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Abstract NL. In Nederland is meer fosfaat uit dierlijke mest beschikbaar dan binnen de gebruiksnormen toepasbaar is op het totaal aan landbouwgronden. Het teveel aan fosfaat dient daarom op een duurzame en kosteneffectieve wijze te worden afgezet naar gebieden elders met een vraag naar fosfaatrijke meststoffen. Een alternatief voor de huidige mest export is mestraffinage waarbij mest wordt verwerkt tot waardevolle meststoffen. Dit rapport beschrijft de mogelijkheden tot het scheiden van dikke fractie van varkensmest in een fosfaatmeststof en een nutriënt-arme organische bodemverbeteraar. Deze fosfaatmeststof kan gebruikt worden als grondstof voor meststoffen voor de export terwijl de organische bodemverbeteraar in de regio afgezet kan worden. Het scheidingsproces, genaamd RePeat, bestaat uit een aanzuurstap gevolgd door een scheidingsstap en het terugwinnen van fosfaat door dosering van calcium- of magnesiumhydroxide. Dit rapport borduurt voort op eerder werk (Schoumans *et al.,* 2017) waarin het proof-of-principle voor dit proces is gegeven. Het onderhavige rapport beschrijft aanvullende laboratorium- en pilotproeven met co-vergiste varkensmest en de resultaten daarvan zijn opgenomen in hoofdstukken 2 t/m 4 van dit rapport. Aspecten die hierin centraal staan zijn o.a. het recirculeren van proceswater binnen het proces, het verlagen van het organische stof gehalte in het herwonnen fosfaat en de ontwatering van herwonnen fosfaat na additie van calcium- of magnesiumhydroxide. Hoofdstuk 5 geeft de verwachtte massabalansen van het proces bij verschillende procescondities. Hoofdstuk 6 gaat in op de kwaliteit van de organische bodemverbeteraar en beschrijft o.a. resultaten van incubatieproeven. Een schatting van de business case van het proces is opgenomen in Hoofdstuk 7. De resultaten van de laboratorium- en pilotproeven vormden de basis voor het ontwerp van een grootschalige demonstratie installatie van het RePeat proces welke in 2019 gerealiseerd zal worden bij Groot Zevert Vergisting B.V. in Beltrum.

Abstract UK. In the Netherlands, the agricultural sector produces more manure than can be applied on agricultural land within the P application standards. The excess amount of manure should be exported to other regions with a demand for P fertilisers. An alternative for current manure export is manure processing in which manure is processed into valuable fertiliser products. This reports describes a process in which the solid fraction of co-digested manure is processed into a concentrated P fertiliser and a nutrient-poor organic soil improver. The recovered P fertiliser can be used as a secondary raw material for fertiliser production or for export whereas the soil improver can be used on arable soils in the nearby region of the manure treatment plant. The separation process, called RePeat, consists of a acidification and dilution step to extract P from the solid fraction followed by a base addition step to recovery P. The proof of principle was given in a previous report (Schoumans *et al.,* 2017). This reports describes additional laboratory and pilot tests (Chapter 2-4). Attention was given to the reuse of water within the process, the dewatering of calcium phosphate versus struvite and the selection of separation equipment for a demonstration plant. Chapter 5 gives the process mass balances calculated using a mass balance model. Chapter 6 assesses the quality of the organic soil improver in terms of its carbon- and nitrogen mineralisation rate. An example of a business case for the process is included in Chapter 7. The results were used to design a demonstration plant for the RePeat process to be built at Groot Zevert Vergisting B.V. in 2019.

Keywords: RePeat, phosphorus recovery, manure, digestate, struvite, magnesium phosphate, calcium phosphate, organic soil improver

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Photo cover: Photo of manure treatment plant of Groot Zevert Vergisting B.V.,
Beltrum, The Netherlands.

Contents

Preface

This report is a result of the ‘Meerwaarde Mest en Mineralen’ (Added Value Manure and Minerals) project (TKI-BBE-1704/AF16137b) which was initiated by the Farmers organisation ‘Land- en Tuinbouw Organisatie Nederland’ (LTO, Agricultural and Horticultural Organisation of the Netherlands) and funded by the Ministry of Economic Affairs of the Netherlands as part of the ‘Topsector agreement’.

The agricultural sector of the Netherlands produces about 25% more phosphorus (P) in the form of manure than can be applied on agricultural land in the Netherlands within the P-application standards. Hence, innovative approaches are needed to process the surplus manure. One promising solution to deal with the surplus of P in manure is to recover P in the form of a (mineral) P product for use as a P fertiliser (for export) or as a raw P feedstock for the P fertiliser industries. This idea for ‘closing the manure P cycle of The Netherlands’ has been buzzing for a while but was never investigated until in 2013 a Public Private Partnership (PPP) was set up with the Farmers Organisation LTO and the Ministry of Economic Affairs. The first step of the Public Private Partnership study was to set up simple laboratory experiments to explore the technical opportunities of P recovery and was published by Schoumans *et al.,* (2014). This study gave the ‘proof of principle’, showing that P can be recovered from the solid fraction of ((co-)digested) animal manure against reasonable costs for acid-base consumption. The concept was given the name ‘RePeat’ being an abbreviation of ‘Recover of P to eat’. In 2016, the RePeat concept was further tested on lab scale with manure samples from different farms. Thereafter, a pilot installation was built at Groot Zevert Vergisting B.V. in Beltrum which allowed tests to be performed with larger quantities of manure. The results of these pilot tests were published in Schoumans *et al.,* 2017.

The results of the pilot tests were promising and the ambition arose to construct a full-scale demonstration plant at the anaerobic digestion plant of Groot Zevert Vergisting B.V. in Beltrum, The Netherlands. However, during the design of the full scale plant, new research questions arose meaning additional laboratory- and pilot tests and more elaborate analyses on the products. Results of these tests are reported in this report and were used to finalise the design for the demonstration plant to be built in 2019.

Summary

In the Netherlands, the intensive agricultural production system has led to environmental problems because in the past, fertilizer application rates were higher than crop uptake. These include losses of nutrients like nitrogen (N) and phosphorus (P) to ground and surface water. Nowadays, manure application standards restrict the amount of nutrients that can be applied on agricultural land in the Netherlands. More phosphorus is produced by animal husbandry than can be applied on agricultural land meaning that the surplus amount needs to be processed or exported. Export of animal manure is costly and leads to CO_2 emissions due to the large volumes being transported over hundreds of kilometres. To overcome these issues, there is a need for innovative, simple and cheap manure treatment technologies to process the P available in animal manure or digestate into a concentrated and valuable product.

The previous report (Schoumans *et al,* 2014) described the proof of principle of a methodology of separating the solid fraction of manure or co-digested manure into a mineral P fertiliser and a P-poor organic soil improver. This methodology was afterwards further developed and tested at laboratory and pilot scale (Schoumans *et al,.* 2017). The P recovery process, called RePeat[1], starts with separation of the animal manure or digestate into a solid and a liquid fraction. Then the solid fraction is acidified to pH 5 in order to solubilize mineral P and this acid slurry is separated into a solid and liquid fraction separating the P-poor organic soil improver from the P-rich acid solution. Phosphorus is thereafter recovered from the acid solution as precipitated calcium phosphate or struvite by increasing the pH through addition of $Ca(OH)_2$ or $Mg(OH)_2$. Groot Zevert Vergisting B.V. constructed a pilot installation in Beltrum, The Netherlands. A full scale demonstration plant with a yearly capacity of 16,000 ton of solid fraction of digestate will be constructed there in 2019. During the design of the demonstration plant, new research questions arose which led to new laboratory and pilot tests. Results of these are reported in this report and used to finalise the process design for the full scale demonstration plant.

Chapter 2 describes results of practical tests with the pilot plant operated in batch mode. Their goal was to investigate the effect of reuse of process water on product quality. The solid fraction of co-digested manure, with a P content of 6.3 g P/kg, was diluted with process water from the previous batch in a 1:4 (w/w) ratio and acidified by addition of 77 kg 50% sulphuric acid per ton solid fraction manure. Thereafter the diluted solid fraction was separated into a solid fraction and liquid fraction by means of a screw press. The solid fraction was once more diluted, acidified and screw pressed in the same way. This lead to a 90% phosphorus removal from the solid fraction resulting in an organic soil improver with a relatively low P content of 1.2 g/kg which can be used as soil conditioner on arable land. Phosphorus was recovered from the acid liquid fraction, which had a P content of 1.5 g/L, by raising the pH to 8 by addition of $Ca(OH)_2$ resulting in precipitation of calcium, phosphate and possibly sulphate (Ca~P~S). The Ca~P~S sludge had a dry matter content (DM) of 6% and an organic matter content was 40% (based on DM). Nearly all via sulphuric acid added S ended up in the Ca~P~S sludge, mainly as dissolved SO_4^{2-} in the water fraction of the Ca~P~S sludge. Hence, further dewatering of the Ca~P~S sludge will result in a decrease of the amount of S separated with the Ca~P~S sludge but leads consequently to an increase in the S content of the P-poor organic soil improver.

Chapter 3 describes the outcomes of experiments on the precipitation of P from the by screw press separated acid liquid fraction. Their goal was to find an approach to recover P as an easily dewaterable product. The use of $Ca(OH)_2$ or $Mg(OH)_2$ for P precipitation was compared. The use of $Mg(OH)_2$, to increase the pH of the acid liquid fraction from 5 to above pH 7, led to the formation of struvite. This was evident from the simultaneous precipitation of P and ammonium (NH_4) in a 1:1 molar ratio. Phosphate precipitation by addition of $Mg(OH)_2$ took a couple of hours whereas it took only a couple of

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[1] RePeat: acronym: Recovery of Phosphorus to eat

minutes after addition of $Ca(OH)_2$. The settling velocity of struvite formed in a batch-wise approach amounted to 100 cm/h which was much larger than the settling velocity of Ca~P~S sludge (4 cm/h). The DM content after centrifugation amounted to 21% and 13% for struvite and Ca~P~S sludge, respectively. Struvite can form coarser particles when particles are retained within the reactor allowing them to growth. This principle was tested in a continuously fed laboratory reactor with an hydraulic retention time of 5 hours. After three days, an easily dewaterable struvite product with 40% DM was formed. This benefit of struvite is likely to outweigh the higher costs for $Mg(OH)_2$ compared to $Ca(OH)_2$ and the costs for a larger precipitation tank needed to increase the particle retention time.

In Chapter 4, the outcomes of tests with various separators at Groot Zevert Vergisting B.V. are described. Their goal was to select separation- and dewatering equipment for the full scale demonstration plant. The first objective was to remove fine particulate OM from the acid liquid fraction prior to it reaching the precipitation tank. This had the aim to reduce the OM content of the recovered P product. It was found that a lamella separator could remove a substantial amount of the particulate OM. The second objective was to dewater the Ca~P~S sludge. A rotating drum screen was found to be unsuitable for this purpose because particulate matter passed the 80 µm pore size filter whereas the 40 µm pore size filter immediately clogged. A decanter centrifuge dewatered the Ca~P~S sludge to a DM content of 28% at a low feeding rate of <1 m^3/h and to a DM content of 9% at a normal feeding rate of 4 m^3/h. This is equivalent to a Ca~P~S sludge production of respectively 200 and 600 L per ton of ingoing solid fraction and an additional drying step is required in order to produce a dry Ca~P~S product. As an alternative, also a struvite precipitation test was performed in a continuously fed tank. Struvite formed as sand-like precipitates after three days of continuously feeding the reactor. This is in line with the results of the laboratory tests described in chapter 3. However, due to various practical constraints, the tests could not be continued and it was not possible to make a mass balance.

Chapter 5 summarises the process design and gives the expected mass balance for the RePeat demonstration plant producing struvite, P-poor organic soil improver and a gypsum-rich sludge.
The mass balance model was set-up using data from the lab- and pilot experiments plus knowledge on the solubility product of gypsum. The P-poor organic soil improver contains S, in the form of SO_4^{2-} and gypsum, due to the addition of sulphuric acid in the extraction process. The concentration of S in the soil improver is not known yet as it depends on the process conditions. It however is expected to vary between 7-14 g S/kg. The lower value is gained in case the precipitated gypsum is separated by means of a lamella separator.

In Chapter 6, the quality of the P-poor organic soil improver is assessed with respect to criteria for organic soil improvers and criteria for potting soil ingredients. An incubation experiment was performed to assess the carbon- and nitrogen mineralisation rate using compost from vegetable-, fruit- and garden (VFG) waste as a reference. The humification coefficient, calculated using a 2-pool model, was70% for the P-poor organic soil improver and 92% for the compost. Nitrogen was immobilised during the two weeks of the incubation experiment due to the high C/N ratio of the OM.
A comparison with other organic fertilisers showed that the ratio between phosphate (P_2O_5) and effective organic matter (EOM), which is defined as the OM that remains in the soil for at least one year, is profitable. Example fertilisation schemes are given in which 60 kg P_2O_5/ha is applied by combinations of manure and P-poor organic soil. Compared to fertilisation with untreated pig slurry, a farmer can reach a threefold increase in the dosage of EOM by replacing 10% of the P-application standard by P-poor organic soil improver which requires a dosage of 4 ton/ha. Thereby the advised S dosage of 30 kg S/ha for most arable crops is not surpassed. For this scenario, the overall EOM dosage amounts to 2 ton/ha of which 75% originates from the P-poor organic soil improver.

Alternatively, the P-poor organic soil improver may be a suitable secondary raw material for potting soil production as an alternative for peat. The physical properties of the OM of P-poor soil improver, including water holding capacity and porosity, are very similar to peat. The slightly acidic pH fits requirements of potting soil producers and the oxygen consumption rate is sufficiently low.
An additional leaching step with clean water is however needed in order to leach out SO_4^{2-} and to lower the EC value.

Chapter 7 addresses the business case for a demonstration plant with a processing capacity of 100,000 ton manure /digestate per year in which the solid fraction, amounting to 16,000 ton per year, is treated with the RePeat process. That RePeat business case is compared to a reference situation in which transport and disposal costs for the solid fraction of digestate are €25.00 per ton. With the RePeat process, these costs could be lowered to €14.00 per ton of solid fraction, assuming that arable farmers are willing to use the P-poor organic soil improver in exchange for paying its transportation costs.

1 Introduction

The agricultural sector of the Netherlands faces severe challenges related to the environmental impact of intensive agriculture due to an excess amount of nutrients in terms of manure. Although the number of animals of intensive livestock farms has declined slightly during the last decade, nutrient balances are still positive. This means that the amount of nutrients in manure exceeds the amount that can be used on agricultural soil in The Netherlands within the application standards. In 2017, livestock in the Netherlands produced 77 billion kg manure containing 169 million kg P_2O_5 and 448 million kg of N. In terms of phosphate, the majority was produced by cattle (57%) whereas pigs and poultry contributed another 22% and 17%, respectively (Figure 1.2).

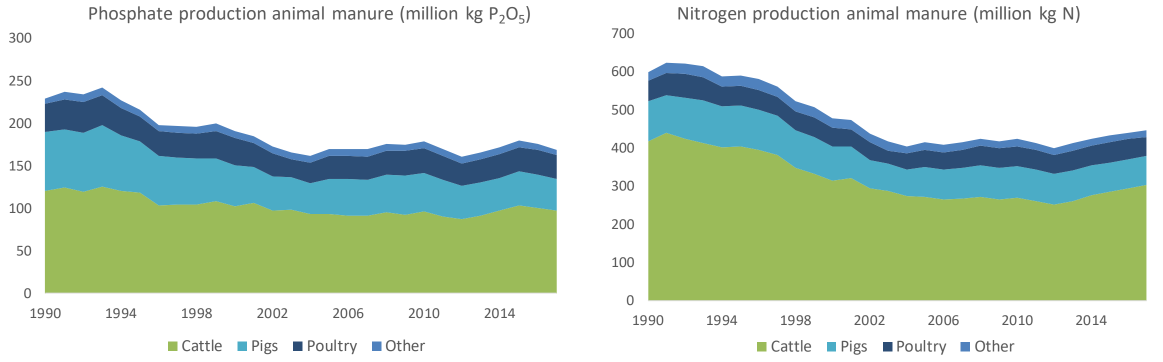

Figure 1.1 *Phosphate and nitrogen production in the form of animal manure in the period between 1990 and 2017*[2]

The amount of phosphate applied on agricultural land has been halved since 1990 due to the introduction of P-application standards (Figure 1.2). The P-application standard have since then decreased until their current values which corresponds to a situation of equilibrium fertilisation (or maintenance fertilisation). The strong decrease in P-application standards led consequently to a strong increase in the surplus of phosphorus in manure that cannot be applied on agricultural land.

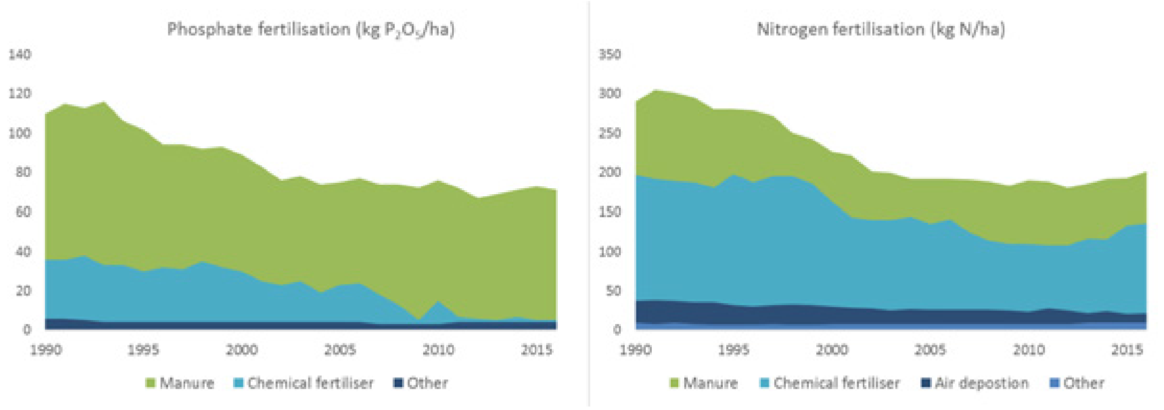

Figure 1.2 *Average phosphate and nitrogen fertilisation rates on Dutch agricultural soils in the period 1990-2017* [2]

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[2] https://www.clo.nl/indicatoren/nl0093-stikstof--en-fosfaatbalans

The manure application rate is not just limited by phosphorus but also by nitrogen as the Nitrates Directive of the European Commission states that farmers cannot apply more than 170 kg N/ha as manure (or 230 or 250 kg/ha on grassland in case of derogation of a farm). For dairy manure, the nitrogen content can be the factor limiting manure application meaning that a fraction of the P application standard remains unused. For example, in 2017, the amount of phosphate that could be applied on agricultural land in the Netherlands amounted to about 135 million kg P_2O_5 [3] of which 10% remained unused due to the unfavourite N/P ratio of the manure. Hence, 122 million kg P_2O_5 were used on arable land whereas the remaining part, equalling 28% of the overall P produced as manure, had to be exported. Farmers preferably use their own manure for fertilisation and it is therefore that export of P from manure is mainly from poultry and pig manure. Nearly all poultry manure is processed or exported after being processed through either incineration, composting or after being pelletized. For pig manure, roughly 40% is nowadays exported whereas this is only 5% for cattle manure[3].

The surplus of pig manure is dominantly exported to Germany as slurry or as a solid fraction obtained after mechanical separation (NCM, 2018). Export of manure in the form of slurry or solid fraction is costly due the fact that large volumes of slurry need to be transported over distances of 100-300 km. In 2017, average manure disposal costs of farms amounted to €20 and €11/ton for pig manure and diary slurry, respectively[4]. The higher disposal costs for pig manure are due to the higher phosphate content and the lower N/P ratio as compared to dairy manure, which makes pig manure less attractive for use in fertilisation schemes. Another reason that pig manure has higher disposal costs is that dairy farmers can use most of their manure on their own land which is not the case for pig farmers who usually own little land. In an attempt to reduce manure disposal costs, the interest in manure separation and manure processing techniques has strongly increased during the last decade. At this moment, manure separation followed by composting or drying of the solid fraction and thereby producing a pelletized organic fertilising product is still considered as best-practice.

As an alternative, the solid fraction of manure can be treated with water and acids to solubilise and extract phosphate from the OM which can subsequently be recovered through the addition of a base such as calcium- or magnesium hydroxide. This process, called RePeat[5], has been developed and tested by Wageningen UR in laboratory- and pilot tests which took place in 2016-2017 (Schoumans *et al.*, 2014, 2017). These tests showed that over 80% of the phosphorus could be extracted from the solid fraction of manure or solid fraction of co-digested manure after dilution with water and acidification to pH 5. The acidified slurry can then be separated into a solid fraction and an acidified liquid fraction by means of a screw press. After this separation phosphate can be recovered from the liquid fraction. In the previous work, phosphorus was recovered through the addition of $Ca(OH)_2$, forming calcium phosphate precipitates. In theory also other bases such as $Mg(OH)_2$ could be used. The precipitated phosphate can be separated from the solution after settling. The process produces a concentrated phosphate fertiliser to be used for export or as secondary raw material for mineral P fertilisers. It also produces a nutrient-poor organic product which can be used as soil improver or as replacement for peat-based growing media in horticulture.

The previous reports described results of laboratory and pilot tests (Schoumans *et al.,* 2014, 2017). Though results were promising, also some bottlenecks were encountered which led to the following research questions:

1. how can the dewaterability of the Ca~P~S sludge be improved
2. how can the OM content of the recovered phosphate precipitate be reduced and
3. what are the consequences of recirculation of process water on the sulphur content of the end products?

Since project partner Groot Zevert Vergisting B.V. had decided to invest in a full scale installation, these bottlenecks needed to be solved in order to be able to make a final design for the full scale plant. Results of the laboratory and pilot tests performed in 2018 are documented in this report. These results were used to make final decisions in the process design for the full scale plant which will be installed at Groot ZevertVergisting B.V's anaerobic digestion plant in Beltrum in spring 2019.

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[3] CBS statline, data 2017.

[4] www.agrimatie.nl Mestafzetkosten. Accessed at 28-01- 2019

[5] RePeat: acronym: Recovery of Phosphorus to eat

2 Pilot test: continuous recirculation of process water

2.1 Introduction

The RePeat process makes use of an extraction step in which the solid fraction of manure or digestate is mixed with water and subsequently acidified to pH 5 by addition of sulphuric acid. The P-rich solution is separated from the solids and treated with $Ca(OH)_2$ in order to increase the pH. Thereby orthophosphate (orthoP) precipitates with Ca^{2+} into an amorphous calcium phosphate ($CaHPO_4$) mineral which can be collected after settling. After settling of the calcium phosphate, a solution remains with a low P concentration but a relatively high concentration of salts including sulphate. Disposal of this water should be prevented since it would create a bulky waste stream. Hence, reuse of this process water in the next batch cycle is important and it reduces the intake of clean water.. Recycling of process water will lead to accumulation of salts, including sulphate, in the process water. It is currently unknown if and how elevated salt levels may affect the extraction or precipitation process due to a shift in chemical equilibria in the RePeat system. Moreover, the distribution of sulphur between the two end-products, recovered phosphate sludge and nutrient-poor organic soil improver, is of interest. Preferably, sulphur accumulates in the phosphate product were it adds to the plant nutrient content of the fertiliser. High sulphur concentrations in the nutrient-poor organic soil improver may be disadvantageous because it gives a risk of unbalanced fertilisation of sulphur when used in large quantities.

