

Struvite: technology, fertilizer legislation and cleaning of scaling by caustic Soda.

Thesis submitted by

Diederick Bakker (Environmental Sciences)

Student number 911002001

Student at: van Hall Larenstein University of Applied Sciences (Leeuwarden, The Netherlands).

Internship at: Paques BV (Balk, The Netherlands)

Corresponding author: TEL: +316 17144660 Email: diederick.bakker@hvhl.nl

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Abstract

The limited natural phosphorus reserves in the world are gradually depleting. This makes it interesting to look for other ways of recovering phosphorus. One of the possibilities is the recovery of phosphate (PO_4) from industrial and municipal waste water, by the precipitation of struvite. By dosing magnesium to waste water, Ammonium (NH_4^+), Phosphate (PO_4^{3-}) and Magnesium (Mg^{2+}) might form a crystal together called struvite ($\text{MgNH}_4\text{PO}_4(\text{s})$). Struvite has a low solubility, which makes it interesting to use as a slow-release fertilizer. With struvite, crops would be longer enriched with nutrients, which means less fertilizer is needed in the long run. This thesis will investigate on what level struvite- and other P-recovering technologies, can possibly contribute to the demand for phosphorus in the EU. Struvite is a fairly new product, which means that European legislation still has to catch up to the fact that struvite from waste water can be effectively used as a fertilizer. This thesis aims to clarify the current and upcoming European legislation concerning the use of struvite (from waste water) as a fertilizer. Struvite can also form and precipitate naturally (uncontrolled). In waste water treatment plants (WWTP), this can cause pipe clogging. Conventional methods for dealing with this problem are mostly expensive, environmentally unfriendly or simply inefficient. In theory it seems possible to dissolve struvite by adding caustic soda (NaOH), which would be a better alternative as it does not create as much problems as conventional cleaning methods. This thesis will investigate if and how caustic soda can effectively remove struvite scaling inside industrial piping.

The maximum contribution of phosphate recovery from waste water is estimated to be around 1%, if all WWTP would use some of the best technologies available to recover phosphate. Although this percentage is small in terms of fully securing phosphate demand in the EU, it could increase in the future by efforts such as an increased focus on the use of sustainable farming methods.

Currently struvite produced from waste water can indeed be sold and used as a fertilizer across the EU, as long as it meets certain criteria. Because the criteria is different across most EU member states, the European commission has proposed a draft legislation called the Circular Economy Package. The implementation of the Circular Economy Packages will specifically mean for struvite (from waste water) that it will officially be considered by the EU as a (valuable) trade product, which will hopefully be the result of higher production, and selling of, products such as struvite across the EU.

Performed lab experiments indicated that 1 molar and higher concentrations of caustic soda (NaOH) can remove struvite scaling. The research also showed that ammonia gas (NH_3) may be released in great quantities by the reaction of caustic (OH^-) with struvite. A possible effective and cheap cleaning process would be to add 5 molar caustic soda to a clogged pipe and close it off for a certain amount of time. The caustic soda has the effect that the scaling will become partially degraded and very loose, which makes it possible to flush the scaling out of the pipe by using WWTP effluent. The removed scaling can then be treated further in a phosphate recovering system. The dissolved ammonia can possibly be stripped away by aeration, which is a coming technique in struvite precipitation reactors.

List of terms and abbreviations

Ammonia: compound NH_3 .

Ammonium: compound NH_4^+ .

Anammox: Energy efficient process that removes nitrogen in WWTP's.

Caustic soda: compound NaOH (sodium hydroxide, lye).

CE marked product: declaration that the product complies with the essential requirements of the relevant European regulation.

Crystallization: is a natural (or artificial) occurring process where a solid forms, where the atoms or molecules are highly organized in a structure known as a crystal.

EBPR: enhanced biological phosphate removal.

End-of-waste: waste product that has undergone a treatment process and no longer can be seen as waste, but a possible valuable market product.

Jar test: Machine that can stir multiple separate containers at the same speed and at the same time

K_{sp}: solubility product, a term to describe the maximum amount that a solute can dissolve in a solution (mostly water).

Legislation: a law which has been enacted by a legislature or other governing body or the process of making it.

Magnesium: compound Mg , occurs in this thesis as: magnesium oxide (MgO) and magnesium chloride ($\text{Mg}(\text{Cl})_2$).

Molar(ity): measure of concentration of a solute in a solution, amount of substance in a specific volume. Described by a capital M after the amount.

Molar mass: mass (in grams) of 1 mole of a particular substance, e.g. the atom hydrogen (H) is 1,008 grams per mole.

PAO: Phosphorus-Accumulating-Organisms.

pH: A term to describe the level of acidity.

Phosphate: common form of phosphorus. Described in the fertilizer industry as molecule form ' P_2O_5 ', and described in chemistry as molecule form ' PO_4 ' ion.

Phosphorite: sedimentary rock which contains high amounts of phosphate minerals

Phosphorus: element ' P '.

Reynolds number: dimensionless number to describe the level of actual turbulence of a solution

REACH: Regulation Evaluation Authorisation and Restriction of Chemicals. European regulation for the safety and control of chemicals.

RPM and RPS: rotations per minute and rotations per second

Struvite: compound MgNH_4PO_4 , also called MAP

SSR: supersaturation ratio, a term to describe the excess of solutes in a solution.

Viscosity: The viscosity of a fluid is a measure of its resistance to gradual deformation by shear stress or tensile stress. It is a term for the description of the 'thickness' of a solution. For example, syrup has a higher viscosity than water.

w/w %: mass fraction in chemistry, the ratio of the mass of one substance, to the mass of the total mixture.

WWTP: Wastewater Treatment Plant, also known as WWTW (Wastewater Treatment Works).

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Chapter 1: Introduction

1.1 Context of the thesis subject

The limited natural phosphorus reserves in the world are gradually depleting. The current most cited estimation, made by the Institute of Ecology in 1971, was that the world natural phosphate reserves would last for another 90-130 years before they deplete [1]. This was in 1971, this number will be much lower today, taken into account elapsed time and population growth. Newer estimations are still heavily discussed in the science community.

The largest and least expensive source of phosphorus is obtained by mining phosphorite or phosphorus rock. Phosphorite is mainly used to create fertilizers (source for 80% of phosphorus fertilizers), which is very important to secure worldwide food supply [2]. Phosphorite is not native to Western Europe, but is mined mainly in East Asia and Africa [3]. Partly for the reasons above, a great deal of companies and researchers in Europe are looking for ways of producing phosphorus in alternative ways.

Paques, based in Balk the Netherlands, and other companies, have developed technologies that can recover phosphate (PO_4) from industrial and municipal sewage sludge. In the Paques PHOSPAQ™ reactor, phosphate is precipitated and recovered by using magnesium oxide (MgO). This forms the substance struvite, or also MAP, which is short for Magnesium Ammonium Phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$). This substance is separated from the waste water and can then be used as a slow-release fertilizer. Slow release fertilizers flush out less easily into the soil and are thus longer useful for plant growth. As a result less fertilizer is needed which possibly can, in part, secure phosphorus supply in Europe and also alleviate eutrophication caused by lesser quality fertilizers.

1.2 Problem description and objectives

Technologies

An increased number of phosphate recovering technologies (such as Paques PHOSPAQ™) are being developed in- and outside of the EU. This thesis gives a clear overview of current and upcoming phosphate recovering installations and technologies. An explanation of each technology's, general workings, annual struvite producing capacity and operational costs must be researched. It is also interesting to know how much these technologies can theoretically contribute to the EU demand of phosphate.

Legislation

European legislation still has to catch up to the fact that struvite from WWTP (waste water treatment plants) can be effectively used as a fertilizer. Paques would like a clear overview of current and future legislation concerning the (European) selling and use of struvite fertilizers.

Caustic soda struvite removal agent

Struvite can also form and precipitate naturally. In WWTP, this can cause pipe clogging. Conventional methods for dealing with this problem are mostly expensive, environmentally unfriendly or simply inefficient. It would be interesting to test a new method that has sprung up in the science community. In theory, it seems possible to dissolve struvite by adding caustic soda (also called lye, sodium hydroxide NaOH). This thesis investigated whether if the use of caustic soda as a struvite

'cleaner' is applicable. The main research question is: How can caustic soda effectively remove struvite scaling inside industrial piping?

The main research question has been split into sub questions:

- How fast does hydrogen chloride (HCl) degrade struvite?
- How fast does sodium hydroxide (NaOH) degrade struvite?
- How fast does water break down a lump of struvite?
- What chemical reaction describes the cause of the destruction of struvite by caustic soda?
- What effect does mixing have on the degradation rate of struvite in caustic soda solutions?
- What effect does temperature have on the degradation rate of struvite in caustic soda solutions?
- Is struvite dissolved or simply broken apart into smaller pieces by caustic soda?
- How could struvite be effectively cleaned in a practical situation?

1.3 Layout of the thesis

The points in paragraph '1.2 Problem description and objectives' will be answered as best as possible in chronological order in separate chapters. Chapter 2 will describe the first objective 'Technologies' and chapter 3 the second objective 'Legislation'. Chapter 4 contains theoretical background, methodology, results and finally a conclusion that aims to answer the main- and sub questions as mentioned in the previous paragraph.

Chapter 2: European phosphorus demand and its supply from WWTPs waste water

This chapter describes how much phosphate recovery (specifically from waste water) can contribute to the demand for phosphate fertilizers in the EU. Secondly, an overview was created of currently operating phosphate recovering plants in the world.

2.1 Contribution of phosphate recovery to phosphate demand

As mentioned in the introduction, the natural supply of phosphorite (a rock very rich in phosphorus) is estimated to be exhausted in 90-130 years. This rock is the biggest contributor to the creation of P-fertilizers, which in term are hugely responsible for securing the world's food supply [2].

The cost for this rock will sky rocket as supply (much like oil) will decrease and demand may continue to increase due to worldwide population growth [4]. As reserves deplete, countries may seize to export their phosphorite entirely, to secure their own national food supply. The EU is also highly dependent on regions currently subject to political crisis [5].

A reliable source for phosphorus will always be needed. The EU (and the world for that matter) will need to find new, more sustainable ways of recovering phosphorus.

Main reasons for the promotion of P-recovery in the EU

Firstly, there is a possible lucrative market available in the export of P-fertilizers: "Last years, the EU-27 has imported between 1 and 1,2Mt (mega tonnes) of phosphate fertilisers (P_2O_5) mainly from Russia, Morocco and Tunisia. As the EU-27 also exports phosphate fertilizers, net imports only reached 0.4/0.5 Mt each year since 2008." [5] A large market is available for the EU to export P-fertilizers. Secondly, reduced eutrophication can be achieved by slow-release fertilizers such as struvite. Combining phosphate recovery with processes such as Anammox [6] can create a cost-efficient and sustainable method for the treatment of industrial- and municipal waste water effluent. And lastly, Europe could become (partially) independent in phosphorus supply.

Phosphate recovering technologies are being studied and developed all over the world. Technologies such as PHOSPAQ™ and PEARL that are operating for some time already seem very promising. But how much can these actually produce? What level of contribution can they make to the phosphate fertilizer demand in the EU? Estimation from the European commission shows that in 2005, 9 Mt of dry matter sewage sludge was produced [7]. The European PhosphorusPlatform reported that in 2010 the total demand for phosphate (molecule form: P_2O_5) was 4.9 Mt [8].

Can Europe create enough P-fertilizer from sewage sludge?

To answer this question a theoretical situation will be used where all phosphorus removal in the EU would take place by EBPR and would be treated by anaerobic digestion for biogas (see next paragraph). This sustainable theoretical situation can be used to estimate what the maximum contribution of phosphate recovery from waste water-sludge could be, to the annual demand for phosphate in the EU:

Table 1: Maximum contribution of phosphate from P-recovery to EU phosphate demand

Annual sludge (dry weight) production in the EU:	9 Mt per year
Average phosphate % from dry weight <u>digested</u> sludge: [9]	0,48% – 0,77% *

Average phosphate production from sludge:	0.056 Mt per year
Recovery efficiency of top technologies:	90% (see next paragraph)
Average phosphate recovery from sludge:	0.051 Mt per year
Annual phosphate demand in the EU:	4.9 Mt per year
Contribution from sludge P-recovery to EU P-demand:	~ 1%

Taken into account with Table 1: Not all technologies are >90% efficient, most have lower efficiencies (see next paragraph). This particular percentage was used to show a maximum (sustainable) production capacity. Other assumptions were also made for Table 1, for example the amount of sludge production comes from a 2005 source and the amount of P-demand comes from a 2010 source. Also, many WWTP in Europe use chemicals to remove phosphorus from their influent. This immobilizes the phosphorus in a way that it cannot be precipitated as struvite later on. This will be discussed further in paragraph '4.1.2 Conventional substances for the removal of struvite scaling'. Chemical phosphorus removal was not taken into account with Table 1, so that a maximum contribution percentage could be calculated by assuming that all WWTP in the EU would work on EBPR systems.

Although 1% is a small contribution, the demand for phosphate could possibly decrease in the future if the EU would increase focus on the use of sustainable farming methods and more efficient phosphate fertilizers. The EU could also focus on the decrease of the consumption of meat (which is a very inefficient food supply). Other sources of phosphate are also available next to industrial and municipal waste water, such as places with high eutrophication/ p-pollution (case in point: the Everglades [10]).

In the next paragraph an overview will be given of current and upcoming phosphate recovery systems mentioned in Table 1.

2.2 Phosphate-recovering technologies

This section of the report will show an overview of some of the most well known currently operating, or still in pilot phase, phosphate recovering plants across the world. Most of these techniques work on the production of struvite. The technologies shown in the lists all operate on waste water treatment effluent (and sludge).

2.1.1 Description of waste water treatment plant effluent

Most phosphate recovery technologies described in this chapter treat the effluent or sludge that is created by the following processes.

Dissolved phosphate can be removed by forcing certain bacteria to grow on the excess nutrients in waste water. This process is usually called EBPR (enhanced biological phosphorus removal) and uses bacteria in biofilms or sludge. These bacteria are called phosphorus accumulating organisms (or PAO's). PAO accumulate phosphate heavily under aerobic conditions and under anaerobic conditions take up easily biodegradable organic matter and some phosphate. The basic process is described in the figure below:

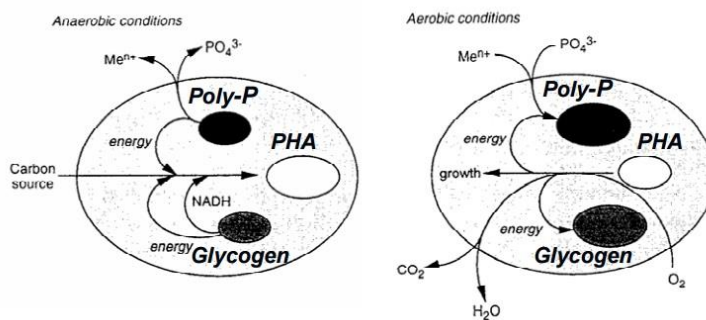


Figure 1: P-uptake by PAO [11]

The alternation of aerobic and anoxic conditions is the main principle of EBPR. An example of the design process is illustrated below. The water travels from an anaerobic stage where the PAO receive their carbon source, to the aerobic stage where phosphate uptake takes place and eventually a precipitation tank where the sludge, containing most of the PAO's, may be separated.

