Phosphorous recovery from iron (III) phosphate sludge

-A suggestion on how to recycle phosphorous in order to reach a more sustainable waste management strategy

Master of Science Thesis in the Master Degree Program; Industrial Ecology – For a sustainable society

CAMILLA BERGQUIST

Department of Chemical and Biological Engineering
Division of Industrial Materials Recycling
CHALMERS UNIVERSITY OF TECHNOLOGY
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ABSTRACT

Phosphorous is an essential element for all living beings with no possible substitute. Phosphorous is a chemical element and is therefore not finite, however the workable findings of phosphorous minerals are. Due to the rapid population growth and depleting phosphorous reserves, there is both an environmental as well as an economical reason to recover phosphorous. As a step towards sustainability and a lower environmental impact, Eka Chemicals wishes to recover phosphorous from the iron (III) phosphate sludge.

The aim of this master thesis is to investigate how a waste stream, rich on iron (III) phosphate, can be utilized and how phosphates can be separated and recycled, at Eka Chemical´s plant in Trollhättan.

From this master thesis it can be concluded that removing unwanted substances from the sludge is the only short-term method which has shown enough satisfying recovering results to be a potential method to be implemented on site. However a suitable user has to be found in order for the approach to be successful. Using the sludge as raw material for the manufacturing of snail pesticide is one alternative and using it as fertilizer is another. Both the extraction as well as the method of changing the precipitation is possible alternatives for long-term approaches in order to reach the goal of waste prevention rather than waste treatment. However other factors such as economy also have to be taken into account when choosing the best alternative.

Key Words: *Phosphorous, recovery, Eka Chemicals, waste prevention, solvent extraction, dissolution*

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1 INTRODUCTION

Phosphorous is an essential element for all living beings with no possible substitute. Phosphorous is a chemical element and is therefore not finite, however the workable findings of phosphorous minerals are. (Swedish EPA, 2002) Through the history, phosphorous has seemed to be inexhaustible and has been used as it was. Due to the rapid population growth and depleting phosphorous reserves, there is both an environmental, as well as an economical reason to recover and reuse phosphorous.

As a step towards sustainability and a lower environmental impact of its production processes, Eka Chemicals AB wishes to recover phosphorous from an iron (III) phosphate sludge which is generated in their internal process water cleaning facility. The intention is to recover the phosphate for reuse instead of sending it to landfill, which is the present situation.

1.1 AIM AND OBJECTIVES

The aim of this master thesis is to investigate how a waste stream, rich on iron (III) phosphate, can be utilized and how phosphates can be separated and recycled from this stream or directly from the process water. This thesis includes proposals of both short-term and long-term approaches to recover phosphorous. The short-term approaches have the aim of treating the sludge in order to use it as a source of phosphates, while the long-term approaches focuses on methods to recover phosphorous without generating any sludge.

1.2 METHOD

This report is divided into two major parts, the literature study and the more practical part, which is supported by different experiments. The literature study had the aim of finding information needed to choose a likely way forward to recover phosphates from the sludge as well as directly from the water. The literature study was followed by the more practical part which includes experiments in order to find functional methods and eliminate the non useful ones.

Instead of working according to a traditional linear approach the so called PDCA-cycle has been used in this thesis. This approach ensures good quality since the results from every action are compared to targets which have been set in the beginning of the process. (Basu, 2004) PDCA stands for Plan-Do-Check-Act, and will generate continuous improvements, instead of the more linear approach of "making right the first time". (Basu, 2004)

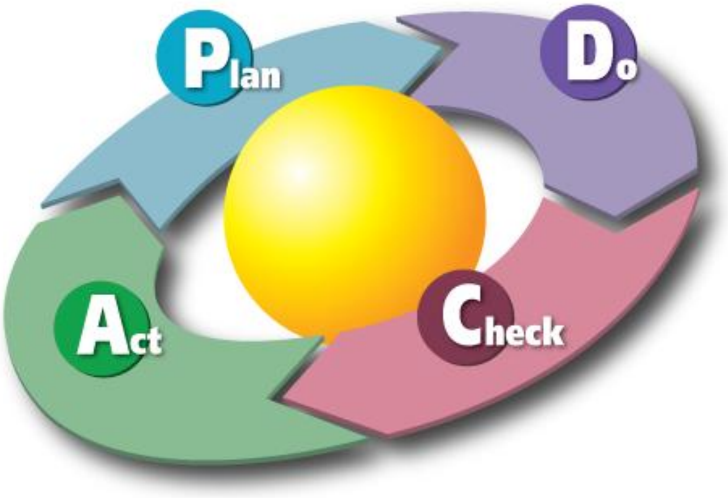


FIGURE 1 the PDCA cycle (BULSUK, 2009)

Basu 2004 means that by using the PDCA cycle two types of actions are generated: temporary and permanent. The temporary actions are explained as actions which simply aim at solving the already existing problem while the permanent action is the ones which will eliminate the root causes of the problem, and generate a more sustainable solution. In this report there are two different actions called short- and long-term approaches. This thesis will follow the PDCA cycle which is illustrated by Figure 2 below. The PDCA cycle has also been used within all experimental work of this master thesis, which can be seen in figure2.

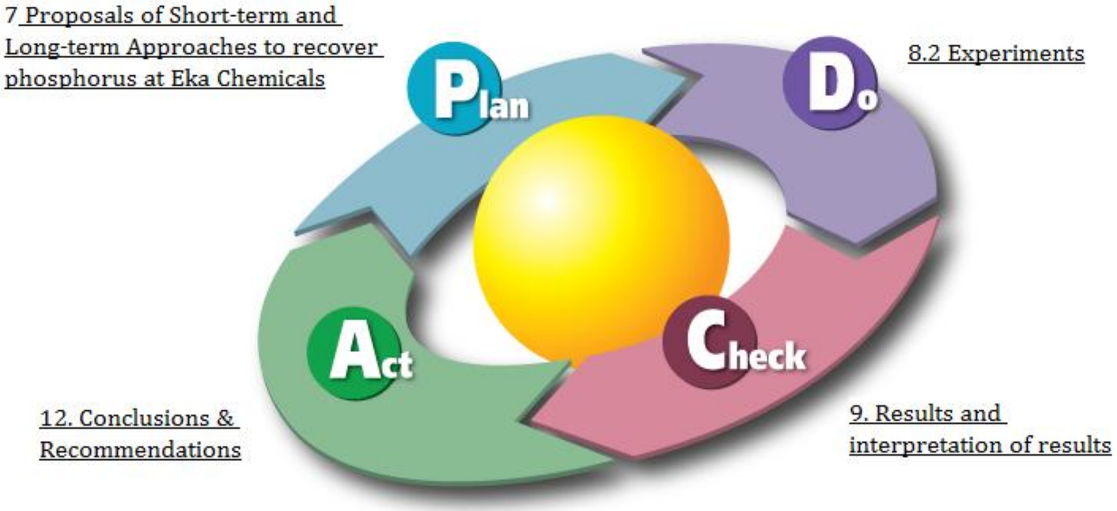


FIGURE 2 how this master thesis will follow the PDCA cycle

1.3 LIMITATIONS

All relevant approaches will be described in section 6 “*Short-term and Long-term Approaches to recover phosphorous*” in the report, even though not all of those are investigated further due to limitation in time. However recommendations for future work can be found at the end of the report

1.4 DISTRIBUTION OF REPORT

Below, the distribution of the report is described in order to make it easier for the reader to orient within the report.