The effects of process water reuse within the system were investigated with the RePeat pilot installation during eight subsequent batches. Mass balances are shown and results are discussed including effects of the accumulation of salts on the sulphur content of the recovered products.

2.2 Materials and Methods

2.2.1 Process configuration

The RePeat process is schematically depicted in Figure 2.1, which shows the input and output materials and internal flows between the different installation components. The numbers in the figure associated with arrows refer to mass flows which are monitored by sampling and measurements. The full process includes two acidification steps to solubilize and leach P from the solid fraction of manure or digestate and a base addition step in order to precipitate and recover P.
The digestate is acidified to pH 5 using 50% sulphuric acid and subsequently separated into a solid and liquid fraction. The acidification and separation step is performed twice in order to obtain a high P release from the solid fraction (>75%; Schoumans *et al.*, 2017). Next, P is recovered from the liquid fraction under alkaline conditions by addition of 30% $Ca(OH)_2$ followed by gravitational solid-liquid separation. Thereafter, the liquid fraction is fed into the acidification tank and reused within the process thereby preventing a new waste stream.

2.2.2 Set-up of the pilot experiment

The pilot test was performed with digestate from the mesophilic anaerobic digestion plant of Groot Zevert Vergisting B.V. in Beltrum, The Netherlands. The plant treated pig slurry (80%) and bio wastes including livestock digestive tract content, crop residues (potato) and food and feed residues (20%). The digestate was separated into a solid and a liquid fraction by means of a centrifuge (decanter) after which the solid fraction was used for the experiments.
The process water (recirculation water) was reused in the process. As a consequence, the composition of the recirculation water changed over time due to accumulation of salts until an equilibrium between inflow and outflow had been established. To mimic this situation, the extraction and recovery process

was repeated eight times (eight batches) while continoulsy reusing the process water from the previous batch.

For each batch, the following procedure was followed; About 400 kg of solid fraction of digestate (Figure 2.1, flow 1) was fed into the first acidification tank and diluted with recirculation water at a ratio of 1:4 (w/w). For the first batch, groundwater was used for dilution.. The slurry was acidified with 50% sulphuric acid to pH 5 using an automatic pH dosage and registration system while being continuously mixed. Thereafter, the slurry was separated by a screw press into a solid fraction (flow 3) which was led to the second acidification tank and a liquid fraction (flow 4), which was led to the precipitation tank. In the second acidification tank, the solid fraction was diluted with recirculation water at a ratio of 1:4 (w/w) and the pH of the slurry was lowered to pH 5 using 50% sulphuric acid. Again, a screw press was used to separate the solid (flow 7) and liquid fraction (flow 8). The latter liquid fraction was used as a diluting agent in the first acidification tank for the next batch. The acid liquid fraction was fed in the precipitation tank (flow. 4). The acid liquid fraction was stirred and treated with a suspension of 30% $Ca(OH)_2$ (flow 9) until the pH had increased to pH 8.
This immediately resulted in the formation of calcium phosphate precipitates. Stirring was then stopped and sedimentation started which continued overnight (approximately 12 hours). The next day, the clear supernatant was removed by siphoning (pumps) (flow 10) and used in the next batch as a dilutant in the second acidification tank. Thereafter, the calcium phosphate slurry was removed by siphoning into a storage tank (flow 11).
During the pilot tests, the mass of all ingoing, internal and outgoing flows was monitored by measuring flows and/or weights of streams and and chemical compositions of streams via samples. The electrical conductivity (EC) value of the acid liquid fraction (flow 4) was monitored in order to assess whether the salt concentration had reached equilibrium.

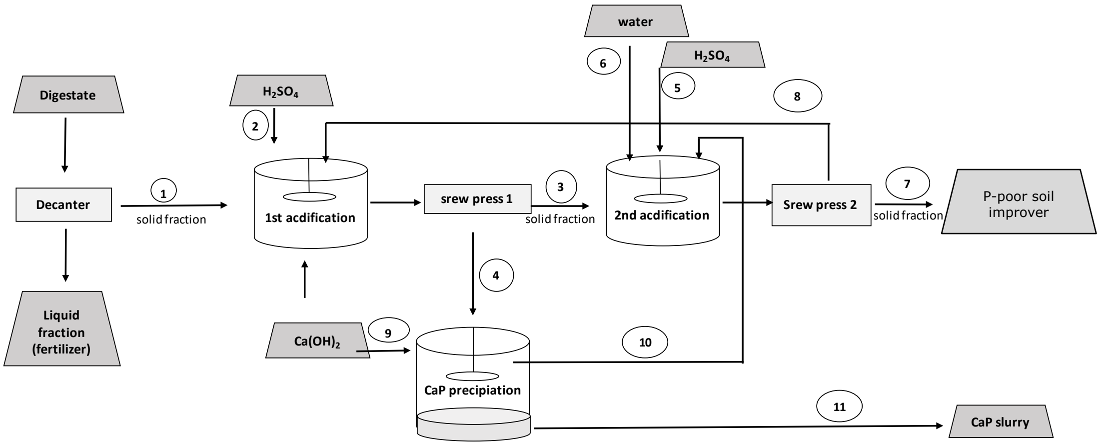

Figure 2.1 *Flow diagram of the RePeat process. The numbers indicate the sampling points.*

2.2.3 Chemical analysis of end products and intermediates

Chemical analyses were performed on samples taken in the sixth, seventh and eighth batch since EC measurements revealed that the salt concentration was in equilibrium after the fifth batch. Samples were analysed by the Chemical Biological Soil Laboratory (CBLB) which is part of Wageningen University and Research. The dry matter (DM) content was determined by drying at 105 ºC and the organic matter (OM) content was determined by loss on ignition (LOI) at 550 °C. The chemical composition was determined after destruction with HNO_3-HCl- (Aqua Regia) followed by analyses of the P, Ca, Mg, K, Na and S content in the solution by ICP-AES. In the solid samples, the total nitrogen (N-t) content was determined after destruction with $H_2SO_4/H_2O_2/Se$. For liquid samples, the pH was measured and ortho-P and N-NH_4 were determined spectrophotometrically with a Segmented Flow Analysis (SFA) device after filtration over a filter with a pore size of 0.45 µm. For solid samples, pH and N-NH_4 were measured in a 1M KCl extract.

2.3 Results and discussion

Reuse of process water led to accumulation of salts as was evident from the increasing EC of the process water. The EC remained constant from the fifth batch onwards implying that the system reached a steady state condition. Hence, samples from the sixth, seventh and eight batch were collected and analysed. Results were averaged over these three batches and the average results are reported in this chapter. Table 2.1 gives the overall mass balance of the system expressed per ton of ingoing solid fraction. Table 2.2 and 2.3 show respectively the average composition of the solid and liquid mass flows. Numbers of sampling locations are depicted in figure 2.1. a table with all measurement data on individual samples is included in Annex 1.

Phosphorus extraction and recovery
The ingoing solid fraction (flow 1) had a P content of 6.3 g/kg and a pH of 8.3. The solid fraction was mixed with process water and acidified to pH 5, consuming 70 kg (or 50 L) of 50% sulphuric acid per ton of ingoing solid fraction. The acidified mixture was separated by means of a screw press into a solid and a liquid fraction. This solid fraction (flow 3) is an intermediate product since it undergoes a second acidification step requiring 7 kg (or 5 L) 50% sulphuric acid per ton of ingoing solid fraction. The acid requirement of the second acidification step is rather low compared to the first acidification step (only 10%). This step should mainly be considered as a leaching step to remove the already solubilised phosphate from the solid fraction. During the first acidification step, the P content of the solid fraction decreased from 6.3 to 1.9 g/kg. During the second acidification step, the P content further decreased to 1.2 g/kg. Though the effectiveness of the second acidification step may seem low, this step is crucial in order to produce an organic solid fraction that can be regarded as 'P-poor' within the Dutch agronomic context. Based on the mass balance (Tabel 2.1), about 90% of the phosphate in the ingoing solid fraction was extracted and subsequently recovered. The P content of the solid fraction decreased with 80% from 6.3 to 1.2 g/kg.

Phosphorus was recovered through precipitation with $Ca(OH)_2$ leading to the formation of calcium phosphate and possibly also gypsum. This sludge is hereafter referred to as a calcium~phosphate~sulphur or as Ca~P~S precipitate. For each ton of ingoing solid fraction, 55 kg of $Ca(OH)_2$ (30%-solution w/w) was dosed to the acid P-rich liquid fraction in order to increase the pH to 8.0. This Ca~P~S suspension was allowed to settle overnight after which the clear supernatant was siphoned to another tank for reuse as extraction solution for the next batch. After settling, the Ca~P~S slurry had a DM content of 6.5%, the installation thus produced 2 ton of Ca~P~S slurry per ton of ingoing solid fraction. The process thus led to an increase in the volume of manure, which is unwanted. a subsequent dewatering step is therefore required in order to reduce the volume of the Ca~P~S slurry and to reduce the amount of heat needed for drying. This issue is further elaborated on in Chapter 3 were the settling rate of CaP is compared with that of struvite and in Chapter 4, were various separation techniques are tested on their ability to dewater the Ca~P~S slurry.

Table 2.1 *Average mass balance (three batches) of the pilot-scale P-extraction and recovery experiment expressed per 1000 kg of ingoing feedstocka. Ingoing solid fraction and end products in bold.*

Sampling point	Flow	Fresh weight	Dry matter	Org. Matter	P	Ca	Mg	S
		kg	kg	kg	kg	kg	kg	kg
1st acidification step								
1	**Feed (SF Digestate)**	**1000**	**239**	**178**	**6.3**	**6.5**	**4.0**	**1.9**
12	Process water	3897	70	n.m.	1.0	3.8	2.1	11.7
4	50% sulphuric acid[b]	70	35	0.0	0	0	0	11.6
2nd acidification step								
3	SF_intermediate	572	176	151	1.1	2.2	0.7	2.9
8	Recirculation water	2391	43	n.m.	0.0	2.5	1.5	9.5
6	Groundwater	1496	0	n.m.	0	0	0	0
5	50% sulphuric acid[b]	7.1	3.6	0	0	0	0	1.1
7	**P-poor soil improver**	**388**	**126**	**110**	**0.5**	**1.5**	**0.3**	**1.6**
Calcium phosphate precipitation step								
4	Acid liquid fraction	4486	185	n.m.	6.5	8.5	5.7	23.0
9	30% $Ca(OH)_2$[b]	55	19.6	0.0	0	10.7	**0**	**0**
11	**Ca~P~S product**	**2194**	**142**	**61**	**6.3**	**13.5**	**4.2**	**13.6**
	Error (IN-OUT, %)	6%	13%	4%	-9%	13%	-13%	-3%

[a] Experiment was performed with 400 kg solid fraction of digestate per batch but the mass balance was expressed per 1000 kg of solid fraction. Locations of sampling points refer to numbers given in Figure 2.1. n.m.; not measured.

[b] 50% sulphuric acid with a density of 1.4 kg/L and H_2SO_4 content of 698 g/L. Density of 30% $Ca(OH)_2$ is 1.25 kg/L. Composition of sulphuric acid and calcium hydroxide based on technical factsheets of the supplier.

[c] Error was calculated as the difference between the mass of the ingoing streams (1, 4, 5, 6, 9) and the mass of the outgoing streams (7, 11) expressed as percentage of ingoing mass (1, 4, 5, 6, 9).

Table 2.2 *Composition per kg of fresh matter of the ingoing solid fraction (feedstock), the solid fraction after one and two acidification steps respectively (SF-1, P-poor OM) and the calcium~phosphate~sulphur slurry (Ca~P~S). Averaged over three batches.*

Sampling point		1	3	7	11
Parameter	Unit	feedstock	SF – 1	P-poor OM	Ca~P~S slurry
DM	(%)	23.9	30.7	32.3	6.5
OM	(% of dm)	74.8	85.7	88.0	42.9
pH	(-)	8.3	6.2	5.9	7.8
P	(g/kg)	6.3	1.9	1.2	2.9
N	(g/kg)	8	n.m.	4.8	2.8
Ca	(g/kg)	6.5	3.9	3.8	6.1
Mg	(g/kg)	4.0	1.3	0.8	1.9
S	(g/kg)	1.9	5.0	4.2	6.2
K	(g/kg)	3.8	1.3	1.0	1.5
N-NH4	(g/kg)	1.8	n.m.	0.8	1.4

[a] The process water was recirculated within the process during eight subsequent batches. The table gives the average composition of feedstock andproducts obtained in batch 6-8. EC-measurements pointed out that the salt levels were at equilibrium from run 5 onwards. Sampling points refer to numbers given in Figure 2.1.

__Tabel 2.3__ Composition of the process water at three positions within the process. Averaged over three batchesa.

Parameter	Unit	Position 4 Acid fraction after tank-1	Position 10 Recirculation water after P precipitation	Position 8 Acid fraction after tank-2
Dry matter	(%)	4.1	1.8	2.0
pH	(-)	5.1	7.2	5.7
P	(g/kg)	1.5	0.0	0.2
N	(g/kg)	n.m.	n.m.	n.m.
Ca	(g/kg)	1.9	1.1	1.0
Mg	(g/kg)	1.3	0.6	0.5
S	(g/kg)	5.1	4.0	3.0
K	(g/kg)	1.5	1.4	0.9
$N\text{-}NH_4$	(g/kg)	1.4	1.1	n.m.
EC	(mS/cm)	19	n.m.	n.m.

[a] The process water was recirculated within the process during eight subsequent batches. The table gives the average composition of feedstock and products obtained in batch 6-8. EC-measurements pointed out that the salt levels were at equilibrium from batch 5 onwards. Sampling points refer to numbers given in Figure 2.1. N.m = not measured.

Organic matter

The ingoing solid fraction had an OM content of 75% of its dry weight, whereas the outgoing P-poor organic soil improver had an OM content of 88%. This increase is due to the removal of salts form the organic matrix. About 62% of the ingoing OM ended up in the P-poor OM whereas the remaining part ended up in the Ca~P~S slurry.

The OM content of the Ca~P~S slurry was 40% OM based on dry weight. The mass balance shows that 34% of the ingoing OM ended up in the Ca~P~S slurry. Hence, the separation efficiency is rather poor. This is disadvantageous in terms of the volume of the organic soil improver produced, which is expected to be a valuable product. It also is disadvantageous for the quality of the recovered phosphate which ideally has a low OM content. The low separation efficiency for OM can be explained by the fact that fine OM is able to pass the filter of the screw press and that these organic colloids coagulate after addition of $Ca(OH)_2$. This phenomenon is clearly visible by the naked eye when one compares the colour of the acid fraction (before the precipitation tank) and the recirculation water after the precipitation tank (Figure 2.2). In order to improve the separation efficiency for OM, the removal of fine particles from the acid liquid fraction must thus be improved. The tests with separation apparatus, including a settler, for this purpose are described in Chapter 4.

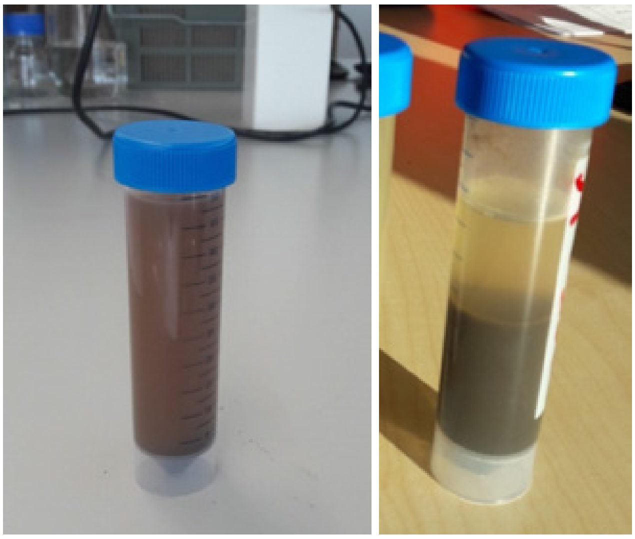

Figure 2.2 *Photo of the acid liquid fraction (just before the precipitation tank) (left) and the Ca~P~S sludge after sedimentation (right). The clear supernatant on top of the Ca~P~S sludge shows that nearly all organic matter had coagulated with the Ca~P~S.*

Fate of the sulphate
The overall acid consumption amounted to 77 kg 50% sulphuric acid per ton of solid fraction.
The average acid consumption during the first acidification step amounted to 70 kg (or 51 L) of 50% sulphuric acid per ton of solid fraction. The acid consumption remained constant during the eight process cycles. Recirculation of process water therefore did not affect the acid consumption rate.
The sulphuric acid dosage corresponds to a sulphur dosage of 13 kg S per ton solid fraction. Hence, this will substantially affect the sulphur content of the end products.

The mass balance of these pilot tests shows that the added sulphur dominantly ends up in the Ca~P~S slurry which can be in the form of gypsum or dissolved sulphate. The distribution of S between these two forms can be elucidated from the composition of the remaining recirculation water fraction (flow 10). This fraction logically has a similar dissolved sulphate concentration as the Ca~P~S slurry. The recirculation water contains 4 g/kg S, which can be assumed to be present as dissolved sulphate since this flow does not contain any settable particles. The Ca~P~S slurry consists for 94% of water and has a sulphur (S) content of 6 g/kg of which we can assume that 4 g/kg is present as dissolved sulphate. Hence about 66% of total S in the Ca~P~S slurry is present as dissolved sulphate whereas the remaining 33% is likely present as gypsum. Thus, the majority of the sulphur in the Ca~P~S slurry is present in a dissolved form. This means that the high sulphur content of the Ca~P~S slurry is largely due to the large water content of the slurry. As a consequence, improved dewatering of the Ca~P~S sludge will result in a higher equilibrium concentration of sulphur in the process water and thus a higher sulphur content in the organic soil improver.

Predicting the sulphur concentration upon improved dewaterability of the Ca~P~S sludge
In the current pilot installation, the formed Ca~P~S is allowed to settle overnight after which the Ca~P~S sludge with a DM content of 6% is separated from the solution. In a full scale plant, a higher DM content of the Ca~P~S sludge must be reached in order to make the process profitable. In that case, the amount of water leaving the system per ton of ingoing solid fraction decreases and hence, the sulphur concentration in the process water increases. Using a simple mass balance calculation, described in equation 1, we estimated the sulphur content of the end products as a function of the DM content of the Ca~P~S sludge. We assumed that the system does not produce any waste water. Furthermore, we assumed that 33% of the added sulphur precipitates as gypsum and ends up in the Ca~P~S sludge. Equation 1 was used to calculate the sulphur concentration in the process water at equilibrium. Equation 2 and 3 were used to calculate the sulphur content of the Ca~P~S sludge and the organic soil improver.

$$S_{H2SO4} + S_{solid\ fraction} - S_{gypsum} = S_{eq} * \frac{((1-dm_{OM})*M_{OM}+(1-dm_{Ca-P-S})*M_{Ca-P-S})}{1000} \qquad \text{(equation 1)}$$

$$S_{OM} = S_{eq} * (1 - dm_{OM}) \qquad \text{(equation 2)}$$

$$S_{Ca-P-S} = S_{eq} * (1 - dm_{Ca-P-S}) + \left(\frac{S_{gypsum}}{M_{Ca-P-S}}\right) * 1000 \qquad \text{(equation 3)}$$

With:
S_{H2SO4} = *amount of sulphur in sulphuric acid, per ton of ingoing solid fraction (13 kg S)*
$S_{solid\ fraction}$ = *amount of sulphur in ingoing solid fraction (2 kg S)*
S_{gypsum} = *0.33 ** S_{H2SO4}
S_{eq} = *equilibrium concentration of sulphur in the water fraction of the RePeat system (g/kg)*
dm_{om}, dm_{Ca-P-s} = *dry matter content of the organic matter and Ca~P~S products (-)*
M_{om}, M_{Ca-P-S} = *mass of organic matter and Ca~P~S product, per ton of ingoing solid fraction (kg)*
S_{OM}, S_{Ca-P-S} = predicted sulphur content in *organic soil improver and Ca~P~S product (g/kg)*

Currently, the Ca~P~S is recovered as a sludge with a DM content of 6% . Using more advanced separation equipment such as a decanter, we expect that the DM content can be increased to 20-30% DM. The consequences hereof in terms of sulphur content of the two end products are shown in Figure 2.3. An increase in the DM content of the Ca~P~S sludge to 30% DM would lead to an increase in the sulphur content of the organic soil improver from 2 to 10 g/kg fresh matter. An top of that, the P-poor organic soil improver may contain some organic S naturally present in manure and digestate. Meanwhile, the S content of the Ca~P~S product will decrease from 56 to 28 g/kg based on DM content.

The elevated sulphur content of the end products may have consequences for the sulphur balance of the soil it is applied to. This is in particular the case for the organic soil improver since farmers may use this product in rather large dosages. This is further elaborated on in Chapter 5.

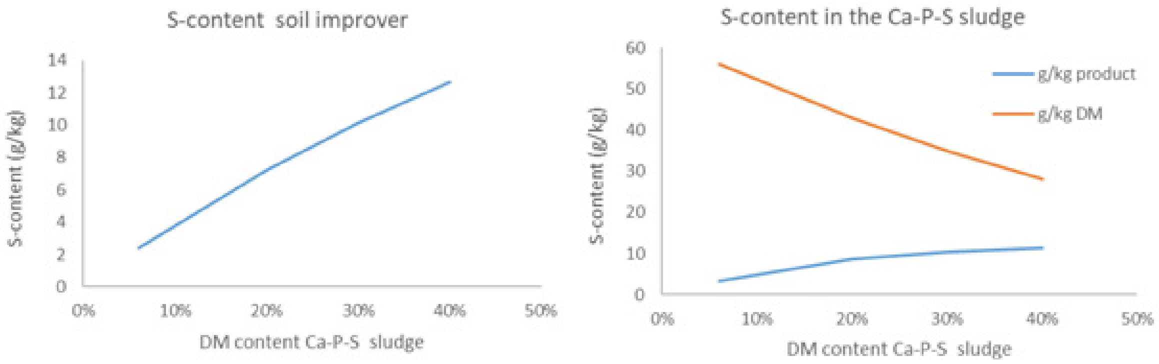

Figure 2.3 *Predicted sulphur content of the P-poor organic soil improver (g/kg fresh matter, left figure) and Ca~P~S product (right figure) as a function of the dry matter content of the Ca~P~S sludge upon removal from the system. For the Ca~P~S product the S content is expressed per kg fresh matter and dry matter. The S content was calculated with equations 1-3.*

2.4 Conclusion

This chapter described results of experiments with the pilot installation at Groot Zevert Vergisting B.V. in the Netherlands. The solid fraction of co-digested pig manure was treated with sulphuric acid to solubilize and remove phosphorus which was subsequently recovered through the addition of $Ca(OH)_2$. After each batch, process water was reused for the following batch in order to study the effects of accumulation of salts, in particular sulphur salts, on the performance of the process and the chemical composition of the end-products.

The experiment led to the following conclusions:
- Two subsequent extractions with sulphuric acid at pH 5 lead to a reduction of the P-content of the solid fraction of digestate from 6.3 g/kg to 1.2 g/kg. Over both steps, about 90% of the phosphorus was extracted and recovered as Ca~P~S sludge.
- After settling overnight, the Ca~P~S sludge had a DM content of only 6% and an OM content of over 40% . Hence, an additional dewatering step is required in order to minimize the amount of heat needed for drying. An additional separation step to remove fine suspended OM is needed to lower the OM content. The Ca~P~S products must be dried in order to have a positive value.
- The use of sulphuric acid, in a rate of 77 kg 50% sulphuric acid per ton of ingoing solid fraction, results in the accumulation of sulphate in the process water. At steady-state, about 66% of the added S ends up in the Ca~P~S sludge and 34% in the organic soil improver , resulting in an S content of 4 g/kg in the organic soil improver.
- Improved dewatering of the Ca~P~S sludge will however result in further accumulation of sulphate in the process water and hence, in a higher S content of the organic soil improver OM. In case the Ca~P~S sludge can be recovered with 30% DM, the sulphur content of the organic soil improver is expected to increase to 10 g/kg.

