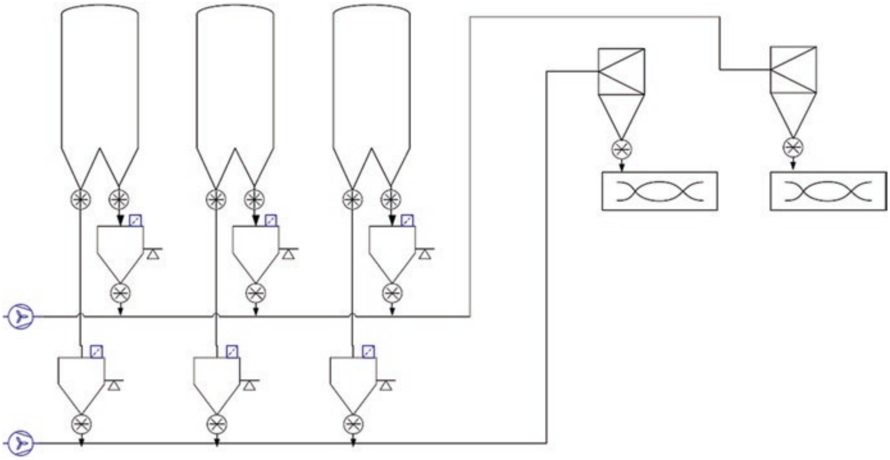

Fig. 16.7 Flow sheet for the storage, mixing and transporting secondary phosphates to the mixer for acidulation at ICL Fertilizers

The expansion will entail several silos with dosing units and transportation systems directly into the mixers for acidulation. An important ability is to achieve a constant flow in the necessary composition of the components. It should also be possible to mix milled phosphate rock from the regular process with, for example, meat and bone meal ash from this system at the mixer input. The pre-engineering led to a proposal for three silos with gravimetrical dosing and pneumatic transportation to the mixers. This way, a flow of 15 t/h can be achieved to each of the mixers. A flow sheet for this system is shown in Fig. 16.7. Apart from this development, ICL is in a process of discussions and trials for its German plant in Ludwigshafen to apply the same concept. However, approval processes go a bit slower in Germany. At the moment a license was obtained for using a limited daily quantity of ashes in the process.

16.5 Challenges and Issues

16.5.1 Legislation

As sewage sludge ash, struvite and meat and bone meal ash are currently regarded as waste. It is imperative that these streams will not be regarded as waste in the future, thus making nutrient recovery from these streams more practicable. The new EU Fertilizer Regulations which are under discussion at the time of writing have to accommodate the use of ashes and struvite as a raw material for production of EU fertilizers in an environmental acceptable way. Missing the opportunity that some conventional fertilizer plants can be a big help in creating a circular economy for phosphate would be very sad and contradicting the new sustainability views.

MBMA processing does not pose any threat to the environment and ecology, but even reduces emissions because of the lack of fluoride and other gas-forming substances. When regarding the processing of SSA, the emissions are also lowered due to the absence of gas-forming substances. During a plant-scale test with struvite addition to the granulation, the emissions of fluorine and phosphate showed lower figures than without struvite in PK production. However another trial with struvite had to be stopped due to smell issues from co-crystallized organic material. It proves each material source needs careful checking before processing.

With regard to struvite, further research is needed to prove that no pathogens, pharmaceuticals or other hazardous contaminants remain present; it is imperative that no risks are carried over to the fertilizer. Use of struvite as a raw material in processes like ICL's fertilizer process will reduce the chances of contaminants to almost zero, since the struvite will be exposed to a very acidic environment and high temperature in the dryer, which will kill all viruses and bacteria.

The cadmium content for both MBMA and SSA is far lower than that of most phosphate rock. This results in lower cadmium levels in the final products. The SSA, however, does contain some elevated levels of trace elements like copper and zinc compared to the phosphate rock. There should be room in the legislation for these beneficial heavy metals that are needed in plant growth.

16.6 Conclusions for the Fertilizer Application

The use of secondary phosphates in the mineral fertilizer industry yields great opportunities. Many different sources are possible, which could guarantee security of supply and keep the market healthy with regard to competition. This also contributes to a healthy phosphate balance, since this way countries with a surplus of phosphate could remove it from the cycle and export it through fertilizer to countries which have a phosphate deficiency.

Technically, it is already possible to replace a great deal of phosphate rock with secondary phosphates from struvite and mono-incineration ashes. However, legislation and safety issues still exist. The classification of these products as 'waste' obstructs their current employment on an industrial scale. It is imperative that the legislation issues are addressed as quickly as possible and high hopes are set to the JRC working group called STRUBIAS to come with practical proposals by the end of 2018. The European Sustainable Phosphorus Platform emphasizes this and could contribute to these issues.

Regarding struvite, it is important that further legislation is developed on the contaminants it could contain. Following this, the struvite could then easily be used in the production of phosphate fertilizer as the phosphate it contains is already soluble and thus plant-available. The processability of struvite does vary, as odour emissions and moisture content vary. These are issues that should be kept in mind, and every struvite source is therefore to be tested and reviewed individually.

