



# Sewage Sludge Ash: An Alternative Source of Phosphate

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## 1. Introduction

As an essential nutrient for food production, phosphate is largely used in fertilizers to enhance crop growth (Baishya et al., 2016; Hasanuzzaman et al., 2018). Regardless of its enormous demand, the only concentrated P source is phosphate rock and the resource is finite (Cordell & White, 2011; Smit et al., 2009). There are no large reserves of phosphate rock left in Europe. Most of European countries import phosphate rock from North Africa and Russia (Ridder et al., 2012). The dependency on a non-recyclable source of phosphate today raises the urgency and ambition among European countries to find alternative sources of phosphate. The aim is to find and develop alternative sources to secure the balance between the demand and supply of phosphate in the future (M. A. de Boer et al., 2018; Schröder et al., 2010).

According to Smit et al. (2010), there is a non-negligible 30 Mkg of P in the Netherlands obtained from society (household and industry waste) and agriculture, but less than 2 Mkg is being recycled. Among the alternative sources, wastewater treatment plants (WWTPs) have currently the highest potential source of P-recycling. Several research studies have addressed the development of P-recovery methods and technologies (Hartmann et al., 2020; Kumar et al., 2021; Zapata & Zaharah, 2002). Approximately 14,000 tons of  $P_2O_5$  total contains in 1,500,000 tons of sludge treated in a year (Ministerie van Economische zaken, 2011; Smit et al., 2009). The phosphorus pentoxide or  $P_2O_5$  is a natural occurring form of elementary phosphorus. It is commonly used in the fertilizer industry to determine the P-content in phosphate rock or other phosphate sources. In 1996, the regulation of P-removal in sewage water treatment plants (SWTP) is applied in the Netherlands to prevent eutrophication (Bunce et al., 2018). The regulation is followed by the prohibition of landfilling and land application of sewage sludge in 1997, leaving incineration as the only viable way for sludge disposal (Mitchell & Beasley, 2011).

The phosphate is captured from the sludge through adsorption, chemical precipitation, enhanced biological phosphorus removal, and constructed wetland (Ramasahayam et al., 2014). Metal compounds, such as aluminum chloride and iron chloride, are commonly used to flocculate and precipitate phosphate in wastewater (Bratby, 2006). Meanwhile polyphosphate accumulating organisms (PAO) are utilized for the enhanced biological phosphorus removal (EBPR). According to Tarayre et al. (2016), the PAOs, which generally are bacteria, are maintained in an aerobic phase. Under this condition, the PAOs take up phosphate and store it in the intercellular polyphosphate form. The dilute solid suspension from both chemical and biological treatment is then incinerated at around 700°C for 3 hours (Kauwenbergh et al., 2007). The incinerated ash is known as sewage sludge ash (SSA) or incinerated sewage sludge ash (ISSA) with around 22-26%  $P_2O_5$  content. The amount is considered to be comparable to the amount of  $P_2O_5$  in phosphate rock (National Research Council, 2000).

The possible use of SSA as alternative phosphate source is being investigated by ICL Fertilizers as one of the leading global chemical company in plant nutrition. They mark the beginning of their research and development of sewage sludge ash (SSA) as the alternative phosphate source by opening the ICL Phosphate Recycling Unit in Amfert. The ash is obtained from two different companies, HVC and SNB. The amount of SSA produced by HVC (Dordrecht) and SNB (Moerdijk) is respectively ±22,000 tons/year and ±35,000 tons/years (Ruijter, 2018). The

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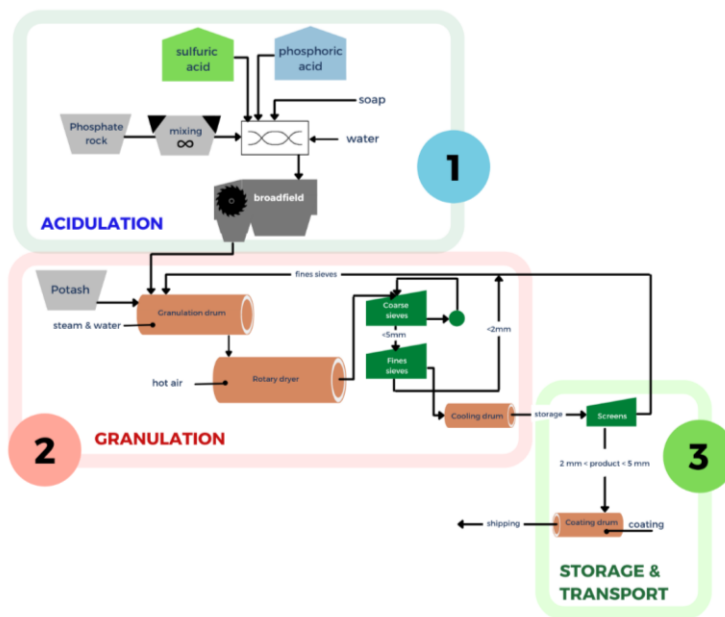
amount of phosphate rock imported and consumed at the ICL Amfert plant is around 100.000 tons/year . Although the demand of phosphate rock is still bigger than the current production of SSA per year, partial reduction of phosphate rock import can reduce the production cost and lower the dependency on phosphate rock (M. A. de Boer et al., 2018; Schröder et al., 2010).

The project aims to produce fertilizers using alternative phosphate sources, such as sewage sludge ashes (SSA) and produce circular and sustainable phosphate fertilizers. The products need to fulfill the quality standards of products made from standard phosphate rock. The development progress on laboratory and plant-scale will be explained and discussed in this report. The discussion will be divided into the two main steps of phosphate fertilizer manufacturing, acidulation and granulation. The report includes the effects of different material addition in each step, such as water and acid in the acidulation process. Furthermore, the report details the influence of changes and main parameters. Finally, the report gives recommendations and suggestions for the upcoming research.