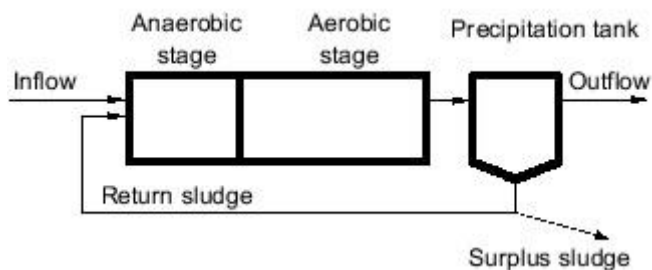


Figure 2: EBPR process design [12]

The sludge produced by a process such as the one in Figure 2 can be further treated by anaerobic digestion, which produces natural carbonic methane gas (CH_4 , CO_2). Sludge from which methane gas is produced can then be further treated for the removal of phosphate.

2.1.2 (Struvite) Precipitation Technologies

Precipitation technologies mainly work on processes that form phosphate minerals such as struvite and calcium phosphate. This technology is the most occurring tech for the recovery of phosphate in waste water. For an example of such a process principle we can look at the PHOSPAQ™ process:

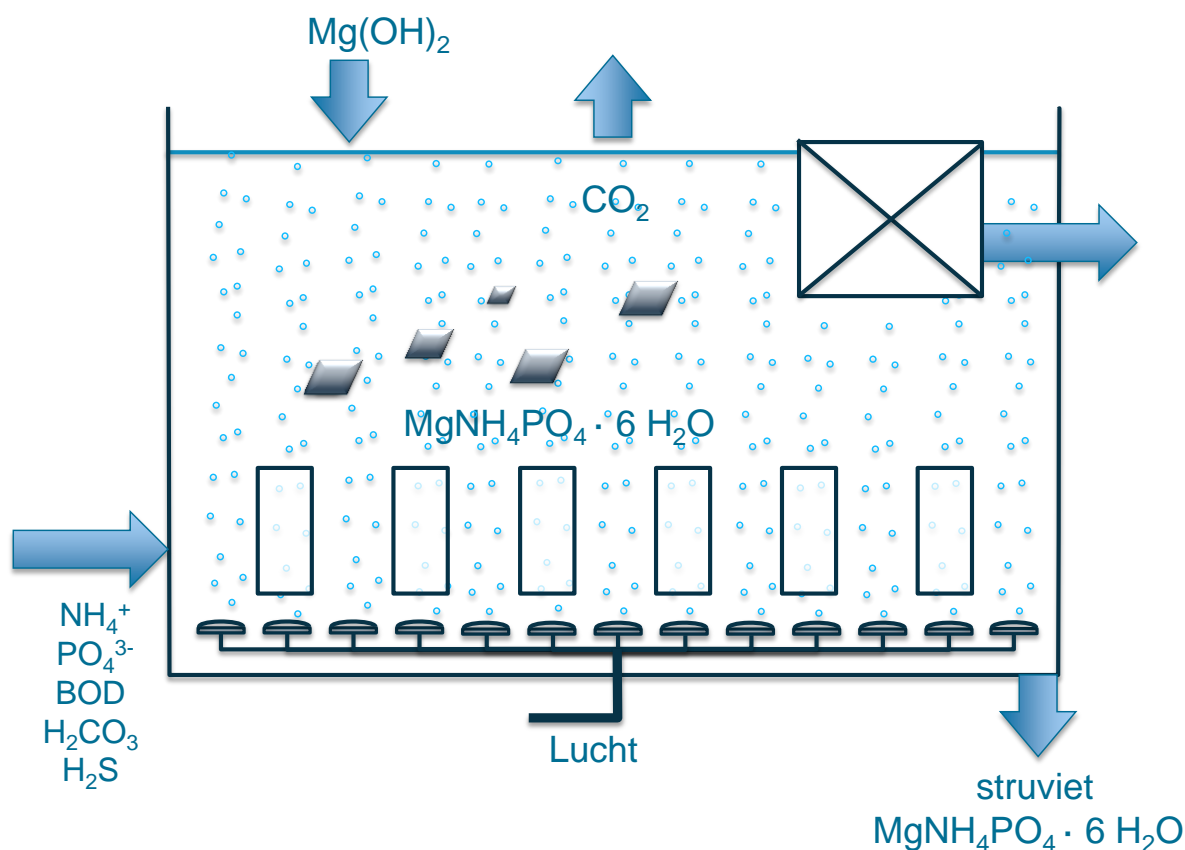


Figure 3: Inside the PHOSPAQ™ reactor [13]

In these types of reactors (Figure 3), waste water (sludge) is continuously aerated to promote optimal pH levels and high turbulence. Magnesium is dosed and struvite can crystallize in the following way:



The precipitated struvite can then be separated from the suspension. Methods such as these are very effective for phosphate recovery as it ‘targets’ phosphate and ammonium specifically. Technologies that work on this principle are also sustainable as the removed struvite can be used as a slow-release fertilizer. A list of some of the top used struvite precipitating technologies can be seen in Table 2.

Table 2: (Struvite) precipitation technologies with the most number of references

Name of tech:	Product type:	Largest facility (annual struvite capacity in tonnes):	Efficiency (percentage P-removal:	Process specifics:	# Referen-ces:	First and latest build
AirPrex	Granular struvite	600-1000	90-95%	Crystallisation, airlift reactor	8	2009/2016

				(CSTR and CO ₂ stripping), precipitation and separation		
AnPhos	(granular or powder) struvite	<i>unknown</i>	80-90%	Crystallisation, airlift reactor (CSTR and CO ₂ stripping), precipitation and separation	6	2005/2017
Multi-form	Struvite pellets	438	<i>unknown</i>	caustic or ammonium for pH adjustment, cone-shaped crystallisation reactors	4	2012/2013
NuReSys	Granular struvite	950	80-95%	Crystallisation, airlift reactor (CSTR and CO ₂ stripping), precipitation and separation	8	2003/2015
Pearl	'Crystal Green' granular struvite	930	85%	Crystallisation, fluidised bed reactor, pre-treated with WASSTRIP® (biological sludge thickener)	14	2007/2013
PHOSPAQ	Granular struvite	400	70-95%	Crystallisation, airlift reactor (CSTR and CO ₂ stripping), precipitation and separation	11	2006/2016

A broader list of currently operating (or pilot) precipitation plants can be found in Appendix 1, more information about Table 2 such as sources can also be found there.

2.1.3 Alternative Processes

There are other processes beside the precipitation of struvite that can recover phosphorus. These are technologies where some form of thermal or chemical process is used. Most of these technologies are very new, and do not have many references. In Table 3 three examples are given:

Table 3: Alternative P-recovering technologies

Name of tech:	Product type:	Largest facility (annual struvite capacity in tonnes):	Efficiency (percentage P-removal:	Process specifics:	# Referen-ces:	First and latest build
AshDEC	CaNaPO ₄	<i>Unknown</i>	98% (P in ASH)	Rotary kiln, P reacts with Na ₂ SO ₄ at 900-1000 degree C	1	2008
MEPHREC	P-slag/ briquett es	<i>Unknown</i>	81%	dewatering and thermal treatment	1	2016 (pilot)
LEACH PHOS	CaP and wet struvite	<i>Unknown</i>	70%	chemical process, extraction by diluted sulphuric acid and crystallisation process	1	2012

A broader list of currently operating (or pilot) plants can be found in

Appendix 2, more information about Table 3 such as sources can also be found there.

2.3 Conclusion

The aim of this chapter was to find out what the maximum contribution could be from phosphate recovery (from waste water) to the EU demand for phosphate. An estimation was made in paragraph 2.1 that this contribution would be around 1%, if all WWTP would use some of the best technologies as described in 2.2. Although this percentage is small in terms of fully securing phosphate demand in the EU, it could increase in the future by efforts such as an increased focus on the use of sustainable farming methods.

Chapter 3: Legislation on the use of struvite as a fertilizer

Struvite produced from waste water sludge can be used as a slow-release fertilizer. It is still unclear what the European policy requires of this. This chapter aims to clarify the present and upcoming situation for the use of struvite originating from waste water as a fertilizer.

3.1 Present and upcoming governing EU legislation

Present legislation

Regulation (EC) no. 2003/2003 of the European parliament and of the council of 13 October 2003 'relating to fertilisers' [14], is the first legislation that governs all the European Union rules that apply to fertilizers (chemical compounds that provide nutrients to plants). It ensures that these highly technical requirements are implemented uniformly throughout the EU. The second legislation that applies to the use of struvite as a struvite fertilizer is REACH. "REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) is a regulation of the European Union, adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. It also promotes alternative methods for the hazard assessment of substances in order to reduce the number of tests on animals [15]". This regulation represents the official requirements for the use and selling of all chemicals in the EU.

These legislations direct that new struvite producers must buy into the research data that 'Berliner Wasserwerke' registered. This company was the first to specifically register struvite. They performed the necessary safety analyses for the REACH regulation, so that struvite (from waste water) could be used as a CE marketed product. New registrants must also pay for the additional registration fees for the chemicals agency ECHA and the cost for outsourcing the registration. The registration requirement for an annual production of at least 100 tons struvite or more will only apply 31 May 2018.

Because struvite can be considered as a recovered substance according to the definitions in the REACH regulation, it may be possible to use the exemption from the registration requirements for recovered substances (Article (2 (7) (d) of the Regulation). The condition for this is that the substance is in compliance with the already registered substance by Berliner Wasserwerke. That is to say, at least 80% of magnesium ammonium phosphate (1:1:1 mol ratio) and no hazardous impurities. Both the Dutch and British REACH helpdesk as the EU Commission have confirmed that for struvite, this exemption possibility can be used [16]. The European Commission has provided a written opinion [17] to (7/12/2015) that Art. 2(d) of REACH applies to recovered struvite. That means that once the substance has been REACH registered by one producer (done by Berliner Wasserbetriebe), other producers do not need to REACH register. A list of these requirements concerning the purity and chemical composition of struvite can be found on phosphorusplatform.eu [18].

Presently, struvite from waste water can be used as a fertilizer in the EU. It is still necessary however to comply with the specific national legislation of EU Member States (see paragraph 3.2 National legislation of EU member states). Because of the current lack of uniformity across EU member states and general ambiguity concerning topics such as these, the European commission has proposed a solution by the adaptation of the Circular Economy Package.

Upcoming legislation

The European Commission has adopted an ambitious new Circular Economy Package to help

European businesses and consumers to make the transition to a stronger and more circular economy where resources are used in a more sustainable way.

The proposed actions will contribute to "closing the loop" of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy. The plans will extract the maximum value and use from all raw materials, products and waste, fostering energy savings and reducing Green House Gas emissions. [19]

For (waste) products which no longer pose any significant risk to public or animal health, an end point in the manufacturing chain may be determined, beyond which they are no longer subject to the requirements of the waste (Directive 2008/98/EC) regulation.

“Article 18 End-of-waste-status: A CE marked fertilising product that has undergone a recovery operation and complies with the requirements laid down in this regulation shall be considered to comply with the conditions laid down in Article 6(1) of Directive 2008/98/EC and shall, therefore, be considered as having ceased to be waste [20]”.

Significance for struvite fertilizers originating from waste water

The Commission will modify the legislation to enable recycled materials to be reclassified as non-waste whenever they meet a set of general conditions, which are the same across the whole EU. This amendment is meant to simplify the legislative framework for operators in the recycling business and ensure a level-playing field. Existing EU-wide end-of-waste criteria (e.g. for glass or copper scrap) will remain in force[21]. This means that struvite will officially be considered by the EU as a valuable trade product. The Circular Economy Package will (hopefully) be the result of higher production and selling of products such as struvite.

As some fertilising products are not produced or traded in large quantities across the EU, the Commission has proposed optional harmonisation, taking into account the principles of better regulation and subsidiarity. Optional harmonisation means that manufacturers within the EU can choose to comply with;

- The revised EU Fertilisers Regulation, affix the CE mark to their product and trade it anywhere within the EU, or
- National rules, which allow them to trade their product in their national market.

The Commission has also pointed out that if a manufacturer wants to trade its product in other EU countries but not comply with the revised EU Fertilisers Regulation, this could only be done if the receiving countries accept the national rules of the producing country (a term described as mutual recognition). For example, if a UK producer's compost complies with national rules (i.e. PAS 100 and the Compost Quality Protocol if producing in England, Wales or Northern Ireland) and he/she wishes to sell the compost to a buyer in France, this could only be done if the competent authority in France accepts the producing country's national rules.

Next steps

The draft regulation was sent to the European Parliament and Council for adoption. Once adopted, it will be directly applicable, without the need for transposition into national law, after a transitional period allowing companies and public authorities to prepare for the new rules. The estimation is that the circular economy package will be active before the end of 2017: “Both European Parliament and

Council of Ministers can amend the legislation but must agree upon an identical text before those bills can become law. This means that a final package will likely not be established until the second half of 2017. Malta, which holds the rotating EU Presidency, has said it will try to reach a deal with the ministers of European Parliament before 1 July, when its six-month Presidential term ends [22].

3.2 National legislation of EU member states

Most EU member states have adopted the current (mid 2017) European legislation in their own national laws. In case of the regulation for the export and import of fertilizers, mutual recognition can be in order: “The principle of mutual recognition stems from Regulation (EC) No 764/2008. It defines the rights and obligations for public authorities and enterprises that wish to market their products in another EU country. Mutual recognition ensures market access for products that are not subject to EU harmonisation. It guarantees that any product lawfully sold in one EU country can be sold in another. This is possible even if the product does not fully comply with the technical rules of the other country. The regulation also defines how a country can deny mutual recognition of a product [23]”.

In cases where mutual recognition is denied, the exporting country will have to comply with the importing country’s national standards.

Dutch

The Dutch Fertiliser law states that struvite can be seen as a ‘recovered phosphate’. This means that struvite (from waste water and agricultural waste) can be used as a fertilizer in the Netherlands, as long as it complies with the regular requirements for heavy metals and organic micro-pollutants applicable for regular fertilisers [24].

Germany

Recovered phosphorus (including struvite) is categorized in Annex II of the Ordinance on Fertiliser Quality (DüMV) as type 6.2.4 phosphate precipitates. This states that struvite needs to comply with the first REACH registered struvite by Berliner wasserwerke. [25]

UK

Fertiliser must be an ‘EC fertiliser’ or ‘EEC fertiliser’ which is listed in the EU Fertiliser Regulation (EC 2003/2003). An EU product that does not meet the GB Fertiliser Regulation (1991) may still be able to be imported under the Mutual Recognition Regulation [26]. It is not yet determined if UK regulations such as these will change when the UK leaves the EU, as the UK’s law is deeply intertwined with EU legislation. An article by the financial times suggests that during the transitional period the UK might continue participation with EU agencies [27].

