2. Kongress: Phosphor - Ein kritischer Rohstoff mit Zukunft -
am 26. und 27. Oktober 2016 im Kursaal Stuttgart Bad Cannstatt

Phosphate recycling in mineral fertilizer production

C.P. Langeveld and K.W. ten Wolde

Summary:

Phosphate recycling is an important issue, since it 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. Different sources present opportunities to recover phosphates, the most important being manure, litter, wood ashes, sewage sludge ashes, meat- and bone meal ashes and struvite.

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. These sources are readily available for implementation and require only little modifications to the current fertilizer production facilities of ICL. Also, the environmental impact of producing fertilizer using these secondary phosphate sources suggests the emissions of phosphate and fluorine is lower than with regular phosphate rock.

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 latest draft of the Fertilizer Regulations of the European Commission, maximum values for heavy metal content in fertilizer were specified in greater detail. The first results show that products produced from sewage sludge ash **will not always be able to meet these demands.** Since heavy metal content in struvite and meat- and bone meal ash is low, no problems are expected in these products.

The use of secondary phosphate in fertilizer production yields great opportunities. A successful implementation will depend on realistic limits on heavy metals in fertilizers as specified in the future Fertilizers Regulations.

Since 2015, ICL is investigating possibilities to recycle sewage sludge and meat & bone meal ashes also into elementary phosphorus (P4) and derivatives (food grade phosphoric acid). Patents and licenses for the thermal RecoPhos process were acquired, now a pilot plant is being designed to collect the data needed for scale up to commercial size.

Potentially ICL will build units producing 36 kt P4 for captive use into fire retardants and lubrication additives. Consumption of sewage sludge ash for this amount of P4 will be 400.000 ton/a!!

2. Kongress: Phosphor - Ein kritischer Rohstoff mit Zukunft -
am 26. und 27. Oktober 2016 im Kursaal Stuttgart Bad Cannstatt

Keywords: secondary phosphate, struvite, sewage sludge ash, meat- and bone meal ash, acidulation, granulation, RecoPhos, P4, food grade acid.

Contents

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, Prud'homme, Muirheid, & Isherwood, 2006). Therefore, usage has to be cut to make the reserves last longer. Still, this will not make phosphorus an infinite resource (Van Vuuren, Bouwman, & Beusen, 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 waste water treatment plants. The sewage sludge can be processed in many different ways to recover the phosphorus (Schick, Kratz, Adam, & Schnug, 2009). These can be summarized into three main categories, the watery sludge, dewatered sludge and sewage sludge ash. At waste water

treatment plants, struvite, which is essentially magnesium ammonium phosphate, can also be formed by crystallisation and precipitation. This feedstock also contains a high level of phosphorus and can be regarded as a secondary phosphate source (Jaffer, Clark, Pearce, & Parsons, 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, Steingrobe, Römer, & Claassen, 2011). The solubility in neutral ammonium citrate and water, which with phosphate rock is realised by acidulating, is important. The processing for this will be discussed in chapter 4.

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.

1.1 ICL Fertilizers' position

ICL Fertilizers runs several fertilizer production units in different parts of the world. All of them are based 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 PK's and on top of that ammonium sulphate to produce NPK's. These processes are very suitable for the recycling of secondary phosphates (contrary to other NPK processes) without any safety issue.

Figure 1.1: ICL Fertilizers' production plant in Amsterdam

At ICL Fertilizers in Amsterdam 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 en meat- and bone meal ash. Acidulation of sewage sludge ash and addition of struvite to fertilizer have also been carried out on plant-scale tests.

As a phosphate fertilizer producer with an own supply of phosphate in the Israeli desert, 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 world-wide 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 plants that export a major part of their products to countries with a deficit on phosphate, help solving the existing surplus in The Netherlands and Germany.