## 2. Phosphorus in Phosphate Fertilizers

### 2.1 Phosphate Fertilizer Manufacturing

The plant operated by ICL Fertilizers Europe C.V in Amsterdam produces various kinds of products using one process. The production process can be divided into three main process parts: acidulation (1), granulation (2), and storage (3).



**Figure 2.1** Block flow diagram of SSA fertilizer production

#### 2.1.1 Acidulation

Acidulation is the first treatment needed to transform the phosphorous in the phosphate rock into water-soluble phosphate. The treatment is required due to unready available phosphorous content in the conventional source of phosphate in the form of phosphate rock (Kauwenbergh et al., 2007). Common treatments involve the use of organic acids, such as sulfuric acid (SAC) and phosphoric acid (PAC) (Turner et al., 2005). The acid is mixed together with the phosphate rock in order to acidulate the phosphate (see *Figure 2.1* Section 1). The amount of acid addition is calculated in liquid-to-solid (L/S) ratio. The reaction creates a cake or foam texture due to CO<sub>2</sub> gas formation (see *Chapter 2.3* for further explanation) (Ivanova et al. 2006). The treated or acidulated phosphate rock with water-soluble phosphorous content is known as run of pile (ROP). The ROP is transported via the Broadfield to the next step in the process. There are different

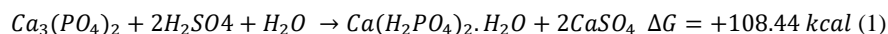
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types of ROP depending on the use of the extraction acid. At ICL Fertilizers, phosphate rock is mainly treated with SAC and/or PAC. The products are known as single superphosphate (SSP) and triple superphosphate (TSP).

#### Single Superphosphate (SSP)

Single superphosphate is one of the first commercial mineral fertilizers for phosphate source (IPNI, 2012). The milled phosphate rock is acidulated using sulfuric acid (68-75%) creating a semi-solid material and increasing the temperature (Plotegher & Ribeiro, 2016). The production of SSP is relatively simple, requires only little technical skill, and low capital investment. The unquestionable efficiency of SSP and the additional supplies of calcium and sulfur in the products makes it one of the crucial phosphate fertilizers today (IPNI, 2012; UNIDO & IFDC, 1979).

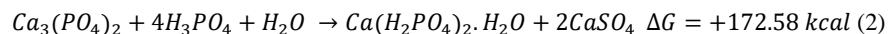
Regardless of its simplicity, the phosphorus content of SSP is relatively low ranging between 16-22% P<sub>2</sub>O<sub>5</sub> (Smit et al., 2009; UNIDO & IFDC, 1979). According to UNIDO & IFDC (1979), the grade of SSP is easily influenced by the grade of the rock used; the production of high grade SSP requires high grade phosphate rock. In addition, the reactivity and the metal content of the rock can affect the SSP quality. Excessive amount of iron and aluminum can decrease P<sub>2</sub>O<sub>5</sub> water-soluble content.



The reaction between phosphate rock and sulfuric acid occurs in two stages (see Eq.1). First, the reaction between sulfuric acid and phosphate will form phosphoric acid and calcium sulfate. Then, monocalcium phosphate will be produced from the reaction of phosphoric acid in the first stage and phosphate. Monocalcium phosphate monohydrate ( $Ca(H_2PO_4)_2 \cdot H_2O$ ) is water-soluble (see Eq. 2). Both stages of the reaction happen in parallel.

#### Triple Superphosphate (TSP)

Similarly, triple superphosphate is produced by reacting phosphate rock and acid. However, acidulation is done by using phosphoric acid instead of sulfuric acid (Sinden & Ltda, 2005; Zapata & Zaharah, 2002).



The direct acidulation with phosphoric acid results in higher P<sub>2</sub>O<sub>5</sub> % content in TSP (see Eq. 2) (D. Boer, 2020). Compared to the other granular fertilizers, TSP has the highest P content with more than 90% of P water-soluble content (P<sub>2</sub>O<sub>5</sub> 40-45% water-soluble content). TSP manufacturing is similar to SSP. The process is simple with low technical skill and small capital investment. The rock reactivity is also important in producing TSP. However, the influence of phosphate rock grade on the TSP is lower than in the case of SSP acidulation (UNIDO & IFDC, 1979).

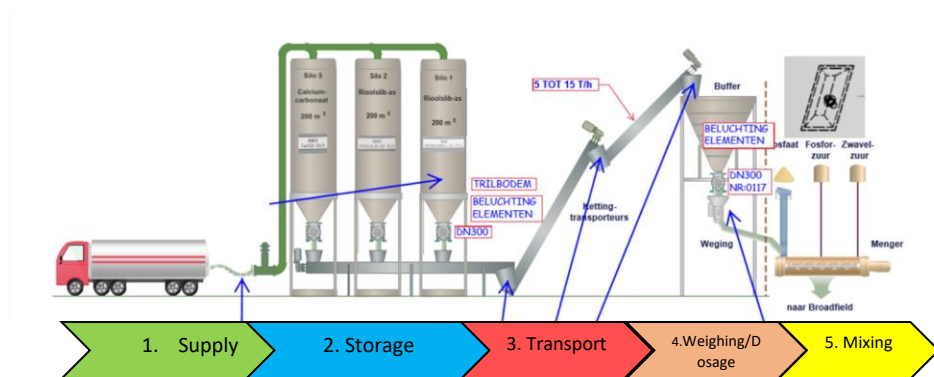
#### 2.1.2 Granulation

The ROP is further processed depending on the desired form of the fertilizer. Various forms of fertilizers include liquid, powder, and granules. ICL Fertilizers is specialized in granular fertilizers (see *Figure 2.1* Section 2). The ROP and potash are added to the granulation drum. The residence time in the granulation drum is 4 minutes. During the granulation, steam and water are added to wet the mixture and help the particles to bind to one another. The addition of water and steam is usually referred to liquid-to-solid ratio used in the granulation. After 4 minutes, the granules roll out the granulation drum to the rotary drying drum. The granules are dried with hot air (around 450°C) for 20 minutes to evaporate the water content. After drying, the granules are sieved. The granules > 5mm diameter are crushed in a grinding machine and used as recycle together with the < 2mm fraction.