As sewage sludge ashes have a high content of heavy metals, this could become an issue with regard to accumulation in the soil where the fertilizer is applied. The products from sewage sludge ash do meet the set limits from the European Commission's WG3 meetings which were based on scientific arguments. However, political battles are now taking place to introduce stricter limits and restrict the recycling potential. As was seen in trial experiments, sewage sludge ashes with a high content of iron did not acidulate as well as the ashes with a lower concentration of iron. If the sewage sludge streams and applied flocculants could be managed in a better fashion, it could be possible to achieve even better results regarding phosphate recovery from sewage sludge ashes.

Meat and bone meal ashes are the best applicable at the moment, as these show most similarities with regular phosphate rock. Therefore, no real issues exist with the implementation of this feedstock into the production of mineral phosphate fertilizer. However a big volume of the meat and bone meal is now being used in cement and concrete production, using only the caloric value of the material and wasting the phosphate in a building material. Hopefully new legislation like in Switzerland and Germany will forbid this kind of applications and will be driving more into phosphate recycling.

16.7 Recycling of Ashes in Industrial Applications

ICL is a big consumer of elemental phosphorus (P_4) and food-grade phosphoric acid in its downstream activities in Europe and the USA (lubricant additives, flame retardants, food and feed salts, fire extinguisher products). Instead of putting all the eggs in one basket for recycling P (the fertilizer route), we are in a process to develop two other processes especially for P_4 and food- grade phosphoric acid.

16.7.1 RecoPhos Thermal Process

This is a process for which ICL obtained the patents in March 2016 and is using sewage sludge ashes as raw material. The ash is mixed with carbon and heated under reducing circumstances by inductive heating to 1600 °C. At this temperature, P_4 is released as a gas which, after cleaning out contaminants, is condensed to pure solid P_4 (Fig. 16.8). The by-products from this process are:

- *Slag*, containing immobilized metals and silicate, which can be treated in a new process to produce cement. If not treated, the slag can be used for road construction.
- *Ferrophos*, a mix of elemental iron and phosphorus used as an additive in the steel industry.
- *Syngas*, mainly CO that can be used in the process to preheat the ashes.

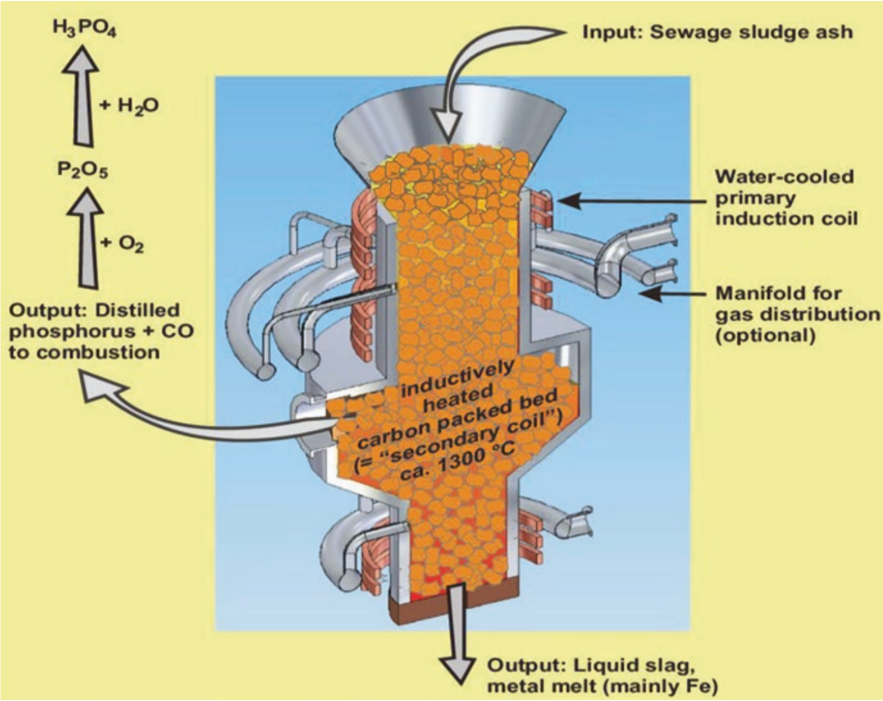

Fig. 16.8 Schematic picture of the RecoPhos thermal process

ICL is preparing the engineering for a pilot plant, to be built in Terneuzen, the Netherlands. Since the investment of the pilot will be major (about Euro 20 million), subsidies are sought as well as partners that want to participate financially in the pilot (ash suppliers, cement companies, etc.). The first commercial unit will be built in Bitterfeld Germany, where big amounts of ash are available and use of the P_4 in the chemical plant of ICL producing fire retardants is secured. RecoPhos is a very interesting process with a potential offtake for sewage sludge ashes of over 400,000 t/a and one of the few processes not generating any waste product but only sellable final products.

Apart from applications in Europe and the USA, there is a great interest for this technology from Southeast Asia where big cities are trying to find outlets for their ashes and RecoPhos (either producing P_4 or alternatively technical-grade phosphoric acid) could be the solution.

16.7.2 Tenova Process for Food-Grade Phosphoric Acid

A different approach for dealing with sewage sludge ashes: ash is treated with by-product hydrochloric acid (HCl), creating a phosphoric acid solution. This solution is purified by several stages of extraction and finally evaporated to commercial concentrations (75 or 83% H_3PO_4). This concept is very interesting in industrial areas where both ash and HCl are available as waste products. The principle was tested on lab scale and feasibility studies are now being made. The next step will be the construction of a continuous pilot plant. Also here partners are sought (HCl suppliers, ash suppliers) as well as subsidy providers (EU, local).

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