The results initiated the following actions:
- Research on the dewatering of Ca~P~S sludge using different solid separation techniques (Chapter 4)
- Research on the possibility to improve P-dewatering using $Mg(OH)_2$ (struvite formation) instead of $Ca(OH)_2$ (Chapter 3)

3 Laboratory experiments

3.1 Introduction

This chapter focusses on two aspects of the RePeat system related to the use of organic acids as alternative for sulphuric acids and the use of magnesium hydroxide in order to improve dewatering of the precipitated phosphate.

The solid fraction of co-digested pig manure shows a relatively high buffering capacity (this study and Schoumans *et al*, 2014 and 2017). This leads to a relatively high use of sulphuric acid with, as a consequence, not unneglectable contents of sulphur (as sulphate) in the P poor organic soil improver and Ca~P~S sludge. Organic acids can replace sulphuric acid with as beneficial side-effect that recirculation water can be used as a carbon source for biogas production without burdening the P poor organic fraction and C~P~S sludge with sulphur. The prospects of the use of organic acids in the RePeat concept were explored.

Precipitation of phosphorus from the acid liquid fraction by means of $Ca(OH)_2$ was shown to produce a Ca~P~S sludge with poor sedimentation and dewatering properties. At first, it was inventoried whether calcium phosphate could be disposed of in the form of a slurry. However, a quick market survey revealed that fertiliser companies strongly prefer to receive a stackable material with a high phosphate content. Mechanical dewatering and drying of Ca~P~S sludge could be one option though this may be rather expensive due to purchase and operational (energy) costs for separators and dryers.. Moreover, energy use for dewatering and drying should be prevented from a sustainability-point of view. Current full-scale P-recovery reactors, such as the AirPrex at Waternet, make use of magnesium to form struvite. Struvite is known for its ability to form crystals which can be recovered from the liquid phase by gravitational force or by low tech separation equipment.

Struvite ($MgNH_4PO_4.6H_2O$) forms upon the reaction of phosphate with magnesium and ammonium in alkaline conditions. Though examples exists of properly functioning full scale struvite reactors, those process conditions may not be applicable to the acid liquid stream to be treated in this study. First of all, the chemical composition of the waste water, in particular the phosphate concentration, pH and concentration of calcium and sulphate, is very different in the influent ofof struvite installations at WWTP's compared to the composition of the acid liquid fraction to be extracted from co-digestate. Moreover, the acid liquid fraction contains substantial amounts of calcium, sulphate and OM of which in particular calcium is known to inhibit struvite formation (Huchzermeier and Tao., 2012). Struvite crystals grow by continuous precipitation of new struvite on the surface of existing particles in the reactor. Hence, retention of precipitates in the reactor is an important requirement in order to allow particle growth. Overall, these uncertainties were reason to study the precipitation of phosphate with magnesium hydroxide in laboratory tests.

3.2 Materials and Methods

3.2.1 Extraction of phosphorus by organic acids

Outline
Four organic acids are tested in the explorative study: citric acid, formic acid, acetic acid and pyroligneous acid (by-product of pyrolysis). The solid fraction of co-digested pig manure was titrated with an organic acid to lower the pH to a desired value. First, by titration it was explored which quantity of acid was needed to reach a certain pH value. With this data, suspensions of the solid fraction in water (1:4) were brought to pH five pH with an organic acid in a second experiment.

After equilibration, a sample was taken to determine pH, dissolved ortho-P by means of segmented flow analysis (SFA) and total-P by means of inductively coupled plasma (ICP).

Sample material

Sample material was of a mixed sample of solid fractions of co-digested pig manure (number 3) of 10 batches with numbers 24, 25, 26, 28.1, 28.2, 29, 30, 31, 32 and 34. Of each batch a sub-sample of 150 g material was taken (total 1.5 kg). Next the 10 sub-samples were carefully mixed and sampled for analysis on DM, OM via(loss of ignition, density, pH, N-total, P-total via ICP, Ca-total, Mg-total and K-total (Table 3.1).

Table 3.1 *Composition of solid fraction of co-digested pig manure.*

Parameter	Unit	Value	Method
Dry matter	% product	32.01	NEN 6499
Organic matter	% in dry matter	81.3	NEN 5754: 2005; loss-on-ignition
Bulk density	g/L	888	In house method CBLB
pH	[-]	7.64	In house method CBLB
N-total	mg/kg product	8867	Destruction with H_2SO_4+H_2O_2+Se followed by analysis of minerals according NEN 6966
P-total	mg/kg product	5783	Destruction with H_2SO_4+H_2O_2+Se followed by analysis of minerals according NEN 6966
PO_4-P	mg/kg product	544	In house method CBLB, determined after centrifuging for 10 minutes at 3500 rpm followed by filtration 0.45 µm
K-total	mg/kg product	4744	Destruction with H_2SO_4+H_2O_2+Se followed by analysis of minerals according NEN 6966
Ca-total	mg/kg product	9417	Destruction with H_2SO_4+H_2O_2+Se followed by analysis of minerals according NEN 6966
Mg-total	mg/kg product	4010	Destruction with H_2SO_4+H_2O_2+Se followed by analysis of minerals according NEN 6966

Stock solutions organic acids

Stock solutions of 2 M organic acids (citric acid, acetic acid, formic acid and pyroligneous acid were made. Citric acid, acetic acid and formic acid were laboratory quality products. Pyroligneous acid originated from a pilot pyrolysis installation (flash pyrolysis).

1st test: Titration curve

To 50 g of solid fraction of co-digested pig manure 200 mL of demineralised water was added and the suspension was continuously stirred with a magnetic stirrer. Next the sample was stepwise titrated with an organic acid to pH 4. The initial pH and the added quantity of acid and the pH after each step were recorded after the pH had stabilized after a few minutes. When the lowest pH value was reached, the suspension was stirred for another 2 hours to determine if a slow process in establishing a pH equilibrium occurred. This was found not to be the case. The pH value reached after a few minutes did not change after two hours.

2nd test: P recovery

Based on the results of the 1st test, the quantities of organic acids needed to reach the pH of 7.5, 7.0, 6.5, 6.0, 55, 5.0, 4.5 and 4 were calculated. Next 25 g of solid fraction of co-digested pig manure was transferred into a flask. The required quantity of acid to reach pH 7.0, 6.5, 6.0, 5.5 or 5.0 (= result test 1) was added. Also a sample with no acid addition was included (in total 6 pH levels). Then demineralised water was added to reach a total volume of liquid of 50 mL. Then the flasks were shaken for 2 hours. After 2 hours the pH was measured. Next the samples were centrifuged at 3500 rpm for 10 minutes. The supernatant and pellet were separated and weighed. The pH of the supernatant was measured. a subsample of the supernatant was then taken and diluted 15 times, filtered over a 0.45 µm pore size filter and analysed on total-P, Ca, Mg, Na, K, Fe and S by ICP-AES. The pellet was decomposed by aqua regia in a microwave and total P, total K, total Mg, total Ca, total S, total Na and total Fe were measured according to NEN6966.

The efficiency of recovery of phosphorus with the supernatant or pellet was calculated according to equation [1].

$$\text{Efficiency} = \frac{[\text{amount of phosphorus in the supernatant or pellet}] \times 100\ (\%)}{[\text{amount of phosphorus in solid fraction co-digested pig manure}]} \qquad [1]$$

The costs of the organic acids for P recovery are based on a survey of prices for these acids given by Alibaba.com. For this analysis the minimum and maximum prices for volumes of at least 20 ton and purity >60% were collected from five competitive suppliers. Collected data were standardised to €/mol H^+. Information on pyroligneous acid is scarce. Data from three suppliers with volumes of 1 ton were given. These data and the assumption that acetic acid is the main constituent of pyroligneous acid led to a price range.

3.2.2 Collection of acid liquid fraction for precipitation experiments

In the pilot installation at Groot Zevert Vergisting B.V., the solid fraction of digestate was mixed with ground water (4400 L per ton solid fraction), acidified to pH 5 using sulphuric acid, and separated into a solid and a liquid fraction by means of a screw press. The acid liquid fraction was sampled and used for precipitation tests described in paragraphs 3.2.3 to3.2.5. The acid liquid fraction had a pH of 5.1 and an ortho-P concentration of roughly 1.5 g/L.

3.2.3 Precipitation: calcium hydroxide versus magnesium hydroxide

A lab test was performed to assess the phosphorus precipitation as a function of $Ca(OH)_2$ and $Mg(OH)_2$ dosage. Ten plastic pots were filled with 100 mL of acid P-rich liquid fraction, collected from the pilot installation. a volume varying between 0 and 10 ml/l of a 30% (w/w) $Ca(OH)_2$ or 50% (w/w) $Mg(OH)_2$ was added to each pot. The pots were put on a horizontal shaker and shaken at a very low speed for four hours. This rather long reaction time was chosen since it is known that the precipitation of phosphorus with $Mg(OH)_2$ is slow but should be completed within four hours. After this the pots were centrifuged (3000 rpm, 6 min). The supernatant was analysed on pH, P, Ca, Mg and K by ICP-AES and ortho-P and N-NH_4 by SFA. The mass of the pellet was weighed and the pellet was analysed on DM content and loss-on-ignition at 105°C. Thereby water bound in the crystal structure was lost which means that the DM content is underestimated in samples with struvite.

3.2.4 Kinetics of phosphorus precipitation with magnesium hydroxide

The objective of this experiment was to determine the reaction rate of phosphorus precipitation upon addition of $Mg(OH)_2$.

Acid liquid fraction was collected from the pilot installation at Groot Zevert Vergisting B.V., see paragraph 3.2.2. The experiment was performed using a 1L beaker glass which was continuously stirred using a magnetic stirrer (Figure 3.1). The beaker glass was filled with 600 mL acid liquid fraction (paragraph 3.2.2). At t0, 7 mL of 50% (w/w) $Mg(OH)_2$ solution was added per liter of acid liquid fraction.. After 15, 30, 60, 90, 120, 180, and 240 minutes, the stirrer was stopped and the sludge was allowed to settle for one minute. The pH was measured and the supernatant was sampled. The supernatant, thus represented the liquid fraction after settling of the precipitated solids, was analysed on P, Ca, Mg and K by ICP-AES) and on PO_4 and NH_4 by SFA, colorimetrically.

3.2.5 Continuous phosphorus precipitation with magnesium hydroxide

Acid liquid fraction was collected from the pilot installation at Groot Zevert Vergisting B.V., see paragraph 3.2.2. a beaker glass was filled with 500 mL acid liquid fraction and 3.5 mL of 53% (w/w) $Mg(OH)_2$ suspension was added. The suspension was stirred for four hours and left overnight.
This suspension was used as a starting point for the continuous experiment. The liquid fraction was stirred on a magnetic stirrer and acid fraction was dosed at a rate of 100 mL/h and 53% (w/w) $Mg(OH)_2$ suspension was added at a rate of 0.4-0.6 mL/h. Each hour, the stirrer was stopped and the sludge was allowed to settle and 100 mL of effluent was decanted such that the hydraulic retention

time (HRT) was 5 hours The pH was measured and the effluent was analysed on total-P, Ca, Mg and K by ICP-AES on PO_4 (ortho-P) and $NH_4$by SFA, colorimetrically.

The 53% (w/w) $Mg(OH)_2$ suspension was supplied by NedMag, Netherlands. This product is commercially available as $Mg(OH)_2$-tech. (see Table 3.2).
All experiments and analyses were performed at the CBLB (Chemical -Biological Soil Laboratory), which is part of Wageningen University and Research-WENR.

Table 3. 2 *Specifications of the Mg(OH)2 suspension used in lab and pilot experiments.*

Parameter	Value
Supplier	NedMag
Commercial name	$Mg(OH)_2$ tech
pH	10
Density (kg/m^3)	1440
Solids (%)	52-54
Particle size (µm)	2-2.5
$Mg(OH)_2$ (% of solids)	98.5

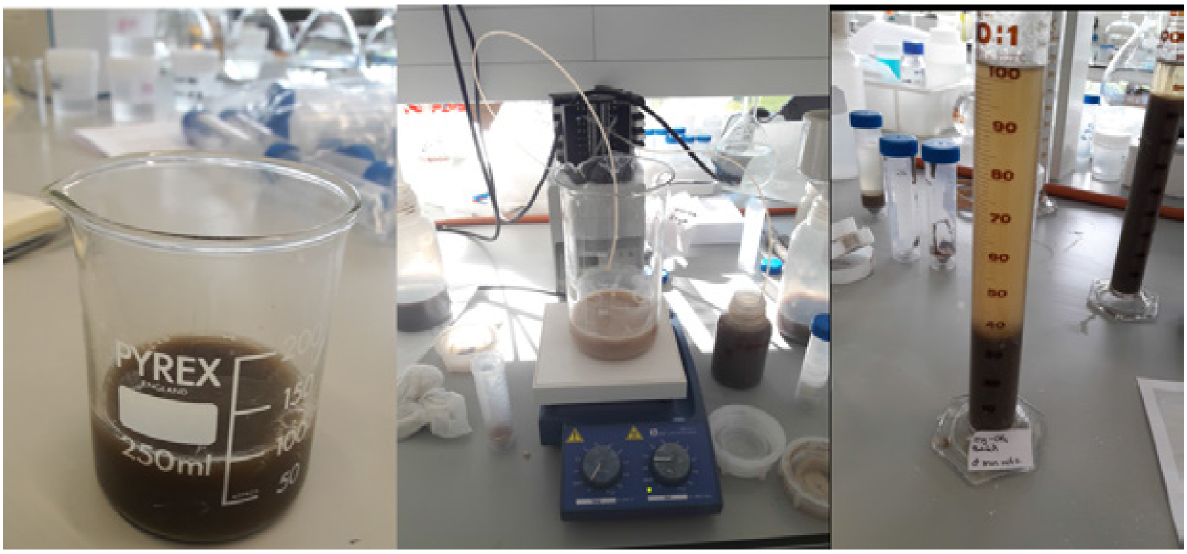

Figure 3.1 *Acid liquid fraction (left), experimental setup (middle) and settled sludge (right).*

3.2.6 Struvite formation in a continuous stirred-tank reactor (lab)

The struvite formation experiment was performed by LeAF, Wageningen. Acid liquid fraction was collected from the pilot installation at Groot Zevert Vergisting B.V. and used as feedstock.
The experiment was performed using a double-walled 10 L continuously stirred reactor which was kept at 40 degrees ºC through a water mantel in order to mimic the temperature in the full-scale plant (Figure 3.2). The reactor was fed with acid liquid fraction at a rate of 1L/h (HRT: 10 h) and 53% (w/w) $Mg(OH)_2$ suspension at a rate of 6 mL/h. The effluent was sampled on a daily basis and analysed on pH, P, Ca, Mg and K by ICP-AES and on PO_4 and NH_4 by SFA, colorimetrically, in the CBLB laboratory. After five days, it was decided to quit the experiment due to various technical problems. The tube used to add magnesium hydroxide clogged and the stirrer was not able to move through the thick layer of sediment formed at the bottom of the reactor. The reactor was emptied and the struvite sludge at the bottom of the reactor was dewatered on a sieve with a pore size of 200 µm.
The collected struvite was dried at room temperature to determine its DM content. The air dried struvite sludge was thereafter analysed for its total element contents after destruction of the material using the H_2SO_4-Se method of CBLB, Wageningen.

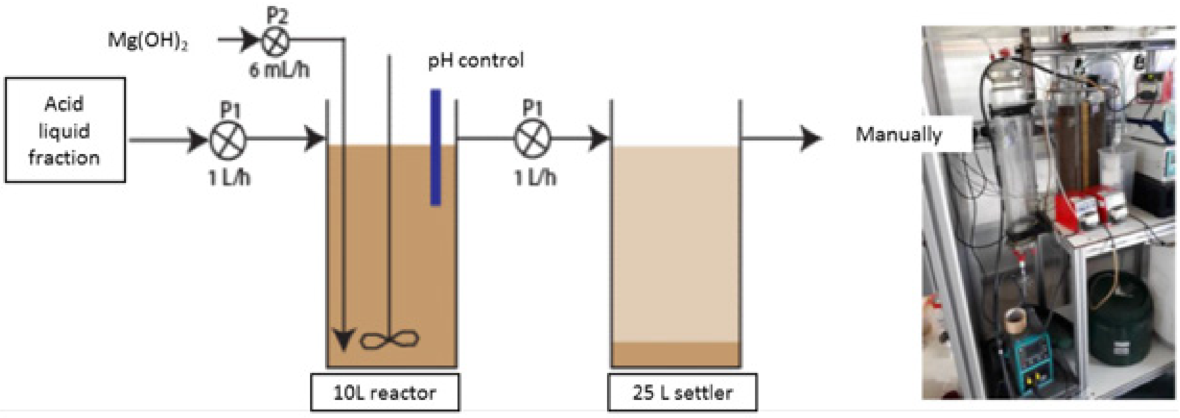

Figure 3.2 *Schematic picture of the experimental set-up of the struvite formation experiment.*

3.3 Results

3.3.1 Organic acids as alternative for sulphuric acid

The organic acids citric acid, acetic acid, formic acid and pyroligneous acid are all able to solubilise phosphorus from the solid fraction of co-digested pig manure (Figure 3.3). Citric acid solubilised more phosphorus at a given pH value than the other organic acids. At pH 5 citric acid performed better than acetic acid and formic acid, which performed equally well. Pyroligneous acid solubilised less phosphorus than acetic acid and formic acid.

Results of chemical analyses on supernatant, including P, K, Ca, Mg, Na, S and Fe, are given in Annex 2. All organic acids increased the concentration of P, K, Ca, Mg and (modest) Na but not S (Annex 2). Compared to the other acids, citric acid solubilised more P, Ca, Mg and (modest) and Na. Only citric acid also increased Fe (Annex 2). Citric acid enables the formation of complexes with Ca and Mg which most likely has contributed to P solubilisation.

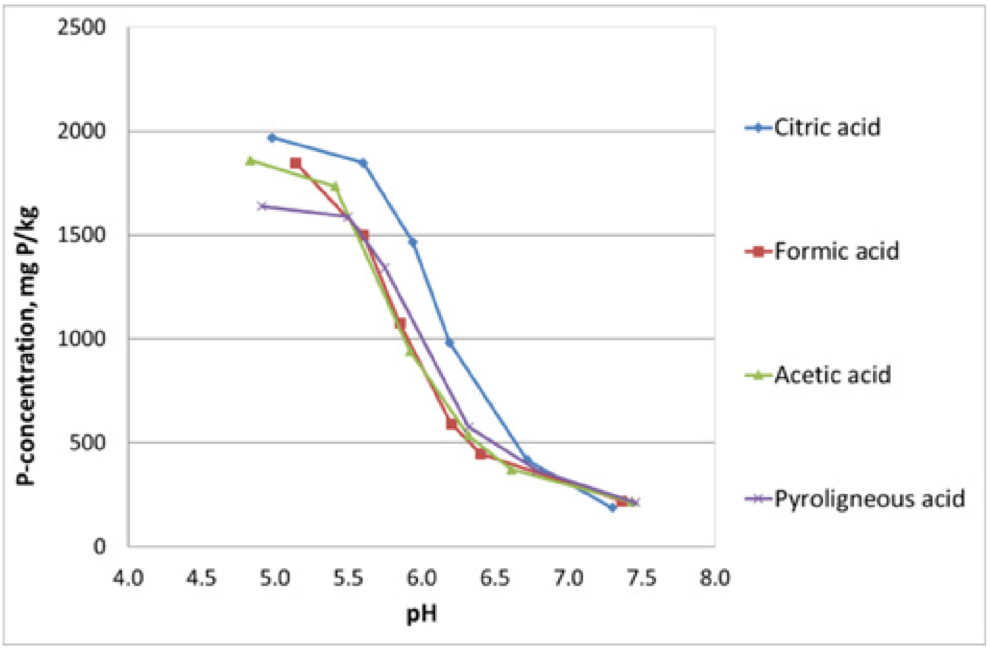

Figure 3.3 *Phosphorus (P) concentration in the supernatant of suspended solids of co-digested pig manure with a range in pH values created by addition of citric acid, acetic acid, formic acid or pyroligneous acid. The initial pH was about 7.5. By addition of different quantities of the organic acids the pH dropped to roughly pH 5.*

By lowering the pH (or by increasing the acidity) the phosphorus concentration in the liquid, the supernatant after centrifugation, increased whilst the phosphorus content of the solids, (pellet after centrifugation, decreased. Based on these measurements the quantity of P in the liquid fraction (supernatant) and solid fraction (pellet) have been calculated. Next these values were compared with the initial quantity of P present in the suspended solids of co-digested pig manure and the efficiency of P recovery (§3.1, equation [1]) was calculated. Lowering the pH from 7.5 to 6.5 led to an increase in P recovery of about 5% (Figure 3.4). Lowering the pH from 6.5 to 5.5 increased the P recovery by an additional 30-35%. Further lowering of the pH yielded an additional increase for citric acid and acetic acid of about 7-9% but not for formic acid or pyroligneous acid. The increase of P recovery in the supernatant coincides with a lowering of the quantity of P that was recovered with the pellet (Figure 3.4). This exploratory laboratory experiment did not result in a complete recovery of P from the pellet. This is most likely caused by an incomplete removal of liquid from the pellet. Liquid with solubilised P probably remained in the pellet.

Although all organic acids can be used to recover phosphorus, their uses without a complementary goal are hindered by their relatively higher cost (Table 3.2). These acids cannot compete with sulphuric acid (Table 3.2). Complementary goals such as reducing sulphur addition to increase broader use of resulting fertilising products (secondary phosphorus raw material for fertiliser production, P poor organic soil improver) or an increase of biogas production (residues of used organic acids) are needed to increase a perspective in the use of these organic acids.