France

In France the Mutual Recognition Regulation also applies. Products that are already approved in other member states, an application for prior approval (shorter procedure) may be applicable. For fertilizers that are not yet approved, a relatively complicated process is required. “Pursuant to Article L.255-2 of the Rural Code, fertilising materials and growing media may be marketed, imported, distributed or even transferred free of charge in France, provided they have been subject to approval or a temporary sales authorisation (APV) or import authorisation. For information on procedures, refer to the ANSES website: www.anses.fr “[28].

Belgium

In Belgium the Mutual Recognition Regulation also applies. Fertilisers are required to comply with the Belgian legal requirements as mentioned in the Royal Decree of 28 January 2013 on the marketing and the use of fertilizers, soil improvers and growing media. Struvite is an end product not included in its Annex. Therefore, the Federal Public Service (FPS) Health, Food Chain Safety and Environment can grant exemptions for the trade of struvite products as fertilizers when the producer applies for mutual recognition [29]. In Flanders the fertilizer product needs to meet the composition requirements regarding the maximum content of pollutants as described in annex 2.3.1 of VLAREMA (Flemish Regulation on Sustainable Management of Material Cycles and Waste Materials) [30].

3.3 Conclusion

Struvite produced from waste water can currently be sold and used as a fertilizer across the EU, as long as it meets certain criteria. The struvite product needs to comply with requirements from EU REACH regulation and it also needs to meet requirements from specific national legislation of the receiving EU member state. Because it is generally very unclear if and how struvite and similar products can be used, the European commission has proposed a draft legislation called the Circular Economy Package. This has, among others, the aim of creating optional harmonisation across the national legislations of EU member states. Optional harmonisation means that manufacturers within the EU can choose to comply with the revised EU Fertilisers Regulation, affix the CE mark to their product and trade it anywhere within the EU, or use national rules, which allow them to trade their product in their national market.

The implementation of the Circular Economy Packages will specifically mean for struvite (from waste water) that it will officially be considered by the EU as a (valuable) trade product. This will hopefully be the result of higher production, and selling of, products such as struvite across the EU.

Chapter 4: A possible solution to struvite scaling by the use of caustic soda

This chapter will look at an alternative method for removing uncontrolled struvite formation from industrial piping. Main goal of this chapter is to answer the following question: How can caustic soda effectively remove struvite scaling inside industrial piping? This research question will be answered as best as possible by carrying out literature study and by performing lab scale experiments (tests in 1 litre beakers). The results from these tests shall be used later on for more representable field-like experiments.

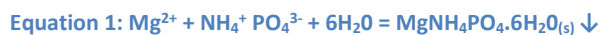
4.1 Theoretical background

This chapter describes some general information and theory which serves as background information for the experiments performed in this chapter.

4.1.1 Optimal conditions for the formation of struvite

High pressure, low temperatures and high concentration of ions are factors for the promotion of scaling. The waste water stream originating from for example anaerobic digesters contains dissolved magnesium, phosphate and ammonium.

Some of these ions may form (uncontrolled) struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}_{(s)}$) and will, under some pressure, attach on the inner walls of the piping. The main chemical reaction behind struvite formation:



In case of phosphate recovery systems such as PHOSPAQ™, struvite scaling mainly occurs in the piping towards the reactor. A PHOSPAQ™ reactor that was operated for 8 years showed little to no struvite scaling inside the reactor and little to no struvite scaling in the drain pipes [31]. An example of a clogged pipe is given in Figure 4.



Figure 4: Struvite clogged pipe [47]

Various process parameters such as increased molar ratio (Mg:NH₄:P), supersaturation, pH, degree of mixing, temperature and seeding conditions are likely to affect the struvite precipitation process [32]. Previous research on the optimal conditions for struvite precipitation indicates that a molar ratio (Mg:P) of 1.5 to 1.6 provides the highest removal efficiency [33][34]. pH between 8 and 8.5 and temperature around 35°C seem to work the most efficient [31]. Struvite has a very low solubility in water of around 160 mg/L at pH 7 and 25 °C, with a solubility product (K_{sp}) between 10⁻¹⁰ and 10^{-13.3} [35]. Supersaturation ratio (SSR) is one of the main driving forces behind crystallisation, which is described as:

$$\text{Equation 2: } \text{SSR} = \text{K}_{\text{sp}} / \text{K}_{\text{speq}} = [\text{Mg}][\text{NH}_4][\text{PO}_4] / \text{K}_{\text{speq}}$$

With K_{speq} = the equilibrium conditional solubility product [33]. Equation 2 can be used to determine the amount of supersaturation in your solution, and thus the amount of struvite that may crystallize and precipitate. As mentioned before, the crystallization is highly dependent on pH (value between 8 and 8.5). Uncontrolled struvite precipitation could also occur in dewatering processes (such as

centrifuges) were water crashes through a collection point. The high flow of the water could have the effect of CO₂ stripping, which increases pH and thus increases the likelihood of struvite scaling.

4.1.2 Conventional substances for the removal of struvite scaling

It is important to remove struvite for two reasons: to clean the clogged pipes and to recover the phosphate in the broken down and or dissolved struvite. A commonly used cleaning acid is hydrogen chloride (HCl). The use of this substance for cleaning purposes is generally environmentally unfriendly, as the acid can also dissolve toxic metals. It can also decrease the efficiency of a downstream struvite recovery process because of its lowering effect on pH. As mentioned before, struvite precipitation reactions work best at pH values between 8 and 8.5. The use of acids can be detrimental to the efficiency of the reactor, as it would be ideal if the removed/ dissolved scaling could be transferred directly towards the system after it is cleaned. This would lower the pH of the reactor, which in term demands more resources to stabilize the pH again to normal operating levels. As acids can also dissolve metal, pipes could be damaged severely after a certain amount of cleaning processes. Increase of pH however, would likely have a lower adverse affect on the reactor which makes the possible use of alkaline interesting. A possible reaction of HCl:



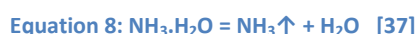
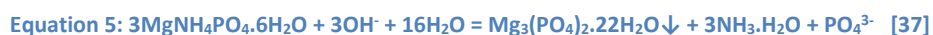
The uses of more complex cleaning agents are also common. Antiscalant products work efficiently and are relatively cheap. However, these antiscalant products are not ideal because they may also inhibit later struvite formation in the reactor [36]. In case of PHOSPAQ™ the ideal situation would be to re suspend phosphate in the pipes leading towards the reactor, and thereafter recrystallize struvite inside the reactor. This way, no unnecessary phosphate will be ‘lost’ or flushed away.

To prevent struvite formation in pipes and to remove phosphate from influent, WWTP’s sometimes use FeCl₃ as an antiscalant. This ‘immobilizes’ the phosphate, which is also not useful in case of PHOSPAQ™, as phosphate becomes unavailable for crystallization as struvite later on:



4.1.3 Alternative substances for the removal of struvite scaling

A research conducted by Haung *et al.* [37], describes that the chemical equations (Equation 5, Equation 6, Equation 7 and Equation 8) are likely to happen when you try to dissolve struvite with sodium hydroxide. These reactions show that ammonia will be released into the air as a gas, which can be an undesirable effect.



These chemical equations will be further investigated in this report, and will be used as the supporting/ backing theory behind the main research question: How can caustic soda effectively remove struvite scaling inside industrial piping? Equations 6 and 7 both have the result of producing a precipitant. The theory describes that 100% dissolution of struvite in caustic is possible. This will be discussed in paragraph ‘4.1.4 Important parameters for the dissolution of struvite’ (Figure 5).

The hypothesis that follows from this: Equation 7 describes the cause of the destruction of struvite by caustic soda which results in Equation 8.

Potential hazards from ammonia release

It can be estimated how much ammonia will be released from a clogged pipe that would be cleaned by caustic soda. For example, let's take a 20cm by 300cm pipe that's clogged for 60% (Table 4):

Table 4: Calculation example of ammonia gas released by the breakdown of struvite

Pipe size (L):	10
Pipe size (cm ³):	94248
Factor volume clogged pipe:	0.6
Volume of struvite (cm ³):	56549
Density of struvite (g/cm ³):	1.7
Amount of struvite (gram):	96133
Factor ammonium in struvite (w/w):	0.07
Maximum amount of released ammonium (gram):	6729
Mol reaction ammonium to ammonia:	1:1
Density ammonia (kg/m ³):	0.73
Ammonia (m ³):	4.9

So just from this example we can calculate that 5 m³ of ammonia gas could be released if we use Equation 7 and Equation 8. This means that ammonia derived from broken down struvite should perhaps be vented out of the pipe before it enters further phosphate recovery systems. It could also be possible that struvite in an unventilated pipe (closed-off) would be 'cleaned' very slowly or at some point would not react at all with caustic soda. As the ammonia cannot escape the solution, NH₃ saturation (distributed in the air and solution) can be achieved somewhere during the process, which may inhibit further reaction of struvite with caustic soda (Table 5).

Table 5: Saturation of ammonia

Pipe size (L):	10
Maximum amount of solution that can fit the pipe (L):	4
Maximum amount of released ammonium (gram):	6729
Maximum solubility of ammonia (g/L) [38]:	428
Maximum amount dissolved ammonia (gram):	1928
Excess ammonia (kg):	4.8
Density ammonia (kg/m ³):	0.73
Excess ammonia (m ³):	3.5

In the example from Table 4 and Table 5 we can see that the maximum solubility of ammonia would be reached. This could mean that the excess ammonia could remain 'intact' as ammonium inside struvite, in an unventilated/ closed-off pipe.

Positive effects of caustic soda as a struvite cleaning agent

Although the release of ammonia can be detrimental, the use of caustic soda still has some interesting effects, mainly because it doesn't increase the acidity:

- No immobilizing effect on phosphate, scaling can be recrystallized later on in the phosphate recovery system
- No damaged pipes which saves on costs and no dissolved toxic metals into the system
- Less adverse effect on the efficiency of phosphate recovering plant, as it does not lower pH levels
- Caustic soda is easy to obtain as it is a very common compound in the chemical industry

Although the positive effects of caustic soda are worth mentioning, caustic soda could also affect the efficiency of struvite precipitation negatively by too high increase of pH. The optimal pH is around 8 to 8.5. Crystallization will still occur when this pH threshold is passed slightly, the crystals however would be much smaller which could affect precipitation in the reactor (struvite does not leave the reactor by settling), see paragraph 2.1.2 (Struvite) Precipitation Technologies). And as mentioned before, caustic (in high enough concentration) can also dissolve struvite. The release of ammonia gas can also be a detrimental effect.

4.1.4 Important parameters for the dissolution of struvite

Research made by Curtin University of Technology shows some interesting data on the solubility of struvite under different conditions [39].

Figure 5 shows that temperature seems to be a very important factor when attempting to dissolve struvite. This graph also seems to indicate that there is an optimum for struvite precipitation around pH 7. This also indicates that caustic soda should be able to dissolve struvite especially in high values of pH.

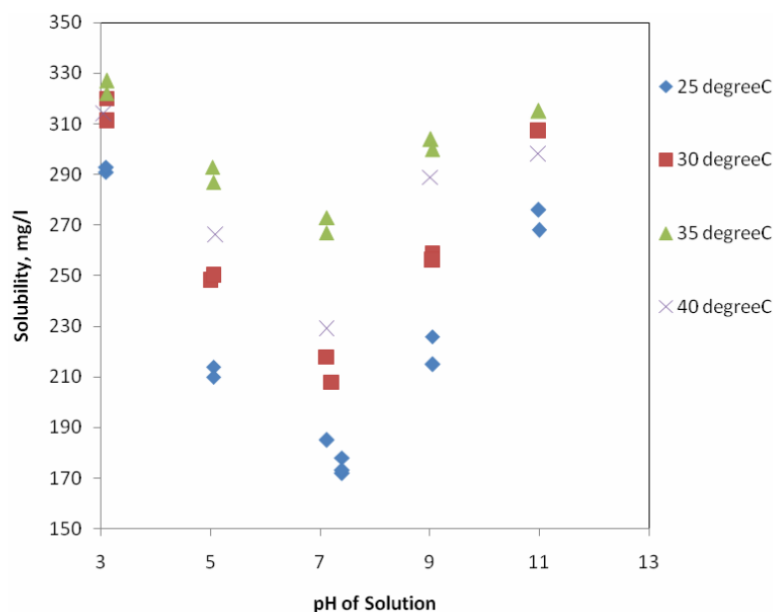


Figure 5: Solubility of struvite under different conditions

4.1.5 Difference in clogging rate by struvite for different types of pipes

Research by JD *et al.* [40] indicates that there is a difference in the rate with which certain types of pipes clog by struvite scaling. The 'smoother' the surface area the more resistant the pipe is to clogging. However, smooth pipes are still prone to clogging [36]. It could be interesting for Paques to spend some research time in finding out what type of pipe is best resistant to struvite scaling. In most WWTP stainless steel is used which has a relative rough surface area.

4.1.6 Ideal type of struvite to be used for testing

The goal is either to fully dissolve or drastically decrease the particle size of the struvite originated from inside a pipe. Complete dissolution might be better for later P-recovery in PHOSPAQ™ reactors and the like. However, the main goal is to clean the pipe and not so much the recovery of the P attached to the pipes. This means that struvite does not have to dissolve for 100% completely. The cleaning process just needs to 'create' small enough particles so that the struvite can be easily flushed out of the pipe.

This means that powdered struvite cannot be used for lab scale tests, as it doesn't have a usable size i.e. it is not possible to measure size reduction with it. Either struvite in granular or lump form can be effectively used. The absolute best would be recovered pieces of struvite from scaling in waste water treatment plants.

4.1.7 Ideal cleaning process

Large WWTP pipes can be difficult to remove, as they can be large and buried underground. An ideal cleaning process is one that is easy, cheap and sustainable. This process could work the following way:

- Add or use a parallel pipe next to the clogged pipe to continue WWTP operations. Although less ideal, the installation could also be shut down for a night until the cleaning process is finished
- Add caustic soda to the clogged pipe and close it off
- Wait until the scaling is loose or dissolved
- Reattach the pipe to the system so that the struvite suspension can be flushed out with influent
- Continue operations and use the pipe again in the next cleaning step
- The dissolved/ degraded struvite scaling can be processed for phosphate recovery.

The possibility for this type of process will be investigated further in the next paragraph.

4.2 Methodology

The main goal of this chapter is to answer the following question: How can caustic soda effectively remove struvite scaling inside industrial piping?

This research question will be answered as well as possible in this part by lab scale testing. These lab scale tests act as preparatory research step before more representative/ field like tests can be performed.

The objective is to measure the rate of which a lump of struvite decreases in weight over time, by mixing it in a beaker with a solution of HCl, NaOH or just clean water. A test reaches 'end' status when the original piece of struvite is visually gone completely, or broken apart in many little pieces that cannot be weighed effectively. Again, the struvite does not have to be dissolved for 100%, it just needs to be reduced to a reasonably small size so it can be flushed out of a pipe.