PART 1 (Chapter 1-6): This part is the main theoretical part of the report. This part aims at giving the reader a well structured background in order to understand the subsequent reasoning and the following more practical chapters.

PART 2 (Chapter 7-9): This part is the main practical part of the report. This part illustrates the purposed approaches as well as the performed experiments made during this master thesis.

PART 3 (Chapter 11-13): This is the last part of the report which consists of discussion, main conclusions and some recommendations.

2 AKZONOBEL AB

AkzoNobel, based in Amsterdam, the Netherlands, is a leading company in Decorative Paints, Performance Coatings and Specialty Chemicals, a subdivision of which is the Pulp & Paper Chemicals business unit. AkzoNobel has approximately 60.000 employees based in more than 80 countries. In the year 2010, AkzoNobel had revenue of €13, 028 million, € 1,044 million from Pulp and Paper Chemicals. The company is found on the top of Dow Jones Sustainability Index. (Akzo Nobel Sverige, 2011)

2.1 EKA CHEMICALS AB

Elektrokemiska Aktiebolaget EKA, is a subsidiary company to AkzoNobel AB and was founded in Bengtsfors, Sweden in 1895 by the founder of the Nobel Prize; Alfred Nobel. Eka Chemicals AB is a business unit within the group of AkzoNobel AB, with Pulp and Paper Chemicals as their main business area. Eka Chemicals is one of the world's leading manufacturers within the field of bleaching and performance chemicals for the pulp and paper industry. (Akzo Nobel , 2011)

2.1.1 THE AKD PRODUCTION IN TROLLHÄTTAN, SWEDEN

Eka Chemicals in Trollhättan, Sweden, manufactures alkylketendimer (AKD) which is a wax used to create liquid resistance in paper (hydrophobicity). The wax is used in for example food packaging in order to avoid the paper to become soaked up. At Eka Chemicals in Trollhättan the AKD wax is produced under a patented process without any solvents. The basic raw materials, which are used to produce AKD, are fatty acids with 6-24 carbon atoms. The fatty acids originate from animal or vegetable fats, oil or wax. (Eka Chemicals, 2011)

The AKD manufacturing process can be divided into two major parts; Chlorination and Dimerisation. In the chlorination process, chlorides are added to the fatty acid to form a so called fatty acid chloride. The chlorination is done in two steps, in order to optimize the chlorination process, and maximize the yield. In the first step phosphorous trichloride (PCl_3) is used to chlorinate about 90 % of the fatty acids, then a second chlorination step is performed with thionyl chloride ($SOCl_2$), to chlorinate the remaining 10 %. Both these reactions are illustrated in reactions (1) and (2). (Eka Chemicals, 2011)

$$5\ R\text{-}CH_2COOH + 2\ PCl_3 \Longrightarrow 5\ R\text{-}CH_2COCl + HCl + P\text{-compounds} \quad (1)$$

$$R\text{-}CH_2COOH + SOCl_2 \Longrightarrow R\text{-}CH_2COCl + SO_2 + HCl \quad (2)$$

The second step of the AKD manufacturing process is the so called dimerisation, a reaction when two identical molecules react with each other. This dimerisation is done by removing the chloride in order to make the two units react. This reaction step is illustrated in reaction (3). The triethylene amine (Et_3N), which is used in the dimerisation step, is recycled by a reaction with sodium hydroxide (NaOH) as can be seen in reaction (4). (Eka Chemicals, 2011)

$$2\ R\text{-}CH_2COCl + 2\ Et_3N \implies R\text{-}CH{=}\ C\ \text{-}CH\text{-}R + 2\ Et_3N.HCl \qquad (3)$$

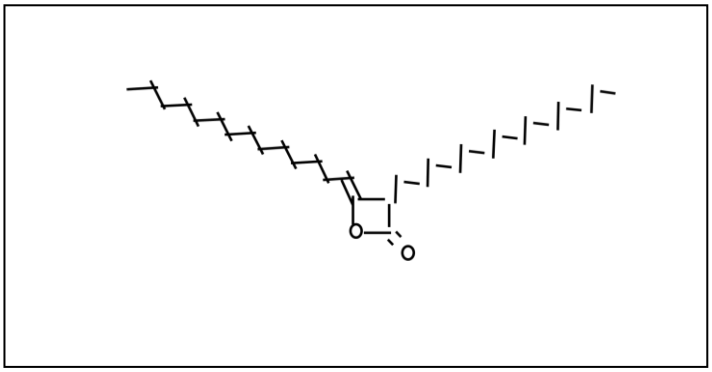


FIGURE 3 the AKD molecule (Eka Chemicals, 2011)

$$Et_3N.HCl + NaOH \implies Et_3N + NaCl + H_2O \qquad (4)$$

The AKD is shipped to the paper industry by trucks as aqueous emulsions with a solid content of 12-25%. (Eka Chemicals, 2011) The total AKD manufacturing process at Eka Chemicals in Trollhättan can be illustrated by the flowchart seen in Figure 4. (Eka Chemicals, 2011) The AKD production process generates a waste stream containing phosphates which are removed from the water within the company's internal water cleaning facility.