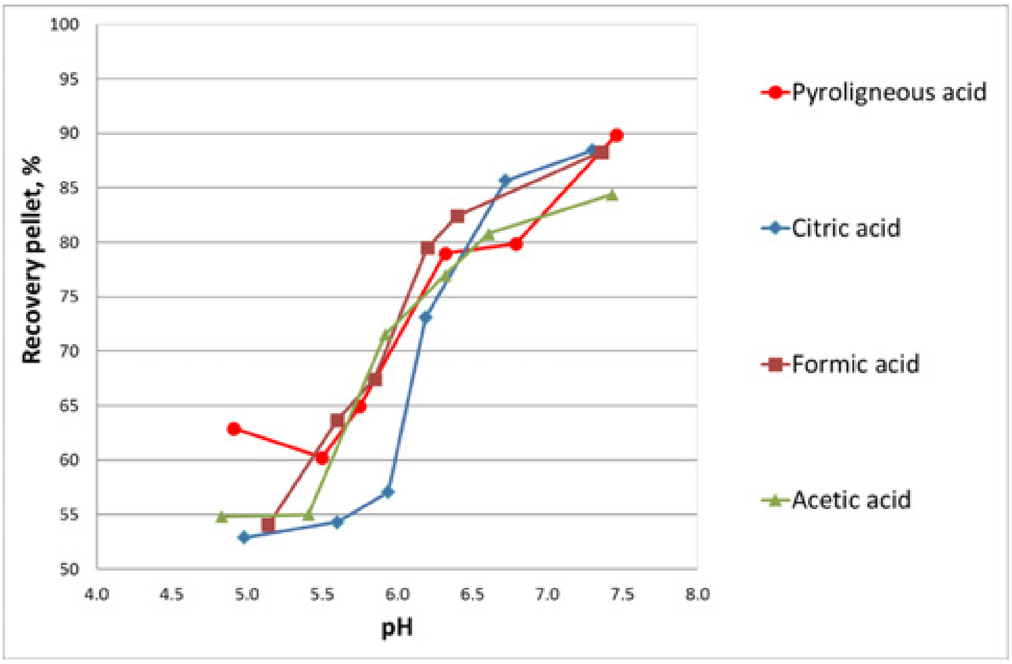

Figure 3.4 *Phosphorus (P) recovery % in the pellet after centrifuging of co-digested pig manure treated with a range in pH values created by addition of citric acid, acetic acid, formic acid or pyroligneous acid. The initial pH was about 7.5. By addition of different quantities of the organic acids the pH dropped to values of about 5. The suspension was centrifuged at 3500 rpm for 10 minutes.*

Table 3.1 *Estimate of the economic cost of the use of organic acids (see § 3.2.1).*

Organic acid	Minimum value, €/mol H^+	Maximum value, /mol H^+
Acetic acid	0.021	0.069
Citric acid	0.033	0.065
Formic acid	0.022	0.043
Pyroligneous acid	0.017	0.098
Sulphuric acid	0.008	0.015

3.3.2 Calcium phosphate versus magnesium phosphate

Table 3.2 shows the results of a simple batch experiment in which acid liquid fraction, containing about 1.5 g/L ortho-P, was treated with either a 30% (w/w) $Ca(OH)_2$ or 55% (w/w) $Mg(OH)_2$ suspension. For the $Ca(OH)_2$ suspension a dosage of 10 mL/L was sufficient to remove all ortho-P from the solution. The thereby acquired pH of the solution was 6.9. The sulphur content of the solution did not decrease upon addition of $Ca(OH)_2$ suspension. This indicates that formation of gypsum did not occur. The magnesium concentration in the solution decreased slightly but this could not be due to struvite formation because the ammonium concentration remained constant. The decrease in magnesium and calcium concentration in the solution may be due to coagulation of cations with OM particles upon increasing the pH.

For the $Mg(OH)_2$ suspension a dosage of 8 mL/L and a pH of 6.6 were sufficient to remove 95% of the ortho-P from solution. Addition of $Mg(OH)_2$ suspension led to the removal of 48 mmol P and 34 mmol NH_4 per liter. The simultanous removal of ortho-P and ammonium suggests that about 70% of the P is precipitated in the form of struvite ($MgNH_4PO_4.6H_2O$). The other fraction of the precipitated phosphate likely precipitated as (amorphous) calcium phosphate or magnesium phosphate.

For the highest dosages, the sludge settling velocity was determined by letting the sludge settle in a measuring cylinder (Figure 3.6). The Ca-precipated sludge settled with a velocity of about 4 cm/h whereas the Mg-precipitated sludge settled with a velocity of 100 cm/h. The use of $Mg(OH)_2$ thus leads to formation of sludge with a much higher settling velocity.

The precipitate was separated from the suspension by means of centrifugation which is thought to mimic a dewatering step of a decanter. Total volume and DM content of the sludge obtained after centrifugation are given in Table 3.3. Addition of calcium hydroxide produced about 130 L sludge with a DM content of 15% per m^3 of initial acid slurry. Addition of $Mg(OH)_2$ produced 94 L sludge with a DM content of roughly 20% per m^3 of acid slurry. These DM contents may give an underestimation of the true DM content since they were determined at 105 °C while it is known that struvite is thermally decomposed at these temperatures releasing mineral-bound NH_4 and H_2O. Struvite ($NH_4MgPO_4.6H_2O$) has a molar mass of 245 g/mol and which 51% of its mass consists of NH_4 and H_2O. Therefore the DM content may be underestimated with about a factor two.

Table 3.2 *Composition of supernatant after addition of Mg(OH)2 or Ca(OH)2 to acid liquid fraction*[a].

	Dosage (mL/L)	pH (-)	$P-PO_4$ (mg/L)	Ca (mg/L)	Mg (mg/L)	N-NH4 (mg/L)	S (mg/L)	P-removal (%)	Sludge volume (mL/L)	Sludge d.m. content (%)
$Ca(OH)_2$, 30%	0	5.1	1570	1480	1140	1250	3.9		42	12%
	6	6.34	365	350	968	1210	3.2	86%	70	23%
	8	6.59	215	600	857	1210	3.3	97%	113	15%
	10	6.92	85.4	740	787	1200	3.5	100%	130	13%
$Mg(OH)_2$, 50%	0	5.1	1570	1480	1140	1250	3.9		40	12%
	6	6.35	216	500	1400	969	3.7	77%	70	23%
	8	6.83	43.4	690	1330	823	3.8	86%	79	22%
	10	8.4	4.13	660	1380	838	3.7	95%	94	21%

[a] $Ca(OH)_2$ or $Mg(OH)_2$ was added to 100 mL acid liquid fraction after which the suspension was shaken for four hours and centrifuged for 5 minutes. Thereafter, the supernatant was sampled and the dry matter content of the sludge was measured. The settling velocity of the sludge was determined prior to centrifugation. P-removal as percentage of ortho-P in solution.

[b] nd: not determined

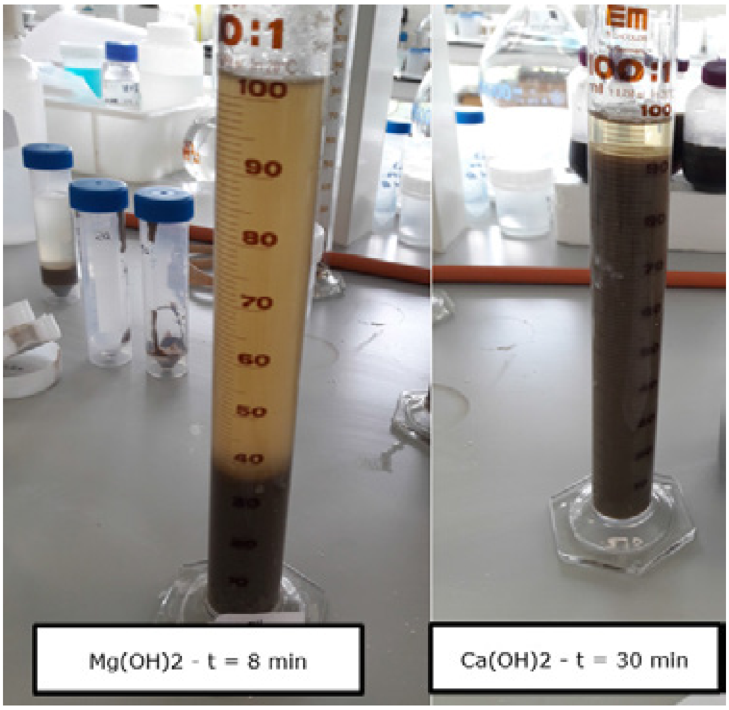

Figure 3.6 *Photo of P-precipitated sludge formed after precipitation of phosphate with either magnesium-hydroxide (Mg(OH)2) or calcium-hydroxide (Ca(OH)2) after a settling time of 8 and 30 minutes respectively. The sludge settling velocity (samples with highest base dosage) amounted to 4 and 100 cm/h for the Ca(OH)2 and Mg(OH)2 treatment, respectively.*

3.3.3 Reaction rate of P precipitation with magnesium hydroxide

In the tests were $Ca(OH)_2$ was used as a base, immediately a precipitation reaction occurs.
In contrast, the pH increase and precipitation reaction took at least one hour when $Mg(OH)_2$ was used as a base. We therefore studied the reaction rate of P precipitation with addition of $Mg(OH)_2$ (Table 3.3, Figure 3.7). The acid liquid fraction had an initial pH of 5.2 and an initial ortho-P content of 1.5 g/L. The pH gradually increased to pH 8.6 over the course of the experiment by addition of $Mg(OH)_2$ suspension. Already at pH 6.0 (t=15 min), about half of the ortho-P was removed from the solution and at pH 6.3 (t=30 min) 96% of the ortho-P had been removed from solution... This high removal efficiency at rather neutral pH may point to a surface precipitation process in which ortho-P precipitates at the surface of $Mg(OH)_2$ colloids. Higher pH-values led to even lower ortho-P concentrations in sollution. For the purpose of P recovery in the RePeat plant, a pH value of 6.5-7.0 is sufficiently high to recover nearly all phosphate by using $Mg(OH)_2$. Considering the fact that the effluent of the struvite reactor is reused in the process in the next RePeat cycle, it is not necessary to aim for a very low ortho-P concentration in solution at the expense of a higher $Mg(OH)_2$ dosage.

Under the conditions in the reactor, both struvite and calcium phosphate may form. The removal of ortho-P and calcium amounted to 48 mmol/L and 12 mmol/L respectively, meaning that at maximum 25% of the phosphate had precipitated with calcium. The ammonium removal amounted to 47 mmol/L which is more than can be explained by the formation of struvite alone if we assume that 25% of ortho-P precipitated with calcium. Such a mass balance calculation is however not without uncertainties. Part of the calcium may have been removed from the solution due to coagulation with organic substances. For ammonium, gaseous losses may have occurred. Hence, we can conclude that the majority of ortho-P precipitated as struvite but that the precise contribution of struvite versus calcium phosphate remains uncertain.

Table 3.3 *Supernatant composition after addition of Mg(OH)2 suspension to the acid liquid fraction as a function of time.*

Time	pH	P-PO_4	P-t	Ca	Mg	N-NH_4	S	K	P-removal
(min)	(-)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(%)
0	5.1	1520	1510	1390	1090	1340	3780	880	0
15	6.02	806	823	620	1510	1250	3630	950	46
30	6.37	54.8	66	900	1300	708	3590	910	96
60	7.61	5.22	12	900	1290	670	3510	900	100
90	8.2	2.55	9	910	1290	684	3610	880	100
120	8.42	1.64	7	960	1320	700	3690	900	100
180	8.51	1	6	900	1300	696	3610	870	100
240	8.58	1.16	6	900	1320	678	3570	890	100

[a] At t=0, 7 mL of 53% (w/w) Mg(OH)2 suspension per litre of acid liquid fraction was added and the increase of the pH value was followed for 4 hours. a beaker glass with 400 mL of acid liquid fraction was stirred and $Mg(OH)_2$ solution was added. At the sampling times, the stirrer was stopped and the sludge was allowed to settle for a minute. Thereafter, pH was measured and supernatant was sampled. P-removal as percentage of ortho-P in solution.

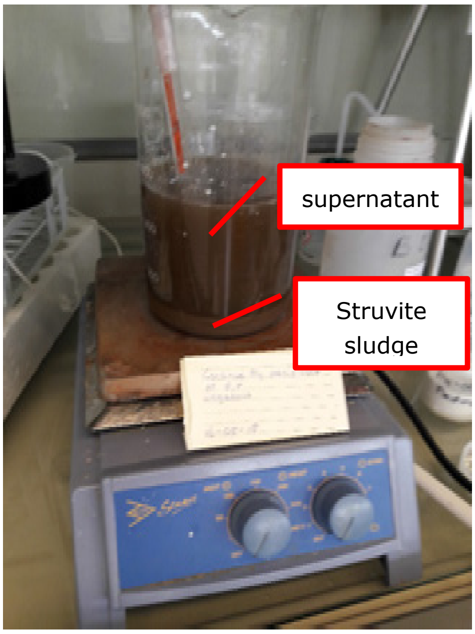

Figure 3.7 *Experimental setup of the batch experiments. The suspension was stirred using a magnetic stirrer. The supernatant was sampled in order to determine P-removal.*

3.3.4 Continuous struvite formation

Phosphorus removal from the acid liquid fraction was studied in a continuously fed beaker glass at a rate of 100 mL/h and a hydraulic retention time of five hours. The pH was monitored and $Mg(OH)_2$ was added in order to keep the pH at about 7.5. This pH is sufficiently high for a near-complete P removal.

The average $Mg(OH)_2$ dosage amounted to 5 mL/L acid fraction, which is lower than the amount needed in the batch experiment (7 mL/L). Thus, the efficiency of added $Mg(OH)_2$ increased due to the longer residence time of solid particles in the system. The removal of NH_4 from the feed solution in a nearly 1:1 molar ratio with ortho-P indicates that nearly all ortho-P has been removed in the form of struvite. Also some calcium phosphate formed as is evident from the decrease in the calcium concentration which corresponds, on a molar basis, to 10% of the removed ortho-P. Overall, we can conclude that, despite the high calcium concentration, most phosphorus was removed in the form of struvite.

The average $Mg(OH)_2$ suspension dosage amounted to 6 mL/L and can be expressed per ton of ingoing solid OM. One ton of solid OM resulted in roughly 4500 litter of acid liquid fraction. Hence, the 53% (w/w) $Mg(OH)_2$ suspension dosage amounts to 27 L per ton of ingoing solid fraction.

Table 3.4 *Effluent composition during a short-term continuous struvite formation experiment.*

Time	$Mg(OH)_2$	pH	$P-PO_4$	P-t	Ca	Mg	$N-NH_4$	S	K
(min)		mL/L			(-)		(mg/L)		
Feed	-	5.1	1510	1510	1390	1090	1280	3820	880
0	4	8.38	0.96	6	840	1320	632	3620	880
60	7	7.1	19.9	25	870	1240	630	3420	870
120	7	7.66	2.98	11	890	1260	619	3470	890
180	7	7.66	2.87	13	930	1280	615	3560	900
240	7	7.74	2.77	16	950	1270	607	3560	900
300	7	7.46	3.85	22	1000	1260	619	3580	890
360	4	7.74	4.31	21	980	1210	614	3570	880
420	4	7.74	2.59	27	1010	1240	606	3590	870

[a]. a beaker glass with 500 mL of acid liquid fraction was stirred, 3 mL of 53% (w/w) $Mg(OH)_2$ suspension was added. At the sampling times, the stirrer was stopped and the sludge was allowed to settle for a minute. Thereafter, pH was measured and supernatant was sampled.
The hydraulic retention time was 5 h.

3.3.5 Struvite formation in a continuously fed 10 L reactor

The struvite experiment in the continuously fed reactor was stopped at day five due to practical problems. a thick layer of sludge, which later turned out to be struvite, had formed on the bottom of the reactor because the mixer was not capable of keeping these particles in suspension. This layer of sludge inhibited the injection of the influent because the injection point was near the sludge layer. Despite the practical problems encountered and the rather short duration of the experiment, the experiment gave valuable information about the possibilities to produce struvite from the acid liquid fraction of the acid treated solid fraction of digestate.

The effluent pH was lower (pH < 8) than expected which was attributed to poor mixing in the reactor leading to settling of the $Mg(OH)_2$ particles. Nevertheless, the results show that struvite formation occurs already at pH 6 as is shown by the decrease in both $P-PO_4$ and $N-NH_4$ in a nearly 1:1 molar ratio in the effluent samples (Table 3.6). At pH 6.7, ortho-P in the effluent amounted to 43 mg/L meaning that already 95% of the ortho-P in the influent had precipitated (Table 3.6).

The high P-total concentrations in the effluent indicate a flush out of fine struvite particles. This was to be expected since no precautions had been taken to prevent such a flush out of fine particles because the initial idea was to let these particles settle in the settler and feed them back into the reactor.

Figure 3.4 shows the sediment as it was scooped out of the reactor. This material, prior to dewatering, had a DM content of 40%. Table 3.6 shows the composition of the struvite material. The air-dried struvite had a P_2O_5 content of 17.6%. The molar Mg-P ratio amounted to 1.5 indicating that part of the added $Mg(OH)_2$ had not reacted with phosphate. XRD analysis revealed that the product consists for about 15% of amorphous material and 85% of crystalline material. The crystalline part consisted for about 75-85% of struvite and 15-25% of magnesium hydroxide.

Table 3.5 *Composition of influent and effluent samples taken during the continuous flow experiment.*

	pH (-)	$P-PO_4$ (mg/L)	$N-NH_4$ (mg/L)	P-total (mg/L)	Ca (mg/L)	Mg (mg/L)
Influent	5.3	1595	1326	1631	1431	1185
Effluent day 1-a	5.8	1236	1170	n.m.	n.m.	n.m.
Effluent day 1-b	5.9	551	1006	n.m.	n.m.	n.m.
Effluent day 2	6.2	279	793	886	997	1638
Effluent day 5	6.7	43	643	740	1032	1680

Table 3.6 *Composition of the sediment recovered from reactor at the end of the 3-days precipitation experiment expressed as g per kg of product. The product was dried at room temperature and thereafter analysed.*

	N-total (g/kg dry product)	P-total	Ca	Mg
Sediment	25	77	36	92

Figure 3.4 *Sediment recovered from the precipitation reactor at the end of the 3-days struvite precipitation experiment.*

3.4 Discussion

This chapter presents results on additional laboratory experiments that focussed on alternatives for sulphuric acid in the extraction process and on alternatives for calcium hydroxide in the precipitation process.

Possibility to use organic acids as alternative for sulphuric acid
Sulphuric acid is cheap and therefore often the preferred acid used in manure processing. However, despite sulphur being a macro-nutrient, accumulation of sulphur in the end-products is a drawback because it creates a risks for over-fertilisation of sulphur in agriculture. This problem does not occur when using organic acids.

Laboratory tests show that organic acids, including acetic acid, citric acid and formic acid, are well capable of extracting phosphorus from manure. An advantage of organic acids is that accumulation of sulphate in the end products and effluents is prevented. However, given the business case, the high prices of industrial grade organic acids do not allow usage of these products in manure treatment at this moment. For example, industrial grade citric acid has an equivalent market value of about €0.033 to €0.065 per mol of H^+. For comparison, 96% (w/w) sulphuric acid has an equivalent value of €0.008 to €0.015 per mol H^+. Sulphuric acid is thus about 4-5 times cheaper compared to the organic alternative citric acid (mol H^+ basis).

Biological processes for the production of citric acid from organic substrates are described in literature. These may offer a cheaper source of citric acid. Further research on the TRL of these processes and associated costs was beyond the scope of this study. Alternatively, acid waste streams may be used in the extraction process. Pyroligneous acid, tested in the laboratory (figures 3.3-3.5), is an example of an acidic waste stream originating from flash pyrolysis of woody biomass for 2-3 minutes. However, such products may also contain pollutants, for example organic micropollutants or poly aromatic hydrocarbons.. The product from flash pyrolysis that was tested had a low concentration. Therefore, a concentration step is needed to prevent an increase of the total volume of recycling water. Organic acids, in contrast to sulphuric acid, can contribute to biogas production but this requires another design of the RePeat module. Such a redesign is necessary as organic acids may have the drawback of odour emission and bio sludge formation.

Calcium hydroxide versus magnesium hydroxide

In the RePeat process, phosphorus minerals are released from the solid fraction of co-digested pig manure due to the addition of acid. This is followed by solid-liquid separation creating an acid liquid fraction with a pH of 5 and a phosphorus concentration of 1500-2000 mg/L. Subsequently, the phosphorus is recovered in a precipitation step by increasing the pH. In the pilot tests, calcium-hydroxide was used as a base because it is a cheap chemical which quickly reacts with phosphate to from an amorphous calcium phosphate precipitates. However, a serious drawback of $Ca(OH)_2$ is that it forms a slurry with a low DM content, a very low settling velocity and dewatering of the sludge is difficult. Therefore, laboratory experiments were performed in which precipitation with $Ca(OH)_2$ was compared with $Mg(OH)_2$ in terms of settling velocity and dewatering.

By addition of calcium hydroxide an amorphous precipitate consisting of fine particles was formed that hardly settled (settling velocity 4 cm/h). In pilot tests, settling gave a calcium phosphate sludge with a DM content of roughly 6% (Chapter 2). In the laboratory, a DM content of 15% was reached after centrifugation which is thought to mimic a separation step by means of a decanter. Hence, an additional drying step is needed in order to process the calcium phosphate sludge into a dry and marketable product.

In contrast, by addition of magnesium hydroxide a more crystalline product formed. The fresh precipitate, formed in batch experiments, had a settling velocity of about 100 cm/h and a DM content of 20% after centrifugation. The precipitate formed was struvite, which is in line with the simultaneous removal of NH_4 from the acid solution. Struvite is known for its ability to form large crystals. WWTP's use this principle to recover struvite from sewage sludge. Examples are the AirPrex reactor in Amsterdam, the NuReSys reactor in Apeldoorn and the Ostara reactor in Amersfoort. In order to observe crystal growth, a precipitation experiment was performed in a continuously fed 10 L reactor. a continuously fed reactor allows for optimal conditions for crystal growth compared to a batch fed reactor. a struvite material with the texture of course sand was formed which was easily dewatered by sieving. Thus, struvite could be produced as a dry and stackable material which does not require thermal energy for drying.

Calcium phosphate precipitation is a very fast process and hence it can occur in a small continuously stirred reactor. In contrast, the kinetics of struvite formation are rather slow, fine struvite particles therefore need relatively much time to grow out to larger particles. Based on the laboratory tests, an HRT of 4-5 hours should be sufficient for an almost complete removal of phosphorus from the solution. Recirculation of fine solid particles is required in order to promote crystal growth and hence formation of coarse grained particles. This means that the struvite tank should be equipped with build-in plates or an external settler in combination with recirculation of the fine particles.

In terms of costs for chemical consumption, $Ca(OH)_2$ is about twice as cheap as $Mg(OH)_2$ (Table 3.8). However, to compare the overall costs for the production of calcium phosphate versus struvite , also other costs including investments in a decanter and dryer for the calcium phosphate sludge and their operational costs must be included. Table 3.9 summarizes the pros and cons of $Ca(OH)_2$ and $Mg(OH)_2$. In decision making, also local circumstances should be considered such as the availability or residual heat for calcium phosphate drying.

Table 3.7 *Price comparison of various base products.*

Base	€/ton	Molar mass	€/kmol OH-
Ca(OH)2, 45%	€120,-	74	€4,50
Mg(OH)2, 53%	€310,-	58	€9,04
NaOH, 50%	€330,-	40	€13,20

Table 3.8 *Pros and cons of using Ca(OH)2 and Mg(OH)2 in the precipitation process.*

	Calcium-hydroxide	**Magnesium-hydroxide**
Price chemical consumption	Low	High
Reaction rate	Seconds	Hours
Settling velocity	Very slow	Very fast
Dewatering	Poor	Good
Thermal drying step required	Yes, high capacity	No, or low capacity dryer
Market value products	For dry products, no difference in market value is expected	

3.5 Conclusion

- The organic acids citric acid, formic acid, acetic acid and pyroligneous acid are capable of lowering the pH of a suspension of the solid fraction of co-digested pig manure sufficiently to recover phosphorus. However these organic acids are too expensive given the business case context of manure treatment at this moment. Additional goals such as control over the sulphur content of end products and/or an increase in biogas production have to be included to overcome their cost. Alternative biological production processes for these acids may enhance the prospects.
- The precipitation reaction of $Ca(OH)_2$ with phosphate is very fast compared to that of $Mg((OH)_2$ with phosphate. However the settling velocity of a phosphorus precipitate formed by addition of $Mg(OH)_2$ is superior to that formed by $Ca(OH)_2$, when both are produced in a batch-wise manner.
- In a continuously fed laboratory reactor, struvite crystallises and forms a coarse grained product which could be easily dewatered through a combination of settling and sieving. a drawback of the struvite route is however the costs for $Mg(OH)_2$. They are about twice as high as those for $Ca(OH)_2$ when expressed per mole OH^{-1}.