The following tests (Table 6) were performed to answer the research questions as described in chapter 1, and to test the possibility for the situation as described in '4.1.7 Ideal cleaning process':

Table 6: Setup for lab work

Test #	Type	Temperature	RPM	Molarity
1	Degradation of struvite by HCl, NaOH and water	Room temperature	210	-1M HCl, -1M NaOH -Clean water
2	Degradation of struvite by different NaOH concentration	Room temperature	210	1M ,2M ,3M , 5M and 8.25M NaOH
3	Determining chemical reaction	A sample will be taken from one of the solutions (with dissolved struvite) from test #2.		
4	Effect of mixing and Effect of air access	Room temperature	0 (open containers and closed of containers)	(best from test 2)
5	Effect of temperature	Room temp. and 35 °C	0	(best from test 2)
6	Artificially clogging pipes	-	-	-
7	Representable field-like test	Room temperature	0	(best from test 2)

4.2.1 General information

The tested material

Struvite lumps of around 0.8 grams were used for testing. The weights and shapes were chosen as uniform as possible and noted before performing the tests. The used struvite was extracted from scaling inside a pipe from a WWTP (picture in Figure 6).



Figure 6: Left: struvite from a WWTP pipe, right: struvite cut into uniform sizes for testing

The exact purity of this particular struvite is unclear. The assumption was made that it has a purity level greater than 90% of MgNH_4PO_4 and this will be verified with measurements. The struvite for testing does not have to be 100% pure struvite. It just needs to be representative for actual struvite scaling from WWTPs. This could be struvite with lower purity percentages, possibly mixed with other scaling such as CaCO_3 .

To put it into perspective; pure struvite (lab made) looks very different as it is much clearer (Figure 7).

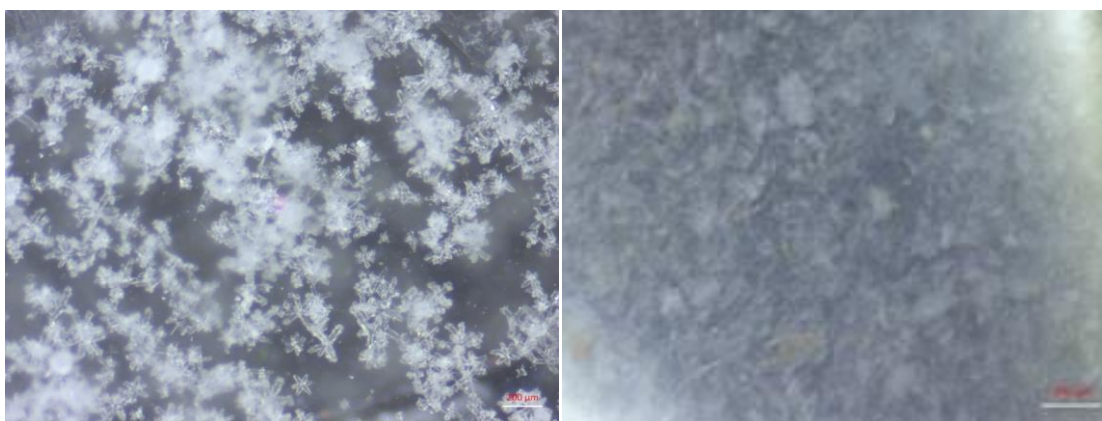


Figure 7: Lab made struvite (left) and dissolved struvite from WWTP scaling (right)

Beakers

1 litre beakers with a diameter of 8.5 cm and height of around 20 cm were continuously used. Used volumes (demineralised water with added caustic or acid) were continuously 200 ml.

Solutions

A 33% w/w (8.25 molar) stock solutions of high purity caustic soda was used to create different concentrations (such as 1, 2, 3 and 5 molar (20% w/w) NaOH) needed for testing. A 1 molar stock solution of HCl was used for the first Jar Test. Different molarities of HCl were not used in this research. The 1 molar HCl test only served as a baseline for comparison reasons with caustic soda. These specific concentrations of caustic soda were used because they are easily accessible in large quantities (no dilution steps needed), which is very useful in terms of creating an easy cleaning process at industrial scale.

Amount of measurements

Measurements were taken at 0 minutes (wet weight) and every +30 minutes thereafter to keep track

of the struvite mass loss over time. Measurements were stopped when either the original piece breaks into several little pieces (as the measurement will be very inexact from all the added water the struvite absorbs), or when a 100% size reduction (observed by eye) was achieved. A visual example of this will be given in the next chapter 'Results'.

4.2.2 Method for test #1 and #2

Measuring size reduction

The size reduction over time of struvite had to be measured in these test to determine the effect of different solutions on the degradation of struvite. This was accomplished by weighing the struvite multiple times during the test. Struvite was taken out of the solution by using a pincer. The struvite was put on a petri dish for weighing on an analytical balance. After weighing the struvite was immediately resubmerged for continuation of the test. The weight of the remaining water on the petri dish was subtracted from the struvite weight. Although this is not a very exact method (as it is not a dry weight measurement and the struvite loses contact time with the solution), it still gives a good indication of the weight reduction of a struvite lump over time. Other methods where struvite did not have to lose contact time with the solution, such as measuring turbidity, pH or measuring size decrease with photo's did not yield much useable data ([Appendix 4](#)).

Mixing and temperature

A Jar test (Figure 8) was used with stirring blades of 7.5 cm (width) by 2.5 cm (height). RPM during tests was set to around 210 and temperature was around 17-22 °C (room temperature).



Figure 8: Jar test setup, 4 stirrers rotating at equal speed

The stirrers of the jar test only stirred the top layers of each suspension so that for the majority of the time it would not make direct physical contact with the struvite lumps during mixing. The reason for this was to minimize the impact of mechanical stress on the struvite by direct physical contact with the rudders, so that the major influence on the degradation of the lump would be the type of solution and turbulence.

4.2.3 Method for test #3: Effect of mixing and effect of air access

From tests #2 we can find out how fast struvite degrades in different caustic soda solutions that were mixed. In test #3, the fastest of the two caustic solutions from test #2 can be used again. This time no mixing will be applied. It can be determined if mixing has an effect on the degradation of struvite by comparing the results from test #2 and test #3.

The difference between a sealed-off and an open container can also be examined, as it is clear from the theory that ammonia gas is likely to escape when caustic is added to struvite. It could be possible that struvite dissolves much slower when ammonia gas cannot escape the solution. It is useful to know if the pipe needs to be ventilated or not. Mechanical mixing will not be applied in this test.

Effect of Viscosity levels

It is necessary to take the effect of viscosity into account when the effect of mixing will be determined in test #3. The 4th edition of Chemical Engineering by R.K Sinnott [41] describes how it is possible to calculate the Reynolds number in solution filled beakers:

Equation 9: $Re = N D^2 \rho / \mu$ [41]

Re = dimensionless number that describes the level of turbulence

N = agitator rotational speed (rotations per seconds RPS)

D = diameter of agitator (m)

ρ = density of compound (kg/m³)

μ = dynamic viscosity (Ns/m²)

RPM in test # 1 and #2 was continuously at 210, which is 3.5 RPS. The diameter of the agitator (propeller) is 0.075m. Filling in the Reynolds equation gives the following results for each caustic soda concentration that will be used in test #1 and #2.

Table 7: Viscosity of caustic soda solutions and corresponding Re numbers

(Molar) Caustic Soda	(w/w%) Caustic Soda	Density kg/m ³ [42]	Dynamic Viscosity (Ns/m ²) [43]	Reynolds Number
1M	4%	1040	0.001	20475
2M	8%	1090	0.001	21459
3M	12%	1130	0.002	11123
5M	20%	1220	0.005	4804
8.25M	33%	1360	0.015	1785

Table 7 shows that although the stirrer speed will be constant (210 RPM), the level of turbulence will be very different over different concentrations. For example, because 8.25 molar caustic soda has a high viscosity (syrup likeness) compared to lower concentrations, the turbulence in that solutions is relatively much lower. It could be possible that the degradation of struvite is much slower in 8.25 molar caustic soda because of this fact, or maybe the difference in relative level of mixing will be simply negligible because of the high molarity itself.

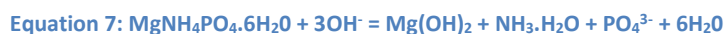
4.2.4 Method for test #4: Effect of temperature

Figure 5 in paragraph '4.1.4 Important parameters for the dissolution of struvite' describes that increased temperature correlates with increased solubility of struvite. A thermal bath can be used to test if this effect is true. If a significant difference in the degradation of struvite can be observed between room temperature and 35 °C than this effect is likely true. This effect is interesting to know in terms of creating a cleaning plan described in paragraph '4.1.7 Ideal cleaning process'. This effect will be measured by observing a single piece of struvite (0.8 g) inside a 200ml 5M caustic soda

solution. Photo's will be taken every +30 minutes to see the struvite degradation process. The degradation can be deemed finished when the original piece of struvite has lost all its surface area.

4.2.5 Method for test #5: Determining chemical reaction

Literature study (4.1 Theoretical background) showed some insight into what the causes could be for the breakdown of struvite by NaOH, HCl and water. A possible reaction involving caustic soda could be (Equation 7):



HACH test kits were used to determine if the struvite really dissolves completely into separate ions as the reaction above suggests. Test LCK 303 was used to measure ammonium (N-NH₄) and test LCK 350 was used for the determination of phosphate (P-PO₄) concentration. The method for these are described in paragraph '4.2.7 Material and method for standard tests'.

By using Equation 7, we can estimate what the concentration of phosphate will be if a piece of struvite dissolves completely. Each tests for this research used about 0.8 grams of struvite (as seen in Figure 6). The composition for these would be:

Table 8: Composition of 0.8 gram 100% pure struvite

	Mass %	Amount (mg)	Mw (g.mol)
Struvite	100%	800	245,41
PO ₄ ³⁻	39%	310	94,9714
NH ₄ ⁺	7%	59	18,042
Mg ²⁺	10%	79	24,31
6H ₂ O	44%	352	108,096

This means that if Equation 7 is true, we will measure around 310 mg of dissolved phosphate when all of the struvite (originated from 0.8 grams of struvite) in our solution dissolves, assuming it is 100% pure struvite. We would also measure 0 mg dissolved NH₄, as it is converted to NH₃·H₂O(aq) and thereafter possibly released (Equation 8) in the air as a gas.

Effect of either sodium or hydroxide

The theory describes that hydroxide (OH⁻) is the main cause of the degradation of struvite. It could also be possible however that sodium (Na⁺) may be the main cause by ionic exchange. The theory behind this is that sodium might interchange with magnesium and thus destroying the struvite crystal structure. By using two solutions with the same ionic strength (measured with electric conductivity) we can test whether NaCl is as fast as NaOH in the degradation of struvite.

4.2.6 Method for test #6: Artificially clogging pipes

To give a more representative answer for field like conditions actual clogged pipes will be required for experiments. As these were hard to obtain, some pipes will need to be artificially clogged with struvite in the lab. Several methods were tested:

Method 1

By pumping a solution of NH₄+PO₄ and injecting either MgOH or MgCl₂, scaling might form inside a pipe. This was attempted in the following way (Figure 9, Figure 10):

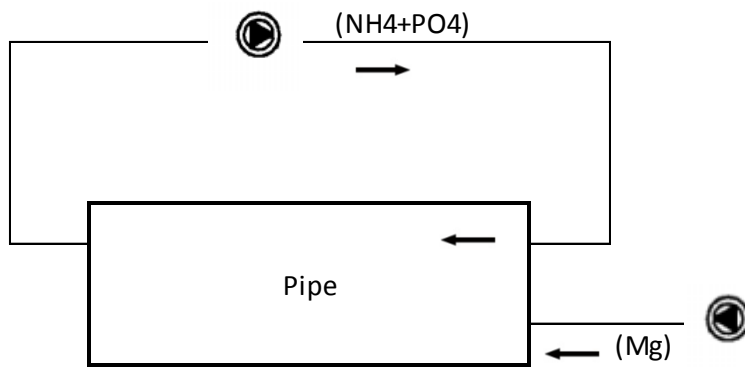


Figure 9: Method 1 pipe clogging

This setup can be observed in the pictures below:



Figure 10: Method 1 artificially clogging pipes

Figure 10, a mixture of NH_4+PO_4 and a solution of MgCl_2 was continuously pumped through the pipe by using compressed air. The air flow causes the mixture to flow upwards through the pipe which should in theory result in the formation of struvite crystals on the pipe.

Method 2

By thoroughly closing each side of a pipe before adding highly concentrated NH_4 , PO_4 and MgO , scaling might form on the pipe. The pipe can be left to rest for a weeks or so.

4.2.6 Method for test #7: Representable field-like test

The goal of this test is to find out if '4.1.7 Ideal cleaning process' can be effectively implemented in a practical/ real-life situation. If '4.2.6 Method for test #6: Artificially clogging pipes' does not work, than an answer must be given by using results from smaller scale lab tests.

The problem with these smaller lab scale tests (tests #1 and #2) is that the contact area of caustic soda with struvite is very different for lab scale tests (such as tests #1 and #2) compared to a field-like situation described in '4.1.7 Ideal cleaning process'. In a beaker, struvite is highly (but not completely) surrounded by the solution and thus it has a relative high contact area. In this specific field-like situation, the contact area is much lower as the pipe is closed-off, which means only a limited amount of solution can be added. Only a relative (Table 9) small amount of caustic soda would be present to react with the struvite scaling.

Table 9: Comparing struvite/ caustic soda ratio in lab scale with ideal cleaning process for field conditions

Amount of struvite in a beaker (g)	0.8
Density of struvite (g/cm ³)	1.7
Amount of struvite in a beaker (ml)	0.47
Volume of caustic soda in a beaker (ml)	200
Struvite/ caustic soda in lab scale (ml/ml)	0.0024
-	-
Amount of struvite in field condition, random example of a clogged pipe (%)	40%
Struvite/ caustic soda ratio in field condition (ml/ml)	0.4

This means that the degradation rate of struvite will be much slower in a pipe compared to the degradation rate of a small amount of struvite in a beaker. From Table 9, it can be determined what a more realistic volume of caustic soda would be (Table 10):

Table 10: Representable struvite/ caustic soda ratio in lab scale

Amount of struvite (g)	0.8
Density of struvite (g/cm ³)	1.7
Amount of struvite (ml)	0.47
Amount of struvite in field condition, random example of a clogged pipe (%)	40%
Struvite/ caustic soda ratio in field condition (ml/ml)	0.4
Volume of caustic soda needed (ml)	0.705

To create a representable picture of field-conditions as described in '4.1.7 Ideal cleaning process' by performing lab scale test, 0.71ml of caustic soda (Table 10) needs to be used instead of 200ml of caustic soda (Table 9). This representable ratio of struvite to caustic soda cannot be used for tests #1 and #2, as 0.71ml of caustic soda is a too small amount of volume to use to determine the effect of mixing.

4.2.7 Material and method for standard tests

HACH equipment

Test #3 was performed by using predesigned methodology of HACH [44] for the determination of phosphate and ammonium. These were test LCK 303 (ammonium) and LCK 350 (phosphate) and can be observed in Figure 11.



Figure 11: HACH tests LCK 303 and LCK 350

The methodology was performed closely as described by the test kits. After sample preparation the cuvettes were put in an automatic HACH sample reader (Figure 12).



Figure 12: HACH reader

Sample preparation

Additional steps were added with the test kits LCK 303 and LCK 350. The samples for LCK 350 (phosphate) were centrifuged before reading it with the HACH reader to remove any suspended solids and to optimize the determination of dissolved amount of phosphate.