### 2.1.3 Storage

While the > 5mm and < 2mm fraction are transported back to the granulation drum, the granules with the desired size (2 – 5 mm) are cooled down and stored for 2 weeks in the warehouse. During the 2 weeks storage, the components inside the granules further react until the remaining acid has fully reacted. The step is known as a ripening time. Finally, the granules are coated in the coating drum before shipped to clients. The coating is applied using a coating drum. The coating oil can reduce the moisture uptake, reduce dust formation and caking of the granules.

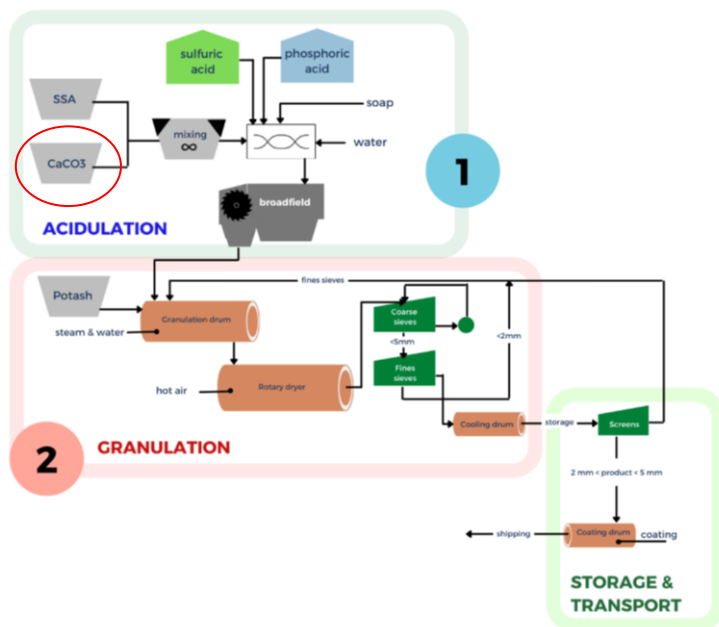
## 2.2 Sewage Sludge Ash in Phosphate Fertilizer



**Figure 2.2** Ash silo and transport system

At ICL Amfert plant, a Phosphate Recycling Unit is specifically built to store and transport alternative phosphate sources (see *Figure 2.2*). The system starts with material supplied by trucks. The dry materials in the form of powder are transported into the silos with the help of air pressure. The system is known as a pneumatic transport system. There are three materials stored in the silos:  $\text{CaCO}_3$ , SSA SNB (Moerdijk), and SSA HVC (Dordrecht). Each material is stored separately in a different silo. During the production process, the materials are transported by three chain conveyors from the silos to buffer silo. The feeding of material from the three silos to the buffer silo is adjustable, it can be operated individually or simultaneously. Flow indicators are installed at the bottom of silos to indicate the material flow. At the bottom of the buffer silo, a

weighing machine is installed to indicate the overall weight of dry materials flowing into the mixer.



**Figure 2.3** Block flow diagram of SSA fertilizer production

The production of phosphate fertilizers using sewage sludge ash (SSA) is similar to products made using phosphate rock. In the acidulation process, sulfuric acid (SAC) and/or phosphoric acid (PAC) and soap are used to acidulate the SSA. The main differences lie in the  $\text{CaCO}_3$  addition and higher addition of soap in acidulation step (see *Figure 2.3* Section 1). The dry materials, SSA and  $\text{CaCO}_3$ , are fed to the process from the silos of the Phosphate Recycling Unit. While the other components are transported in the same way as during production of conventional phosphate fertilizers. The addition of  $\text{CaCO}_3$  aims to improve the mixing process. The reaction of  $\text{CaCO}_3$ , acid and surfactant forms  $\text{CO}_2$  gas, enhancing the solid-liquid mixing process (see *Chapter 2.3* for further explanation). Meanwhile, steam and water are also added in the granulation step to stick the materials together and form granules. However, higher ratio of steam and water is used in the SSA granulation compared to regular phosphate fertilizer production (see *Figure 2.3* Section 2).

### 2.3 Phosphorus Extraction

Before the acidulation process, phosphorous content in phosphate sources commonly comes in the form of apatite (Food and Agriculture Organization of the United Nations, 2004). This form



of phosphorous is not water soluble and cannot be absorbed by plants. A phosphorous extraction is required to convert it into water-soluble phosphate. There are some factors influencing the phosphorus extraction efficiency, including acid concentration and liquid-solid ratio (L/S ratio) (Fang, 2021). Fang (2021) also stated that the increase of acid ratio creates more intense condition and produce more available protons to break down the metal-P bonds. Besides these parameters during the acidulation, mineralogy of the phosphate sources and the addition of surfactant can affect the P-extraction efficiency.

#### 2.3.1 $\text{CaCO}_3$ addition in P-extraction

The mineralogy of phosphate rock is classified according to its origin, igneous rock and sedimentary rock (UNIDO & IFDC, 1979). Sedimentary apatite formed near the surface of the earth under relatively low temperature and pressure in various environment (Zhang, 2019). According to Broom-Fendley (2021), the conditions near the surface forms a wide spectrum of secondary minerals, such as iron and aluminum phosphate, clays, and iron oxides. Moreover, most of the deposits consist of different carbonate-fluorapatite, called francolite. The reaction of carbonate, acid and surfactant forms  $\text{CO}_2$  gas during the acidulation. The released gases result in a porous structure of acidulated phosphate rock or known as run of pile (ROP) (UNIDO & IFDC, 1979). Igneous rock is shaped under very high temperature and pressure. Different rock forming conditions influence the crystal structure of the two rocks (Selley, 2005). The high temperature and pressure in the igneous rock formation creates hard-rock and mildly weathered rocks (Zhang, 2019). The rock creates microcrystalline and leads to potential carbonate substitution with secondary apatite. The carbonate substitution leads to lower carbonate content rocks with harder and denser ROP. Moreover, studies showed this condition also leads to granulation difficulties and poor ammonization characteristics (UNIDO & IFDC, 1979).