4 Testing separation equipment and struvite production at the pilot installation

4.1 Introduction

The RePeat process, as described in detail in Chapter 2, has been developed to separate the solid fraction of digestate into a nutrient-poor organic soil improver and a P-rich mineral product by means of extraction (using sulphuric acid) and precipitation (using calcium- or magnesium hydroxide).
The process consist of two acidification tanks, one precipitation tank and four devices for solid-liquid separation. The overall performance of RePeat strongly depends on the performance of the separation devices. Upscaling of the pilot installation to a full-scale installation thus requires selection of the best available separators in terms of separation efficiency, investments, maintenance and durability.

This chapter describes the results of tests with various separators working on different flow streams within the RePeat process. The report pays attention to options for the removal of fine organic particles from the acid liquid stream in order to improve the purity of the recovered phosphorus.
This research was initiated because tests with the pilot installation revealed that the recovered calcium phosphate contained on DM basis over 40% OM (Chapter 2.3). Furthermore, the research focused on the efficiency of separators and their dewatering capability of the precipitated sludge of either calcium phosphate or struvite. This is a critical step in the overall process since the market research revealed that there are no opportunities for disposal of calcium or magnesium phosphate sludge to the mineral and organic fertiliser industry. This is because current processes in that industry are based on processing dry raw materials. For logistic reasons and further industrial processing the recovered phosphate product must be stackable.

This chapter gives separation efficiencies of the pilot tests and discusses the consequences for the quality of the end-products.

4.2 Materials and Methods

4.2.1 Process description

The principle units of the process scheme are similar to those in Chapter 2 but the scheme is now extended with (i) a separation step to remove fine suspended particles prior to phosphorus precipitation and (ii) a dewatering step for the precipitated phosphorus. This chapter describes the results of the tests for the following three separation steps that are also encircled in Figure 4.1:

1. Separation of the solid and liquid fraction of digestate from the digester by means of decanter centrifuge;
2. Removal of fine organic matter from the acid liquid fraction prior to the precipitation reactor;
3. Dewatering of calcium phosphate

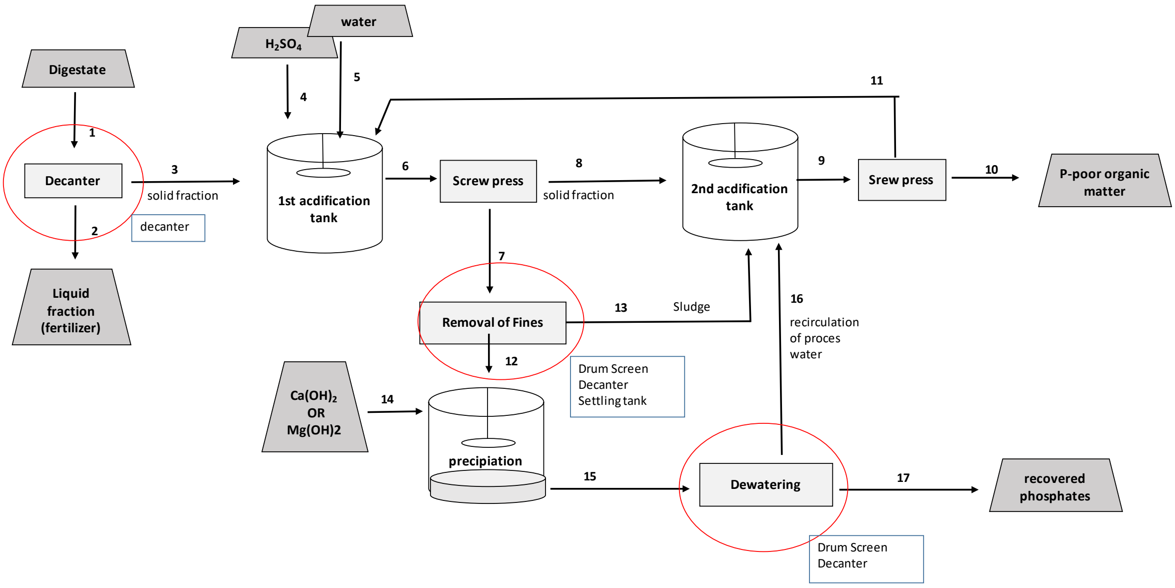

Figure 4.5 *Process scheme of RePeat. For the encircled separation steps, several separation apparatus have been tested on their performance.*

4.2.2 Solid-liquid separation of digestate

Digestate was separated by means of a decanter of GEA Engineering, ’s-Hertogenbosch, Netherlands. The solid and liquid fraction were analysed at the laboratory of Wessling GmbH located in Altenberge, Germany.

4.2.3 Removal of fine particles from the acid liquid fraction

Previous pilot tests revealed that the solid-liquid separation of the acidified solution (1^{st} acidification tank; see figure 4.1) with a screw press generated a liquid P-rich stream with a DM content of about 3.5-4%. About thirty percent of the OM of the solid fraction of digestate was recovered in the calcium phosphate sludge which consequently had an OM content of about 40% based on DM. Hence, fine organic particles are able to pass the screw press and coagulate after the addition of a base. To increase the purity of the phosphate precipitate, pilot tests were performed with a drum filter, a decanter and a settler in order to remove these fine particles from the acidified P-rich liquid fraction.

The acid liquid fraction was produced with the pilot installation as follows. Solid fraction of digestate was mixed with water (groundwater) and acidified with sulphuric acid to pH 5. The mixture was separated with a FAN screw press equipped with a 250 µm pore size filter screen. The acid liquid fraction was stored in intermediate bulk containers (IBC’s) until the start of the experiments with the following separators:

The *rotating drum filter* was made available by Nijhuis Industries, Netherlands. About four cubic meter of the acidified P-rich liquid fraction was fed over the drum screen which was equipped with a 80 mµ pore size filter. Samples were taken from the feed, centrate and sludge and were analysed by CBLB, part of Wageningen UR.

The *decanter centrifuge* was made available by GEA Engineering (UCD 205-00-32). The test was performed at a feed rate of 2 m^3/h. The corresponding DM feed rate was 80 kg/h which is well within the capacity range of the decanter (50-100 kg/h). The decanter was allowed to reach a steady state condition and was thereafter ran for 45 minutes, treating 1.6 m^3 of acid liquid fraction. Samples were taken from the feed, separated centrate and sludge and were analysed by Wessling GmbH located in Altenberge, Germany.

The *settler* (lamella separator) was equipped with lamella with a distance of about 15 mm, the settler was about 2.7 m high and had a surface area of about 5 m^2. The volume of the settler amounted to

4 m^3. The tests with the settler were performed at a feed velocity of 4 m^3/h. The sludge purge rate, removing the thickened sludge from the bottom of the settler, was set at 0.4 m^3/h. The test was continued for two hours in order to obtain an equilibrium situation within the settler. The feed and separated liquid and solid fraction were sampled and the samples were analysed in the laboratory of Wessling GmbH.

4.2.4 Dewatering of the precipitated calcium phosphate

All experiments described in par. 4.2.4 – 4.2.6 were performed with the acid liquid P-rich fraction which was obtained as follows: solid fraction of digestate was mixed with groundwater (1000 kg digestate on 3500 L groundwater) and acidified with 50% (w/w) sulphuric acid to pH 5.0. The mixture was thereafter separated into a solid and a liquid fraction by means of a 250 µm pore size screw press. The liquid fraction, hereafter referred to as acid liquid fraction, was stored in 1 m^3 containers until further testing. Various batches of acid liquid fraction were prepared.

To precipitate calcium phosphate, the pH of the acid liquid fraction was increased to pH 8.0 by addition of calcium hydroxide. The $Ca(OH)_2$ dosage differed among the various batches and amounted to 6-10 L of 30% (w/w) $Ca(OH)_2$ suspension per m^3 of acid liquid fraction. The produced calcium phosphate slurry was stored in IBC’s for further processing on the separators.

A *rotating drum screen* was made available by Nijhuis Industries and equipped with a 80 µm mesh size filter cloth. This mesh size was chosen because a previous test (not described here) with the filter cloth showed that a smaller mesh size of 40 mµ led to immediate clogging of the filter. The calcium phosphate slurry was pumped over the drum screen with a feed rate of 1-2 m^3/h. Once a steady condition was reached, samples were taken from the resulting centrate and sludge.

A trailer with *decanter* was made available by GEA Engineering (type UCD 205 trailer, capacity 1-3 m^3/h; DM capacity of 50-100 kg/h). The content of the IBC was continuously stirred in order to ensure a homogenous feed to the decanter. Three tests were performed with feed rates of 2, 1 and 0.5 m^3/h. The feed, centrate and sludge were sampled and analysed in the laboratory of Wessling GmbH.

4.2.5 Dewatering of precipitated magnesium phosphate

The solid fraction of digestate was acidified. The acid liquid fraction contained about 1.6 g/L $P\text{-}PO_4$ and was treated with 50% (w/w) $Mg(OH)_2$ suspension in order to precipitate phosphate. The initial pH was 5.5. The $Mg(OH)_2$ dosage amounted to 1 L per 100 L of acid liquid fraction after which the pH gradually increased. The next morning, after about 14 hours, the pH was 8.7.

4.2.6 Struvite formation

Laboratory tests with a 10 L reactor showed the formation of coarse struvite particles that could be easily dewatered. This test was repeated at a somewhat larger scale at the plant of Groot Zevert Vergisting B.V.. a 1 m^3 IBC was used as a reactor and equipped with pumps for influent, effluent, $Mg(OH)_2$ addition and a stirrer (figure 4.2). The tank was continuously stirred. The water volume in the tank was kept constant at 350 L and the influent (acid P-rich liquid fraction) and effluent flow rate were set at 70 L/h to reach the desired HRT of 5 hours. a constant $Mg(OH)_2$ suspension dosage of 0.7 L/h was used.

The experiment ran for three days. After three days, the sludge was allowed to settle and the clear effluent water decanted. Samples were taken from the influent, effluent and sludge and wereanalysed by Wessling GmbH.

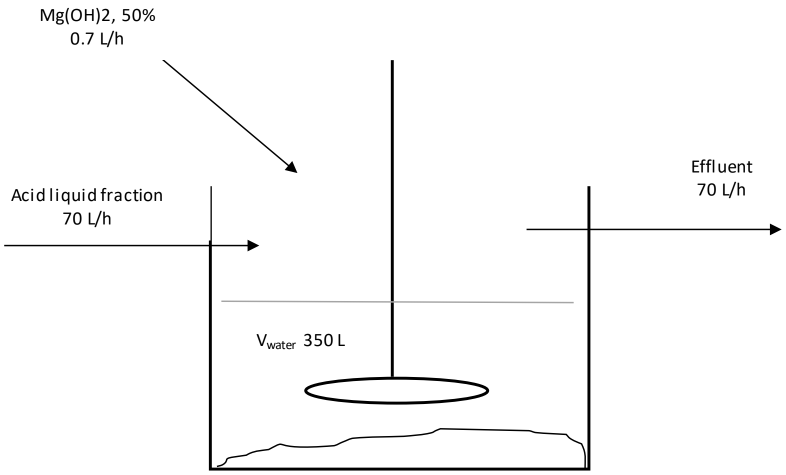

Figure 4.2 *Schematic depiction of the struvite test performed with an IBC as reactor.*

4.3 Results

4.3.1 Solid-liquid separation of liquid digestate

Table 4.1 shows the separation efficiencies of the GEA Salomon decanter used for separation of the digestate of Groot Zevert Vergisting B.V. into a solid and a liquid fraction. About 14% of the overall mass ended up in the solid fraction. This solid fraction contained 60% of the phosphorus and 22% of the nitrogen (N) of the digestate. The solid fraction of the digestate had a P content of 7.8 g/kg.

Tabel 4.1 *Separation of liquid digestate of GZV using a GEA decanter. Product composition and separation efficiency.*

	Mass	DM	OM	P	N	Ca	Mg	K	S	N-NH4
Composition	(kg)	(%)	(%)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)	(g/kg)
Liquid digestate	1000.0	8.5	71	1.86	7.70	2.03	0.95	4.50	0.8	4.30
Solid fraction	144.0	31.2	76	7.77	12.0	7.79	5.31	5.05	1.8	3.30
Liquid fraction	856.0	4.7	2.6	0.69	6.9	0.87	0.12	3.69	0.6	4.40
Separation efficiency	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Liquid digestate	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Solid fraction	14%	53%	57%	60%	22%	55%	81%	16%	33%	11%
Liquid fraction	86%	47%	37%	32%	77%	37%	11%	70%	67%	88%
Error (In-out)	-	0%	6%	8%	1%	8%	9%	14%	0%	1%

[a] DM = dry matter; OM = organic matter, expressed as percentage of dry matter

4.3.2 Removal of fine organic matter from the acid liquid fraction

Pilot tests were performed in order to test the suitability of a drum filter, decanter centrifuge and settler for the removal of the fine particles from the acid liquid fraction which had a DM content of 5%. Table 4.2 shows the DM removal efficiency achieved with the drum filter, decanter, and settler, they were 14%, 27% and 19% respectively. Thus, the removal efficiency increased in the order; drum filter, settler, decanter. The DM content of the produced sludge differed substantially among the tested separators. The decanter was able to produce a sludge with a DM content of 33% whereas the drum filter and settler produced a fluid sludge with a DM content of only about 6%.

The tests revealed that the removal efficiency of the settler was sufficiently high. The low DM content of the sludge is not regarded as a problem since this sludge can be fed into the second acidification tank. a settler was preferred over a decanter because of the lower investment- and maintenance costs.

All tests were performed without the use of coagulants or flocculants despite the fact that it is known that the separation efficiency improves using polymers or iron salts. However, from an environmental and an agronomic point of view, Groot Zevert Vergisting B.V. wants to omit coagulants and flocculants in their P recovery system.

The effluent acid liquid fraction of the settler was used in subsequent precipitation experiments were it was found that the OM content of the Ca~P~S sludge had decreased from 50% to 30% of the DM content due to the use of the settler

Table 4.2 *Separation efficiencies of rotating drum screen, decanter and settler for the removal of fine particulate matter from the acid liquid fraction.*

	Drum filter	Decanter	Settler
Removal efficiency - % dry matter removed from acid liquid fraction	14	27	19
Sludge production (L/m^3)	36	36	210
Dry matter content sludge (%)	5.8	33	5.8

[1] Percentage of dry matter (total solids) removed from the liquid fraction

4.3.3 Dewatering of calcium phosphate sludge

Tests with the drum screen equipped with an 80 µm pore size filter showed almost no recovery of calcium phosphate; only 10% of the total phosphorus was collected on the filter cloth whereas the remaining part passed the filter cloth. The collected sludge had a higher DM content of 18%. Because of this poor separation efficiency, no additional chemical analyses were performed on the samples and no table with results is given.

Separation efficiencies of the decanter are given in Table 4.3. The decanter removed almost all P from the solution and produced a sludge with a DM content of 28% and a P content of 19 g/kg. However, in order to reach such a high DM content in the sludge, the decanter had to be operated at a low feed rate of 0.5 m^3/h. a lower feed rate increases the residence time of the sludge within the decanter and therefore improves dewatering. The decanter was also tested with a feed rate of 2 m^3/h, which is within the advised feed rate based on the machines specifications, and this gave a calcium phosphate sludge with a DM content of only 9% (results not shown). So, from a technical point of view calcium phosphate can be recovered with a DM content of almost 30% at a low feed rate in a small installation. However, for large scale applications such as at Groot Zevert Vergisting B.V. with a Ca~P~S slurry flow rate of about 6-8 m^3/h, this requires a large investment in 2 or 3 decanters. This would be needed to obtain sufficient capacity to run the decanters at a feeding rate within the advised range as based on product specifications.

One ton of liquid fraction resulted in 52 kg of calcium phosphate sludge after separation with a decanter (Table 4.3). Since one ton of solid fraction produced four tons of liquid fraction, this equals a calcium phosphate production of 208 kg per ton of ingoing solid fraction (about 20% reduction in terms of mass). This is however for a situation in which fine OM is removed from the solid fraction by a settler and in which the decanter is operated at a very low feeding rate of 0.5 m^3/h. In practice, these settings may not be feasible due to the high investment costs for a decanter centrifuge. At a normal feeding rate of 2 m^3/h, the amount of calcium phosphate sludge produced per ton solid fraction is a factor three larger, about 600 kg per ton of ingoing solid fraction. For any of the cases, a manure drying system is needed in order to produce a dry product.

Table 4.3 *Separation of calcium phosphate sludge with a with a GEA decanter at a feeding rate of 0.5 m3/h.*

Flow	Mass (kg)	DM (%)	OM (% of DM)	P (g/kg)
Acid liquid fraction + Ca(OH)2 at pH 8	1000	3.1	43	2.2
Centrate of decanter	948	1.7	39	0.0
Sludge of decanter	52	28.5	32	30.1
Separation efficiency	**(%)**	**(%)**	**(%)**	**(%)**
Acid liquid fraction + Ca(OH)2 at pH 8	100	100	100	100
Centrate of decanter	91	52	65	2
Sludge of decanter	9	48	35	98

[a] DM = dry matter content, OM = organic matter content.

4.3.4 Dewatering of struvite sludge

First, experiments were done in which Mg(OH)2 suspension was added to the acid P-rich liquid fraction in order to precipitate orthophosphate with magnesium. These experiments, performed in IBC’s , confirmed the outcome of laboratory tests that the settling velocity of struvite sludge is superior (40 times higher) compared to that of calcium phosphate sludge (Table 4.4).

Table 4.4 *Settling velocity of calcium phosphate sludge and struvite sludge*[a].

	Calcium P sludge	struvite sludge
Settling velocity – cm per 10 min	0.5	22
Settling velocity (cm/h)	3	132

[a] Settling velocity was determined twelve hours after addition of Ca(OH)2 suspension or Mg(OH)2 suspension to the P-rich acid liquid fraction.

Acid liquid fraction which contained 1600 mg/L P-PO_4 was treated with 50% (w/w) $Mg(OH)_2$ suspension in order to precipitate phosphate. The initial pH of the acid liquid fraction amounted to 5.5. The $Mg(OH)_2$ suspension dosage amounted to 1 L per 100 L of acid liquid fraction after which the pH gradually increased. The kinetics of $Mg(OH)_2$ dissolution are slow. After 14 hours (overnight) the pH was 8.7 and a magnesium phosphate sludge had formed and had settled.

The struvite sludge was continuously stirred and pumped from the bottom of the IBC to the drum screen. Despite the use of a stirrer, a thick layer of dense sludge remained at the bottom of the container. The mass balance (Table 4.5) reveals two important results. Firstly, the removal efficiency of the drum screen is insufficient for struvite because the high volume of centrate, which passed the 80 µm pore size filter, still contains a high concentration of P (0.6 g/kg). Secondly, the majority of the magnesium phosphate sludge remained on the bottom of the IBC (even with continues stirring) which indicates that the sludge has a very high settling velocity. Hence, these result imply that the struvite particles are best recovered through settling in a conus-shaped reactor tank in which the sludge can be removed at the bottom of the reactor. Such a design is common for struvite reactors. The struvite sludge produced in this batch test differs however from struvite formed in regular struvite reactors in which struvite particles are kept in the reactor for a long time to support particle growth.
Such an approach, with the aim to produce coarser precipitates, was also tested and is described in paragraph 4.3.5.

Table 4.5 *Separation of struvite sludge with a drum screen[a].*

Composition	Mass (kg)	DM (%)	OM (%)	P (g/kg)	Mg (g/kg)
Acid liquid fraction (prior to $Mg(OH)_2$ addition)	1000	2.5	28.9	1.6	1.2
Centrate after drum screen	839	2.5	28.3	0.6	2.4
Sludge after drum screen	10	21	47.9	14	24
Separation efficiency	**(%)**	**(%)**	**(%)**	**(%)**	**(%)**
Acid liquid fraction (prior to $Mg(OH)_2$ addition)	100	100	100	100	b
Centrate after drum screen	84	84	83	32	b
Sludge after drum screen	1	8	13	8	b
Difference (≈sludge IBC)	15	8	4	60	b

[a] DM. ; dry matter content, OM.; organic matter content.

b For Mg, the separation efficiency in percentages is not given because no sample was taken from the acid liquid fraction after addition of Mg(OH)2.

4.3.5 Struvite formation

The purpose of the tests were twofold; (i) to determine whether an HRT of five hours is sufficient to remove phosphorus and (ii) to determine whether a solid retention time of three days is sufficient to form sand-like struvite particles. The solid retention time refers to the average retention time of precipitated P within the reactor. In the chosen experimental approach, precipitates remain in the reactor over the course of the experiment (three days) and hence, the solid retention time is three days.

During the tests, $Mg(OH)_2$ suspension supply tubes got clogged several times. When this happened, $Mg(OH)_2$ was regularly dosed by hand in order to maintain the set $Mg(OH)_2$ dosage. The pH of the effluent varied between 6.0 and 6.3 during the course of the tests. This low pH value was unexpected since a preliminary batch test had shown that the chosen magnesium hydroxide dosage was sufficient to increase the pH of the acid fraction to pH 8 within two hours. It was argued that the rather low pH of the effluent was caused by inadequate mixing of the reactor. As a result, $Mg(OH)_2$ would rapidly sink to the bottom of the IBC tank were dissolution would be slow due to the locally high pH in the sediment. This hypothesis was confirmed by the visible presence of white particles in the sediments and the high Mg/P ratio in the sediment indicating that the added $Mg(OH)_2$ had only partially dissolved. As a consequence, also the phosphate concentration in the effluent was still high. However, only total-P was measured meaning that the high P concentration in the effluent could also indicate a flush-out of fine struvite particles.

At the end of the test, a thick layer of sand-like struvite or magnesium phosphate precipitate had formed on the bottom of the tank (which contained probably also quite some $Mg(OH)_2$). The DM content of the settled sludge, determined at 105 °C, was 20% (Table 4.6). Since it is well known that struvite decomposes at 105 °C, the actual DM content is likely a factor two higher because 50% of struvite’s mass is present as H_2O and NH_4. Because of the rather course structure, it is expected that the struvite sediment could be easily dewatered. The wet struvite had a P content of about 17 g/kg which is equal to a P_2O_5 content of 15% based on dry weight. The Mg:P molar ratio amounts to 3:1 showing that at maximum one third of the added $Mg(OH)_2$ reacted with phosphate and that possibly large amounts of other Mg products such as (hydr)oxides and other salts are available in the sludge.

Overall, the results confirm that the use of magnesium hydroxide in a continuously fed reactor leads to formation of a magnesium phosphate/struvite sludge which has, based on visual observations, a coarser structure than struvite sludge formed in a batch system. However, due to inadequate mixing and consequently a too low pH in the reactor, this test could not be used to confirm the laboratory results in which we showed that the chosen HRT is sufficient to obtain a nearly complete P removal from the acid liquid fraction. Moreover, the relation between the solid retention time and particle size distribution of the struvite remains uncertain.