Both LCK 303 and LCK 350 samples were diluted with demineralised water so that they would fall in the specific measuring range of each specific kit. This was achieved by using the calculated expected value as described in Table 8.

4.3 Results

This paragraph shows the results derived from the experiments as described in paragraph '4.2 Methodology'.

4.3.1 Results Test #1: Degradation of struvite by HCl, NaOH and water

The results from experiment 1 can be seen in Figure 13:

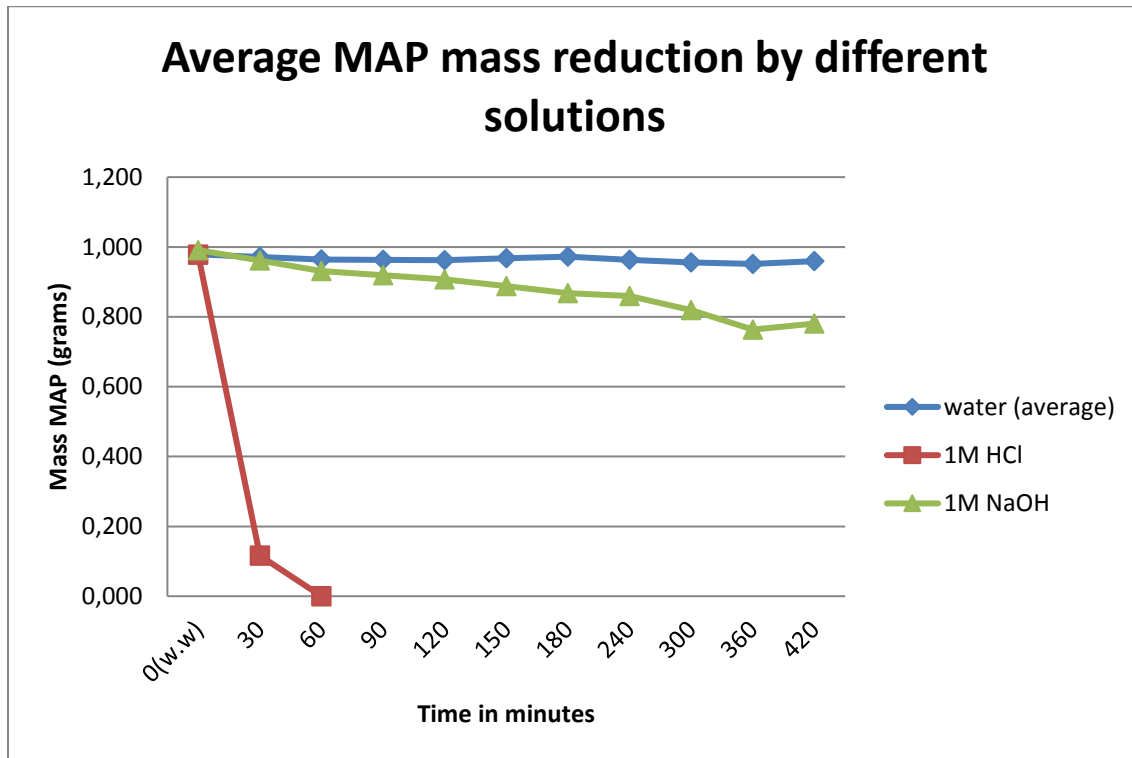


Figure 13: Overview of struvite mass reduction in different solutions (averages)

Example of the process by HCl can be seen in Figure 14 (the drawn squares on the beaker are 1 by 1 cm):



Figure 14: Start (left) to finish (right) of 0.8 g MAP in 1M HCl ~45min. mixing

Figure 14 shows that 1 molar of HCl completely reduces the struvite lump in about 45 minutes of mixing. The struvite in water and 1 molar of caustic soda was still largely intact after 420 minutes of mixing (Figure 13).

4.3.2 Results Test #2: Degradation of struvite by different NaOH concentration

The results from experiment 2 can be seen in Figure 15:

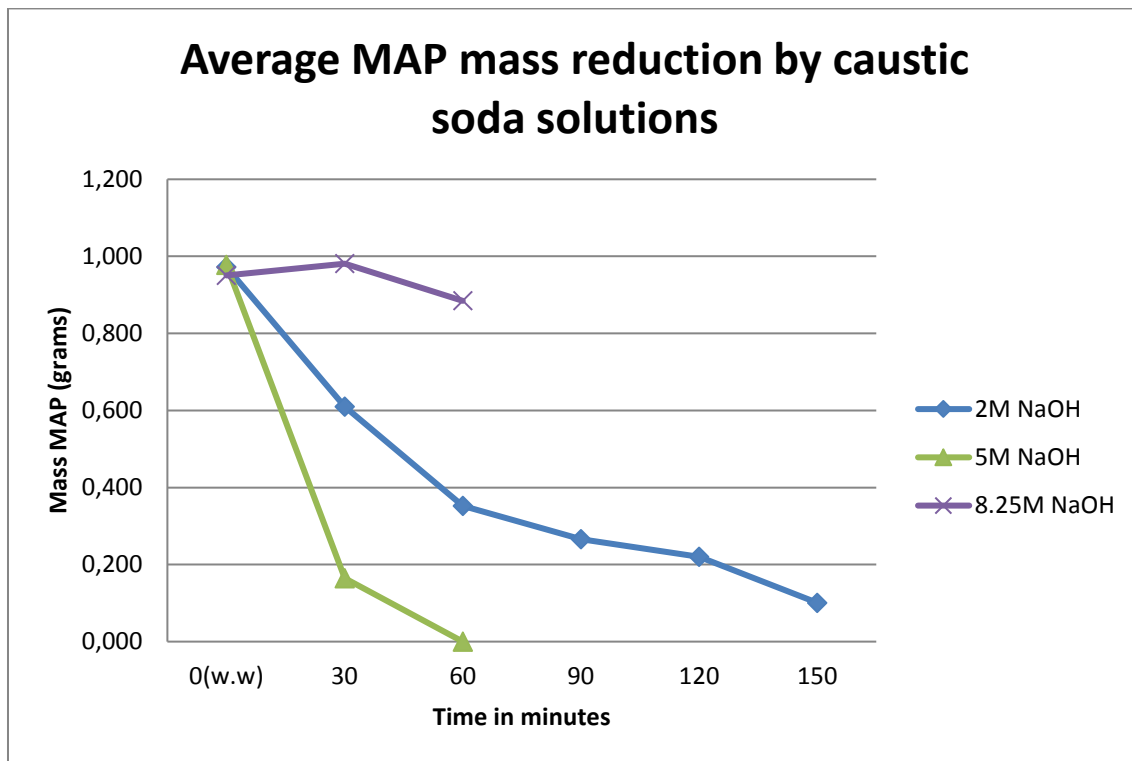


Figure 15: Overview of struvite mass reduction in caustic soda solutions (averages)

Figure 15 shows that 5M of caustic soda degrades struvite the fastest when mixing is applied. With 8.25M NaOH, the struvite breaks into smaller parts after around 120 minutes. The structure is very soft which makes it very hard to remove with a pincer without accidentally breaking the lump further. An example of this is shown in Figure 16.



Figure 16: Soft struvite in a 8.25M NaOH solution after 120 minutes of mixing

Although there wasn't a 100% degradation of the struvite in 8.25M, the test was still deemed as 'finished' after 120 minutes. If struvite gets as soft as this it can be easily flushed out with effluent as it will most likely not be attached to the inside of the pipe anymore. The difference between 5M and 8.25M will be discussed further in the next paragraph 'Discussion'. The 3M caustic soda test was only performed two times. This result is not shown in Figure 15 because the result between these two

tests varied greatly and because no repeats were performed later on. The two 3M caustic soda tests can still be found in [Appendix 3](#).

Organoleptic observation

A heavy NH_3 smell was observed during the mixing of struvite in 2M NaOH and higher concentrations. When a piece of struvite dissolves, the smell also disappears. This could indicate that NH_4 indeed converts to NH_3 and releases through the air as the theory describes.

Overview of test #1 and #2

Table 11 shows the estimated time needed for a piece of struvite to completely lose its original surface area. As it is difficult to estimate if a struvite piece is gone (difficult to weigh and see by eye), estimation were made. For example with 2M NaOH, the exact time was unclear but is somewhere in between two measuring points, measuring point 150 minutes and measuring point 180 minutes. Both the water tests and the 1 molar NaOH tests needed longer than 420 minutes of mixing to degrade the struvite. More data about these results can be found in [Appendix 3](#).

Table 11: Degradation rate of (0.8 g) MAP in different solutions

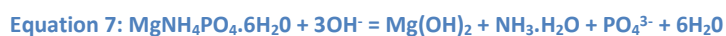
	Average required time (minutes) somewhere between:	Average from notes (minutes)	Number of tests
Water	>420	>420	2
1M HCl	40-50	~45*	3
1M NaOH	>420	>420	2
2M NaOH	150-180	150-180	5
5M NaOH	30-60	~45*	3
8.25M NaOH	60-90	60-90	3

*These averages were easier to estimate, since there was less deviation across repeat tests.

Table 11, Figure 13 and Figure 15 indicate that 5 molar seemed to be the fastest working concentration of NaOH on the dissolution of struvite in mixed conditions. It also shows a big difference in effective dose between HCl and NaOH, as 1M HCl seems to degrade struvite about as fast as 5M NaOH.

4.3.3 Results Test #3: Determining chemical reaction

The assumption in this research is that the struvite is near 90% pure. The hypothesis is that struvite dissolves completely into separate ions when it reacts with caustic soda (Equation 7), and that ammonia gas will be released through the air (Equation 8).



An expected value can be calculated from this equation. The hypothesis has a good chance to be true if the expected value is approximately equal as the measured value. Samples were taken from the 5M caustic soda test, after 50 and 180 minutes of mixing. After 40 minutes, the struvite in the test was reduced to a small enough size that the test could be deemed as 'finished'. At that point it still had some smaller particles in suspension. After 180 minutes the struvite was completely gone and the solution was very murky. The samples taken from these were prepared as described in paragraph '4.2.7 Material and method for standard tests'. All tests were performed in duplicates. Table 12 shows the results from the HACH test LCK 350 and the expected value from Equation 7:

Table 12: Expected versus measured, dissolved phosphate from 0.8 gram struvite

P-PO4 (mg/L)	5M NaOH (180 min.)
Expected (from 0.804g MAP):	503.4
Measured by LCK 350:	478.2
% deviation	-5% *

* After 180 minutes of mixing a clear solution was observed. The reasonably small 5% deviation indicates that this MAP is around 90 to 100% pure and also that the hypothesis (Equation 7) is likely correct.

Table 13 shows the results from the HACH test LCK 303 and the expected value from Equation 7. Samples were taken after 40 minutes and 180 minutes of mixing 0.8g of struvite in 5 molar caustic soda:

Table 13: Expected versus measured, dissolved ammonium from 0.8 gram struvite

N-NH4 (mg/L)	5M NaOH (40min. of mixing)	5M NaOH (180 min. of mixing)
Expected (from 0.8g MAP):	<1	<1
Measured by LCK 303:	58.7 *	<1

* Not all of the struvite was visually gone in the suspension. Not all of the NH_4 was likely converted yet as NH_3 .

NaCl test for the effect of sodium

A Jar Test was performed in duplicate; the results are shown in Table 14:

Table 14: Map mass loss of struvite in either NaOH or NaCl (averages from duplicates)

(Time in minutes)	Map weight (grams) in solutions	
	2 Molar ,350 mS/cm NaOH	350 mS/cm NaCl
0 (wet weight)	1,02	0,92
30	0,61	0,93
60	0,29	0,92
90	0,16	0,90
120	0,062	0,90

Table 14 shows the average taken from tests result from duplicates. It shows that after 120 minutes struvite in 350 mS/cm NaOH is almost completely gone, while the struvite in salt solution is still largely intact. This indicates that hydroxide is indeed the main cause for the breakdown of struvite as mentioned in the reaction from (Equation 7).

4.3.4 Results Test #4 Effect of mixing and effect of air access

Test 4 shows a big difference in degradation rate of struvite between closed container and open container (Table 15). Struvite in open containers dissolves considerably faster compared to closed container. The reason for this could be that NH_3 saturation (distributed in the air and solution) was achieved somewhere during the process. The gas cannot escape the container and thus slowing down the reaction (Equation 7, Equation 8). 'End' is defined as a 100% decrease of the original particle size of the struvite piece.

Table 15: Degradation rate of struvite in open and closed containers (no mechanical mixing occurred)

	End (minutes)
2M NaOH (open container)	~240
2M NaOH (closed container)	>300
5M NaOH (open container) *	~120
5M (closed container)	>300

Table 15: the 2 molar (closed) and the 5 molar (closed) tests were stopped after 300 minutes, as the goal of the test was to see if a difference could be observed between closed and open containers, which seemed true based on the result. Comparing Table 15 with Table 11 also shows that mixing has a significant effect on the degradation of struvite at 2M and 5M caustic soda.

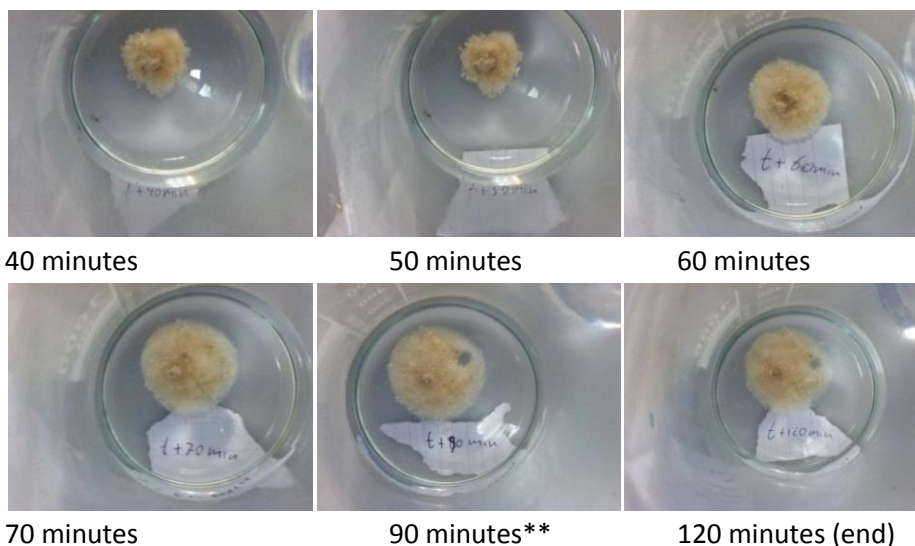
A time lapse of the degradation of struvite in the 5M open container test can be observed below:



10 minutes

20 minutes

30 minutes



*A sample was taken here for microscopic observation

Organoleptic observation

Bubbles coming out of a struvite piece were observed in the closed-off containers, which could be NH_3 gas.