#### 2.3.2 Soap addition in P-extraction

In addition, surfactant is often added to improve P-extraction (Hrenovic et al., 2010). It is a substance with the ability to attract water and oil (Stebe & Lin, 2001; Davidovits, 2019). The presence of soap decreases the surface tension, allowing longer reaction to occur. It is also commonly used in the acidulation treatment to enhance the homogenous mixing and the overall efficiency. The higher the homogeneity, the better the quality of the final ROP product.

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### 3. Materials and Methods

#### 3.1 Composition of SSA

The sewage sludge ash used in the project are produced in municipal waste incineration plants from Dordrecht (HVC) and Moerdijk (SNB). The ashes are in the form of a very fine powder. The  $P_2O_5$  content varies depending on the source of sewage sludge. Every batch of sewage sludge ash from both companies is different. The content ranges between 22-26%  $P_2O_5$  total. Besides P content, the SSA contains heavy metals. The main heavy metals are Arsenic (As), Chromium (Cr), Nickel (Ni), Manganese (Mn), Lead (Pb), and Zinc (Zn). The heavy metal content is present because of the use of metals in piping, paint, building materials, etc. Due to the lead piping used in old houses and neighborhoods in the Netherlands, the SSA from Dordrecht (HVC) has a higher Pb content (see *Table 3.1*).

*Table 3.1 Heavy metal content of HVC and SNB ashes*

Sample	Fe <sub>2</sub> O <sub>3</sub> %	Al <sub>2</sub> O <sub>3</sub> %	As ppm	Cd ppm	Cr ppm	Cu ppm	Hg ppm	Ni ppm	Pb ppm	Zn ppm
EU Limit	N.A	N.A	40	60	N.A	600	1	100	120	1200
Phosphate Rock	3% (total)		40	40	N.A	600	1	50	120	1500
HVC SSA (2020)	12.5	7.5	58	3	109	1326	0.1	96	350	3445
SNB SSA (2020)	13.5	6.8	21	3	114	925	0.1	62	180	2447

#### 3.2 Lab Procedure

Several acidulation and granulation tests were done on pilot-scale using both ashes. Smaller batch size helped analyzing the use of specific compounds and/or techniques in a controlled environment. Unlike the system in the factory, the pilot-scale tests are batch experiments. Each equipment has to be manually performed. Before the direct acidulation tests in the factory, pilot-scale tests were carried out to give insights in the process and reaction. Some granulation experiments were also done with SSA. Further description and explanation of the equipment and experiments will be discussed below.

##### 3.2.1 Acidulation

The pilot-scale acidulation tests are done by using an anchor blade mixer (see *Picture 3.1*). The mixer is set vertically on a ring stand. The dry materials (SSA and  $CaCO_3$ ) and the wet materials (acid and soap) are prepared separately. The dry materials are prepared on one small bowl while the wet materials are in a 500 ml beaker. The blade is set at the center of the beaker. The bottom of the beaker is also equipped with ring lock. It is installed to keep the beaker from falling. When the acidulation is about to start, the blade is set down to its safety lock and the mixer is turned on. After a few seconds, the dry materials are poured into the beaker. The mixer is turned off after four to five seconds. The short mixing time is set to mimic the same condition of the mixing

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system in the factory. The mixer is then set back up to its original position and the beaker is removed from the ring lock. After that, the ROP is left for 20 minutes to react. Finally it is passed through a sieve into powder.



**Picture 3.1** Pilot scale equipment: (1) the mixer and (2) granulation drum.

**Picture 3.1** Pilot-scale equipment: (1) the mixer and (2) granulation drum.

### 3.2.2 Granulation

As for the granulation, three various equipment are involved in the process: a granulation drum, a rotary drying drum, and a sieving tower. The amount of dry material added is around 2 kg. Liquid is added in a form of steam and water. The steam is blown into the granulation bed using a rubber hose. The hose is directed in the granulation bed and moved back and forth to evenly distribute the steam. A similar technique is also used for the water, it is sprayed into the granulation bed to disperse the water evenly. The granules are dried with hot air for 20 minutes to evaporate the water content. After drying, and the granules are sieved in a sieving tower for 10 minutes. The products are sorted and stored as in the factory; the fines are used as recycle and the granules with the right size are analyzed and stored. The tower consists of 8 fractions to give information about the distribution and average size of the granules.



**Picture 3.1** Rotary drying drum on pilot-scale

### 3.2.3 Laboratory analysis

Samples of acidulation and granulation tests are taken for analysis. There are four main analysis techniques: the manual ROP quality analysis, the composition analysis by the ROBOT, the moisture uptake in a climate chamber, and strength analysis by using a manual Brinell hardness testing tool in the laboratory. The detailed procedures will be discussed further below.

#### Manual ROP Quality Analysis

The manual ROP quality analysis is to facilitate the selection of ROP recipe for the factory. As it is mentioned above, the manual ROP quality measurement is done by utilizing the sense of touch. The parameters are classified into five categories: stickiness, powdery texture, cake formation, dryness, and crushable. The scale used is from 1 to 5, with 5 as the highest number. The texture of ROP made from phosphate rock is the standard of the 5 parameters.