Table 4.6 *Composition of influent, effluent and sediment formed in the struvite test[a].*

		Influent (Acid liquid fraction)	Effluent	Sediment (Struvite)
pH	(-)	4.8	6.1	9.2
Dry matter	(%)	3.9	2.4	≈26
Organic matter	(% of dm)	-	-	19
P-total	(g/kg)	1.7	0.8	16.9
Ca-total	(g/kg)	1.6	0.8	12.5
Mg-total	(g/kg)	1.1	1.7	46.3
N-total	(g/k)	1.9	1.4	5.4

[a] The measured dry matter content of struvite amounted to 19% but was determined at 105 degrees °C and hence may contain an underestimation of the real content. The given dry matter content was calculated based on the elemental composition and the assumption that all P was present as struvite, which has a molar mass of 245 g/mol.

4.4 Conclusion

The engineering of the full-scale RePeat installation requires knowledge on the performance of separators. This chapter described results of tests with a decanter centrifuge, drum screen, and settler. There were two objectives; (i) removal of particulate OM from the acid P-rich liquid fraction in order to increase the purity of the recovered mineral phosphorus product and (ii) dewatering of the recovered mineral phosphorus product.

For the first objective, removal of particulate matter from the acid liquid fraction, it was concluded that a settler is preferred over a decanter because the settler removed a substantial amount of particles and the investments and operational costs are much lower than for a decanter which has a somewhat higher removal efficiency. The rotating drum filter had a lower separation efficiency than the settler and decanter centrifuge.

For the second goal, dewatering of the recovered phosphorus product, it was found that dewatering of calcium phosphate requires the use of a decanter. a decanter produced a calcium phosphate sludge with a DM content of 9% and 30% at feed flow rates of 2 m^3/h and 0.5 m^3/h respectively. Other more low-tech apparatus, such as a drum screen and settler were not suitable because the calcium phosphate particles were too fine and did hardly settle.

Additionally, the formation of struvite was tested in a small pilot test. Struvite formation seems to be an attractive alternative for calcium phosphate formation because the settling velocity of struvite is about forty times higher. Continuous circulation of struvite particles leads to particle growth as has been shown in a laboratory test described in paragraph 3.3.4. Due to practical constraints, the test described in this chapter did not give conclusive results about the minimally required HRT and solids retention time.

5 Process design and mass balance calculations

5.1 Process design

The laboratory and pilot tests described in this report were used to come to the final design of the demonstration plant to be built at Groot Zevert Vergisting in Beltrum. Based on the results, the following decisions were made with respect to the final design:

1. The acidified manure is separated by a screw press after which the liquid fraction is led over a settler to remove fine particulate OM thereby lowering the OM content of the recovered phosphate. The sludge from the settler can be fed back into the second acidification tank or collected as a separate product. We expect that the organic sludge will contain a substantial amount gypsum which needs to be quantified in more detail in the demonstration plant.
2. The demonstration plant will recover phosphorus in the form of struvite because we expect that this product can be harvested from the reactor as sand-sized particles which can be easily dewatered in a filter bag. The alternative product, calcium based phosphate precipitates, requires an additional investment to achieve the required dewatering or an installation to dry it. The latter requires a substantial amount of heat or energy in another form. Groot Zevert Vergisting B.V. therefore preferred the use of magnesium hydroxide over calcium hydroxide.

Figure 5.1 gives a schematic overview of the process steps to be included in the demonstration plant at Groot Zevert Vergisting. Groot Zevert produces about 100,000 ton of digestate per year and their plant is operational for 24 hours a day, 365 days a year. Hence, the digestate production rate amounts to 14 m^3/h and the solid fraction production rate of the decanter is 2-3 ton/h with a DM content of 30%. The RePeat plant is designed to have a processing capacity of 2 ton of solid fraction/hour.

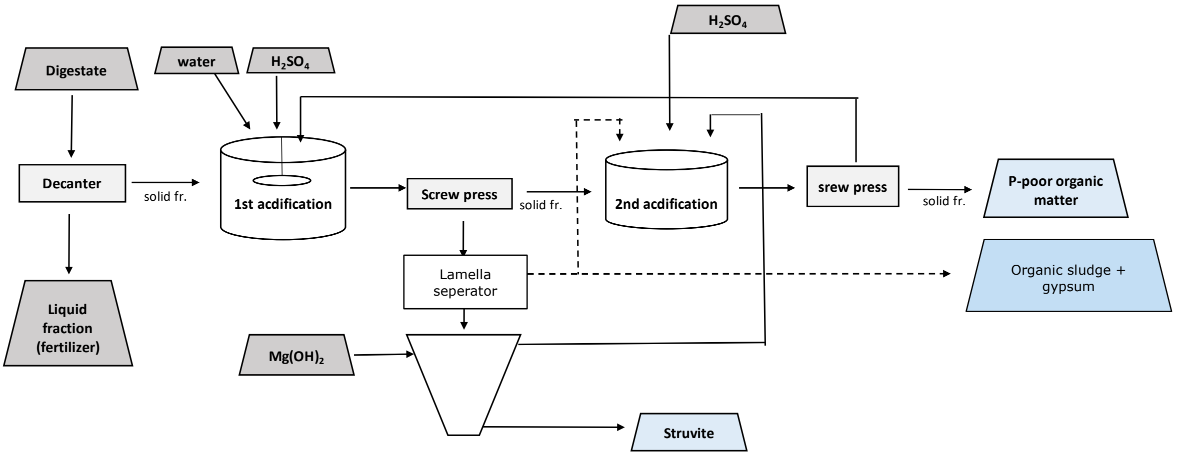

Figure 5.6 *Simplified scheme of the RePeat plant to be built at Groot Zevert Vergisting B.V.*

5.2 Modelling approach

A simple mass balance model was set-up in Microsoft Excel in order to calculate the composition of end products for a system with a closed water balance and mass balance. The input parameters including the chemical consumption rate and the distribution of OM and DM over the end products were estimated based on results of the pilot installation. Based on a given composition of the ingoing solid fraction and given DM content of the end products, the model calculates the distribution of solid matter and water over the end products. The model thereafter uses the water balance to calculate the concentration of salts in the liquid phase by dividing the amount of ingoing salts over the amount of water that is removed from the system per hour. The salt concentration in the water phase is thereafter used to predict the salt content in the end product by multiplying its water content with the predicted salt concentration.

In more detail, the model included the following calculations and assumptions:

- Ten percent of phosphorus in the solid fraction is supposed to be non-extractable. Ninety percent is extracted and recovered in the form of calcium phosphate or struvite.
- The total sulphuric acid dosage for two acidification steps amounts to 38 kg (21 L) 96% (w/w) sulphuric acid per ton of ingoing solid fraction. Of this dosage 95% is used for the first acidification step (§2.5).
- For the struvite route, the magnesium dosage was set to 37 kg (27 L) of 50% (w/w/) $Mg(OH)_2$ suspension per ton solid fraction (§3.3.4). Struvite ($MgNH_4PO_4{\cdot}6H_2O$) has a molar mass of 245 gram/mol.
- OM is distributed between the products based on best guess values derived from the mass balances of the pilot tests. The P-poor soil improver, the sludge produced by the settler and the struvite are modelled with respectively 85%, 5% and 10% of the OM in the ingoing solid fraction (§2.5, §4.3.2 and expert judgement).
- The model needs an estimate for the DM content of the end-products which is used as starting value in the calculation. The calculated DM content is the sum of the OM, precipitates (gypsum, struvite) and all dissolved elements (PO_4, Ca, SO_4, Mg, Na, Cl, K, N). For the soil improver, the DM amounts to 34% (§2.5). For the sludge after the settler, we use a DM content of 10% and struvite is assumed to be harvested with a DM content of 70% which is similar or lower as DM values of struvite produced by installation at waste water treatment plants.
- The water balances are closed. Intake of water occurs only in scenario's were the amount of water in the end products is larger than the amount of water in the ingoing solid fraction.
- Gypsum precipitation is included by assuming that 60% of the calcium present in the ingoing solid fraction precipitates with sulphate to form gypsum. (best guess based on molar Ca and SO_4 ratios and gypsum solubility product). Gypsum is expected to form in the first acidification tank due to the elevated calcium concentrations therein (gypsum precipitation also occurs under acidic conditions). It is assumed that gypsum forms fine particles which pass the screw press and are recovered in the sludge after the settler. The remaining sulphate is assumed to behave as a salt. The organic sludge removed from the acid liquid fraction by the settler can be fed into the second acidification tank or kept apart and disposed of as an organic gypsum-rich fertiliser. In the presented scenario, the sludge from the settler was kept apart.
- Salts (SO_4, Cl, K, Ca, Mg, NH_4) were distributed between the end products based on their water content. Removal of Ca, Mg and NH_4 via precipitates was accounted for.

5.3 Mass balance

Table 5.1 and 5.2 show the predicted mass balance for the RePeat system producing struvite, P-poor organic soil improver and a gypsum-rich organic sludge. The latter product was separately recovered as a liquid in order to lower the S content of the organic soil improver and to keep the chloride concentrations within an acceptable concentration. In this best-guess scenario, it is predicted that one ton of solid fraction of digestate can be processed into 0.7 ton of P-poor organic soil improver, 0.2 ton struvite and 0.2 ton of gypsum-rich sludge. 90% of the ingoing phosphorus is recovered in the form of struvite. Sulphur is dominantly present in the P-poor organic soil improver and in the gypsum-rich organic sludge. About 30% of the sulphate added in the form of sulphuric acid is expected to precipitate with calcium to form gypsum; the calcium content of the manure is the limiting factor. This gypsum is expected to be recovered in the sludge of the settler treating the acid liquid fraction. Hence, the produced sludge is expected to be an organic sulphur-rich product. The P-poor organic soil improver is expected to have an S content of about 10 g/kg due to the presence of sulphate.
The mineral nitrogen content of the P-poor organic soil improver is expected to be low (1.6 g/kg).

Table 5.9 *Estimated mass balance of the RePeat system per ton of ingoing solid fraction.*

Parameter	unit	In				Out		
		Solid fraction	**Water**	**Sulphuric acid**	**Magnesium hydroxide**	**P-poor organic soil improver**	**Struvite**	**Gypsum-rich sludge**
Mass	ton	1.00	0.03	0.03	0.02	0.73	0.11	0.19
Dry matter	ton	0.32	00	0.03	0.01	0.23	0.077	0.019
Water	ton	0.66	0.03	0	0	0.50	0.03	0.17
Organic matter	ton	0.25	0	0	0	0.21	0.03	0.013
P	kg	7.50	0	0	0	0.76	6.5	0.27
Ca	kg	7.50	0	0	0	2.35	0.1	5.1
Mg	kg	7.90	0	0	6.6	5.81	6.8	1.7
S	kg	2.20	0	13	0	8.09	0.5	6.6
K	kg	4.30	0	0	0	3.04	0.2	1.1
N-org	kg	6.00	0	0	0	5.07	0.6	0.3
N-NH4	kg	5.00	0	0	0	1.76	2.6	0.6
Cl	kg	1.3	0	0	0	0.92	0.1	0.3

Table 5.10 *Composition of the ingoing solid fraction and estimated composition of the end- products of the RePeat system.*

Parameter	unit	In	Out		
		Solid fraction	**P-poor organic soil improver**	**Struvite**	**Organic S-rich sludge**
Mass	ton	1.00	0.73	0.11	0.19
Dry matter	%	30	36	70	14
Organic matter	% of dm	73	90	33	67
P	g/kg	7.5	0.99	66.8	1.25
Ca	g/kg	7.5	3.08	0.58	23.72
Mg	g/kg	7.9	7.63	70.7	8.13
S	g/kg	2.2	10.6	5.53	30.54
K	g/kg	4.3	3.99	2.08	4.92
N-org	g/kg	6	6.66	6.36	1.44
N-NH4	g/kg	5	2.31	27.1	2.85
Cl	g/kg	1.3	1.21	0.63	1.49

Final product composition may deviate from these calculations due to e.g. differences in the composition of the ingoing solid fraction or unforeseen effects in the process due to reuse of process water and accumulation of salts. The mass balance calculations are based on parameters derived from lab tests and ‘expert judgement’.

The P-poor organic soil improver can also be used as a sulphur fertiliser. Fertilisation schemes including this P-poor soil improver are given in Chapter 6. Another option is to use the P-poor organic soil improver as a secondary raw material for potting soil. The latter requires an additional leaching step with clean water to leach out sulphate and other salts in order to lower the EC value. The EC value is a critical parameter for potting soil producers since a high EC value can inhibit germination of seeds, lower the growth rate of potting plants or cause phytotoxicity (salt intolerance). The P-poor organic soil improver produced in the pilot installation has an S content of 4 g/kg and an EC value of 2.6 dS/m which was considered acceptable since the EC is dominantly due to nutrients. The P-poor organic soil improver produced by the demonstration plant is expected to have an S content of 8 g/kg and hence the EC value will double. One ton of P-poor organic soil improver contains 650 L of water, based on a DM content 35%. Thus, to reduce the salt concentration with a factor 2, the solid fraction must be leached with another 650 L of water. Using this approach, we estimate that about 850 L of water is needed per ton of P-poor organic soil improver in order to reduce the salt content to an acceptable level.

6 Quality of the P-poor organic soil improver

6.1 Introduction

The P-poor organic soil improver produced by the RePeat pilot installation can be used as a soil improver in regions were the application of OM on agricultural land is limited by N and P application standards. This chapter focusses on the characterisation of the P-poor fraction in order to determine its agronomic value as a soil improver. For this purpose, the carbon and nitrogen mineralisation rate of the P-poor fraction were determined in incubation tests and fertilisation schemes with P-poor OM were formulated. Besides, the quality of the P-poor OM, which is a fibrous material, is discussed in relation to its potential use as ingredient for potting soil.

6.2 Materials and Methods

6.2.1 Chemical analyses on P-poor soil improver

P-poor organic soil improver was collected from the pilot installation at Groot Zevert Vergisting B.V. Details on the extraction process from which this fraction originates are given in Chapter 2. The organic soil improver was stored in a refrigerator until the start of the experiment. The DM content was determined at 105 ºC and the OM content was determined by loss-on-ignition (LOI). Total amounts of P, Ca, Mg, K, Na and S were determined after destruction by the aqua regia method (Houba *et al.*, 1997) followed by analyses of the destruate by ICP-OES. Total N was determined after destruction with $H_2SO_4/H_2O_2/Se$ ((Houba *et al.*, 1997) followed by colorimetric analysis on $N\text{-}NH_4$. Mineral nitrogen ($N\text{-}NH_4$ + $N\text{-}NO_3$) and pH were determined in a 10 mM $CaCl_2$ extract (1:10 m/v ratio; (Houba *et al.*, 1997). Heavy metal contents were analysed by Eurofins Agro (analysis compost certificate).

6.2.2 Carbon and nitrogen mineralisation rate

An incubation experiment was performed in order to determine the carbon and nitrogen mineralisation rate of the P-poor organic soil improver . The approach was similar to the approach of Van Groenigen and Zwart (2007).
Sandy soil was collected on the Droevendaal experimental farm of Wageningen UR. The fresh soil was stored in a refrigerator at 4 °C until the start of the incubation test. The soil had a low $N\text{-}NH_4+NO_3$ content of 2.3 mg/kg (table 6.1) and was therefore considered to be suitable for this incubation test.

The incubation tests were performed using P-poor organic soil improver (P-poor OM) obtained from pilot tests (§2.2). As a reference material, compost from vegetable, fruit and garden waste (VFG) was used. The compost was collected by Attero from their processing location in Venlo. The composition of the used organic products is given in Table 6.2 and subsequent incubation treatments and product dosages are given in Table 6.3. Each treatment received 3 gram TOC per kg of soil except for the control treatment which did not receive any carbon or nitrogen. The P-poor organic soil improver has a relative high C/N ratio of 29 and hence nitrogen may be a limiting factor in the microbial degradation of the OM. To exclude N-limitation, we tested the P-poor organic soil improver in three treatments with extra added nitrogen. Those comprised of an additional dos of 0, 1.2 and 3.0 mg N per 100 gram of soil, targeting a C/N ratio of 29, 26 and 21, respectively. These treatments are hereafter referred to as SI, SI+N and SI+2N. The additional N was given as a NH_4NO_3 solution. Overall, the experiment consisted of three treatments with P-poor organic soil improver and varying N levels, a reference treatment with compost and a control treatment.

The product dosage, corresponding to 3 gram of TOC per kg of soil, was chosen based on similar experiments described in literature (Van Groeningen and Zwart, 2007) from which we concluded that a high TOC dosage is needed in order to obtain a sufficiently large difference in CO_2 emission rates between the treatments and the control. When the dosages are expressed per hectare of soil, assuming that the product is mixed homogenously through a 25 cm thick soil layer with a bulk density of 1000 kg/m^3, the dosages are far above N and P application limits. For the P-poor organic soil improver, the dosage corresponds to 18 ton organic matter, 306 kg N and 159 kg P_2O_5 per hectare. For the compost, the dosage corresponds to 18 ton OM, 720 kg N and 530 kg P_2O_5 per hectare.

The carbon mineralisation experiment was performed through incubation of 100 gram soil in a 0.7 L incubation flasks. The soil was thoroughly mixed with the respective organic fertilising products and N fertiliser and thereafter brought to 60% of the soil's water-holding capacity. The amount of water added was corrected for the amount of water supplied with manure and mineral N fertiliser.
The water-holding capacity was determined visually by adding water to the soil until the point where the soil becomes muddy. The treatments were performed in triplicate resulting in 15 flasks. Concentrations of CO_2, N_2O, and CH_4 in the headspace were measured after 1, 3, 10, 17, 31, 44 and 87 days. The flasks were initially flushed with air and thereafter closed for 1-8 hours in order to allow CO_2 to accumulate. The gas composition was measured by a photo acoustic infra-red gas monitor (Innova 1312). The headspace volume amounted to 531 mL was determined at the end of the experiment by defining the volume of water needed to fill the flask.

The mineralisation experiment was performed through incubation of 100 gram of soil in polyethylene bags (Audiothene 0.10 mm), which is permeable to O_2 and CO_2 but impermeable to water. Samples were prepared as described above for the humification rate experiment. There were six sampling times (day 0, 10, 17, 31, 44 and 87) and treatments were triplicated resulting in 90 single bags. Upon sampling, soils were dried at 40 ºC and thereafter analysed. Dried soil was extracted with 10 mM $CaCl_2$ using a soil solution ratio of 0.1 kg/L and an extraction time of 2 hours. The supernatant was filtrated over a filter with a pore size of 0.45 uM prior to analysis of N-NH_4, N-NO_3, N-total and dissolved organic carbon (DOC).

The samples were initially stored in a climate room controlled at 20 degrees C. In the period between the 44th and 87thday, the laboratory moved to another building in which the climate-conditioning system was not yet working satisfactory and as a result the temperature was above 20 ºC.

The humification coefficient at 10 ºC was calculated using a two-pool model as described in Van Groenigen and Zwart (2007).

Tabel 6.1 *Dissolved nitrogen and dissolved organic carbon (DOC) in the fresh Droevendaal soil prior to the incubation experiments*[a]*.*

Soil	**N-NH4 (mg/kg)**	**N-NO3 (mg/kg)**	**N-total (mg/kg)**	**DOC (mg/kg)**
Droevendaal soil	<0.1	2.3	3	4

[a] Determined after extraction of the fresh soil with 10 mM CaCl2 in a 0.1 kg/L soil to solution ratio.

Tabel 6.2 *Composition of the P-poor organic soil improver (SI) and compost.*

Product	**DM (%)**	**OM (%)**	**N-t (g/kg)**	**TOC (g/kg)**	**C/N (-)**	**N-NH4 (mg/kg)**	**N-NO3 (mg/kg)**
SI	34	89	5.2	153	29	478	44
VFG Compost[b]	55	25	5.5	69	13	2	1

[a] DM; dry matter content determined at 105 ºC, OM; organic matter content determined as loss-on-ignition at 650 ºC, N-t was determined after destruction with H2SO4-Se, N-NH4 and N-NO3 were determined after extraction with 10 mM CaCl2.

[b] Vegetable, fruit and garden waste compost (VFG) of Attero B.V., Venlo

Tabel 6.3 *Dosages of P-poor organic soil improver or compost and their corresponding organic carbon (TOC), nitrogen and phosphate dosages per kg of soil in the treatments of the incubation experiment.*

Treatment	Product	Product dosage per kg of soil Dosage (g/kg)	TOC (g/kg)	N (mg/kg)	P (mg/kg)	Additional N fertiliser Additional N[a] (mg N/kg)	C/N ratio[b] (g/g)
SI-1	Organic soil improver	20	3	102	40	0	29
SI+N	Organic soil improver	20	3	102	40	12	26
SI+2N	Organic soil improver	20	3	102	40	30	21
Compost	VFG Compost	24	3	242	50	0	13
Control	-	-	-	-	-	-	

[a] Additional mineral N was given as NH4-NO3 solution

[b] C/N ratio of the organic soil improver or compost including the additional nitrogen.

6.2.3 Water-extractable nutrients and physical properties

Water-extractable nutrients, physical properties including bulk density, pF curves and shrinkage, and the oxygen consumption rate were analysed by the laboratory of Eurofins, Wageningen (RHP, Potting soil certificate[6])

6.3 Results

6.3.1 Product composition

Table 6.4 gives the composition of the P-poor organic soil improver as produced in two separate pilot tests. Batch B67 was also used in the incubation experiments whereas B80 was used for further testing on parameters relevant for potting soil (Regelink *et al.*, 2019).

The P-poor organic soil improver consists dominantly of OM (>88%). The two batches differ somewhat with respect to their P-content (1.2 and 2.0 g/kg) which may be due to variations in time in the amount and type of organic P present in the co-digested material from Groot Zevert Vergisting B.V. Organic P cannot be solubilised and removed with sulphuric acid.

The sulphur content of the P-poor soil improver amounted to 4.2-4.3 g/kg and did not differ between the two batches though the batches were obtained through different process steps. For B80, the solid fraction of manure was diluted with groundwater, acidified with sulphuric acid to pH 5 and thereafter dewatered by means of a screw press. This process was repeated twice. For B67 process water from the previous batch was used for dilution rather than groundwater. The solid fraction was acidified twice and the process water was reused during eight subsequent cycles. This process is described in detail in Chapter 2. Recirculation of process water was expected to lead to a higher sulphur content in the end product due to accumulation of sulphate in the process water. However, this was not the case due to the fact that the calcium phosphate product was recovered as a slurry with a DM content of only 6%. Hence, the majority of the sulphate left the system via the water phase of the calcium phosphate slurry. Once the precipitated phosphate product can be dewatered to a DM content of about 30%, the P-poor organic soil improver will have a higher sulphur content (Chapter 5).

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[6] https://www.rhp.nl/en/product/potting-soil

Table 6.4 *Composition of the P-poor organic soil improver[1].*

Parameter		B67 (2017)	B80 (2018)
Recirculation process water		YES	No
Dry matter	(%)	32	38
Organic matter	(%)	88	90
pH-KCl	(-)	5.9	5.7
P	(g/kg)	1.2	2.0
N	(g/kg)	4.8	5.4
Ca	(g/kg)	3.8	6.0
Mg	(g/kg)	0.8	1.3
K	(g/kg)	1.0	2.6
Na	(g/kg)	0.4	1.7
S	(g/kg)	4.2	4.3

[1] Dry matter determined at 105 ºC, organic matter determined as loss-on-ignition at 650 ºC. pH measured in a 1 M KCl extract. Total amount of elements determined after destruction with H2SO4-Se (N) or Aqua regia (P, Ca, Mg, K, Na, S)

6.3.2 Carbon mineralization rate of the P-poor organic soil improver

An incubation experiment was performed with the P-poor organic soil improver in order to assess the carbon mineralisation rate and to calculate the humification coefficient.