1.2 Value chain agreement

In The Netherlands, ICL Fertilizers Europe has taken part in the so-called value chain agreement, initiated by The Nutrient Platform in 2011. Together with nineteen other parties the ambition is to create a sustainable market where reusable phosphate streams will be returned to the cycle in an environmental-friendly way. ICL Fertilizers Europe’s ambition is to base its entire fertilizer production on secondary phosphates by 2025. By 2015, a figure of 15% was thought to be attainable (Dutch Nutrient Platform, 2011). In 2014 and 2015, the consumption of secondary phosphates was increasing, but due to technical problems in processing, had to be stopped. Currently, ICL Fertilizers still is confident that the 15% replacement can be achieved in the coming years.

Since the Netherlands has a surplus of phosphate, the expansion to a European Union based platform was desirable. In 2013, at the 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).

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 produced fertilizers. In this chapter, the properties of the sources will be discussed.

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 are 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, Kersten, & Kootstra, 2013) and the gasification of chicken litter (Kaikake, Sekito, & Dote, 2009). The products from these processes could also be implemented in the production of phosphate fertilizer.

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.

2.2.1 Sewage Sludge Ash

At wastewater treatment plants, contaminants are precipitated using iron- or aluminium compounds. Here sewage sludge accumulates. This sludge contains a number of nutrients that can be recycled, such as phosphate. The substitution potential of recovered phosphorus from sewage sludge in Germany is estimated at 40% (Schaum, Cornel, & Jardin, n.d.). There are a lot of differences in the EU regarding sewage sludge; in The Netherlands, 100% is incinerated while in Spain almost all sewage sludge is used agriculturally as reported by Eurostat in 2009. Even within countries such as Germany, differences can be significant: in the northern part, 60% is used in agriculture whereas this is only 20% in the southern part.

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 as not to introduce more contaminants from other streams such as industrial waste, 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 & Schaum, 2009). Another advantage of incineration of the sewage sludge is that it has a caloric value, so it yields energy on incineration.

Currently, a fair amount of sewage sludge ash is disposed to landfill. This is being limited by the EU Landfill Directive, which in turn will increase the availability of sewage sludge ash for the use in fertilizer production.

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 in chapter 3. Since the flocculants for sewage sludge vary, several different analyses are shown in table 2.1 and 2.2. A sewage sludge ash sample is depicted in figure 2.1.

Figure 2.1: sewage sludge ash

Table 2.1: 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 2.2: 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	Average 252 SSA samples Germany	Phosphate rock
As	20,1	19,9	9,4	9,0	8,1	18	17,8
Cd	2,1	1,0	2,2	<0,1	1,7	3.1	25,9
Cr	115,5	124,5	25,0	79,5	18,1	267	53,0
Cu	760,3	1146,0	404,0	749,6	365,0	916	13,5
Ni	44,6	49,6	17,8	37,7	7,8	106	30,7
Mn	871,6	825,5	3070,0	719,4	207,0	1914	6,7
Pb	273,0	254,0	157,6	84,4	82,4	151	< 0,1
Zn	3053,0	2139,0	876,0	1624,0	209,0	2535	260,2

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 decease 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, Gea, & Arauzo, 2012).

This meat- and bone meal ash is very similar to regular phosphate rock in terms of chemical composition. Also the content of contaminants is very low, as can be seen in table 2.1 and 2.2. The product received at ICL fertilizers for testing can be seen in figure 2.2.

Figure 2.2: meat- and bone meal ash

2.2.3 Wood ashes

Several initiatives are taking place to incinerate clean waste wood as a bio-fuel. 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. For analysis results, see table 2.1 and 2.2

2.3 Struvite

At wastewater treatment plants, struvite crystallization is a widely used technique to remove phosphorus, ammonium from digested sludge liquors (Martí, Pastor, Bouzas, Ferrer, & Seco, 2010) by adding a source of soluble Mg in the proper stoichiometric ratio. 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 equation (2.1).

$$Mg^{2+} + NH_4^{+} + PO_4^{3+} + 6\ H_2O \rightarrow MgNH_4PO_4.6H_2O \qquad (2.1)$$

The spontaneous formation of struvite can cause scaling in piping and equipment at wastewater treatment plants and the controlled removal of the building blocks is thus also beneficial for these plants (Jaffer et al., 2002). Analysis of struvite has also shown a very low content of heavy metals, which is beneficial with regard to the possible use in fertilizer.