#### ROBOT analysis

At ICL Fertilizer Amfert, samples are analyzed automatically by a ROBOT. The ROBOT does chemical analysis from raw materials, ROP, and granules. However, the samples need to be dry and in a free-flowing powder-form before analyzed by the ROBOT. 50 g of sample is weighted and put into a barcoded bottle. If the powder is very coarse or granules need to be analyzed, the material is first grinded to powder. The operator decides which analysis the ROBOT needs to do, and this is registered by the software. Then, the bottle is scanned and put on the conveyor belt.

The analysis usually takes around 30 minutes to 1.5 hours depending on the number of analysis the ROBOT needs to perform. The main analysis is the chemical content of the samples, such as  $\text{NH}_4\%$ ,  $\text{P}_2\text{O}_5\%$  total,  $\text{P}_2\text{O}_5\%$  water soluble,  $\text{K}_2\text{O}\%$ . Additionally, the ROBOT can also measure pH, water content and free acid content.

The factor represents the amount of free acid present in the sample that still can react with phosphate. If the factor is zero, there is equal acid as phosphate to react. In the case the factor is positive, there is more acid present than available phosphate for the reaction. In that case the sample is over acidulated. The reverse case, where the factor is negative, the amount of acid present is not enough to react with all available phosphate (see Eq.3).

$$\text{Factor} = \text{free acid} - 2 * (\text{P2O5\% total} - \text{P2O5\% water soluble}) \quad (3)$$

#### Climate Chamber Test

The climate chamber test is specifically for granules. The purpose is to see the effect of extreme humidity conditions (70% humidity at  $21^\circ\text{C}$ ) on the granules. The focus is the moisture uptake and granules strength. Before preparing a sample, the climate chamber needs to be turned on and set at the desired conditions. An aluminum foil is weighed, and the weight is recorded. Approximately 100 g of granules are weighed in the aluminum foil. Then, the granules are carefully spread over the entire surface and put in the climate chamber for  $\pm 24$  hours. After 24 hours, the sample is weighed together with the aluminum foil. The flow of granules and the structure are analyzed and noted. For the moisture uptake calculation, the final weight of granules with aluminum foil is subtracted from the weight of the empty aluminum foil and the initial weight of granules. The calculation result is divided by the weight of the initial sample (see Eq.4).

$$\% \text{Moisture Uptake} = \frac{(\text{final weight aluminum foil \& granules}) - (\text{empty aluminum foil}) - (\text{initial weight of granules})}{\text{initial weight of granules}} \quad (4)$$

#### Brinell Strength Measurement

In the laboratory, the strength measurement is done by using a portable hardness tester. The tester is first set on zero. Then the granules are placed under the machine and the tester is pressed onto the granules. The result is shown in Brinell Hardness Number (BHN) unit. The granules are tested before and after the climate chamber. Before the climate chamber, strong granules can reach 5-7 BHV while after the climate chamber the regular NPK granules reach  $\pm 3$  BHN.

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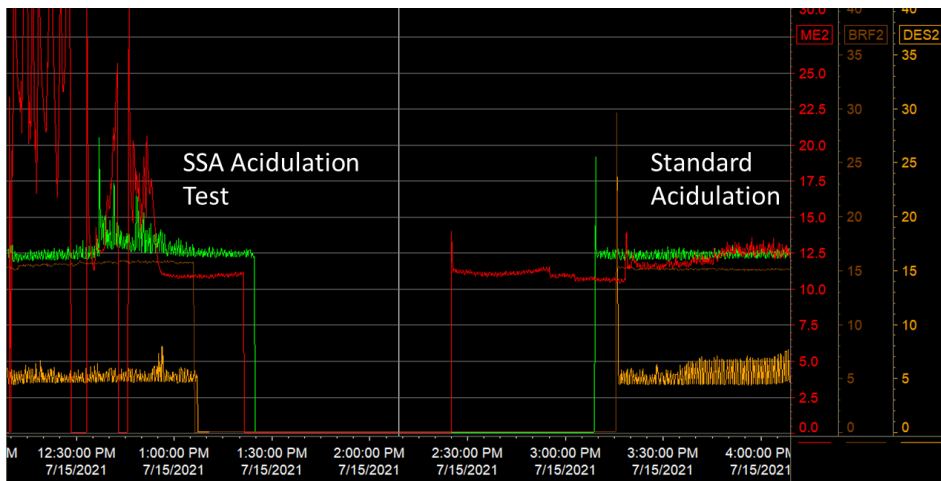
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## 4. Results and Discussion

### 4.1 Acidulation

The SSA acidulation was done previously on a plant scale. Two different products, SSP and TSP were tested in the factory. At the beginning, the ROP quality was poor. Instead of fine free flowing powder, the ROP consisted of big chunks and hard rocks. The mixer also had some difficulties to run (see *Figure 4.1*). The Figure 4.1 shows the energy used for each equipment during the acidulation in the factory (red line). The ME2 represents the mixer amperage, BRF2 indicates the Broadfield amperage and DES2 shows the disintegrator amperage. Among the three equipment, a significant difference can be seen in the mixer amperage of the SSA acidulation compared to standard acidulation. The SSA acidulation test resulted in higher and non-stable mixer amperage. Meanwhile, the amperage of mixer in the standard acidulation is relatively lower and stable. In order to improve the mixing process and increase the ROP quality, parameters changes were tested. The addition of soap,  $\text{CaCO}_3$  and changes in L/S ratio were tested. Each modification resulted in different effects on the mixer and ROP quality

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**Figure 4.1** SSA acidulation vs Standard Acidulation