4.3.5 Results Test #5: Effect of temperature

0.8g Of struvite in closed-off containers with 200ml of 5M NaOH was put in a heating bath of 35 °C. These can be compared to the result of 5M closed-off containers in test #4 (Table 15). 'End' is defined as a 100% decrease of the original particle size of the struvite piece. The results of duplicates can be seen in Table 16:

Table 16: Effect of temperature in duplicate

	End (minutes)
5M NaOH #1	~200
5M NaOH #2	~200

Comparing the result from Table 15 with Table 16 shows that the increase of temperature does increase the degradation rate of struvite as the literature in paragraph '4.1.4 Important parameters for the dissolution of struvite' suggests.

4.3.6 Test #6: Artificial clogging pipes

Method 1

Results this method showed little success. The goal was to artificially clog pipes with struvite. The struvite seemed to form mostly outside the pipe (Figure 17, Figure 18 and Figure 19):



Figure 17: Struvite on the clamp and on the outside of the pump

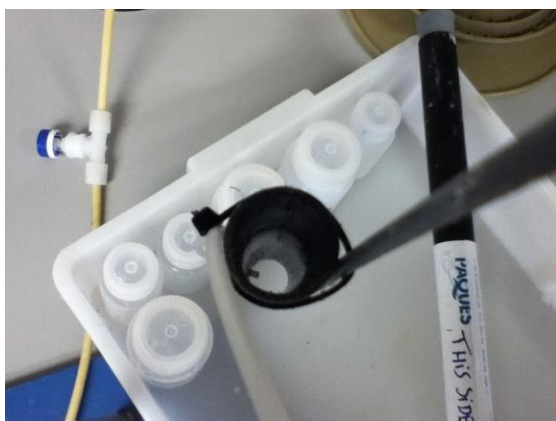


Figure 18: No struvite inside the plastic pipe



Figure 19: Thin layer of struvite or magnesium oxide on a stainless steel pipe

Method 2

A mixture of NH_4Cl , KH_2PO_4 and MgCl_2 was added to a pipe of approximately 46.8 cm long with an inner diameter of 2 cm. The pipe was sealed with rubber stops and thereafter left to rest for approximately one week. The result can be seen in the following pictures:



Figure 20: Pipe successfully filled for 50%

Although the test seems successful, it only has substance attached on one side of the pipe. The pipes in the field are clogged on all sides of the inner walls. The white substance that can be seen in Figure 20 could also simply be dried up magnesiumoxide or magnesiumphosphate and not struvite.

4.3.7 Results Test #7: Representable field-like test

Since the results from test #6 did not deliver usable material to test field-conditions (as described in paragraph '4.1.7 Ideal cleaning process'), the method in paragraph '4.2.6 Method for test #7: Representable field-like test' was used.

Time lapse of the degradation of struvite

In this particular test 7.7 grams of struvite scaling (same material as in other tests) was used to react with 6.8ml of 5M caustic soda. The ratio struvite to caustic soda was calculated for a pipe that would be clogged for ~40% of caustic soda. For an example of the calculation please see Table 10. In Figure 21 a time lapse can be seen of this test. After 50 minutes of waiting the struvite had absorbed all of the solution. At this time the struvite was very loose and easy to break apart as can be seen in the photo in the bottom left photo. This was easily done by gently stirring it with a gloved finger. The struvite was washed with water which shows that some intact struvite pieces were still there (the last photo in the bottom middle).

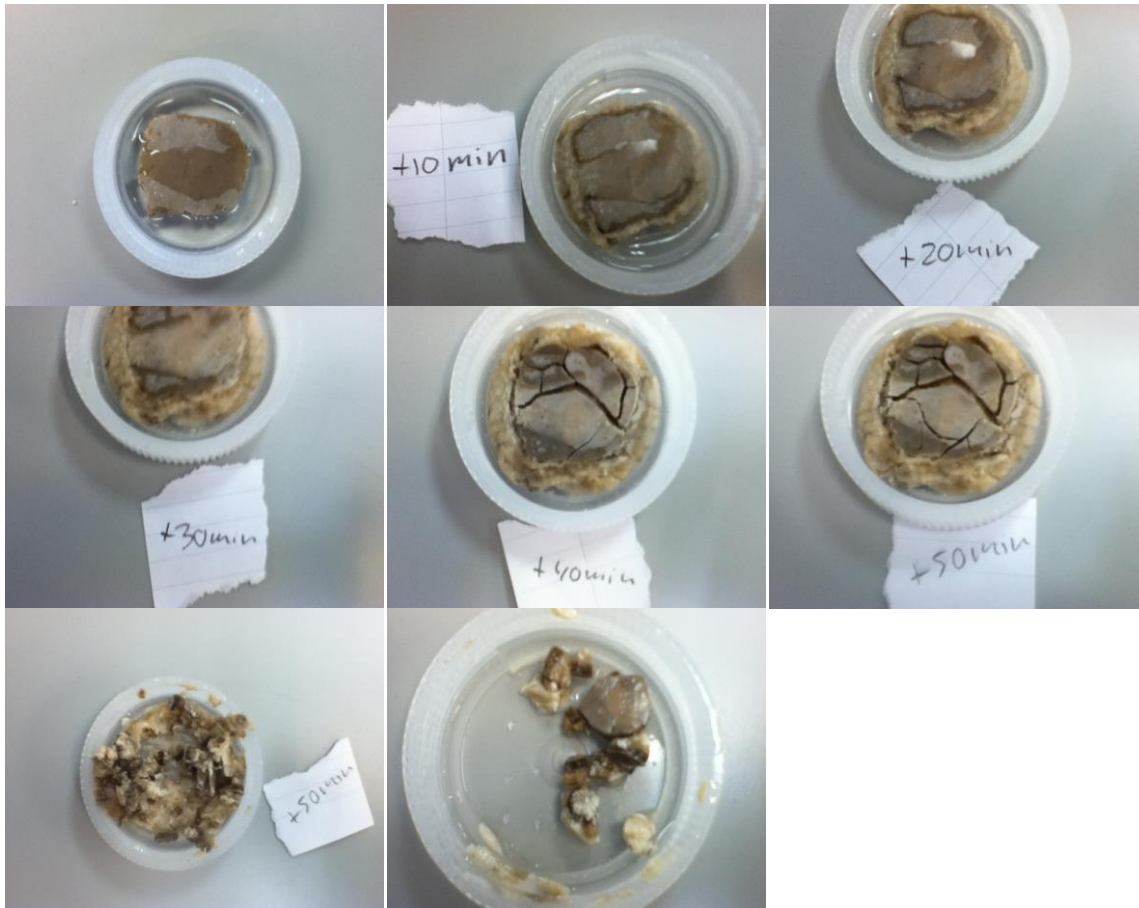


Figure 21: Time lapse of the degradation process of 7.7g of struvite in 6.8ml 5M NaOH

Figure 21 shows that it is possible to clean struvite in a process such as described in paragraph '4.1.7 Ideal cleaning process' for $\leq 40\%$ clogged pipes. The test does not show if higher percentages than 40% also work in this way. With higher clogging percentages, lower volumes of caustic soda can be added.

Difference between 5M and 8.25M

The test in Figure 21 was repeated. This time one struvite piece was put in 5M caustic soda and one in 8.25M caustic soda (Figure 22), to see if there was an observable difference between the two molarities (a struvite to caustic ratio for a 40% clogged pipe was used again).



Figure 22: Start of test ~3g of MAP reacts with 5M and 8.25M caustic soda

After about 60 minutes of waiting the added solutions of caustic soda was absorbed by the struvite; no fluid was left. Figure 23 shows that the struvite was easily broken apart. Both the struvite in 5M

and in 8.25M still had large intact pieces left. No clear difference between the two molarities was observed.



Figure 23: End result of ~60 minutes waiting, 5M (left) and 8.25M (right)

Comparing Figure 21 with Figure 23 shows that the general shape of the struvite is very important in the way it degrades, as the result from Figure 23 left far bigger intact struvite pieces.

4.4 Discussion

The performed experiments in the previous paragraph showed that caustic soda can indeed be used as a cleaning agent for the removal of struvite scaling. Although the results are promising, some aspects of the tests require additional discussion which will be explained in this paragraph.

Test material

Some of the tests were repeated (mainly 2M caustic soda in test #2), because results between the duplicates showed varying result. One possibility is that the test material has a general bad uniformity. As you can see in Figure 6, the pieces cut have somewhat the same shape but they still 'acted' very different inside beakers. Round-like pieces usually remained somewhat stationary in the middle of the beakers when mixing; they didn't seem to be propelled around much in suspension. Flat pieces however were agitated much easier in suspension. This could be the main explanation between the varying results of degradation rates for struvite in 2M NaOH mainly; as the fastest result was 90 minutes and slowest was 150 minutes ([Appendix 3](#)).

Relative flat pieces of struvite were only used in the first couple of tests (tests #1 and #2). The supply of flat pieces was exhausted later on, so only round-like pieces were used in later Jar Tests. Although these were all somewhat round they still had varying shapes which could be the reason behind the deviation in results of test #2 mainly and also test #1.

This is most likely the main explanation as other test variables such as applied concentrations, type of beakers and mixing speed were always uniform across this research. Another possible explanation could be the used method for the weighing of the struvite.

Measurements methodology

The method used for measuring the struvite weight reduction over time for tests #1 and #2 is not ideal. The reason is that the struvite had to be physically removed from suspension to weigh it on an analytical balance, and thus it loses reaction time with the solution by not being in suspension for a brief moment. This also means that a percentage of water will always be weighed beside the struvite. As mentioned before, other methods where no suspension time was lost such as change in electrical conductivity, pH change and turbidity (in the unit NTU) increase all showed unusable data ([Appendix 4](#)). They either showed little correlation with MAP mass reduction or were very inexact.

The loss of suspension time was continuous during this research; around 0.5 minutes was needed for each weighing. This still may have a negative effect on representability for lab scale versus field like scale, as no contact time of the struvite has to be lost with the solution inside an actual pipe.

Concerning paragraph test #3 it has to be mentioned that the HACH tests are not very accurate to begin with, as dilution steps were somewhat inaccurate because samples are never 100% homogeneous (suspended solids still present in solution). Also mentioned before in this paper is the fact that the purity of the struvite is unsure, but estimated to be at least 90% or higher.

Difference between 5M and 8.25M NaOH

The notable difference between 5M and 8.25M NaOH (Figure 15) in test #2 could be explained by the fact that 8.25M NaOH has a much higher viscosity than lower concentrations. Higher viscosity correlates with lower turbulence inside beakers (Table 7). Turbulence has a correlation with the degradation rate of struvite in caustic soda, which we know from test #4. For example, 5M caustic soda degrades a piece of struvite in ~45 minutes when it's mixed (Table 11), compared to ~240 minutes not mixed (Table 15).

Also, 5M caustic soda is faster than 8.25M caustic soda when mixing is applied to both (Figure 15). The opposite might be observed however, when no mixing is involved, then 8.25M could degrade struvite faster than 5M caustic soda because viscosity would not have an effect. This makes sense; higher concentration of hydroxide equals faster degradation rate of struvite. This effect was tested (Figure 23), but did not show a significant difference. The test in Figure 23 should be repeated more (and in larger scales) to fully show this effect.

4.5 Conclusion and recommendation

Experiments were performed to answer the following question: How can caustic soda effectively remove struvite scaling inside industrial piping?

4.5.1 Conclusion

A) Effective caustic soda concentration

Concentrations of 1 molar and higher of caustic soda degrades struvite faster than simple water (Figure 13). Which confirms that caustic soda does dissolve or degrade struvite. When mixing is applied, 5M caustic soda will be the fastest working concentration of caustic soda (Figure 15), which seems about as fast as 1M of hydrochloride. Higher concentrations of caustic soda are slower in mixed situations because of the correlation of concentration with viscosity, which has an effect on turbulence (Table 7). Which means that when mixing is applied to the cleaning of struvite scaling inside pipes, the best working concentration of caustic soda seems to be 5M.

When no mixing is applied to the cleaning of struvite by caustic soda, such in situations as described in 'paragraph 4.1.7 Ideal cleaning process, 8.25M might work faster than 5M caustic soda. Because no mixing would be applied, viscosity would not have a significant effect. However, Figure 23 shows that no difference was observed between 5M and 8.25M in representable lab test. Figure 23 is only an indication, and needs to be researched further to fully understand this effect of no mixing and higher molarities of caustic soda.

Although lower molarities of hydrochloride are needed compared to caustic soda molarities for the same effect, caustic soda still has benefits over the use of acid (described in paragraph 4.1.3 Alternative substances for the removal of struvite scaling). The results from tests #1 and #2 alone, strongly indicates that caustic soda can indeed be used effectively as a cleaning agent for struvite scaling inside industrial piping.

B) Confirming the chemical reaction

Chemical reaction (Equation 7: $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O} + 3\text{OH}^- = \text{Mg}(\text{OH})_2 + \text{NH}_3 \cdot \text{H}_2\text{O} + \text{PO}_4^{3-} + 6\text{H}_2\text{O}$) as found in literature was confirmed by test #3, the HACH LCK 350 phosphorus test. The expected value (calculated from Equation 7) vs measured value (as seen in Table 12) only showed a small deviation, which indicate that the purity of the test material is at least >90% and which indicates that the hypothesis (Equation 7) is correct. This result is promising. However, because of the lack of repetitions and of the inaccurate test method (see Discussion), there is not enough evidence to support that the hypothesis (Equation 7) is correct from the phosphate test alone. The HACH LCK 303 ammonium test showed that no NH_4 was present after the degradation of struvite by caustic soda (Table 13). Also, a strong NH_3 smell was observed and bubbles were seen coming out of struvite lumps in the non mixing tests. This indicates that Equation 8 derived from Equation 7 is likely correct. The ammonium test and phosphate test together seem to indicate that hydroxide indeed can dissolve struvite completely. Comparison of NaCl test (Table 14) with NaOH test (Table 11) confirms that hydroxide (OH^-), and not sodium (Na^+) degrades struvite.

C) Ideal cleaning step

The situation as described in 'paragraph 4.1.7 Ideal cleaning process' was researched by performing test #4, #5 and #7. Test #4 was performed to see if struvite will degrade when a clogged pipe is closed-off. The test showed that struvite degrades faster in open containers versus containers that are closed-off (Table 15). The difference can be explained by NH_3 saturation; NH_3 cannot escape the

solution which inhibits/ slows down the reaction. Although the reaction is much slower, struvite will still degrade.

Next part was to see if temperature has any influence on the degradation rate. Test #5 shows that there is a correlation between degradation of struvite by caustic soda and increased temperature (Table 16). Although the application of increased temperature towards 35 °C does not matter in terms of the use of 'ideal cleaning process', as it would require allot of energy, it still shows that the weather for example would have a significant effect on the required time for the process. The cleaning process might take significantly longer in cold winter days.

Finally, test #7 was performed to see if representable volumes of caustic soda are enough to clean pipes that are clogged for 40% or less. Figure 21 and Figure 23 shows that struvite to caustic soda ratio's that are relevant for 40% clogged pipes are enough to significantly reduce struvite scaling. The struvite absorbs the caustic soda and becomes very easy to break apart into smaller pieces. These smaller pieces can then be flushed out with WWTP effluent.