Figure 6.1 shows the CO_2 production rate measured over the course of the incubation experiment. The lowest CO_2 production rates were measured in the control treatment. The treatment with compost showed elevated CO_2 production rates compared to the control. Treatments with the P-poor organic soil improver showed substantial higher CO_2 production rates as compared to the compost treatment. The dosage of additional mineral N did not affect CO_2 concentrations during the first 44 days of the incubation experiment indicating that the degradation of OM was not hampered by the C-N ratio of the P-poor organic soil improver. However, at the last measurement point (day 88), CO_2 production rates were higher in the SI+2N treatment as compared to the SI and SI+N treatment. It remains unclear whether this effect is due to the addition of N or due to some other artefact. In all treatments, CO_2 production rate were somewhat higher at day 88 as compared to day 44 which was against our expectations. In between day 44 and day 88, the samples had to be moved to another laboratory were the climate control was not yet working perfectly and we expect that this may have affected the CO_2 production rate. We therefore excluded data for day 88 in the calculation of the humification coefficient.

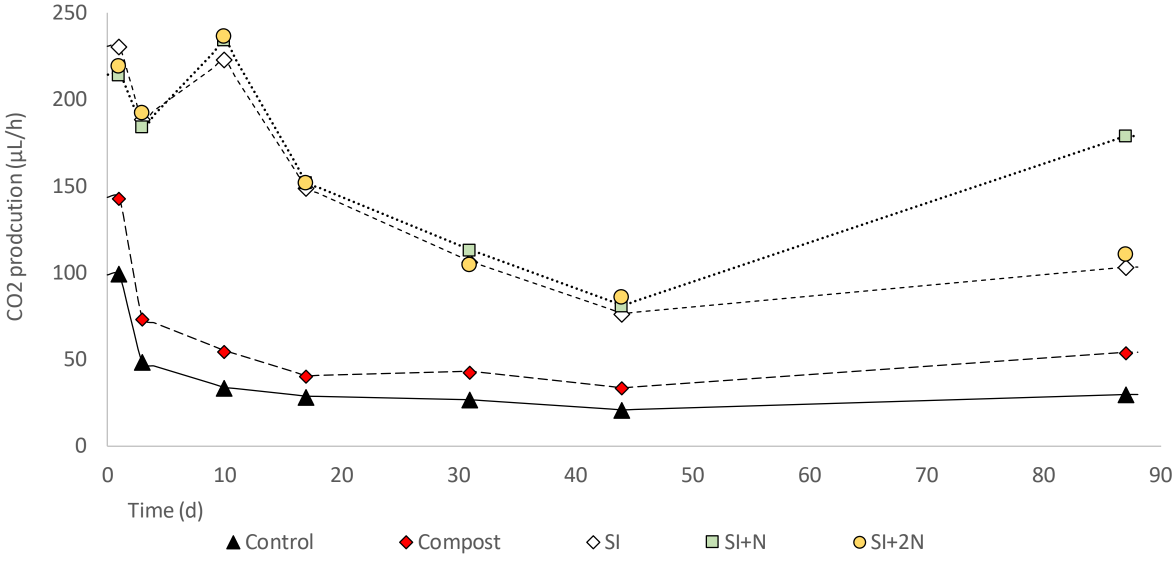

Figure 6.7 *Average CO2 production rate in the incubation flasks (n=3) over the course of the incubation period for treatments with compost, P-poor organic soil improver (SI) with and without additional NH4NO3 (SI+N, SI+2N), and the control treatment. Dashed lines were calculated through linear interpolation.*

Table 6.5 shows the cumulative amount of CO_2 released over the course of the incubation experiment and shows it as a percentage of the amount of added total organic carbon (TOC). After 44 days, 22% of the TOC added as P-poor soil improver was dissimilated. For compost, 3% of the added TOC was dissimilated after 44 days.

Table 6.5 *Cumulative CO_2 release from soil for the various treatments with P-poor solid organic soil improver (SI), compost and the blanc treatment (n=3).*

Treat-ment	TOC added	Cumulative CO_2 release (mg C-CO_2/kg soil)							% of TOC added	% of TOC added
	(g/kg)	t1	t3	t10	t17	t31	t44	t87	T44	T88
SI-1	3	17	69	221	356	533	645	(1005)	22%	33%
SI+N	3	15	63	219	359	546	667	(1251)	22%	42%
SI+2N	3	15	67	226	368	546	664	(1069)	22%	36%
VFG Compost	3	6	19	40	54	79	103	(205)	3%	7%
Control	0	13	41	77	105	154	193	(332)		

[a] Cumulative amount of CO_2 released from treatments with organic products minus the cumulative CO2 released from the control treatment.

VFG compost = compost of vegetable-, fruit- and garden waste

The laboratory data obtained over a period of 44 days were used to fit a two-pool model (as described in Van Groenigen and Zwart, 2007),the model was thereafter extrapolated in order to predict the amount of organic carbon left after one year at 10 ºC. The percentage of added carbon that remains in the soil after one year is called the humification coefficient and is given in Table 6.6. For the P-poor organic soil improver, the calculated humification coefficient amounts to 70% whereas the VFG compost was found to have humification coefficient of 90%. For comparison, humification coefficients of other organic products were taken from literature. Humification coefficients for organic manure and other products were taken from the 'Handboek Bodem en Bemesting'. With the exception of dairy slurry since recently, the Dutch 'commissie deskundigen meststoffen (CDM[7])' advised, based on a literature study and own measurements, to use a humification coefficient of 45% for dairy slurry rather than 70% as is given in the Handbook. Comparison of the humification coefficients shows that the humification coefficient of the P-poor soil improver lies in-between those of non-treated manure and compost.

Table 6.6 *Humification coefficient, i.e. the percentage of organic carbon remaining in the soil after 365 days at 10 ºC, of the P-poor organic soil improver, GFT compost and reference products[a]*

Product	Humification coefficient at 10 ºC (%)
P-poor organic soil improver (this study)[a]	70
VFG Compost (this study)[a]	92
VFG compost b	90
Champost, (spent mushroom compost)[b]	50
Pig manure – slurry[b]	33
Cattle manure – slurry[c]	45
Chicken manure[b]	33

[a] Calculated using a two-pool model as described in Van Groenigen and Zwart (2007).

[b] Humification coefficients taken from 'Handboek Bodem en Bemesting' Tabel 9.3, accessible via www.handboekbodemenbemesting.nl

[c] Humification coefficient of dairy slurry is 45%, following the advice of CDM (Oenema, 2017) accessible via http://library.wur.nl/WebQuery/wurpubs/539359

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[7] CDM-advies 'criteria voor organische stofrijke meststoffen' 29-11-2017 https://library.wur.nl/WebQuery/wurpubs/539359

6.3.3 Nitrogen Mineralisation Rate

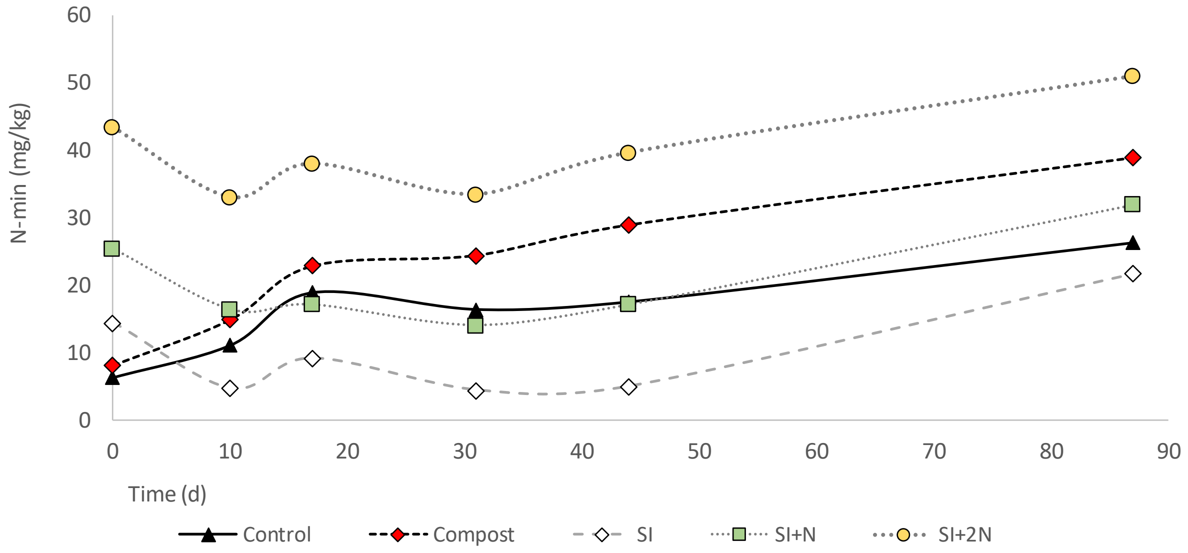

Figure 6.2 *Average N-min (N-NH4+N-NO3) concentration in the soil, expressed in mg per kg soil, during the incubation experiment in treatments with compost, P-poor organic soil improver (SI) with and without additional NH4NO3 (SI+N, SI+2N) and the control treatment (n=3).*

Figure 6.2 shows the mineral N (N-min =N-NH_4+N-NO_3) concentrations in the soil during the incubation experiment. For the P-poor soil improver , nitrogen immobilisation occurred during the first 44 days of the incubation experiment. During this period, the N-NH_4 concentration decreased while the N-NO_3 concentrations increased. This means that the soils remained aerobic and that we can probably exclude gaseous nitrogen emissions due to anaerobic conditions. However, also under aerobic conditions, gaseous emissions of nitrogen can occur which we cannot exclude. After 44 days, the mineral N concentration in the soils slowly increased but remained below that of the control treatment. At day 88, the amount of immobilised N amounts to 0.2 g per kg soil improver which is equal to 4% of its total N content (Table 6.7). Compost shows a continuous increase in N-min due to nitrogen mineralisation. Nitrogen mineralisation from compost amounts to 0.3 g/kg compost or 5% of its total N content over a period of 88 days.

Tabel 6.7 *Measured nitrogen mineralisation in mg/kg product for P-poor organic soil improver and compost during 88 days of incubation at 20 ºC.*

Product	Product composition N-t (g/kg)	 N-min (g/kg)	 N-mineralised (88 days) (g/kg)	 (% of Nt)
P-poor organic soil improver	5.2	0.522	-0.23	-4
VFG Compost	5.5	0.003	+0.29	5

6.3.4 Organic matter as potting soil ingredient

The organic soil improver separated from digestate has a fibrous structure and is free from odours. Table 6.8 shows the parameters which are of major concern for potting soil ingredients. The organic soil improver has a porosity of 90% and a for plants easily available water content of 35% which reflects the fibrous nature of the product. In terms of physical properties, the organic soil improver meets all criteria for potting soil. The oxygen consumption rate is somewhat larger than desired for potting soil indicating a risks for anaerobic conditions in the material. The EC value and sodium concentration also exceed the criteria for a potting soil mix. Potting soils always consists of multiple ingredients and hence the organic soil improver could be mixed with a low-salt product such as peat to create a mixture that meets the criteria.

As explained in Chapter 5, the demonstration plant will produce an organic soil improver with a higher salt content as compared to the pilot installation. This is due to a substantial increase in the water use efficiency and hence a lower water refreshment rate. Hence, to obtain a product with a similar EC value as tested in this study, the demonstration plant shall be equipped with a third leaching step in which salts, in particular sulphate, are removed from the organic soil improver. The perspectives for the use of organic soil improver as potting ingredient depend therefore on the possibility to discharge the sulphate rich leachate against low costs. Since this leachate contains hardly any salts or contaminants except for sulphate, discharge to the sewer may be an option.

This is an exploratory assessment. Follow-up work should also include analyses on pathogens, micro-pollutants (herbicides, pesticides, veterinary medicines) and phytotoxic substances.

Table 6.8 *Assessment of organic soil improver from digestate on criteria for potting soil.*

Product	unit	Organic matter	Criteria potting soil mix
Water max	%-v/v	89	>50
Easily available water	%-v/v	35	>25
EC value	dS/m	2.6	<1.0
Sodium	mmol/L	2.8	<1.0
Dry bulk density	kg/m^3	142	-
Bulk density	kg/m^3	410	-
Porosity	%-v/v	90	>60
Shrinkage	%-v/v	17	<25
Oxygen consumption rate	mmol/g/h	14	<10
pH	(-)	5.5	<6.0

6.3.5 Fertilisation schemes

Table 6.9 gives the composition of the P-poor soil improver and other organic fertilisers including manure and compost. The ratio between phosphate and OM determines the amount of OM that can be applied within the P-application limits. For dairy manure, for example, each kg of phosphate comes with 47 kg of OM of which 33 kg is EOM, meaning that it remains in the soil for at least one year. For the P-poor soil improver, the EOM/P_2O_5 ratio amounts to 75 kg/kg meaning that a farmer can apply 2.3 times more OM per kg of phosphate as compared to dairy manure. For VFG and green compost, the EOM/P_2O_5 ratio amounts to 90 and 146 kg/kg, taking into account the 50% exemption for P_2O_5.

Table 6.9 *Composition of organic fertilising products in kg per ton product[a].*

Product	DM	OS	OS	HC	EOM	P_2O_5	OS/P_2O_5	EOM/P_2O_5	N	N-min	S[e]
	(kg/ton)	(% of dm)	(kg/ton)	(%)	(kg/ton)	(kg/ton)	(kg/kg)	(kg/kg)	(kg/ton)	(kg/ton)	(kg/ton)
P-poor solid fraction of co-digested pig slurry[b]	340	90	306	70	214	2.8	109	75	5.2	0.5	7-14[e]
Solid fraction of co-digested pig slurry[b]	316	75	237	-	-	18	13		12	3	
VFG Compost[b,f]	550	25	140	92	129	2.1 (4.1)	68	62	5.5	3	*n.d.*
VFG Compost[c,f]	696	35	242	90	218	2.2 (4.4)	110	90	8.9	0.8	*n.d.*
Champost, spent mushroom compost[c]	336	63	211	50	106	4.5	47	24	7.6	0.4	*n.d.*
Green Compost[c]	599	30	179	90	161	1.1 (2.2)	162	146	5.0	0.8	*n.d.*
Pig manure – slurry[d]	107	74	79	33	26	3.5	23	7	5.0	3.3	0.6
Dairy manure – slurry[c]	92	77	71	45[c]	32[c]	1.5	47	33	4.0	1.9	0.7
Chicken manure[c]	562	74	416	33	137	23	18	6	28.4	2.9	2.5

[a] DM.; dry matter content, OM; organic matter, HC; humification coefficient, EOM: effective organic matter, defined as the amount of organic carbon present in the product after one year in the field, N-min: NH_4+NO_3. nd.: no data

[b] This study

[c] Data taken from 'Handboek Bodem en Bemesting' Tabel 9.3, accessible via www.handboekbodemenbemesting.nl

[d] Humification coefficient of dairy slurry is 45% as obtained from CDM[8]

[e] The sulphur content is expected to lay between 7 and 14 g/kg depending on whether the formed gypsum is recovered as a separate product or not. Mass balance calculations and underlying assumptions are given in §5.2 and §5.3.

[f] Values for compost are calculated taking into account the 50% exemption for P2O5. Actual P content is given in between brackets.

Table 6.10 shows some example fertilising schemes with manure, P-poor soil improver and compost. The phosphate dosage of each scheme is 60 kg/ha, which is the Dutch P-application standard for arable soils with a neutral P status. By replacing 10% of the applied amount of phosphate organic soil improver, the EOM application rate increases by 50% and 180% respectively, as compared to a situation in which only dairy slurry or pig manure is given. The corresponding sulphur application rate amounts to 30 kg S/ha. The sulphur application rate was calculated with the assumption that the P-poor OM has a sulphur content of 7 g/kg. This corresponds with a situation in which the gypsum is recovered as a separate product. An application rate of 30 kg S/ha is at the upper side of the sulphur fertiliser advice for arable crops. For example, advised sulphur fertiliser application rates vary between 10-30 kg/ha for maize and 0-10 kg/ha for potato and wheat[9]. In case gypsum is not recovered as a separate product, the sulphur content of the P-poor OM will be twice as high and hence, the product application rate must be lowered with a factor two in order to prevent over-fertilisation with respect to sulphur. Though no application standard exists for sulphur, excessive application rates must be prevented from an environmental point of view. For the other organic manure products, sulphur was not included in the fertilisation schemes this sulphur is partly or dominantly present as organic sulphur which is not directly available for plants[10]. For the P-poor soil improver however, sulphur is dominantly present as sulphate which originates from the sulphuric acid used in the extraction process.

The amount of N added with the P-poor soil improver is very small and amounts to 22 kg N/ha in the example fertilisation scenario's. The effect of N immobilisation on N availability is also very small.

In the laboratory, N immobilisation amounted to 0.5 g N per kg soil improver (day 88). With a soil

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[8] CDM-advies 'criteria voor organische stofrijke meststoffen' 29-11-2017 https://library.wur.nl/WebQuery/wurpubs/539359

[9] www.bemestingsadvies.nl

[10] http://eurofins-agro.com/nl-nl/expertise/bemesting/artikelen/s-advies-aangepast-op-geringe-depositie

improver dosage rate of 4 ton/ha, nitrogen immobilisation amounts to 1.6 kg N/ha. Hence, if a farmer applies 250 kg N/ha, less than 1% will be immobilised. This N is temporarily fixed within bacterial biomass which grew on the P-poor soil improver.
In the calculated fertilisation scenario's, the organic soil improver application rate amount to 4 ton of product per hectare per year. This is too little to be spread over the field as is done for f.e compost or solid manure. It may therefore be practical to mix the P-poor soil improver with liquid manure such as dairy- or pig slurry or with the liquid fraction of digestate. The organic enriched manure can then be applied with a common manure injector. Also, blending the organic product with f.e. compost or solid manure products is an option.

When P-poor OM is mixed with other types of manure and fertilising products, preventative measurements must be taken to minimize the risk of hydrogen sulphide (H_2S) gas formation. H_2S is a highly toxic compound which can form under anaerobic conditions. Any type of manure and digestate is a potential source for the formation of H_2S but the addition of sulphate or sulphur-rich products may raise the risks for H_2S formation. Formation of H_2S gas requires anaerobic conditions where sulphate (SO_4^{2-}) is microbially reduced to sulphide (S^{2-}) which can subsequently form H_2S. The latter step is pH-dependent, H_2S formation increases with decreasing pH. The addition of fresh manure, which contains biodegradable substances, increases the risk for anaerobic conditions and thereby the risk for sulphide formation. It is important that employees on manure treatment plants and farmers, who work with untreated manure or digestate, are well informed about the risks for H_2S formation and that precautions are taken to minimize the risks for intoxication by H_2S. To prevent H_2S formation, mixing P-poor organic soil improver with manure should occur shortly before application to the field.

Table 6.10 *Possible fertilisation schemes for combinations of manure and P-poor organic matter. Each scenario adds up to 60 kg P_2O_5/ha[a].*

Scenario	Product (ton/ha)	P_2O_5 (kg/ha)	N (kg/ha)	N-min (kg/ha)	OM (kg/ha)	EOM (kg/ha)	S-min[b] (kg/ha)
1. Dairy slurry							
Dairy slurry	40	60	160	76	2840	1278	-
2. Pig slurry							
Pig slurry	17	60	86	57	1354	446	-
2. Dairy slurry plus nutrient poor organic soil improver from digestate							
Dairy slurry	32	48	128	61	2272	1022	-
P-poor OM	4	12	22	2	1311	917	30
SUM		60	150	63	3583	1940	30
3. Pig slurry plus nutrient poor organic soil improver from digestate							
Pig slurry	14	48	69	45	1083	357	-
P-poor OM	4	12	22	2	1311	917	30
SUM		60	91	47	2395	1274	30

[a] N-min: Mineral nitrogen; OM = organic matter; EOM = effective organic matter.

[b] S-min: Mineral sulphur. For the P-poor solid fraction, we used a sulphur content of 7 g/kg. Sulphur in manure and compost is dominantly present as organic sulphur and therefore excluded. '-' = not calculated.

6.4 Conclusion

The P-poor organic soil improver has a P content of about 1.2 - 2 g/kg, an N content of 4.8 – 5.4 g/kg and contains 88% OM based on its DM content. The humification coefficient is 70% and was derived from the CO_2 production in an incubation experiment. This is lower than the humification coefficient derived for VFG compost, which was 92%. The P-poor organic soil improver contains nearly no mineral nitrogen and upon incubation some was immobilised due the high C/N ratio of the product (C/N = 29).

The ratio between P_2O_5 and OM is similar to that of compost (taking into account the 50% exemption for P_2O_5 in compost) and this allows farmers to apply a large amount of OM on their field within the P application limits. Example fertilisation schemes show that by replacing 10% of the phosphate gift by phosphate in P-poor organic soil improver, the EOM application rate increases with 50% and 180% compared to fertilisation with respectively only dairy slurry or pig manure. With this product dosage, sulphur application rates are still within the advised fertilisation rates and N immobilisation is less than 2 kg N/ha.

7 Business case

7.1 Costs for chemicals

Sulphuric acid consumption

The acid consumption rate was determined previously in lab- and pilot tests and varies between 17 and 32 L 96% (w/w) sulphuric acid per ton of solid fraction of digestate. The largest acid consumption was measured in pilot tests in 2018 during which a solid fraction was used with a P content of 11 g/kg. This content is far above the normal P content of about 6-8 g/kg. On average, the acid consumption amounts to 24 L 96% (w/w) sulphuric acid per ton of solid fraction and this value is used in the business case. For the quantities needed at Groot Zevert Vergisting B.V., this chemical can be delivered in bulk for a price of €92,- per ton (personnel communication with Dutch suppliers).

Table 7.1 *Sulphuric acid dosage determined in lab and pilot test expressed in L and kg 96% sulphuric acid and accompanying costs, all expressed per ton of solid fraction of digestate*[a]*.*

	96% sulphuric acid (L/ton SF)	96% sulphuric acid (kg/ton SF)	Price (€/ton SF)
Lab results 2017b	17	31	€2.90
Pilot test 2017c	22	39	€3.60
Pilot tests 2018d	32	58	€5.40
Average	24	42	€3.98

[a] 96% (w/w) sulphuric acid, density 1.8 kg/L, H_2SO_4 content of 1762 g/L, price €92,-/ton

[b] Schoumans *et al.*, 2018.

[c] solid fraction was acidified twice, see Chapter 2

[d] Average of four batches, solid fraction was acidified once

Magnesium consumption

In continuous flow laboratory experiments, 27 L (35 kg) of 55% (w/w) $Mg(OH)_2$ solution was dosed per ton of solid fraction. This amount was needed to maintain the pH in the precipitation beaker above 7.5 which was found to be sufficient for a nearly complete P removal (§3.3.4). In batch experiments not all added $Mg(OH)_2$ was consumed due to the slow reaction rate of $Mg(OH)_2$ with ortho-phosphate. Therefore higher $Mg(OH)_2$ dosages were used in the batch tests. a 55% (w/w) $Mg(OH)_2$ suspension can be purchased for about €250,- per ton of product (personal communication with Dutch suppliers). Hence, the costs for $Mg(OH)_2$ amount to €8.75 per ton solid fraction of digestate. a cheaper alternative is a 99% (w/w) magnesium oxide (MgO) powder which can be purchased for about €300,- per ton. a dosage of 11 kg MgO per ton solid fraction would be sufficient if we assume that the reactivity of MgO is similar to that of $Mg(OH)_2$. Under that assumption, the costs for MgO amount to €3.30 per ton of ingoing solid fraction of digestate. However, it may be that solid MgO has a lower dissolution rate than $Mg(OH)_2$ in suspension. Therefore somewhat larger amounts may be needed. The $Mg(OH)_2$ suspension underwent a wet-milling treatment which gave it a higher reactivity compared to the solid MgO. Besides, particle size and hence reactivity of $Mg(OH)_2$ and MgO may differ among different products and suppliers. Prices may also differ between suppliers..