#### 4.1.1 Effects of $\text{CaCO}_3$ addition

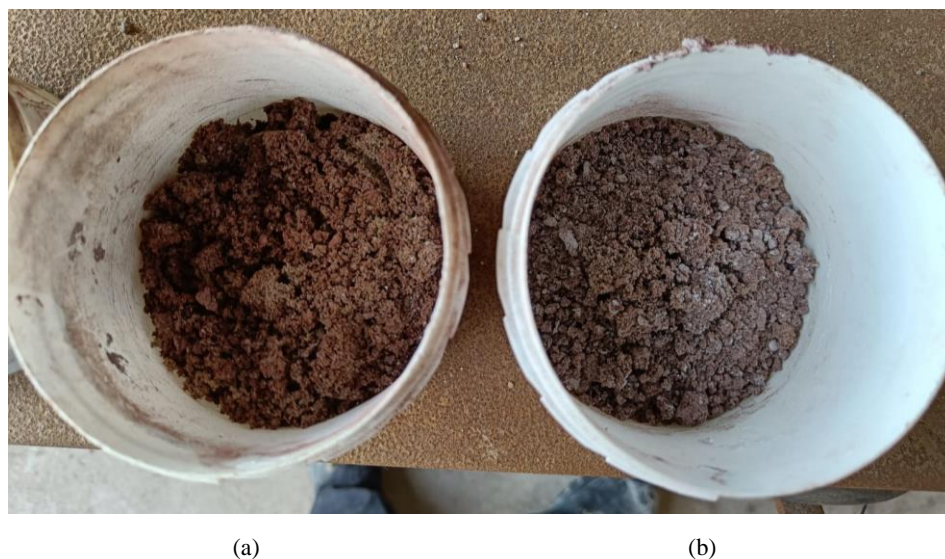
The addition of calcium carbonate ( $\text{CaCO}_3$ ) is related to  $\text{CO}_2$  gas formation. Sufficient  $\text{CaCO}_3$  addition can affect the ROP quality during mixing. As the mixer has difficulty to operate longer periods of time, finding the optimum amount of  $\text{CaCO}_3$  is one of the approaches tested in the laboratory and factory. Low to high percentage of  $\text{CaCO}_3$  were added and verified in the laboratory and factory.

In the experiment with low percentage of  $\text{CaCO}_3$ , the cake formation is affected the most. Cake in this case is a foam or bubble formation due to the presence of  $\text{CO}_2$  gas in the mixture. As



insufficient amount of  $\text{CaCO}_3$  is added, inadequate  $\text{CO}_2$  gas forms to induce cake formation in the mixture.

On the other hand, high percentage of  $\text{CaCO}_3$  resulted in finer and lighter powder ROP with more greyish color (see *Picture 4.1*). A fluffier cake also forms with higher addition of  $\text{CaCO}_3$ . A fluffier and lighter ROP are expected to lower and stabilize the mixer amperage, hence reduce the amount of energy needed to rotate the blade inside the mixer. In addition to the texture enhancement, higher percentage of  $\text{CaCO}_3$  gives positive effects to the free acid and  $\text{P}_2\text{O}_5\%$  water-soluble of both SSA ROP from SNB (Moerdijk) and HVC (Dordrecht). As more  $\text{CO}_2$  gas forms during the acidulation, more ideal mixing occurs resulting in a more efficient reaction between acid and  $\text{P}_2\text{O}_5$  content of SSA. The reaction resulted in more  $\text{P}_2\text{O}_5\%$  water-soluble content in the ROP and less free acid content (see *Table 4.1*).



**Picture 4.1** The SSA ROP with sufficient  $\text{CaCO}_3$  addition (a) and excessive amount of  $\text{CaCO}_3$  addition (b) in the pilot-scale acidulation test.

**Table 4.1** Analysis results of  $\text{CaCO}_3$  addition

$\text{CaCO}_3$ content	$\text{P}_2\text{O}_5\%$ water-soluble	$\text{P}_2\text{O}_5\%$ total	Free acid	Factor	Yield
1X	28.6	39	2.7	-18	73.3
2X	30.4	40	0.7	-18.5	76

However, excessive amount of  $\text{CaCO}_3$  in the factory resulted in huge rock formation (see *Picture 4.2*). The formation occurred 20 minutes after the ROP is produced. The noticeable effect was seen in the disintegrator. The rock was too big to crush and cause clogging inside. The rocks blocked the whole transport system causing a delay or stop. Moreover, the addition of  $\text{CaCO}_3$  in the factory cannot be precisely controlled or investigated due to the lack of input measurement.



**Picture 4.2** Material built-up in the mixer with higher percentage of  $\text{CaCO}_3$  during plant-scale acidulation test.

#### 4.1.2 Effects of soap addition

Lowering or increasing the addition of  $\text{CaCO}_3$  does not solve the mixture problem in the factory. The next parameter that was tested is the soap addition. Soap improves the mixing process by decreasing the surface tension of the liquid phase and thus improving the mixing. The soap molecules, surfactants, improve the mixing by increasing the cake state of ROP. The mixture of SSA and acid stays as a slurry for a longer time and the dispersion of the solids in the liquid is enhanced. This is due to a layer of surfactant keeping the bubbles in the mixture longer intact. The surfactant molecule is composed of a water attraction (hydrophilic) part on the head and a water-repellent (hydrophobic) part on the tail.

In a standard acidulation, soap is added in low percentage. However, the amount is insufficient for the SSA acidulation. Higher flow of soap is needed for better mixer performance and ROP quality. In the lab, the higher addition of soap resulted in bigger and fluffier cake formation (see *Picture 4.3*). The ROP is also finer and free flowing after 20 minutes.