Since struvite is not incinerated, a certain fear exists that it could contain pathogens, pharmaceuticals, hormones and other contaminants encapsulated in the crystals (Decrey, Udert, Tilley, Pecson, & Kohn, 2011; Ronteltap, Maurer, & Gujer, 2007). 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 to 55 °C causes it to decompose, releasing gaseous ammonia (Bhuiyan, Mavinic, & Koch, 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. Analyses from these struvite are shown in table 2.3 and 2.4, with a phosphate rock analysis for comparison.

The Airprex process was developed by the Berlin Wasserbetriebe in 2007 in order to reduce the problems with spontaneous struvite precipitation. By aerating the digested sludge, CO_2 is stripped which increases pH while simultaneously magnesium is added to the system to promote crystallisation. The crystals will then settle at the bottom and are removed through the outlet. A schematic presentation of the position in a waste water treatment plant and the setup is shown in figure 2.3. The washed struvite crystals are shown in figure 2.4.

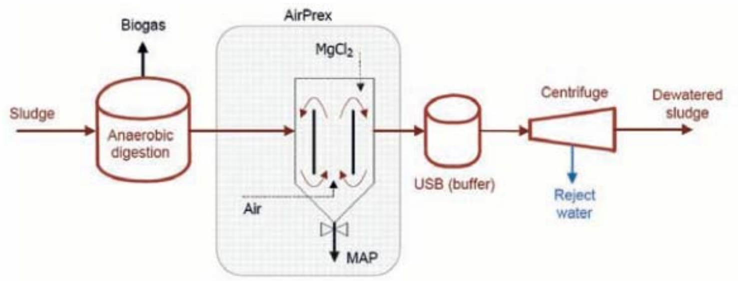

Figure 2.3: schematic of the Airprex process' position in a WWTP (STOWA, 2012)

Figure 2.4: Struvite crystals from the Airprex process (STOWA, 2012)

The Anphos process is very similar to the Airprex process, as it also involves a pH-shift by aerating and magnesium dosing. The struvite from the Anphos process received at ICL Fertilizers was crystallised from the washing water of a potato processing facility. A photograph of the struvite in figure 2.5.

Figure 2.5: struvite from the Anphos process as received in bulk

Table 2.3: 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 2.4: 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

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 in Amsterdam. The results of these tests will be discussed in this chapter, as well as the technical implications it has on the current infrastructure at the production location in Amsterdam. Since the plant in Ludwigshafen, Germany is quite similar to that in Amsterdam, the implementation can also be done here.

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 and thus not plant available. With phosphate rock, acidulating the rock with either sulphuric- or phosphoric acid will yield single or triple superphoshate respectively. These fertilizers have a typical water and NAC solubility of 90-92% and 95-97%. The reaction equations of the acidulation to single- and triple superphosphate are shown in equations (3.1) and (3.2) (Kongshaug et al., 2000).

$$2\ Ca_5(PO_4)_3.F + 7\ H_2SO_4 \leftrightarrow 3\ Ca(H_2PO_4)_2 + 7\ CaSO_4 + 2\ HF \qquad (3.1)$$

$$2\ Ca_5(PO_4)_3.F + 7\ H_3PO_4 \leftrightarrow 5\ Ca(H_2PO_4)_2 + 2\ HF \qquad (3.2)$$

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, 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 is desirable.

3.1.1 Meat- and bone meal ash

Meat- and bone meal ash shows most similarities with apatite; the phosphate is mainly present as calciumphosphate. This reacts with acid in a similar way as apatite, as can be seen by comparing equations 3.1 and 3.2 with 3.3 and 3.4.