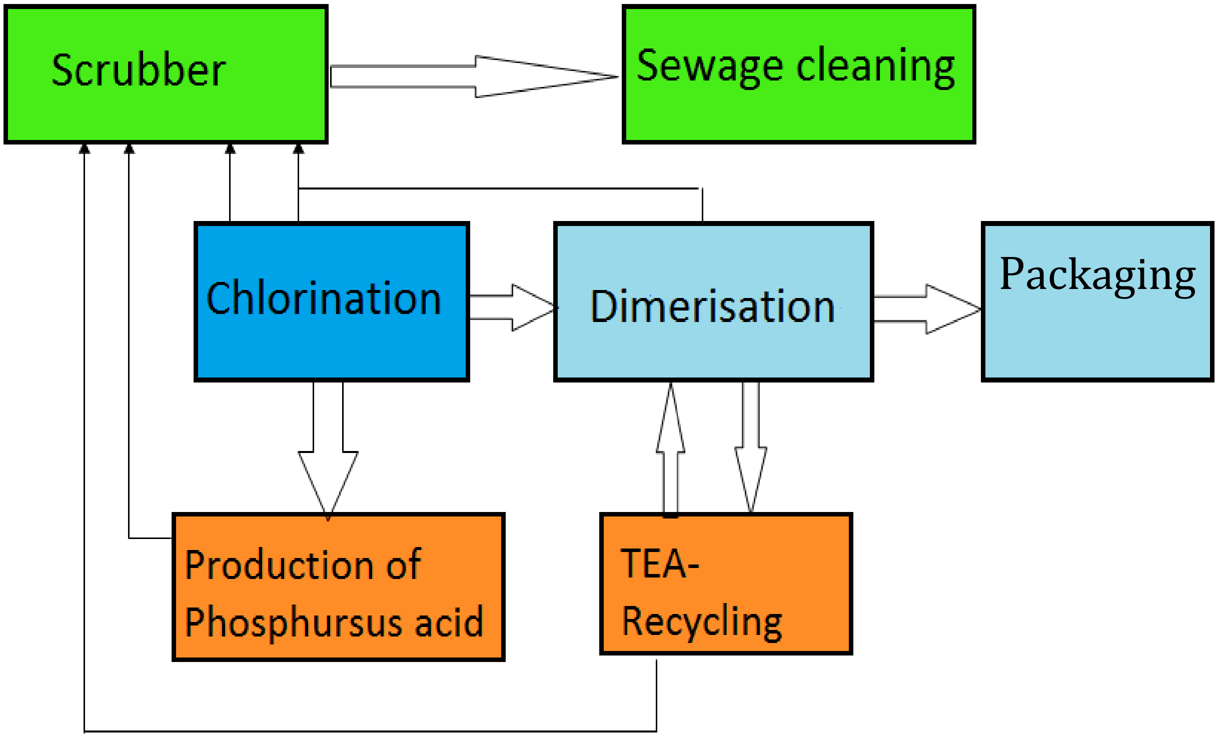


FIGURE 4 flowchart of the AKD process at Eka Chemicals in Trollhättan

3 SUSTAINABLE DEVELOPMENT

Sustainable development has many different definitions. However the definition from the so called Brundtland report from the world conference on environment and development in 1987 is generally known and accepted. (World Commission on Environment and Development, 1987) From this conference it was declared that the poverty in the south as well as the overconsumption in the north is the largest source of our global environmental problems. They concluded that there was a need for a new concept, a concept which could unify environment and development. The new formed concept was given the name "*Sustainable Development*". (Marten, 2007) In the report from 1987, called our *common future*, Sustainable development is defined as *"development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs."* (World Commission on Environment and Development, 1987)

Sustainable development is often described to have three focus areas: Environmental, Economical and Social. These three focus areas can metaphorically be described as three connected circles. The aim of sustainable development is to fulfill the purpose of all three circles. Sustainable development is reached when these three circles intersect, as the green are in FIGURE 5 illustrates. (Elliott, 2006)

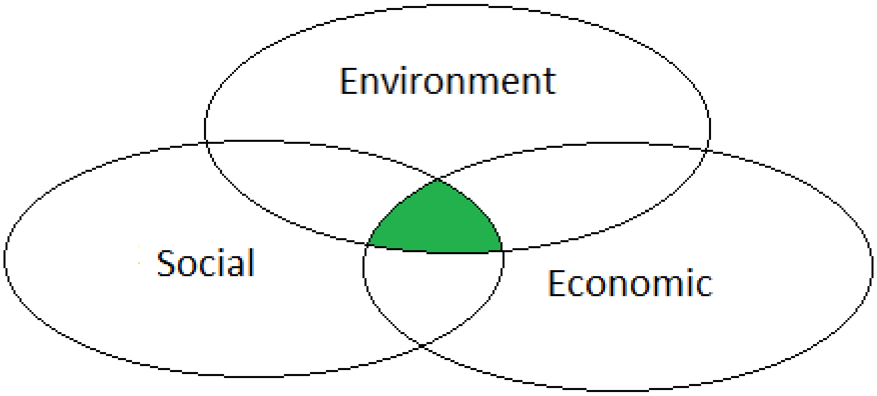


FIGURE 5 sustainable development (Elliott, 2006)

3.1 SUSTAINABLE WASTE MANAGEMENT

"Waste management includes the formation, treatment and disposal of waste materials and its resulting products." (Lemann, 2008) Sweden follows the strategies of waste management stated by the European Union. The so called waste hierarchy is often used to prioritize between different available waste management strategies. The hierarchy is developed by the EU legislatives and is solely based on an environmental perspective when it emphasizes that source reduction and prevention is the best alternative among all waste management strategies. This means that strategies on the top of the hierarchy will lead to the lowest negative environmental impact while the strategy in the bottom of the hierarchy will lead to the largest environmental impact. The hierarchy has a life cycle perspective, where the waste is seen as a resource rather than something unusable and where disposal only is used in cases where there is no other option. (Hill, 2010) The waste hierarchy illustrated in FIGURE 6 has the form of a triangle which is upside down. This triangle illustrates what we wish to accomplish within sustainable waste management, where source reduction is the waste management strategy which is used most, while landfilling is used least.

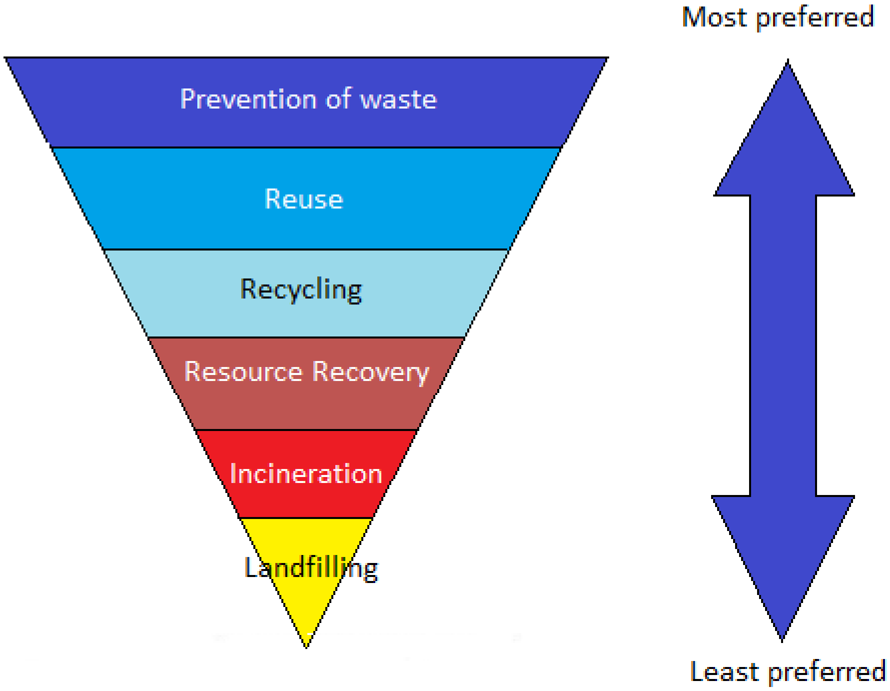


FIGURE 6 the solid waste management hierarchy Fagan, 2009)

3.1.1 FRAMEWORK FOR WASTE MANAGEMENT IN EU

The Directive on waste management from 2006 has been revised in order to reach a more accurate waste management strategy within the member states of the European Union. The new EU-directive 2008/98/EC will act as a framework for the management of waste and work to protect the environment as well as human health by minimizing the negative effects from wastes.

The new framework has modernized the current EU waste legislation by: (Eubusiness.com, 2011)

- *"clarifying the notions of recovery, disposal, end of waste status and by-product;"*
- *"defining the conditions for mixing hazardous waste;"*
- *"providing for measures to encourage the separate collection of bio-waste with a view to the composting and digestion of bio-waste;"*
- *"Requiring EU countries to take measures in terms of control of hazardous waste."*

The objective of the new framework is to implement waste prevention as the first choice within waste management. The new directive states that all member states of the European Union shall have implemented a waste prevention program by 12th of December 2013. (EU- DIRECTIVE 2008/98/EC, 2008) The waste hierarchy explained in section 3.1 in this report is used within this directive to work as a prioritizing scheme when member states are establishing their national waste policies. (EU- DIRECTIVE 2008/98/EC, 2008)

Furthermore the directive also includes the extended producer responsibility which enables countries to take measures to ensure that the producer of the product has the responsibly for the product thought the products life cycle. The extended producer responsibility has the aim of strengthening the re-use-, prevention-, recycling- and other recovery methods of waste. (EU- DIRECTIVE 2008/98/EC, 2008)The Directive 2008/98/EC was put into force the 21th of December 2010.