(a)

(b)

**Picture 4.3** The comparison of cake formation with low soap addition (a) and high soap addition (b).



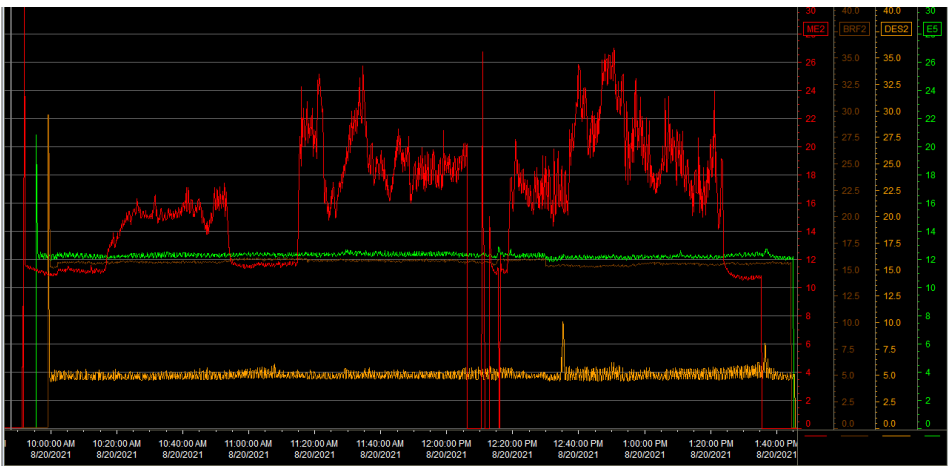
(a)

(b)

**Picture 4.4** The comparison of cake formation with low soap addition (a) and high soap addition (b).

The same result is obtained in the factory. Soap addition has a significant effect on the cake texture. As a result, the amperage of the mixer fluctuates less (see *Figure 4.2*). Compared to the SSA

acidulation test without constant addition of soap (see *Figure 4.1*), the mixer amperage in *Figure 4.2* is relatively lower and constant. The mixer is also able to operate longer without blocking.



*Figure 4.2* SSA acidulation with soap addition

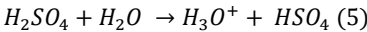
*Table 4.2* Analysis results of soap addition

Soap addition	P <sub>2</sub> O <sub>5</sub> % water-soluble	P <sub>2</sub> O <sub>5</sub> % total	Free acid	Factor	Yield
1X	28.6	39	2.7	-18	73.3
8X	29	39.2	2.4	-18	74

Despite the improvement from soap addition, it was not possible to increase the solids input to standard production levels. The amperage of the mixer is still too high when the material input is increased above 6 t/h.

#### 4.1.3 Effects of liquid-to-solid (L/S) ratio

Liquid-to-solid (L/S) ratio is one of the most crucial parameters in the acidulation. Without the presence of acid in the mixture, the apatite will not be extracted. The liquid added in the acidulation does not only contain acid, but also water is added. The addition of water with the acid solution results in an exothermic reaction (see Eq.5).



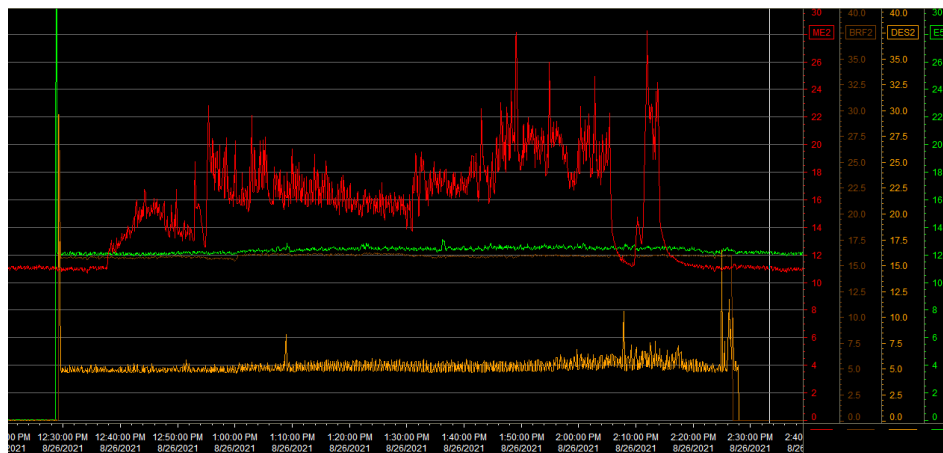
Heat formation from the exothermic reaction fasten and/or improves the reaction between the acid and the phosphate. In general, the higher the temperature, the faster the chemical reaction

is. As a result of the heat formation, a part of the water in the acid turns into steam. The exothermic reaction inside the mixer cannot be controlled and the expectation is that the mixture is very chaotic. The reaction between the acid and water creates a lot of splatters and reduces the ideal mixing. Furthermore, the formation of steam does not stay inside the mixer and steam escapes the mixer forming an unsustainable and unsafe situation (see *Picture 4.5*).



***Picture 4.5*** Steam formation due to water addition in SSP production

After the soap addition was optimized, the SSA input is still less than using phosphate rock in the standard acidulation. As a result, a different acid ratio is tested in the factory. A new ratio of PAC, SAC and water is formulated. In the latest factory test, the mixer amperage (see *Figure 4.3*) is even more constant than the previous tests (see *Figure 4.2*). Using the updated ratio, it is possible to operate the process using a higher SSA input comparable to standard operation.



*Figure 4.3* SSA acidulation with improved L/S ratio

## 4.2 Granulation

Granulation experiments using SSA were only carried out on pilot scale. Some parameters related to granulation are still being investigated. The parameters are liquid-to-solid ratio, minimum amount of SSA ROP needed in the mixture, and potential additives to improve the granulation and quality of the granules.

### 4.2.1 Liquid-to-solid ratio in granulation

The liquid-to-solid (L/S) ratio in granulation is the relation between the added water and/or steam and the solids. Currently, a good L/S ratio has been found for ROP made from SSA and phosphoric acid. The addition of  $\pm 60\%$  steam from the overall liquid addition resulted in the highest granulation efficiency of 80%. It is the highest efficiency obtained for SSA granulation, compared to the average granulation of 40%. However, the high amount of steam needed is inapplicable in the factory, due to the lower input limit of steam than water. If the efficiency cannot be improved, modifications will have to be implemented in the factory set-up.