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \leftrightarrow 3\ Ca(SO_4) + 2\ H_3PO_4 \qquad (3.3)$$

$$Ca_3(PO_4)_2 + 4\ H_3PO_4 \leftrightarrow 3\ Ca(H_2PO_4)_2 \qquad (3.4)$$

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 regards 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.

3.1.2 Sewage sludge ash

As shown in table 2.1 and 2.2, 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.

As can be derived from Gibbs free energy calculations (Dean, 1979; Langeveld & ten Wolde, 2013; Lide, 2008), the formation of iron phosphate and superphosphate are highly favoured thermodynamically in standard conditions. As phosphoric acid is formed during the acidulation of the sewage sludge ash, the available iron oxide is suspect to form iron phosphate which results in less free phosphoric acid to react to superphosphate.

Acidulation

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 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 that 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 (7wt% Fe_2O_3) per hour. No optimised 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.

Granulation

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 10ºC 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 equation (3.5). 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, Bauer, Schachl, Hagedorn, & Schmittinger, 2000). In the used setup, it was impossible to determine the cause of this.

$$KCl + H_2SO_4 \rightarrow KHSO_4 + HCl \qquad (3.5)$$

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 there could be a reaction taking place during granulation, which could also attribute to the temperature increase.

At the moment of this writing, no plant-scale granulation test has been carried out yet where a significant amount of acidulated sewage sludge ash was employed.

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% moisture, 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.

4 Future perspective

There are several different processes in development, based on different principles such as leaching and thermic treatment. These will not be discussed in this report.

4.1 Implementation at ICL Fertilizers

At the moment of this writing, an investment proposal is being prepared at ICL Fertilizers in Amsterdam in order to store and process sewage sludge- and meat- and bone meal ashes. If the process proves itself, a significant increase in the use of sewage sludge ash in Germany can be achieved by implementing the same set-up at ICL's Ludwigshafen plant, provided legislators will cooperate in giving ICL a new BImSch license.

The project 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 e.g. 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 ton per hour can be achieved to each of the mixers. The project has now proceeded into detailed engineering and this will be finished by the end of 2016. When finalizing this and having the full budget approved, it is expected full implementation will start in 2018.

5 Challenges and issues

5.1 Legislation

As sewage sludge ash, struvite and meat- and bone meal ash are currently regarded as waste, at this moment they cannot be employed as feedstock in commercial fertilizer. It is imperative that these streams will not be regarded as waste in the future, thus making nutrient recovery from these streams more practicable.

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 regards 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. Research on the Airprex-derived struvite employed during tests at ICL Fertilizers is being executed by an external laboratory for possible risks. Several Dutch waterboards are currently also working on a joint research with ‘Stichting Toegepast Onderzoek Waterbeheer’ in order to research the contaminants present. At the moment of this writing, no further information was available regarding this issue.

The cadmium content for both MBMA and SSA are far lower than that of phosphate rock. This results in lower cadmium levels in the final products. The SSA however, does contain heavy metals that are not present in the phosphate rock. The acidulated sewage sludge ash was compared to the latest draft of the Fertilizer Regulations for heavy metal content ; the maximum values are shown in table 5.1 (Berend & Severin, 2012). Comparing the heavy metal content in acidulated sewage sludge ash with these numbers, it can be seen that this does not exceed the set limits. Also, when a mixture of acidulated phosphate rock and sewage sludge ash is granulated, the values, except for cadmium, will be even lower.

Table 5.1: Draft Fertilizer Regulations limits for heavy metals in fertilizer compared to acidulated sewage sludge ash

ppm	**As**	**Cd***	**Cr**	**Hg**	**Ni**	**Pb**
Acidulated SSA	7	17	74	0,1	31	84
Draft Fertilizer Regulations	40	60	100	1	100	120

***MG/KG P2O5**

Remark: due to great fluctuations the acidulated ashes can lead to trespassing the draft limit values in many cases

6 Conclusions on secondary phosphates for fertilizers

The use of secondary phosphates in the mineral fertilizer industry yield great opportunities. Many different sources are possible, which could guarantee security of supply and keep the market healthy with regards 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 it should get the full attention at the European Committee. The launch of the European Phosphorus Platform emphasises this and could contribute to solving these issues.