4.5.2 Recommendations

a) For a fast cleaning process

The use of 5M caustic soda will be recommend for the cleaning of struvite clogged pipes. This is fast, easily available, and also safer and cheaper than 8.25M caustic soda. Applied mixing is recommend and can be achieved by pumping the caustic soda solution in a loop trough the pipe, which achieves faster degradation and helps disposal of ammonia through the air. Heating could be applied to further increase the speed of the cleaning process, but is not recommend, as the energy demand is high and the cleaning process is likely fast enough without it.

The required flow of the caustic through the pipe is ideally at a Reynolds number of 1000 (this is the threshold for turbulent flow inside a pipe) or higher. This can be calculated by using the Reynolds equation for pipes.

b) For a slower cleaning process

When time is less of an issue, an easy and cheap cleaning step can be achieved by the following process:

- Add or use a parallel pipe next to the clogged pipe to continue WWTP operations. Although less ideal, the installation could also be shut down for a night until the cleaning process is finished
- Add caustic soda to the clogged pipe and close it off
- Wait until the scaling is lose or dissolved*
- Reattach the pipe to the system so that the struvite suspension can be flushed out with influent
- Continue operations and use the pipe again in the next cleaning step
- The dissolved/ degraded struvite scaling can be processed for phosphate recovery.

*This point requires a follow-up research, as it is unsure how long this process would take. In test #7 the required time was 50 to 60 minutes. However, the struvite had open contact with air and a relative small amount of struvite was used compared to field-like situations (Figure 4). It is not yet determined if the result from test #7 would be the same on larger scales. Table 5 describes that

ammonia gas might be released in great quantities (dissolved or released through the air). This problem could be handled by stripping the ammonia by applied aeration. In terms of Phospaq, aeration is already used for the stripping of CO₂.

c) Follow-up research

- Point 'A' of the conclusion seems to indicate that even higher concentration than 8.25M caustic soda may work even faster in none mixed solutions. Because of safety issues and time shortage this was not researched for this thesis.
- Both points 'A' and 'C' in this recommendation need a thorough follow up research, to give an estimation of required resources and time for the cleaning processes.
- An alternative to point 'A' of the recommendation would be the use of 8.25M caustic soda. This might work even faster than 5M when the amount of mixing would be increased proportionally to overcome the effect of viscosity on turbulence. Because 8.25M caustic soda has such a relative high amount of viscosity, the amount of required energy for the pumping of the solution would also be much higher. Follow-up research would be needed to evaluate this possibility.
- As described in paragraph '4.1.5 Difference in clogging rate by struvite for different types of pipes', it could be interesting for Paques to further investigate the use of scaling-resistant piping.

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Appendix

Appendix 1

A list of technologies based on precipitation technologies can be found here.

AIRPREX

Company contact: www.cnp-tec.com

Produced product: (granular) struvite

Process specifics: Crystallisation, airlift reactor (CSTR and CO₂ stripping), precipitation and separation

Origin of product: UASB effluent Onsite wastewater treatment plants

P removal efficiency: 90-95%

Average operational costs: Electricity demand 10.3 kWh/ kg P. Average chemical demand 14.5 kg MgCl₂/ kg P

Reference list:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Berlin Wassmannsdorf (GER)	2009	600 - 1,000
Mönchengladbach Neuwerk WWTP (Niersverband)	2009	600
Waternet (NL), RWZI Amsterdam-West	2014	1,500
WEB Wolfsburg dewatering plant (GER)	2016	unknown
Tianjin Capital Environmental Protection Group Company Limited (CN)	2016	unknown
ASG wastewater facility Salzgitter GmbH – (GER)	2015	unknown
Stadt Uelzen (GER)	2015	unknown
Echten WWTP (NL)	2011	165

Anphos

Company contact: www.colsen.nl

Produced product: unspecified struvite product

Process specifics: Crystallisation, airlift reactor (CSTR and CO₂ stripping), precipitation and separation

Origin of product: UASB effluent Onsite wastewater treatment plants

P removal efficiency: 80-90%

Average operational costs: 0.3 euro/ kg P

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Land van Cuijk (NL), Aa en Maas	2011/2017	unknown
Odiliapeel (NL), Peka Kroef	2005	unknown
Kruiningen (NL), Lamb Weston Meijer	2005	unknown

Bergen op Zoom (NL), Lamb Weston Meijer	2007/2016	<i>unknown</i>
Budrio (IT), Pizzoli	2010	<i>unknown</i>
Oosterbierum (NL), Lamb Weston Meijer	2016	<i>unknown</i>

Crystalactor

Company contact: www.royalhaskoningdhv.com

Produced product: Struvite pellets, calcium phosphate pellets and others

Process specifics: coagulation/ flocculation/ crystallisation, airlift reactor (CSTR and CO₂ stripping), precipitation and separation

Origin of product: Sewage sludge

P removal efficiency: 70-90%

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Nanjing (CN)	2010	<i>unknown</i>
DHV B.V. Water Amersfoort (NL)	2003	<i>unknown</i>
Alto Dairy Cooperative, Waupun (Wisconsin USA)	2003-2005	<i>unknown</i>

EloPhos

Company contact: www.eliquostulz.com

Produced product: Unspecified struvite product

Process specifics: Degassing, crystallisation (CSTR)

Origin of product: UASB effluent Onsite wastewater treatment plants

P removal efficiency: 95%

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Lingen (GER)	2016	<i>unknown</i>

EXTRAPHOS

Company contact: www.budenheim.com

Produced product: DCP (dicalciumphosphate)

Process specifics: Crystallisation, airlift reactor (CSTR and CO₂ stripping)

Origin of product: UASB effluent

P removal efficiency: ~ 50% removal efficiency of P in sludge input

Average operational costs: *unknown*

References: *unknown*

Company	Start of operations	~ Annual phosphate capacity (tonnes)
MZ-Mombach (GER), Wirtschaftsbetrieb Mainz	2017 (pilot)	<i>unknown</i>

J-oil

Company contact: J-Oil Mills Co.

Produced product: HAP

Process specifics: *unknown*

Origin of product: Onsite wastewater treatment plants

P removal efficiency: *unknown*

Average operational costs: *unknown*

References: *unknown*

Company	Start of operations	~ Annual phosphate capacity (tonnes)
Yokohama (JP), J-Oil Mills Co	<i>unknown</i>	<i>unknown</i>

JSA

Company contact: Japan Synthetic Alcohol Co. (P-REX source 1998)

Produced product: HAP

Process specifics: *unknown*

Origin of product: Onsite wastewater treatment plants

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual phosphate capacity (tonnes)
Kawasaki (JP), Japan Synthetic Alcohol Co	1998	<i>unknown</i>

Kurita

Company contact: www.kurita.eu/en/

Produced product: Struvite

Process specifics: *unknown*

Origin of product: Onsite wastewater treatment plants

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Fukuoka (JP)	3 plants 1997	<i>unknown</i>

Kyowa Hakko

Company contact: www.kyowahakko-bio.co.jp/english/

Produced product: HAP

Process specifics: *unknown*

Origin of product: Onsite wastewater treatment plants

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Hofu (JP)	2006	<i>unknown</i>

Multiform

Company contact: www.multiformharvest.com

Produced product: Struvite pellets and other

Process specifics: caustic or ammonium for pH adjustment, cone-shaped crystallisation reactors.

Origin of product: Onsite wastewater treatment plants

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Yakima, WA	2012	350
Boise, ID	2012	438
Massey, MD, Jones Family Farms (dairy)	2013	20
Green Bay, WI	<i>unknown</i>	<i>unknown</i>

NASKEO

Company contact: <http://www.naskeo.com>

Produced product: (granular) struvite

Process specifics: Crystallisation, fluidised bed reactor

Origin of product: Onsite wastewater treatment plants

P removal efficiency: 85-90 %

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Castres WWTP (FR)	2015	33

Nippon Phosphoric Acid

Company contact: www.nippon-chem.com

Produced product: H₃PO₄

Process specifics: *unknown*

Origin of product: Downstream wastewater treatment plants and ash treatment

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Chiba (JP)	2009	<i>unknown</i>

NuReSys

Company contact: www.nuresys.be

Produced product: Granular Struvite

Process specifics: Crystallisation (CSTR) and CO₂ stripper

Origin of product: UASB effluent, primary sludge leachate, centrate

P removal efficiency: 80-95%

Average operational costs: 1.31 Euro/ kg P

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Milchunion Germany Dairy (GER)	2006	<i>unknown</i>
Agristo Belgium Deep frozen French Fries (BE)	2006	274
Clarebout Potatoes (Chaussée de Lille, BE)	2012	402
Clarebout Potatoes (Nieuwkerke, BE)	2012	657
Land van Cuijck (NL) Municipal WWTP	2015	<i>unknown</i>
Waterschap Valei en Veluwe (NL)	2003/2015	950
AQUAFIN (BE)	2013	<i>unknown</i>
Remondis Aqua "REPHOS" (Altentreptow, DE)	2006	<i>unknown</i>

NutriTec

Company contact: <http://sustec.nl/> and <http://www.saniphos.eu/>

Produced product: (granular) struvite

Process specifics: Crystallisation (MgCl₂ dosing), airlift reactor (CSTR and CO₂ stripping)

Origin of product: UASB effluent, separately collected urine

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
WWTP (Venlo, NL)	2015 (pilot)	<i>unknown</i>
WWTP ARA Neugut (GER)	2014 (pilot)	<i>unknown</i>
WWTP (Leeuwarden, NL)	2013 (pilot)	<i>unknown</i>
SANIPHOS	2010	<i>unknown</i>

PHOSPAQ™

Company contact: en.paques.nl/products/other/phospag

Produced product: (granular) struvite

Process specifics: Crystallisation, airlift reactor (CSTR and CO2 stripping)

Origin of product: UASB effluent

P removal efficiency: 70-95%

Average operational costs: *unknown*

References:



#	Industry	Country	kg P/d	year
11	Ethanol	China	60	2016
10	Food	China	958	2015
9	Food	Germany	1087	2014
8	Solids waste	China	100	2013
7	Ethanol	USA	540	2013
6	Municipal	The Netherlands	115	2012
5	Municipal	United Kingdom	550	2012
4	Beer&beverage	Poland	350	2011
3	Beer&beverage	China	750	2011
2	Food	The Netherlands	190	2007
1	Municipal & food	The Netherlands	245	2006

PhosphoGREEN (suez, partner with Grundfos)

Company contact: www.suezwaterhandbook.com

Produced product: (granular) struvite

Process specifics: degassing chamber, precipitation tank

Origin of product: Wastewater sludge

P removal efficiency: 90%

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Aaby (DK), Aarhus Water	2013	180
Marselisborg (DK), Aarhus	2018	<i>unknown</i>

Water		
Herning (DK), Herning Water	2016	<i>unknown</i>

PHORwater

Company contact: www.phorwater.eu

Produced product: (granular) struvite

Process specifics: Crystallisation (CSTR), precipitation

Origin of product: Wastewater sludge

P removal efficiency: >90%

Average operational costs: unknown

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Calahorra WWTP (El Cidacos, ES)	2015 (pilot)	<i>unknown</i>

Pearl

Company contact: <http://ostara.com>

Produced product: Granular Struvite “Crystal Green”

Process specifics: Crystallisation, fluidised bed reactor, pre-treated with WASSTRIP® (biological sludge thickener)

Origin of product: UASB effluent

P removal efficiency: 85%

Average operational costs: Electrical demand: 2.2 kWh/ kg P, heat demand 1.8 kWh/ kg P, Chemical demand: 3.1 kg MgCl₂/ kg P,

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Gold Bar WWTP (Edmonton, CA)	2007	<i>unknown</i>
Clean Water Services (Tigard, USA)	2009	<i>unknown</i>
Nansemond WWTP (Suffolk, USA)	2010	<i>unknown</i>
Rock Creek AWWTP (Hillsboro, USA)	2012	930
London (slough, EN)	2013	150
City of York WWTP (York USA)	2010	<i>unknown</i>
H.M. Wier WWTP (Saskatoon, USA)	2013	<i>unknown</i>
Nine Springs WWTP (Madison, USA)	2014	<i>unknown</i>
F. Wayne Hill WRC (Burford, USA)	2015	<i>unknown</i>

City of Amersfoort (NL)	2015	<i>unknown</i>
Stickney WRP (Stickney, USA)	2016	<i>unknown</i>
Truckee Meadows WRF (Reno, USA)	2016	<i>unknown</i>
Madrid Sur (Spain)	2016	<i>unknown</i>
Opequon WRF (Winchester, USA)	2016	<i>unknown</i>

P-ROC

Company contact: see reference

Produced product: Calcium phosphate, HAP

Process specifics: CSH (calcium silicate hydrate) seed material, crystallisation (CSTR), fixed bed and precipitation

Origin of product: wastewater sludge

P removal efficiency: 80-100%

Average operational costs: unknown

References:

Company	Start of operations	~ Annual phosphate capacity (tonnes)
Institute for Technical Chemistry, Water- and Geotechnology Division (ITC-WGT) (GER)	lab scale pilot	<i>unknown</i>

Seaborne/ Gifhorn process

Company contact: Seaborne EPM AG and WWTP Gifhorn

Produced product: Mix of struvite and HAP (Hydroxyapatite), CaP

Process specifics: Pre-treated by acidic dissolution, crystallisation and precipitation, low Mg dosing to promote CaP production and prevention of struvite scaling in the reactor

Origin of product: sewage sludge

P removal efficiency: 49% removal efficiency of P in sludge input

Average operational costs: Electricity demand 6,9 kWh/ kg P. Average chemical demand 8,2 kg HSO/ kg P, 2,9 kg NaOH/ kg P, 0,2 kg Mg(OH)/ kg P, 0,8 kg NaS/ kg P.

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Gifhorn WWTP (GER)	2007	99
Owschlag (GER)	2000 (pilot)	18

Stuttgart process

Company contact: www.iswa.uni-stuttgart.de/lsww

Produced product: Struvite powder

Process specifics: Pre-treated by acidic dissolution, crystallisation by magnesium

Origin of product: sewage sludge

P removal efficiency: 45% removal efficiency of P in sludge input

Average operational costs: Electricity demand 4.8 kWh/ kg P. Average chemical demand 11.9 kg HSO/ kg P, 1.5 kg MgO/ kg P, 2.7 kg NaOH/ kg P, 3.9 kg CHO/ kg P

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Offenburg Pilot plant (GER)	2011	18

Struvia

Company contact: <http://technomaps.veoliawatertechnologies.com>

Produced product: (granular) Struvite

Process specifics: Crystallisation, precipitation tank with Turbomix™/ Turboflo®.

Origin of product: UASB effluent

P removal efficiency: >85%

Average operational costs: Electricity demand 1.2 kWh/ kg P. Heat demand (optional) 0.9 kWh/ kg P.

Chemical demand 3.2 kg MgCl₂ / kg P.

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Helsingør Southcoast (DK)	2015	40
Samoens WWTP, (FR)	<i>unknown</i>	<i>unknown</i>
Brussels-North WWTP (BE)	2013 (pilot)	<i>unknown</i>

Swing

Company contact: Swing Corp.

Produced product: Struvite

Process specifics: *unknown*

Origin of product: Onsite wastewater treatment plants

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Kobe (JP)	2012	<i>unknown</i>

Appendix 2

A list of alternative P recovering technologies can be found here.