4 SUSTAINABILITY AT AKZONOBEL AB

As a business unit within AkzoNobel, Eka Chemicals compile with AkzoNobel´s sustainability policies and guidelines. Sustainability is integrated in all areas of profession within AkzoNobel. Since 2008 AkzoNobel has a Sustainability strategy, with the following three specific sustainability targets; (Akzo Nobel Corporate, 2011)

- *"Remain in the top three in the Dow Jones Sustainability Indexes "*
- *"Reduce our total recordable injury rate"*
- *"Deliver a step change in people development"*

For 2010 these targets ware reevaluated and updated to focus more on; (Akzo Nobel Corporate, 2011)

- *"Top quartile safety performance"*
- *"Top three position in sustainability"*
- *"Top quartile performance in diversity, employee engagement and talent development"*
- *"Top quartile eco-efficiency improvement rate"*

4.1 SUSTAINABLE WASTE MANAGEMENT AT EKA CHEMICALS AB

In order to strive towards a more sustainable waste management AkzoNobel has developed a ten step to step approach on how to make a new usable product from what today is called waste. (Akzo Nobel , 2011) The approach is based on the fact that good waste management begins with preventing or minimizing waste generation in the first place. However, where waste material is produced, management and treatment solutions are necessary. By seeing the different waste streams produced at all the AkzoNobel sites as raw materials, formulation components or reusable packaging for third parties, they contribute considerably to saving valuable natural resources and reduce costs. (Akzo Nobel , 2011)

With this step by step approach AkzoNobel wishes to improve the operational eco efficiency on all production sites within AkzoNobel, in accordance with their ambition to attain sustainable growth. This master thesis is a part of Eka Chemicals work towards using different waste streams produced as raw materials. Specifically, Eka Chemicals wishes to find out how a waste stream, rich on iron (III) phosphate, can be utilized instead of landfilled.

5 PHOSPHOROUS

Phosphorous is an essential element for all organisms with no possible substitute. Phosphorous is needed for the synthesis of DNA and the substance which are controlling the energy transport in cells, ADP and ATP. (Valsami-Jones, 2004) Phosphorous cannot be found in its elementary form; however it is often found integration with for example calcium, sodium, or chlorides. (Naturvårdsverket) Phosphorous is the eleventh most abundant element on earth, but the reserves are unevenly spread. Phosphorous is often the limiting factor of growth for plants on land, since most soils contains small amounts of phosphates naturally. Therefore phosphorous is often applied on agricultural lands in order to increase the yields of crops. (Spoolman, 2009) About 80 % of the global consumption of phosphorous is used as a fertilizer in order to increase the yield from agricultural lands. (Valsami-Jones, 2004)

Phosphorous is a chemical element and is therefore not finite, however the workable findings of phosphorous minerals are. (Swedish EPA, 2002) Phosphorous has seemed to be inexhaustible and has therefore also been used generously throughout the agricultural history in Europe. As a result, the phosphorous reserves are being depleted. Due to the rapid population growth and depleting phosphorous reserves, there is both an environmental as well as an economical reason to recover and reuse phosphorous. (Driver, 1998) To estimate for how long the reserves of usable phosphorous will last is very difficult. The difficulty lies in the economy of extracting the ore and the shifting demands with respect to the price. With a more expensive ore, the incentive for recycling will increase and the reserves may last longer. In the "Aktionsplan för återföring av fosfor ur avlopp", the Swedish EPA mentions three completely different estimations, from three liable sources with different perspectives. The answers range from 350 - 90 years until the reserves will run out. (Swedish EPA, 2002)

Excavating large amounts of phosphorous ore to make fertilizers or clearing large amounts of forests in the tropics are examples on how human activities can interfere with the natural phosphorous cycle on earth. Large amounts of phosphates can erode from fertilized agricultural lands into nearby streams, lakes or the ocean, which can lead to eutrophication. (Spoolman, 2009) As a consequence, industries which are using phosphates have to clean the water from phosphorous, before it is being discharged. Today different methods of chemical phosphorous removal from waste- and process water streams exist. These techniques often generate a solid waste containing valuable phosphorous, which today is landfilled. Chemical phosphorous removal by precipitation will be explained in section 6 of this report.

5.1 IRON (III) PHOSPHATE

Iron (III) phosphate ($FePO_4$) is a solid substance. It is sparingly soluble in water and has no known negative effect on humans or the environment. (Swedish Environmental Protecting Agency , 1997)

Iron (III) phosphate is used as human nutrition supplement as well as a counter measure against the Spanish forest snail called “the murder snail” in Sweden. The iron (III) phosphate interferes with the metabolic system of the snails forcing them to stop eating and the snails will die within a period of three to six days. (US EPA, 2010) *“Ferramol Snigel Effekt”* is a Swedish substance against snails. The product contains mainly flour and sugar, substances which will attract the snails. 1 % of the active substance, iron (III) phosphate, is enough for the substance to be effective. Iron (III) phosphate is accepted to be used within the ecological cultivation in Sweden and is also accepted by KRAV. However, it will require bigger amounts than other snail pesticides, 10–25 kg/ha, in order to be effective. (Swedish Board of Agriculture, 2008) Moreover, the “Ferramol Snigel Effekt” is not classified as a health, fire or environmental hazard. (MIljöcenter, 2008)

In addition to this, iron (III) phosphate has also been used as a fertilizer with relatively good results; however this is something which needs to be further investigated. (Hasselström, 2001) (Nieminen, 2011)

6 COMMON APPROACH OF CHEMICAL REMOVAL OF PHOSPHOROUS FROM WATER

One commonly used approach of chemical removal of phosphorous from water is precipitation with different metal ions.

6.1 PRECIPITATION WITH METAL IONS

The overall principle of chemical removal of phosphorous, by precipitation, is to transfer dissolved phosphorous into a solid form with low solubility. This is often done by using metal salts. With ideal conditions in terms of pH and dose the removal efficiency can excess 90 % with metal salt precipitation. (Valsami-Jones, 2004)

The chemical removal of phosphorous from wastewater is normally divided into four different stages; (Henze, 2002)

I. Precipitation
II. Coagulation
III. Flocculation
IV. Separation

6.1.1 PRECIPITATION AND COAGULATION

The first two stages are very rapid and they often take place at the same time. These two steps are often carried out under mixing conditions. By the addition of metal salts, which are the so called precipitants the phosphorous is converted into a particles of low solubility. The particles are colloidal particles with a diameter between 5 and 200 nm. At present, the most widely used precipitants are the salts of iron, aluminum and calcium.

During the subsequent coagulation the aim is to form larger particle aggregates of about 10-50 µm size. These particles are called primary particles. (Henze, 2002)

6.1.1.1 Iron and aluminum precipitation

The precipitation with iron and aluminum ions are very similar and can therefore be described with the same reaction formula, using M as a symbol for both iron and aluminum in reaction (5) and (6): (Henze, 2002)

Primary reaction $M + H_2PO_4^- \rightarrow MPO_4 + 2 H^+$ (5)

Side reaction $M + 3HCO^{3-} \rightarrow M(OH)_3 + 3 CO_2$ (6)

According to Henze 2002 both the iron and aluminum precipitation is accompanied by a pH reduction. The side reaction should be seen as something positive since it will make the flocculation process more efficient. The hydroxides will attract small particles, which should not have been settled without this side reaction. However this is a simplified overview of the reactions and in reality this is much more complex.