Regarding struvite, it is important that further research is done 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 the odour emissions and moisture content varies. 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 regards to limits on heavy metals in the new Fertilizer regulations. The products from sewage sludge ash do not always meet the set limits from the European Commission’s Draft Fertilizer regulations. Hopefully the draft regulations will still be adjusted in order not to stop the use of ashes in fertilizer production.. 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.
Other sources, such as manure, litter and wood ashes also pose interesting sources. Technology is still being developed to optimise the recovery of phosphate from these sources, such as pyrolysis of manure and wood ash. If the phosphate content is high enough in a certain stream, it could become an interesting source to look into.

7. Recycling ashes in industrial applications: Circular Economy 2.0.

Next to the recycling of phosphates in fertilizers, ICL is investigating possibilities to recycle sewage sludge and meat & bone meal ashes also into elementary phosphorus (P4) and derivatives (food grade phosphoric acid). Patents and licenses for the thermal RecoPhos process were acquired, now a pilot plant is being designed to collect the data needed for scale up to commercial size.
Potentially ICL will build units producing 36 kt P4 for captive use into fire retardants and lubrication additives. Consumption of sewage sludge ash for this amount of P4 will be 400.000 ton/a!!
Since this is somewhat out of the scope of this paper, we will not go too deep into this subject.

8. References

Azuara, M., Kersten, S. R. A., & Kootstra, A. M. J. (2013). Recycling phosphorus by fast pyrolysis of pig manure: Concentration and extraction of phosphorus combined with formation of value-added pyrolysis products. *Biomass and Bioenergy*, *49*, 171–180. doi:10.1016/j.biombioe.2012.12.010

Berend, K., & Severin, K. (2012). *Working Group 3 – Contaminants, hygene and other risks* (pp. 1–14). Brussels.

Bhuiyan, M. I. H., Mavinic, D. S., & Koch, F. A. (2008). Thermal decomposition of struvite and its phase transition. *Chemosphere*, *70*(8), 1347–56. doi:10.1016/j.chemosphere.2007.09.056

Cabeza, R., Steingrobe, B., Römer, W., & Claassen, N. (2011). Effectiveness of recycled P products as P fertilizers, as evaluated in pot experiments. *Nutrient Cycling in Agroecosystems*, *91*(2), 173–184. doi:10.1007/s10705-011-9454-0

Cascarosa, E., Gea, G., & Arauzo, J. (2012). Thermochemical processing of meat and bone meal: A review. *Renewable and Sustainable Energy Reviews*, *16*(1), 942–957. doi:10.1016/j.rser.2011.09.015

Cornel, P., & Schaum, C. (2009). Phosphorus recovery from wastewater: needs, technologies and costs. *Water science and technology : a journal of the International Association on Water Pollution Research*, *59*(6), 1069–76. doi:10.2166/wst.2009.045

Dean, J. A. (1979). *Lange's Handbook of Chemistry*. *Lange's Handbook of Chemistry* (12th ed.). McGraw-Hill.

Decrey, L., Udert, K. M., Tilley, E., Pecson, B. M., & Kohn, T. (2011). Fate of the pathogen indicators phage ΦX174 and Ascaris suum eggs during the production of struvite fertilizer from source-separated urine. *Water research*, *45*(16), 4960–72. doi:10.1016/j.watres.2011.06.042

Dutch Nutrient Platform. (2011). Phosphate Value Chain Agreement. The Nutrient Platform.

European Commission. (2000). Disposal and recycling routes for sewage sludge, (October 1999).

European Phosphorus Platform. (2013). Press Release ESPC13. Brussels: The Nutrient Platform.