ASHDEC

Company contact: www.outotec.com and www.bam.de

Produced product: CaNaPO₄

Process specifics: Rotary kiln

Origin of product: sewage sludge ash

P removal efficiency: 98% of P in sewage sludge ash

Average operational costs: Average electricity demand: 0.8 – 0.9 kWh/ kg P. Average total natural gas demand: 5.2 kWh/ kg P. Average chemical demand: 3.3 kg Na₂SO₄/ kg P, 1.3 kg dried sludge/ kg P, 0.1 kg CaOH₂ / kg P, 0.1 kg NaOH / kg P.

References:

Company	Start of operations	~ Annual P capacity (tonnes)
ASHDEC	2008	<i>unknown</i>

CleanPhos

Company contact: AVA-CO₂

Produced product: DCP

Process specifics: *unknown*

Origin of product: sewage sludge

P removal efficiency: *unknown*

Average operational costs: *unknown*

References: <http://news.bio-based.eu/valuable-phosphorus-from-sewage-sludge-ava-cleanphos-pilot-plant-comes-online/>

Company	Start of operations	~ Annual P capacity (tonnes)
AVA Green Chemistry Development GmbH (Karlsruhe, GER)	2016 (pilot)	<i>unknown</i>

EcoPhos

Company contact: www.ecophos.com

Produced product: H₃PO₄/DCP/MCP precipitants, chemical process

Process specifics: *unknown*

Origin of product: Downstream wastewater treatment plants and ash treatment

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Varna (BG)	2016	<i>unknown</i>

DecaPhos Dunkerque (FR)	under construction	<i>unknown</i>
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Hitachi-Zosen (Unitika)

Company contact: <http://www.hitachizosen.co.jp/english/>

Produced product: Struvite/ HAP / phosphate rock

Process specifics: pyrolysis, anaerobic heating, separation

Origin of product: Onsite wastewater treatment plants / swine manure

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Senboku (JP)	2009	<i>unknown</i>
Matsue (JP)	1998	<i>unknown</i>

Kubota

Company contact: www.kubota-global.net

Produced product: P-slag

Process specifics: thermal treatment and addition of Fe₂O₃ and CaOH

Origin of product: sewage sludge

P removal efficiency: 90%

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Kubota corp. (JP)	<i>unknown</i>	<i>unknown</i>

MEPHREC

Company contact: www.ingitec.de

Produced product: P-slag, briquettes

Process specifics: dewatering and thermal treatment, removal of toxic metals, energy producing technology

Origin of product: Downstream wastewater treatment plants and ash treatment

P removal efficiency: 81%

Average operational costs: electricity demand 12 kWh/ kg P, heat demand 68 kWh/ kg P, 2.3-2.7 kg coke/ kg P, 0.4-0.8 kg O₂/ kg P, 1.3 kg dolomite/ kg P, 0.1 kg Ca(OH)/ kg P.

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Nürnberg (DE)	2016 (pilot)	<i>unknown</i>

LeachPhos

Company contact: BSH Umweltservice AG

Produced product: CaP and wet struvite

Process specifics: chemical process, extraction by diluted sulphuric acid and crystallisation process

Origin of product: sewage sludge ash

P removal efficiency: 70% in sewage sludge

Average operational costs: Electrical demand 1.6 kWh/kg P, Chemical demand 5.6 kg H₂SO₄/kg P, 0.6 kg NaOH/kg P, 3.9 kg Ca(OH)₂/kg P

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
BSH	2012/2013 (pilot)	<i>unknown</i>

METAWATER

Company contact: www.metawater.co.jp/eng/

Produced product: HAP

Process specifics: *unknown*

Origin of product: Downstream wastewater treatment plants and ash treatment

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Gifu (JP)	2010	<i>unknown</i>
Tottori (JP)	2013	<i>unknown</i>

PYREG

Company contact: <http://www.pyreg.de/home-en.html>

Produced product: sewage sludge ash 'Biochars'

Process specifics: combustion chamber

Origin of product: sewage sludge

P removal efficiency: 100% of dry sludge input

Average operational costs: minimum of 10 MJ/ kg sludge

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
ELIQUO, Linz-Unkel WWTP (GER)	2015	Up to 500 t P-Fertilizer with 10 to 20 % phosphorus

RecoPhos

Company contact: <http://www.recophos.org/>

Produced product: H₃PO₄/ P₄

Process specifics: thermo-Reductive RecoPhos Process

Origin of product: sewage sludge and sewage sludge ash

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
RecoPhos	2012-2015 (pilot)	<i>unknown</i>

TetraPhos

Company contact: www.remondis-aqua.com

Produced product: H₃PO₄ chemical process

Process specifics: *unknown*

Origin of product: Downstream wastewater treatment plants and ash treatment

P removal efficiency: *unknown*

Average operational costs: *unknown*

References:

Company	Start of operations	~ Annual struvite capacity (tonnes)
Hamburg (DE)	2015 (pilot).	<i>unknown</i>

Appendix 3

In these tables the weight of each piece of struvite can be seen over multiple measurement times. The weight is displayed in grams. 0 (d.w.) is the first weighing when the original piece was still dry. After this the struvite was put in the solution for at least 1 minute and then measured again (w.w or wet weight).

30-mrt					
Time	demi	Time	[1m] NaOH	Time	[1m] HCl
0 (d.w.)	0,84	0 (d.w.)	0,86	0 (d.w.)	0,85
0 (w.w.)	0,968	0 (w.w.)	0,989	0 (w.w.)	0,9775
60	0,968	60	0,899	10	0,48
120	0,95	120	0,876	20	0,22
180	0,966	180	0,849	30	0,116
240	0,962	240	0,827	40	0,036
300	0,962	300	0,782	50	0
360	0,95	360	0,687	60	0

-

5-apr				
Time	demi	1m NaOH	2m NaOH	1m NaOH nomix
0 (d.w.)	0,844	0,852	0,843	0,847

0 (w.w)	0,99	0,993	1	0,969
60	0,96	0,963	0,961	0,908
120	0,975	0,938	0	0,93
180	0,979	0,887	0	0,914
240	0,965	0,892	0	0,9
300	0,95	0,857	0	0,889
360	0,953	0,84	0	0,879
420	0,959	0,781	0	0,864

-

6-apr				
Time	[2m] Mix flat	[2m] Mix round	[2m] Nomix round	[3m] flat
0 (d.w)	0,796	0,808	0,83	0,793
0 (w.w)	0,91	0,972	1,045	0,931
30	0,635	0,46	1,085	0,572
60	0,507	0,04	1,024	0,23
90	0,407	0	0,959	0,04
120	0,366	0	0,89	0
150	0	0		0

-

11-apr								
Time	20%(#1)	20%(#2)	33%(#1)	33%(#2)	Time	2m NaOH	Nacl 1	Nacl 2
0 (d.w)	0,791	0,817	0,816	0,811	0 (d.w)	0,816	0,8103	0,8045
0 (w.w)	0,963	1,018	0,99	0,981	0 (w.w)	1,0201	0,9161	0,9223
30	0,045	0,146	1,023	0,986	30	0,6134	0,9234	0,932
60	0	0	0,984	0,793	60	0,2859	0,9252	0,9105
90	0	0	?	?	90	0,158	0,8995	0,9056
					120	0,0623	0,9147	0,883
					150	0		

-

20-apr					
Time	2M NaOH	3M NaOH	20% NaOH	33% NaOH	2M NaOH nomix
0 (d.w)	0,7959	0,8061	0,8043	0,7788	0,774
0 (w.w)	0,987	0,85	0,9537	0,8807	1,0277
30	0,7313	0,7064	0,3017	0,9341	0,9185
60	0,5763	0,5758	0	0,8766	0,7305

90	0,4986	0,504	0	?	x
120	0,452	0,4352	0		0,3068
150	0,4034	0,3449	0		0,1777
180	0,3629	0	0		0

-

10- mei				
Time	5% a	5% b	20% a	20% b
0 (d.w)	0,872	0,848	0,8159	0,811
0 (w.w)	1,1336	1,053	1,0546	1,14
30	1,0882	0,9739	1,0626	0,9641
60	1,0524	0,938	1,0516	0,9487
90	1,0459	0,89	1,0805	0,983
120	1,0102	0,8758	1,0961	0,9919

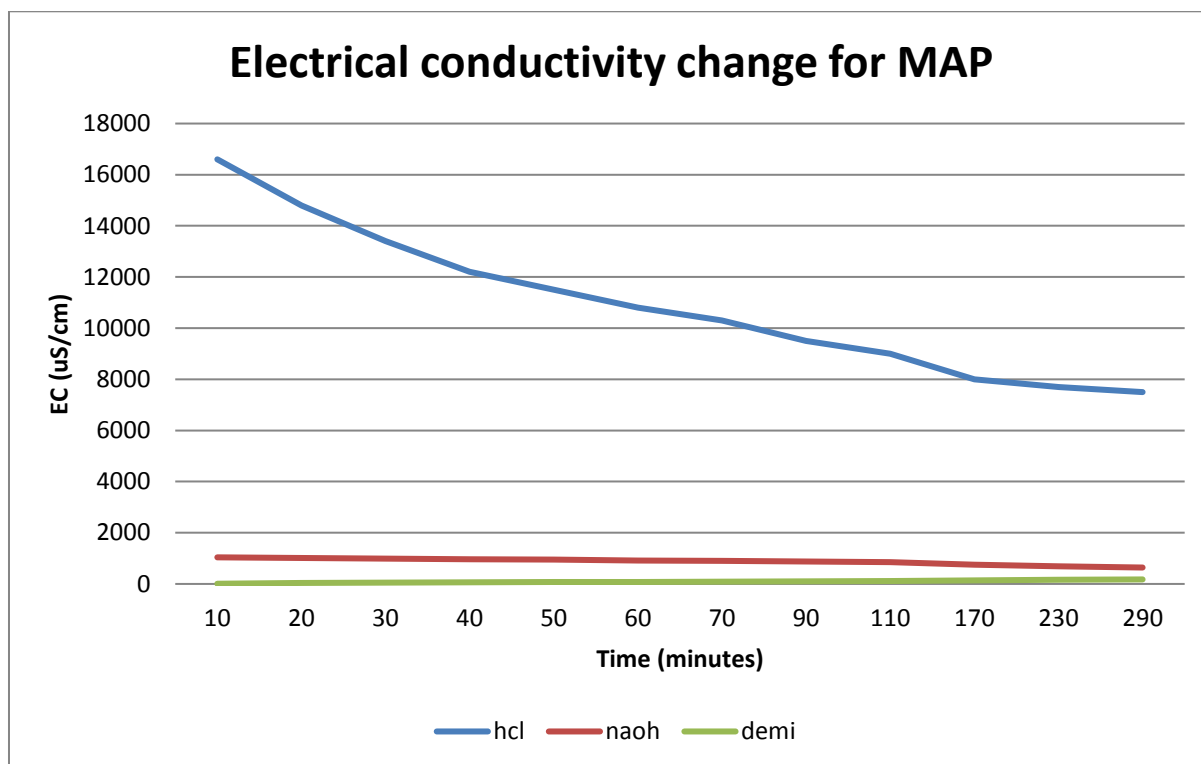
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Appendix 4

This appendix shows the rejected methods for test #1 and #2. The goal of these tests was to track the degradation of struvite 0.8 grams of MAP in different solutions.

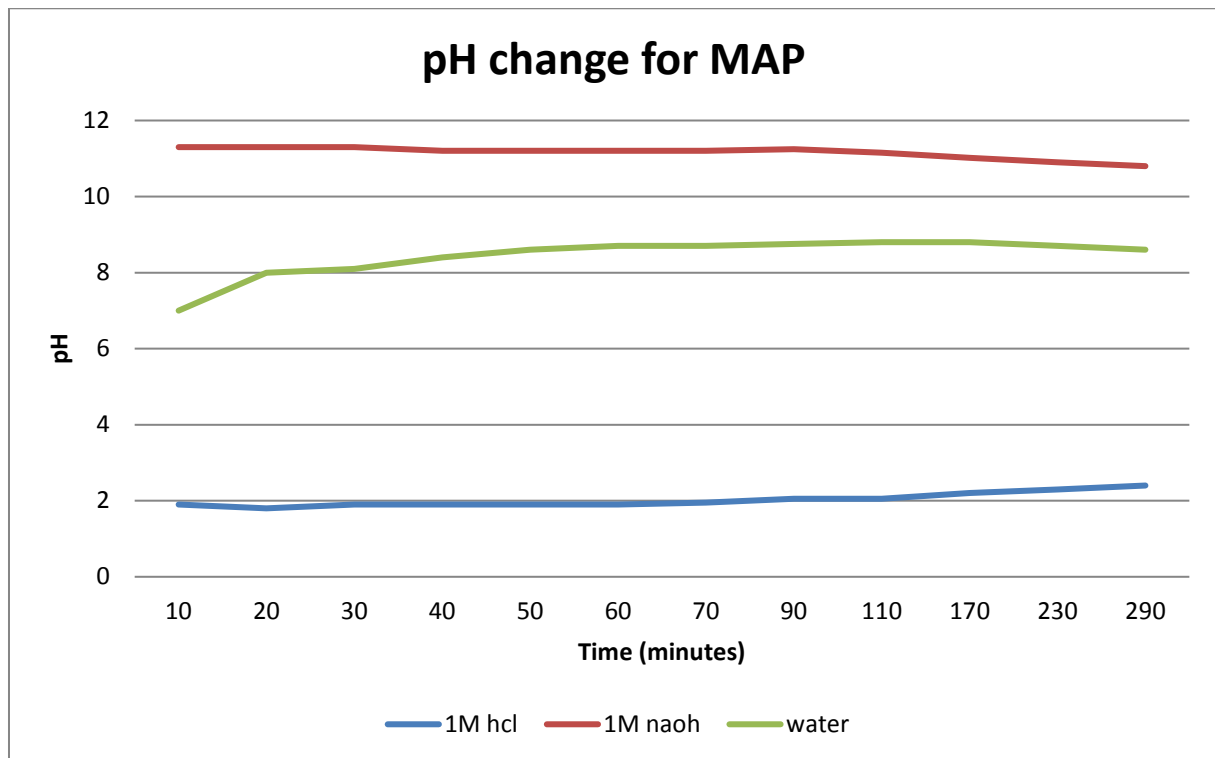
Electrical conductivity

With EC, we would expect a slow increase of the conductivity by the fact that more ions would be released when struvite dissolves. The result however showed a decrease with 1 molar HCl, and no significant change with 1 molar caustic soda and the water test.



pH

Same as the EC test, pH change did not yield enough result. Theory behind this is that when struvite breaks apart into different ions, the pH would also increase as described in equation 7.



Turbidity

The material available at Paques was very outdated and inexact, as it would measure a different NTU amount every time a single same sample was used. Proper samples were also difficult to get, as the solutions were not very uniform (allot of suspended solids present). If two samples were taken at the same time they would look observably very different by eye.



Size reduction

An attempt was made to track the degradation of struvite by measuring the size reduction. Photos were taken every 10 minutes of the struvite on a roster of 1 by 1 cm. Although the pictures look great, the results were not quantifiable enough.