Valsami-Jones 2004 reports some disadvantages of using aluminum instead of iron as a precipitant. Even though the reactions seem to have the same stoichiometric relationships for iron, aluminum precipitation requires higher dosing to reach the same efficiency as iron precipitation. Furthermore aluminum precipitations seem to be more sensitive for the conditions of the incoming wastewater and could result in lower yield if the conditions are not ideal. (Valsami-Jones, 2004)

6.1.1.2 *Calcium precipitation*

The calcium precipitation can be carried out by $Ca(OH)_2$ or CaO as a precipitant, the reactions (7) and (8) illustrate this below.

Primary reaction $5\ Ca^{2+} + 7OH^{-} + 3\ H_2PO_{4-} \rightarrow Ca_5OH(PO_4)_3 + 6\ H2O$ (7)

Side reaction $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ (8)

From the reaction formula this reaction appears to be very beneficial. However according to Henze 2002 it is not as easy as the reactions indicate; the reality is much more complex. For one thing the $Ca_{10}\ (PO_4)_6(OH)\ _2))$, hydroxyapatite, is never formed in practice and secondly the reaction shown above which seems to form apatite in the final step is only one out of a long series of reactions. These series of reactions all have different calcium phosphate products, which all could contribute to the phosphate solubility. (Henze, 2002)

6.1.2 *FLOCCULATION AND SEPARATION*

In the flocculation stage the primary particles of 10-50 µm in diameter are gathered to form even larger particles, so called flocs. The flocculation is carried out in order to increase the particle size further to facilitate the separation stage. The separation step is often done by either sedimentation or by flotation. After the separation the cleaned water can move on and the resulting sludge containing phosphorous has to be further treated. (Henze, 2002)

6.2 THE PHOSPHOROUS REMOVAL AT EKA CHEMICALS AB

The water which enters the internal water cleaning process comes from the triethylamine (TEA) recycling and from the scrubber system at Eka in Trollhättan. This water is alkaline and will in a first step be mixed with a solution of lower pH to achieve a relatively neutral pH. During the neutralization the phosphorous is also oxidized with H_2O_2 in order to obtain PO_4^{3-}. In three steps $FeCl_3$, NaOH and polymers are added in order to precipitate the phosphorous in the form of $FePO_4$. The following reaction (9) illustrates the precipitation step as well as the flocculation. (Eka Chemicals, 2011)

$$Na_2HPO_4(aq) + FeCl_3\,(s) \Longrightarrow FePO_4\,(s) + HCl\,(aq) + 2\,NaCl\,(aq) \qquad (9)$$

The precipitated FePO4 is afterwards settled in a tank, where the iron (III) phosphate is collected as sludge at the bottom. (Eka Chemicals, 2011) The phosphate compounds within the sludge derive from the chlorination process in the AKD production, as described in section 2.1.1. The sludge consists mainly of water, the inert substance iron (III) phosphate and a small amount of organic matter - in particular polyacrylamide used to flocculate the iron (III) phosphate. At present the sludge is compressed to eliminate water and the filter cakes are collected in big containers which are emptied once a week to be landfilled. The remaining filter cake has a dry matter of 35-37% and is classified as non hazardous waste. The content of organic matter in the sludge is very low and therefore combustion as a waste management method is not seen as an alternative. (Eka Chemicals, 2008) The scheme which can be seen in Figure 7 illustrates the described process which takes place at Eka Chemicals´ plant in Trollhättan. (Eka Chemicals, 2011) The treated water afterwards proceeds in a purification system before being finally discharged into the river.

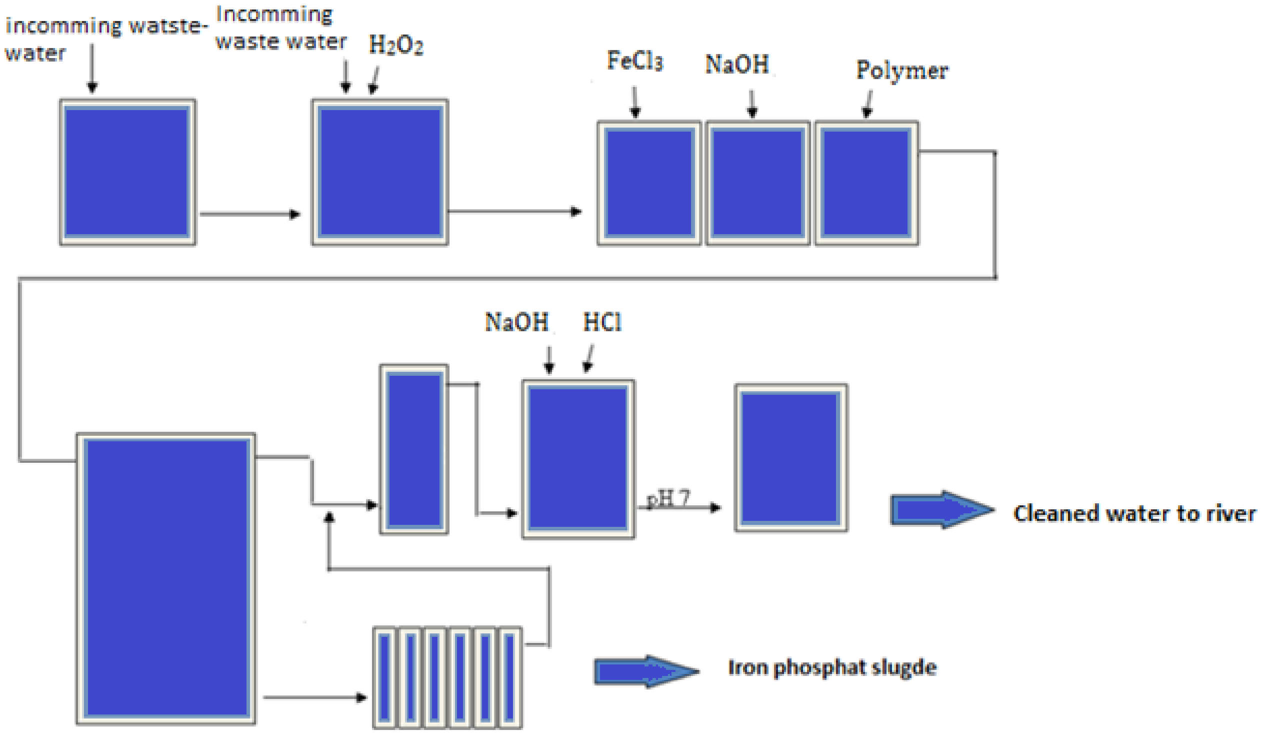


FIGURE 7 a flowchart on the water cleaning process at Eka Chemicals in Trollhättan, Sweden (Eka Chemicals, 2011)

7 PROPOSALS OF SHORT-TERM AND LONG-TERM APPROACHES TO RECOVER PHOSPHOROUS AT EKA CHEMICALS

Different short-term approaches to extract phosphorous from the iron (III) phosphate sludge is described in chapter 7.1. These short-term approaches will be complemented with long-term approaches in chapter 7.2, where the focus is on prevention rather than on sludge treatment.