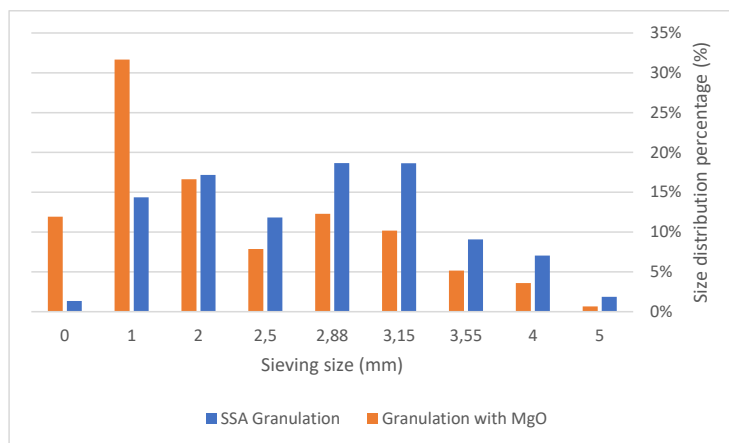
### 4.2.2 Additives in granulation

The SSA granulation efficiency is relatively low using the standard L/S ratio. In order to improve the process, various additives are added.

#### Magnesium oxide

Magnesium oxide (MgO) is commonly used in fertilizer industry as a micronutrient. However, another purpose of MgO addition is to reduce the free acid in the ROP. As mentioned earlier, the heavy metal content in sewage sludge makes the phosphorus extraction more difficult. The acid solution used in the acidulation do not completely react with the apatite in SSA. As a result, the

remaining acid from the solution stays in the ROP in the form of free acid. The relatively high free acid has negative effects on the quality of the granules.



**Figure 4.4** Sieving analysis with and without MgO

However, the addition of MgO does not improve or solve the quality problems. In Figure 4.4, the granule size distribution is shown of the granulation using MgO and without using MgO. The granulation test using MgO has more granules < 2 mm produced with the same amount of water and steam. Furthermore, the percentage of granules with the right size (2.5 mm to 5 mm) is lower.

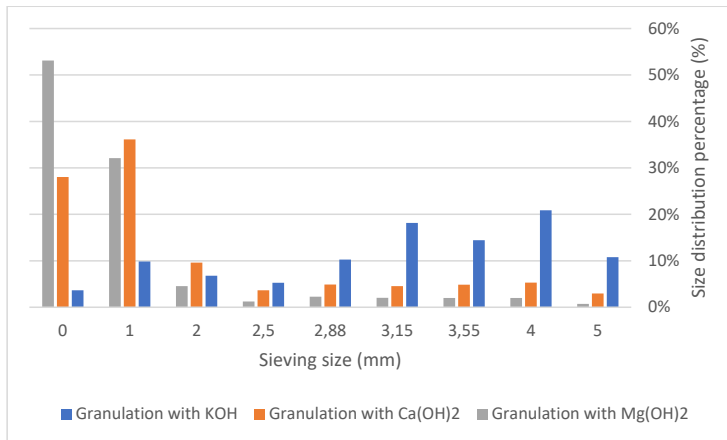
#### Strong Base

##### a. Half-neutralization of ROP

The addition of a strong base was tried to reduce the free acid in the ROP by half before the granulation. The purpose is similar to the addition of MgO, to reduce the free acid of the ROP. Three different bases were used; KOH,  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ . However, the neutralization is unsuccessful. Only around 1% of the free acid in the ROP reacts with the base.

##### b. Base in granulation

Besides the ROP neutralization, the strong bases were also added directly during granulation (see Figure 4.5). When KOH was added, the granulation occurred faster, and less water is needed. The fresh granulation efficiency reached up to 70%. Meanwhile, the addition of the two other bases did not improve the granulation. The granulation efficiency with  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$  is respectively around 30% and 15%. However, the addition of strong base in the granulation process does not produce a hard and strong granule structure. Further research is needed to understand which granulation additives will improve the granulation of SSA ROP.



**Figure 4.5** Sieving analysis with KOH, Ca(OH)<sub>2</sub> and Mg(OH)<sub>2</sub>

## 5. Conclusions and Recommendations

### 5.1 Conclusions

As the research in this paper shows, phosphate fertilizer using one of the alternative sources, sewage sludge ash, is able to produce. The process is divided into three sections: acidulation, granulation and storage and transport. Currently, the focus is improving the acidulation and granulation steps on pilot and plant scale. During the development process, important parameters of each production step are slowly determined. In the SSA acidulation, the parameters include the  $\text{CaCO}_3$  addition, soap addition, and liquid-to-solid (L/S) ratio. While the most crucial factor in SSA granulation is L/S ratio. By changing the parameters above some improvements are obtained in the production process and the final product. In the acidulation stage, the improvements include a better texture of ROP, longer duration of acidulation test in the factory and higher scale of material input comparable to phosphate rock fertilizers. Moreover, SSA ROP produced in the factory is possible to granulate and higher steam addition appears to be the only way to improve the SSA granulation at the present. The use of additive in granulation has not been shown to be helpful. More research is needed to further improve the SSA granulation.

### 5.2 Recommendation

Despite the improvement on the production of SSA fertilizer, further research and development is needed to improve the acidulation and the granulation process. In terms of acidulation, more work on SSP ROP is required to longer the acidulation process with lower mixer amperage and less steam formation around the mixer. Different mixing methods can also be an option to explore. In addition to expand the product selection of SSA fertilizers, more ratios can be developed and tested in the factory. While in the granulation process, the effect of higher steam addition needs to be further tested to find the optimum steam-water ratio. Different additives can also be tested to enhance the granulation efficiency and reduce the use of steam. It is also necessary to plan a granulation test on a plant-scale to check the application of the optimum L/S ratio with higher steam addition.

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