Gilbert, N. (2009). The disappearing nutrient. *Nature*, *461*(October), 716–718. doi:10.1016/j.amjmed.2010.04.007

Heffer, P., Prud'homme, M. P. R., Muirheid, B., & Isherwood, K. F. (2006). Phosphorus fertilisation: Issues and outlook. In *Proceedings International Fertiliser Society*. York: 586.

Jaffer, Y., Clark, T. A., Pearce, P., & Parsons, S. A. (2002). Potential phosphorus recovery by struvite formation, *36*, 1834–1842.

Kaikake, K., Sekito, T., & Dote, Y. (2009). Phosphate recovery from phosphorus-rich solution obtained from chicken manure incineration ash. *Waste management (New York, N.Y.)*, *29*(3), 1084–8. doi:10.1016/j.wasman.2008.09.008

Kongshaug, G., Brentnall, B. A., Chaney, K., Gregersen, J.-H., Stokka, P., Persson, B., … Skauli, Ø. (2000). Phosphate Fertilizers. In *Ullmann's Encyclopedia of Industrial Chemistry*. doi:10.1002/14356007.a19_421

Langeveld, C. P., & Ten Wolde, K. W. (2013). Phosphate recycling in mineral fertiliser production. In *International Fertiliser Society Proceedings 727* Leek, ISBN 978-0-85310-364-6.

Lide, D. R. (2008). *CRC Handbook of Chemistry and Physics* (89th ed.). CRC Press.

Martí, N., Pastor, L., Bouzas, a, Ferrer, J., & Seco, a. (2010). Phosphorus recovery by struvite crystallization in WWTPs: influence of the sludge treatment line operation. *Water research*, *44*(7), 2371–9. doi:10.1016/j.watres.2009.12.043

Ronteltap, M., Maurer, M., & Gujer, W. (2007). The behaviour of pharmaceuticals and heavy metals during struvite precipitation in urine. *Water research*, *41*(9), 1859–68. doi:10.1016/j.watres.2007.01.026

Schaum, C., Cornel, P., & Jardin, N. (n.d.). Phosphorus Recovery from Sewage Sludge Ash – A Wet Chemical Approach, 583–590.

Schick, J., Kratz, S., Adam, C., & Schnug, E. (2009). Techniques for P-recovery from waste water and sewage sludge and fertilizer quality of P-recycling products. In *Phosphorus Recycling and good Agricultural management Practice*.

Schipper, W. J., Klapwijk, a, Potjer, B., Rulkens, W. H., Temmink, B. G., Kiestra, F. D., & Lijmbach, a C. (2001). Phosphate recycling in the phosphorus industry. *Environmental technology*, *22*(11), 1337–45. doi:10.1080/09593330.2001.9619173

Schultz, H., Bauer, G., Schachl, E., Hagedorn, F., & Schmittinger, P. (2000). Potassium Compounds. In *Ullmann's Encyclopedia of Industrial Chemistry*. doi:10.1002/14356007.a22_039

STOWA. (2012). *Struviet productie door middel van het airprex proces* (2012th–27th ed.). Amersfoort: Stichting Toegepast Onderzoek Waterbeheer.

Ten Wolde, K. W. (2012). *Phosphate fertilizer from Sewage Sludge Ash*. University of Twente.

Van Vuuren, D. P., Bouwman, a. F., & Beusen, a. H. W. (2010). Phosphorus demand for the 1970–2100 period: A scenario analysis of resource depletion. *Global Environmental Change*, *20*(3), 428–439. doi:10.1016/j.gloenvcha.2010.04.004

Yamamoto, T., Tsutsui, T., Nonaka, T., Kobayashi, S., Nishiguchi, A., & Yamane, I. (2006). A quantitative assessment of the risk of exposure to bovine spongiform encephalopathy via meat-and-bone meal in Japan. *Preventive veterinary medicine*, *75*(3-4), 221–38. doi:10.1016/j.prevetmed.2006.03.003