7.1 SHORT-TERM APPROACHES

Below, three (I-III) suggestions on how to treat the sludge in order to make it possible to recover phosphorous are described.

I. DISSOLUTION WITH HCL

This approach focuses on investigating the possibility of dissolving the phosphate sludge in hydrochloric acid to recover phosphorous as H_3PO_4 as reported by Clement and coworkers (Clement, 2005) reaction (10). The dissolved phosphates can be recovered by solvent extraction (see section 7.2). Apart from providing a pure phosphorous source which could be used in the process, this approach will also has the benefit of enabling the recovery of $FeCl_3$ which is also used in the water cleaning process at Eka Chemicals in Trollhättan today. This would be both beneficial from an economic as well as an environmental point of view. (Clement, 2005)

$$FePO4(s) + 3HCl\ (l) \rightarrow FeCl_3\ (aq) + H_3PO_4\ (aq) \qquad (10)$$

II. DISSOLUTION WITH NAOH

The sludge may also be dissolved in alkaline medium. (Clement, 2005) The aim would be to precipitate the iron in order to isolate the phosphate to be recovered. The iron is in this approach precipitated with sodium hydroxide to form $Fe(OH)_3$, as illustrated in reaction (11). If it is possible to separate the phosphate from the iron, the remaining PO_4^{2-} can then be recovered by precipitation with $Ca(OH)_2$ to form $Ca_5OH(PO_4)_3$, known as Hydroxyapatite. However, other calcium phosphates will probably be generated as well. Therefore further investigations will be needed if this method would give promising results. The advantage would be that NaOH is available in-house since it is already used in other parts of the process at the plant in Trollhättan. (Clement, 2005)

$$3\ NaOH(l) + FePO_4\ (s) \rightarrow Fe(OH)_3(s) + 3\ Na^+ + PO_4^{3-} \qquad (11)$$

Figure 8 illustrates that the highest stability and so the highest recovery of Ca_5 OH $(PO_4)_3$ is obtained in the pH range of 6-12, as obtained by the programs HYDRA and MEDUSA. HYDRA is a program which is used to select desired components and find complexes for a chosen system. MEDUSA is used to calculate the chemical equilibrium for the system specified by HYDRA. The database which is used within HYDRA has been developed at the department of Inorganic Chemistry at the Royal Institute of Technology (KTH), in Stockholm, Sweden. (KTH, 2011). (Puigdomenech, 2008)

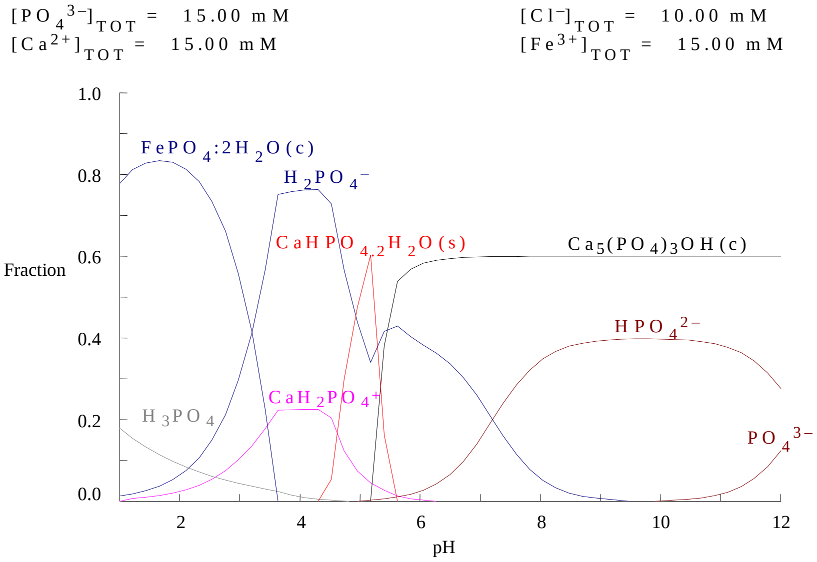


FIGURE 8 illustration of that $Ca_5(PO_4)_30H$ should be stable at pH 6-12

III. REMOVAL OF UNWANTED SUBSTANCES FROM THE SLUDGE

Instead of trying to dissolve the iron (III) phosphate as the earlier methods has aimed at, this method will instead focus on removing other substances from the sludge. As mentioned earlier in the report, iron (III) phosphate is a substance which is effectively used to eliminate snails and slugs. (US EPA, 2010) Today the sludge contains large amounts of iron (III) phosphate together with other elements, as for example Ni, Pb, Zn, Al and Cl, which cannot be accepted when used in gardens or on agricultural lands. The possibility of removing unwanted substances from the sludge will be tested by experimentally examine different solvents to wash out the unwanted elements and achieve a cleaner sludge, containing mostly the iron (III) phosphate.

7.2 LONG-TERM APPROACH TO RECOVER PHOSPHOROUS

Below, two (I-II) long-term approaches are described.

I. SOLVENT EXTRACTION WITH AMINE

Solvent extraction is used for selective refining of one metal or one ion from aqueous solutions containing mixtures of ions. In the extraction process a ligand molecule, soluble in organic solvents, is used to selectively form soluble complexes with the target ions. The ligand is dissolved in an organic solvent which is mixed with the aqueous phase whereby the ions to be recovered are bound to the ligand molecules and transferred to the organic phase. The aim with this approach described by Jiang and co-workers (Jiang, 2010), was to chemically form a phosphate-extractant complex which is soluble in an organic solvent. Kerosene was used as organic phase and benzyldimethylamine as extractant (ligand). The phosphate can be recovered from the organic phase by different methods, the most common is stripping, where the desired component is removed from the organic phase and transferred to a solution of sulphuric acid (H_2SO_4). The stripping is in the method suggested by Jiang done by using 6 M sulfuric acid to remove the phosphate from the organic phase, in another liquid extraction process. This enables the organic phase, free from phosphates to be recycled. (Jiang, 2010)

Jiang and co-workers investigated the effect of different parameters on the phosphorous recovery efficiency. The conclusions from their experiments can be seen in Table 1 and Table 2 below. These parameters have been used as guidelines during the solvent extraction experiments in this thesis. The choice of stripping agent is due to economical reasons since both 6 M H_2SO_4 and 4 M HCl gave the same satisfying result. Jiang et al also concluded that the organic phase can be recycled, however in order to keep the optimum extraction efficiency a volume ratio of 1:2 of fresh to recycled extractant is needed. In addition to this, the stripping agent could also be recycled several times and yet give a satisfying efficiency. (Jiang, 2010)

TABLE 1 Optimal extraction parameters (Jiang, 2010)

Best surfactant	**Benzyldimethylamine**
Best mixing time	6 hours
best separation time	2 hours
Mixing Ration (kerosene ; Surfactant)	2;1
Mixing Ration(aqueous; Organic phase)	4;1
Minimum detection limit	10 µg/L
Maximum extraction efficiency	96,60%

TABLE 2 Optimal stripping parameters (Jiang, 2010)

Stripping agent	**6 M H_2SO_4**
Mixing time	4 hours
Best separation time	2 hours
Mixing ratio (Organic; Acid phase)	1;1
Minimum detection limit	10 µg/L
Maximum stripping efficiency	91,34 %