Magnesium chloride is substantially cheaper than $Mg(OH)_2$ and is often used in struvite reactors on WWTP's. However, magnesium chloride does not increase the pH value and is therefore of no use in the RePeat system without the purchase of another base.

Tabel 7.1 *Required dosage and costs for using 55% (w/w) $Mg(OH)_2$ suspension or 99% (w/w) MgO powder per ton of ingoing solid fraction of digestate.*

	55%, $Mg(OH)_2$ (l) (kg/ton SF)	99%, MgO (s) (kg/ton SF)	55%, $Mg(OH)_2$ (l) (€/ton SF)	99%, MgO (s) (€/ton SF)
Lab tests 2018	29	11a	€8.75	€3.30[a]

[a] Tests were performed using 55% (w/w) $Mg(OH)_2$ suspension. The required amount of MgO has been calculated assuming a similar reaction efficiency of MgO compared to $Mg(OH)_2$ though the reaction efficiency of MgO is likely somewhat lower.

7.2 Market value products

Struvite

The production of struvite requires a continuous flow precipitation reactor. Since the pilot installation was not equipped to be operated in a continuous mode, the struvite precipitation process was only tested in laboratory and short-term pilot tests. As a consequence, the struvite we produced in our tests may not be representative for the struvite that will be produced by a full scale continuous installation. Since struvite recovery is a well-known process, we can make use of knowledge on process parameters and technology from literature and from operators of struvite reactors on waste-water treatment plants. With a so-called continuously stirred-tank reactor, operators can produce struvite with a grain size similar to that of coarse sand. This struvite does not require a thermal drying step. For the business case, we therefore assume that the RePeat system produces a struvite material with a DM content of more than 50% and is a stackable material that can be disposed of as ingredient for the production of fertiliser without further treatment. Struvite from communal WWTP's contains between 17-30% P_2O_5[11] and has a market value of €50,- to €60,- per ton of struvite[12]. We assume that struvite from manure has a similar market value though it is difficult to estimate whether the fertiliser industry is indeed willing to pay this amount for struvite from manure. The price for struvite from manure also depends on upcoming regulation regarding the 'end-of-manure' criteria for products from manure and new EC fertiliser regulations. If struvite from manure can be used as an ingredient for an EC fertiliser product, its market value may rise.

P-poor organic matter – Soil improver

The composition of the P-poor OM equals that of other soil improvers such as compost. The EOM content per ton of product is similar to that of VFG[13] compost. The ratio (P_2O_5/EOM) is twice as high as for VFG compost and similar if we take into account the 50% deduction for P_2O_5 in compost for the P-application standard. We therefore use the market price of VFG compost as an indicator for the market price of the P-poor OM. VFG compost is usually sold for about minus €5 to plus €5 per ton including transport costs which are paid for by the farmer.

P-poor organic matter – Ingredient for potting soil

Alternatively, the fibrous OM may be a suitable ingredient for the production of potting soil and hence an alternative for peat in potting soil. The physical properties of the OM meet all requirements set by potting soil producers. Hygienisation is required to kill pathogens seeds and other propagules. At the demonstration plant Groot Zevert Vergisting B.V., the solid fraction of digestate is hygienisized prior to the RePeat process. a description of the market for potting soil ingredients and a detailed assessment of the quality of the produced OM in terms of potting soil, including results of pot trials, is available elsewhere (Regelink *et al.*, *in progress*). Potting soil producers are interested in alternatives for peat. Assuming that all requirements including the limit for EC are met, the market price for a potting soil ingredient from digestate can be assumed to be similar to that of low-salt green compost used in potting soil and amounts to about €13,- to €18,- per m^3 of product. For comparison, potting soil producers pay about €30,- per m^3 for sphagnum peat. Potting soil producers pay per m^3 of product rather than per ton of product. The fibrous nature and therefore low bulk density of the P-poor organic soil improver (400 kg/m^3) is thus beneficial for the price. P-poor organic soil improver as a potting soil

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[11] Data supplied by Aqua Minerals for struvite from Amsterdam, Beverwijk and Land van Cuijk

[12] personnel communication with operators from Dutch WWTP's

[13] VFG compost: Compost from source-separated vegetables, fruit and garden waste

ingredient would thus have a market value of €32,50 to €45,00 per ton of product. Besides the much higher price, it is also advantageous that potting soil producers need ingredients year round and hence, no storage is needed.

Gypsum-rich organic sludge

Gypsum can be recovered in the sludge of the settler positioned after the first screw press together with the fine organic particulate matter in the sludge. This sludge has a rather low P content of 2 g/kg and can be blended with manure or the liquid fraction of digestate. Due to the rather low N- and P content, we assume that disposal costs are similar to those for dairy slurry (€12.00).

7.3 Business case

Reference scenario

The reference situation is here defined as the costs for disposal of the solid fraction of digestate. Hence, disposal of the liquid digestate fraction is not included in this business case because the RePeat system uses the solid fraction of the digestate as a starting point. Costs for disposal of the solid fraction of digestate, which has a P_2O_5 content of about 14 g/kg, amount to €25.00 per ton including transport to the Eifel region in Germany (personal communication Groot Zevert Vergisting B.V.). a manure treatment plant with a capacity of 100,000 ton manure per year produces about 16,000 ton of solid fraction. In the reference scenario, overall costs for disposal of 16,000 solid fraction of digestate amount to €400k per year.

The liquid manure fraction can be disposed of within The Netherlands on arable soils. This is however rather costly due to long transport distances and the low nutrient content of the liquid fraction and consequently high amount of water. Groot Zevert Vergisting B.V. has therefore decided to invest in a reverse osmosis system mainly to discharge a part of the water directly to the surface water and to produce an NK concentrate. The disposal and/or treatment of the liquid fraction are not considered in the business case. In the business case, we compare a situation in which solid fraction of digestate is disposed of against a situation in which the solid fraction is treated with the RePeat system. Also, revenues from the biogas production are not included in the business case.

Production of struvite and organic soil improver

The business case for the scenario in which the solid fraction of digestate is processed into P-poor organic soil improver, struvite and a gypsum-rich organic sludge is given in Table 7.2. Investment costs are estimated to amount to €700k for an installation with a capacity of 16,000 ton solid fraction per year, which is equivalent to 1.8 ton/hour. The investment costs include all necessary mixing tanks, a struvite precipitation tank, screw presses, buffer tanks, piping, pumping equipment, a settler to remove fine suspended particles prior to struvite precipitation and a settler to separate struvite particles. However, investment costs for decanters for the separation of digestate into a liquid and solid fraction, a hygienisation unit for the solid fraction and air washers are not included.. We calculated the depreciation costs over a period of ten years and assume 7% maintenance costs. Additionally, personnel costs for 0.25 fte are included to operate the installation. Costs for chemical consumption are calculated as described in § 7.1.1. In this example, we assumed usage of the solid MgO product rather than the 2.5 times more expensive $Mg(OH)_2$ suspension. It must however be said that all experiments have been done with the $Mg(OH)_2$ suspension and hence, it is unknown whether MgO has a similar efficiency. Costs for electricity consumption were calculated based on the sum of the power of each separate unit and amount to 20 kWh per ton solid fraction. Costs for electricity were calculated assuming a price of €0.06/kWh. Estimates for product revenues or disposal costs are underpinned in §7.1.2

The yearly costs add up to €270k of which €51k is earned back through the sale of products. The nett costs for treatment of 16,000 ton of solid fraction amount to €218k which results in a €181k profit compared to the reference situation for disposal of untreated manure. The treatment and disposal costs amount to €13.70 per ton of solid fraction which is 45% lower than current disposal costs for the solid fraction of manure.

Table 7.2 *Business case for treatment of 16,000 ton of solid fraction of digestate per year with the RePeat system.*

Reference case – Disposal of solid mineral-rich organic fraction			
	ton/y	€/ton	€/year
Disposal of untreated solid fraction	16,000	€-25.00	€-400,000

Scenario: P-poor organic matter as soil improver			
	Production (ton/y)	Product price (€/ton)	
Investment costs		€700,000	
Depreciation (10 y)			€70,000
Maintenance (7%)			€49,000
Personnel, 0.25 fte			€15,000
Sulphuric acid		€4.00/ton SF	€64,000
Magnesium oxide powder		€3.30/ton SF	€52,800
Electricity consumption			€19,200
Yearly costs			€270,000
Product revenues	Ton product/y	Product price (€/ton)	
P-poor organic matter	11,680	€0.00	€0.00
Struvite	1760	€50.00	€88,000
Gypsum-rich sludge	3000	€-12.00	€-36,480
Yearly revenues			€51,520
Nett (costs – revenues)			€218,480
Profit compared to reference case			€181,520

Organic matter as secondary raw material for potting soil production

Another scenario may be the sale of the fibrous OM as ingredient for potting soil against a price of €37,- ton OM (§7.1.2). Revenues from OM would then increase to €430k. In order to be suitable for application as potting soil ingredient, the OM needs to be leached with clean water in order to lower the salt content. This generates an additional waste stream of 700 L of water per ton of solid fraction. As described earlier, we assume that this leachate, which merely contains sulphate and other salts, can be discharged on the sewage system, be cleaned by reverse osmosis or can be blended with the liquid fraction of manure. Costs for the treatment of the leachate by reverse osmosis are estimated on €8-10,- per m^3 of water. Costs for disposal to the fields are estimated to amount to €12 to €15 per ton. Assuming the latter value, disposal costs for the leachate (12,000 ton/year) would amount to €183k which is still low compared to the revenues of the organic soil improver when sold as potting soil ingredient.

Calcium phosphate instead of struvite

Calcium hydroxide is a cheaper alternative for $Mg(OH)_2$. The $Ca(OH)_2$ consumption, as determined in the pilot test, amounts to 55 kg of a 30% (w/w) $Ca(OH)_2$ suspension which is equivalent to 36 kg of 45% (w/w) $Ca(OH)_2$ suspension (§2.3). Prices mentioned by suppliers with activities in The Netherlands vary between €100-130 per ton for a 45% (w/w) $Ca(OH)_2$ suspension delivered on-site. Assuming a consumption rate of 36 kg per ton solid fraction, costs would amount to €3.60 - €4.68 per ton solid fraction. a solid $Ca(OH)_2$ product costs about €100 per ton, and is thus twice as cheap when the price is expressed per mole OH^-. Costs would then decrease to about €2.00 per ton solid fraction. However, the use of a solid product requires on-site mixing in order to prepare a suspension.

However, precipitation of calcium phosphate results in a poorly dewaterable sludge. At low flow rates (a decanter with flows < 1 m^3/h) a relatively dry product can be made (DM content of 30%. However at high flow rates a sludge with a low DM content of only 6% is produced. This sludge needs further processing or drying in order to produce a dry product. Costs for drying are high and therefore drying does not seem to be a reasonable option for a large scale installation like Groot Zevert Vergisting B.V. (100 000 ton digestate production per year).

Overall, this exercise shows that the business case of digestate separation into struvite and OM is profitable. The investment costs are relatively low due to the simplicity of the process and due to the fact that the solid fraction is only 15% of the total mass of the digestate. The costs for chemical consumption are 43% (€116,000) of the total costs (€270,000) but are to a large extent compensated for by revenues from the products. This is particularly the case for a scenario in with the OM is sold to the potting soil industry. By producing economically valuable products, the business case can still remain positive if costs for manure disposal might decrease in the future.

7.4 Conclusion

An example of the business case was worked out for a manure co-digestation plant with a capacity of 100,000 ton digestate per year. Current costs for digestate disposal amount to about €20 per ton. When separated into a solid and a liquid fraction, disposal costs for the solid fraction amount to €25 per ton. With the RePeat process, overall costs for treatment of the solid fraction of the digestate, including costs for chemical consumption, product disposal, depreciation and maintenance, are estimated at €14 per ton solid fraction. Product disposal costs and revenues are determinative for the profitability of the business case. Product revenues are however uncertain and may turn out to be lower than expected.

8 Outlook

This documentation report gives an overview of all tests and analyses which were done to gather information needed for the design of the RePeat demonstration installation which will be built at the anaerobic digestation plant of Groot Zevert Vergisting B.V. (Beltrum). Groot Zevert Vergisting is a frontrunner in the development and implementation of novel nutrient recovery technologies. In 2019, they will turn their anaerobic digester into the first Green Mineral Mining centre[14] producing valuable biobased fertilisers from digestate.

Groot Zevert Vergisting produces about 100,000 tons of liquid digestate per year. After solid-liquid separation, about 16 kton of solid fraction remains which will be treated in the RePeat demonstration installation which has is designed to have a capacity of 2 ton solid fraction per hour. Running 24 hours per day, the plant will produce about 1700 tons of struvite and 12,000 tons of organic soil improver per year.

Groot Zevert Vergisting recently invested in an advanced RO installation to process the liquid fraction into NK concentrates. This product will be blended with other N-rich fertilises such as ammonium-sulphate, ammonia water or urea to produce the 'green meadow fertiliser'. This product is currently still designated as 'animal manure'. However, the Achterhoek region were Groot Zevert is situated received a pilot status and the product can now be used as a replacement for synthetic N fertilisers as part of the four year project "Biobased fertilisers Achterhoek"[15]

Groot Zevert Vergisting is one the five demonstration plants within the H2020 project SYSTEMIC. This project, which runs from 2017 until 2021, aims to demonstrate novel nutrient recovery technologies at an industrial scale. Monitoring of mass- and energy balances, assessment of product quality and environmental benefits, and dissemination of results are important pillars of the project. In the coming years, both the RePeat and GENIAAL process will be monitored as part of the SYSTEMIC project.

At the time of writing, engineering of the RePeat installation is completed and construction has started. Construction is expected to be finished in May 2019. After start-up, the demonstration plant will be monitored on a regular basis. The demonstration plant will be equipped with multiple flow meters, weigh bars and sampling points in order to ensure that a proper mass balance can be constructed. Also, energy use and consumption of chemicals will be documented. Next year's activities will focus on valorisation of the end products and optimisation of the process. This will include research on the plant-availability of P from struvite and the possibilities to valorise the organic matter as potting soil ingredient. In terms of process optimization, research will amongst others focus on lowering the costs for Mg(OH)2 consumption by using alternatives such as CaO or Ca(OH)2 powder that have not been tested before. Another aspect that will receive attention is how to reduce the sulphur content of the organic soil improver by for example precipitating the sulphur as gypsum and recover this as a separate product.

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[14] www.groenemineralencentrale.nl

[15] https://kunstmestvrijeachterhoek.nl/?lang=en

References

Eriksen, J., P Sorensen, L. Elsgaard., 2008. The fate of sulphate in acidified pig slurry during storage and following application to cropped soil. Journal of Environmental Quality 37:280-286

NCM (Nederlands Centrum Mestverwaarding). 2018. Landelijke inventarisatie export en verwerking dierlijke mest 2018.

Regelink, I.C., Blok, C.,. Perspectives for the use of organic fibres from co-digestated manure as potting soil. Wageningen Environmental Research, Wageningen, *In progress*

Oenema, O., 2017. CDM-advies: Criteria voor en samenstelling van organische stofrijke meststoffen. Accessibele via http://library.wur.nl/WebQuery/wurpubs/539359

Schoumans, O.F., P.A.I. Ehlert, J.A. Nelemans, W. van Tintelen, W.H. Rulkens and O. Oenema. 2014. Explorative study of phosphorus recovery from pig slurry. Wageningen, Alterra report 2514.

Schoumans, O.F., P.A.I. Ehlert, I.C. Regelink, J.A. Nelemans, W. van Tintelen and W.H. Rulkens. 2017. Chemical phosphorus recovery from animal manure and digestate; Laboratory and pilot experiments. Wageningen. Wageningen Environmental Research, Report 2849.

Van Groenigen, J.W., Zwart, K., 2007. Koolstof en stikstof mineralisatie van verschillende soorten compost. Wageningen, Alterra, Alterra-rapport 1503.

Annex 1 Data pilot experiment

			Volumetric weight	Dry matter	organic matter	Ca	Cu	Fe	K	Mg	Na	P	S	Zn	pH	ortho-P	N-NH4	Nt
Batch	Sampling point	Description flow	g/l	%	%	g/kg	mg/kg	mg/kg	g/kg	g/kg	g/kg	g/kg	g/kg	mg/kg	(-)	mg/kg	mg/kg	mg/kg
B64	8	Acid process water	1001	1.8		1.03			0.84	0.56	0.39	0.24	2.95		5.69			
B65	1	Solid fraction digestate	1068	24.1	75.1	6.49	40.8	875	3.60	4.00	1.58	6.26	1.92	116	8.23		1735	8022
B65	4	Acid liquid fraction	1001	4.1		1.89			1.41	1.24	0.63	1.43	5.02		5.05	1060	1349	
B65	3	solid fraction -1	814	31.4	84.8	3.66	33.3	866	1.20	1.15	0.47	1.77	4.66	101				
B65	10	recirculation water	996	1.8		1.1			1.32	0.67	0.61	0.02	3.98		7.05	28	1046	
B65	11	Ca~P~S product	1001	6.1	43.5	5.73			1.36	1.75	0.59	2.65	5.71				1146	2879
B65	8	Acid process water	997	1.9		1			0.87	0.54	0.39	0.24	3.04		5.72			
B65	7	Solid fraction digestate	808	33.5	88.3	3.68	32.2	893	0.90	0.74	0.33	1.13	4.13	94	5.98		850	4864
B66	1	Solid fraction digestate	1033	24.1	74.1	7.02	41.9	913	3.80	4.31	1.63	6.76	2.03	123	8.37		2005	7967
B66	4	Acid liquid fraction	1014	4.1		1.86			1.49	1.25	0.65	1.43	5.08		5.03	1081	1369	
B66	3	solid fraction -1	897	30.1	86.5	3.79	37	912	1.30	1.24	0.52	1.87	5.10	109				
B66	10	recirculation water	1004	1.9		1.07			1.43	0.71	0.64	0.02	4.19		7.14	26	1131	
B66	11	Ca~P~S product	1010	6.1	42.1	5.94			1.48	1.79	0.64	2.81	5.92				1169	2781
B66	8	Acid process water	1001	2.0		1			0.93	0.57	0.41	0.25	3.03		5.68			
B66	7	Solid fraction digestate	819	31.1	87.3	3.87	34.9	900	1.00	0.85	0.39	1.31	4.35	99	5.96		845	5067
B67	1	Solid fraction digestate	1075	23.5	75.1	6.05	36.4	732	3.90	3.64	1.69	5.73	1.85	104	8.4		2277	8671
B67	4	Acid liquid fraction	1004	4.2		1.91			1.57	1.30	0.69	1.51	5.26		5.05	1138	1470	
B67	3	solid fraction -1	818	30.6	85.8	4.28	40.7	921	1.50	1.36	0.58	2.18	5.27	117				
B67	10	recirculation water	1001	1.7		0.99			1.51	0.51	0.68	0.02	3.73		7.51	30	1046	
B67	11	Ca~P~S product	1006	7.2	43.2	6.73			1.55	2.18	0.66	3.19	6.90				1400	3411
B67	8	Acid process water	999	2.0		0.95			1.01	0.49	0.45	0.24	2.95		5.69			
B67	7	Solid fraction digestate	827	32.4	88.3	3.91	36.7	908	1.00	0.72	0.40	1.23	4.24	101	5.97		814	4848

* Raw measurement data on products from the pilot experiments described in Chapter 2

pH and $N\text{-}NH_4$ in solid products were determined after extraction with 1M KCl.

Annex 2 Analytical results of supernatants and pellets per organic acid used

Acid	Suspen-sion before centrifu-ging	Supernatant after centrifuging								Pellet after centrifuging						
			P	K	Ca	Mg	Na	S	Fe	P	K	Ca	Mg	Na	S	Fe
	pH	pH	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[g/kg]	[g/kg]	[g/kg]	[g/kg]	[mg/kg]	[g/kg]	[mg/kg]
Citric acid	7.3	7.42	188	681	42	26	237	140	2.1	3.19	1.40	4.68	2.35	400	1.38	440
Citric acid	6.72	6.83	417	792	147	177	270	136	4.5	3.07	1.30	4.78	2.32	362	1.34	442
Citric acid	6.19	6.32	981	912	420	606	306	134	11.1	2.56	1.20	4.25	1.89	346	1.31	411
Citric acid	5.94	6	1464	966	684	954	315	132	18.6	2.16	1.20	3.97	1.63	329	1.29	403
Citric acid	5.6	5.64	1848	993	1008	1245	321	130	26.7	2.01	1.20	4.00	1.49	334	1.36	576
Citric acid	4.98	5	1968	1026	1602	1314	330	132	53.1	1.95	1.10	4.08	1.49	329	1.38	407
Formic acid	7.36	7.39	219	675	81	53	234	140	3.6	3.25	1.40	4.79	2.40	397	1.36	443
Formic acid	6.4	6.53	447	882	138	174	297	136	2.1	3.02	1.20	4.58	2.29	347	1.32	432
Formic acid	6.2	6.35	591	918	195	284	306	132	1.5	2.96	1.20	4.71	2.24	343	1.35	447
Formic acid	5.85	5.92	1077	1002	423	669	324	131	1.5	2.62	1.20	4.63	1.92	333	1.37	536
Formic acid	5.6	5.65	1500	1038	612	978	333	131	1.2	2.31	1.10	4.26	1.71	330	1.39	493
Formic acid	5.14	5.13	1848	1080	1011	1263	339	130	1.2	2.00	1.10	3.77	1.51	324	1.33	425
Acetic acid	7.43	7.37	216	684	63	52	237	143	2.7	3.03	1.40	4.35	2.24	396	1.29	411
Acetic acid	6.61	6.65	372	831	99	128	282	136	1.8	2.97	1.30	4.52	2.16	357	1.29	411
Acetic acid	6.32	6.36	534	885	138	230	297	133	1.8	2.78	1.20	4.42	2.07	347	1.31	421
Acetic acid	5.92	5.97	942	966	261	540	315	130	1.2	2.65	1.20	4.37	1.93	339	1.30	419
Acetic acid	5.41	5.4	1734	1065	582	1155	336	132	1.2	2.05	1.10	3.94	1.51	327	1.27	408
Acetic acid	4.83	4.89	1860	1110	1056	1284	339	130	1.2	2.06	1.10	3.79	1.44	319	1.28	392
Pyroligneous acid	7.46	7.38	212	681	69	52	237	141	2.4	3.12	1.30	4.67	2.28	382	1.27	408
Pyroligneous acid	6.79	6.76	366	846	93	122	285	139	3.6	2.88	1.20	4.27	2.13	355	1.28	437
Pyroligneous acid	6.32	6.38	576	915	144	265	303	138	6.0	2.76	1.20	4.33	2.07	341	1.28	473
Pyroligneous acid	5.75	5.78	1341	1041	330	885	333	136	6.3	2.42	1.10	4.42	1.70	333	1.29	627
Pyroligneous acid	5.5	5.5	1587	1053	429	1113	336	136	6.3	2.20	1.10	4.10	1.55	329	1.26	725
Pyroligneous acid	4.91	4.93	1638	1056	825	1251	339	131	7.2	2.26	1.10	3.68	1.48	328	1.20	880

* Chapter three, paragraph 3.3.1

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