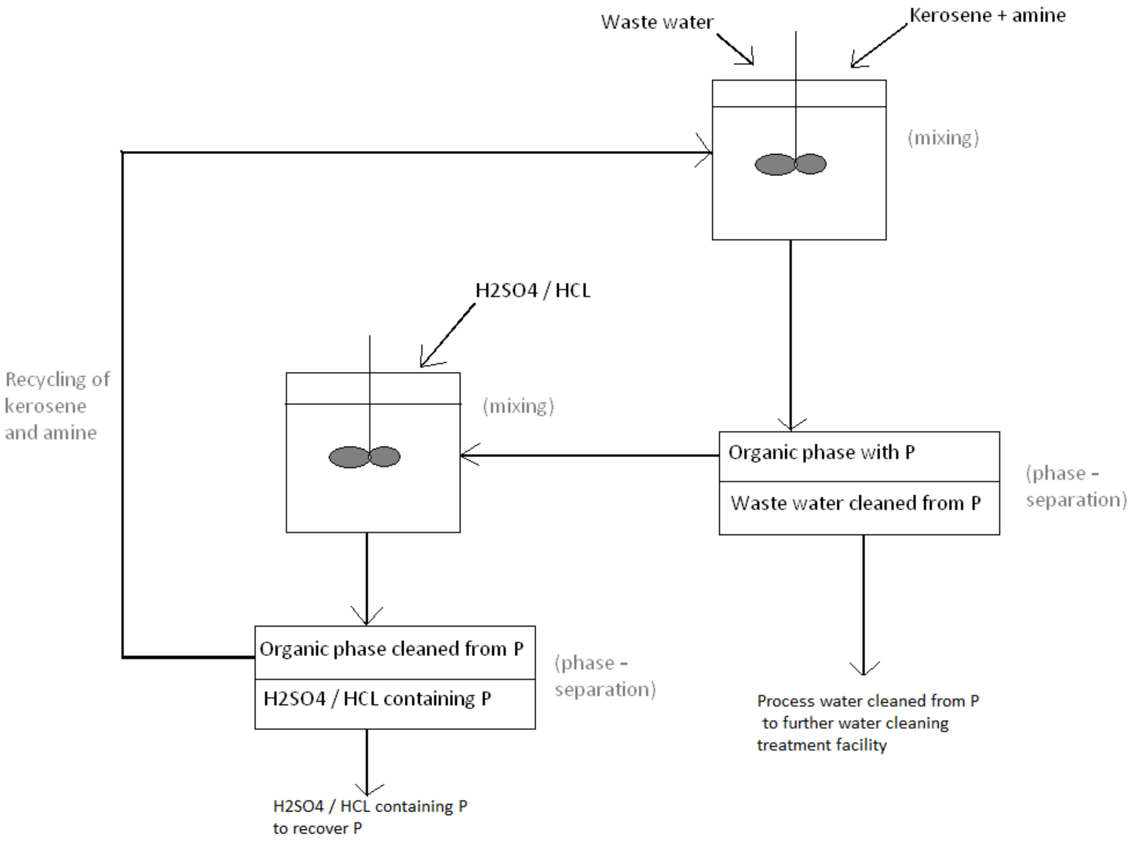


FIGURE 9 Overall description of a solvent extraction process

The solvent extraction process will generate very limited air or water emissions and the process can be seen as relatively environmental friendly. (Choppin, 2004) In Figure 9 an overview of the proposed process of liquid extraction is shown.

Since solvent extraction is an established industrial process, commercial companies offer equipment set ups of different kinds. The company that is closest at hand in Sweden is MEAB Metallextraktion AB. FIGURE 10 illustrates how such turnkey equipment could look like, while Table 3 describes its different components. (MEAB, 2010)

TABLE 3 Description to Figure 9 (MEAB 2010)

	Description		Description
A	Mixing chamber	H	Picket fence distributor
B	Variable speed stirrer motor	I	Outlet weir, heavier solvent
C	Turbine pump impeller	J	Underflow, heavier solvent
D	Inlet, heavier solvent	K	Outflow cavity, heavier solvent
E	Inlet, lighter solvent	L	Adjustable jack-leg outflow, heavier solvent
F	Settling compartment	M	Phase boundary
G	Outlet/inlet mixer/settler		

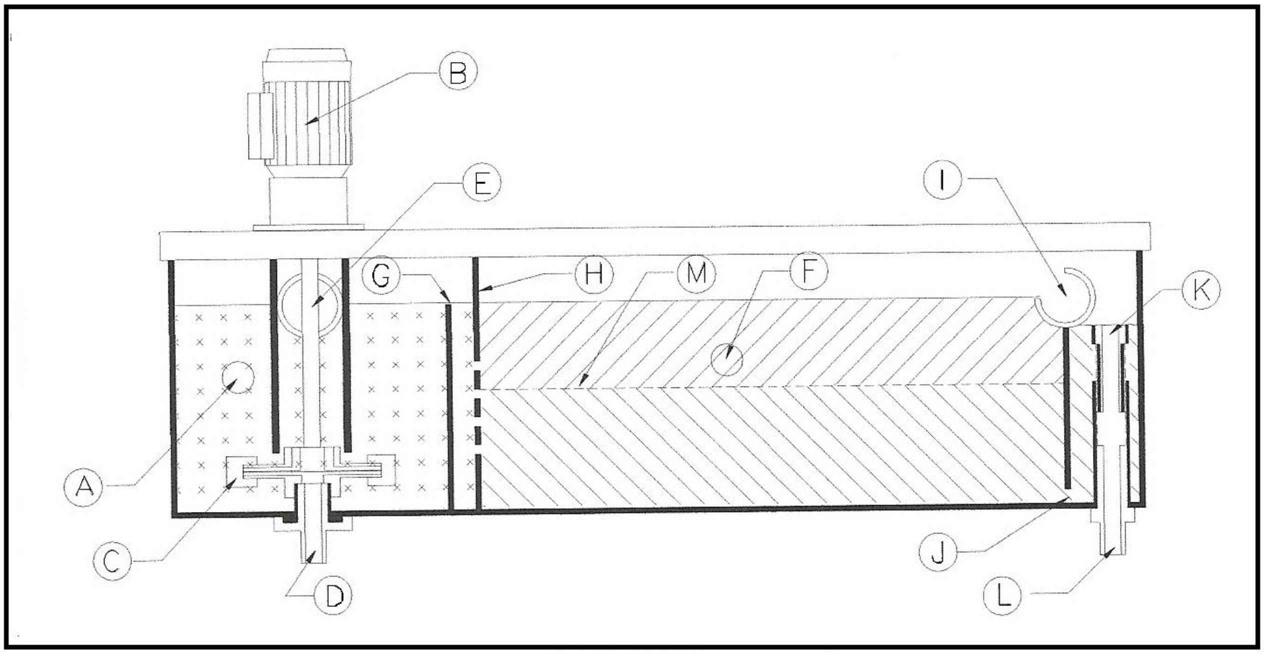


FIGURE 10 Example of mixer-settler unit- construction principles (MEAB 2010)

II. ALTERNATIVE PRECIPITATION METHOD

As discussed in chapter 6 the precipitation can be carried out with calcium or aluminum compounds instead of ferric chloride, which is used today at the plant in Trollhättan. At present the calcium precipitation technique is not efficient enough to be applied at a larger scale. The reason is that the desired product $Ca_5OH\ (PO_4)_3$ is not formed in practical applications due to a large number of side reactions. (Henze, 2002) However if it in the future will be possible to optimize this precipitation method, calcium would be a precipitant to prioritize since this would generate a much more valuable product than the iron precipitation product. In contrast to the solvent extraction this method will still generate a waste stream from the precipitation. However this method is categorized within the long term approach since the waste generated will most probably be a more valuable stream than what is generated today.

8 EXPERIMENTS AND ANALYTICAL TECHNIQUES

8.1 EXPERIMENTS

8.1.1 SLUDGE COMPOSITION

The sludge was characterized to determine its composition. One sample was taken each week and analyzed to show if there were any significant changes in the composition over time. The characterization was done by using ICP-OES/MS technique, both at Eka Chemicals and ALS Scandinavia. The basics of ICP are described in section 8.2.2 in this report. XRD, which basics are described in section 8.2.1 in this report, was also used in order to investigate if the sludge contained any crystalline compounds.

8.1.2 SHORT-TERM AND LONG-TERM APPROACHES TO RECOVER PHOSPHOROUS

From the theoretical background some of the methods were chosen for a deeper investigation. The choice was made after discussions with Eka Chemicals.

8.1.2.1 Short-term approaches

All three, (I, II, and III), proposed short-term approaches were further examined as described below.

I. Dissolution with Hydrochloric acid (HCl)

The first series of experimental attempts to dissolve iron (III) phosphate was made using hydrochloric acid (99, 99 % suprapur from Merck). The calculated weight was added into a graduated conical flask and 100 ml of HCl was added, the first one with a concentration of 0.3M and the next with 0.1M , generating a pH of 0,5 respectively 1. The two flasks were put under mixing with a magnet with a lid on, while a sample was taken every hour.

The second experiment was performed with the same amount of sludge but the double volume of HCl, in order to see how an excess of HCl would affect the results. The samples taken from the three different conical flasks were orange colored with visible particles and were therefore filtrated before an analysis was possible. The samples were filtrated with a 2 ml syringe and a 0.45 μm filter into a plastic test tube.

The ascorbic acid method, described in section 8.2.3 in this report, was used to determine the phosphate (PO_4^{3-}) concentration in the solution. All samples were diluted 10 or 100 times because the phosphate concentration in the samples exceeded the analytical range of the equipment (0.0 to 31, 6 mol $PO_4{}^{3-}$ / dm^3). The measured phosphate content in the solutions was afterwards compared to the calculated total amount of phosphates in the sludge. All samples were prepared in the same way as described in section 8.2.3 before being analyzed.

II. Dissolution with Sodium hydroxide (NaOH)

The next series of experimental attempts to dissolve the iron (III) phosphate was made using 0.01M sodium hydroxide (99, 99 % suprapur from Merck) with a pH of 12. In order to make sure there was enough NaOH in the solution a surplus of NaOH was used. The calculated weight was added into a graduated conical flask and 500 ml of 0.01M NaOH were added. The flask was put under mixing by using a magnet, with a lid on, while a sample was taken every hour.

The second series of experiment was done with the same volume of NaOH and the same amount of sludge; however this sample was put under mixing and heating. The mixture was mixed with a gradual increase of the temperature up to 40 °C, with a starting temperature of 20°C. In parallel to this experiment another sample was prepared with the same proportions, nevertheless with no additional heating and at a temperature of 21 °C. Both flasks were put under mixing, with a lid on, while a sample was taken every hour.

The samples taken from the different conical flasks were orange colored with visible particles and were therefore filtrated before an analysis was possible. The samples were filtrated with a 2 ml syringe and a 0.45 µm filter into a plastic test tube.

The ascorbic acid method, described in section 8.2.3 in this report, was used to determine the phosphate concentration in the solution.

III. Removal of unwanted substances from the sludge

This approach aims at to obtain a clean sludge with as high percentage of iron (III) phosphates as possible. To be successful, the cleaning step has to be optimized to be selective and to only remove the unwanted substances, leaving the wanted substances in the sludge. The first experiment was performed with a 0.1M hydrochloric acid as solvent. This experiment was performed by dissolving the sludge in the solvent, followed by sedimentation of the remaining sludge. When the treated sludge had settled, the remaining solution was filtrated through a membrane filter, eliminating all remaining sludge particles and leaving a clear solution. This solution was afterwards analyzed with ICP-OES/MS to see if any of the unwanted substances had been successfully eliminated from the sludge.

The second experiment was performed with the same procedure as in the first experiment, however in this case sodium hydroxide solution of 0.01M was used as solvent. As with the first experiment, the cleaned solution was afterwards analyzed with ICP- OES/MS, with the aim to see if any of the unwanted substances had been successfully eliminated from the sludge. The specific preparation procedure can be seen in Appendix.

8.1.2.2 Long-term approaches

One (I) out of the two proposed long-term approaches was further examined as described below.

I. Solvent extraction with amine

In the solvent extraction experiment the organic phase (the light phase) and the water phase (the heavy phase) was mixed during six hours using a rotary shaker or a magnetic stirrer in order to ensure efficient phase mixing. After mixing, the samples were allowed to settle during two hours and a separation took place. After these two hours the water phase was separated from the organic phase by using a separating tunnel. The water phase was analyzed with ICP-OES/MS and the ascorbic acid method in order to determine the amount of phosphate and metals remaining.

The first experiment, made within this approach, was done using a HACH standard solution containing 12, 6 mol PO_4^{3-} /dm^3 to act as the water phase, in order to assess the method. For this experiment 8.3 ml of amine (Benzyldimethylamine >=99% from Aldrich), 16.6 ml of kerosene (Solvent 70 from Statoil) and 100 ml of the phosphorous standard were mixed together during 6h as described above, according to the proposals of optimal parameters by Jiang (Table 1 and Table 2).

The same procedure as describes above was used for the next series of experiments; however for those experiments the process water from Eka Chemical´s plant in Trollhättan was used. The first experiment was performed with the same volume ratio of organic phase to aqueous phase as during the test experiment with the phosphate standard. The next two experiments were performed on a smaller scale, using: 4.2 ml amine, 8.3 ml kerosene and 50 ml of process water, but still with the same procedure.

The separated water phases from all three experiments and the process water from Eka´s plant was analyzed by ICP-OES/MS by ALS Scandinavia, as described in section 8.2.2. The untreated process water was analyzed with the aim to determine the initial phosphorous content and the all three water phases were analyzed to show if the phosphate removal was effective.

The third series of experiments was performed with the same volume ratios as describes above. However, the mixing was done using a magnetic stirrer instead of the “shaker plate”. Another important difference was that the process water was oxidized using H_2O_2 before the solvent extraction. Mixing with a magnetic stirrer was chosen in these experiments since it generates better mixing than the “shaker plate”.

For these last two experiments the water phases were analyzed with the ascorbic acid method in order to measure the PO_4^{3-} content in both the samples as well as the oxidized process water. Prior to the analysis, all samples were prepared in the same way as described in section 8.2.3, before analysis.

According to Jiang and co-workers the extracted phosphate can be recovered from the organic phase by breaking the amine-phosphate complex with acid. (Jiang, 2010) Due to limited time, this step was not carried out experimentally in this thesis.

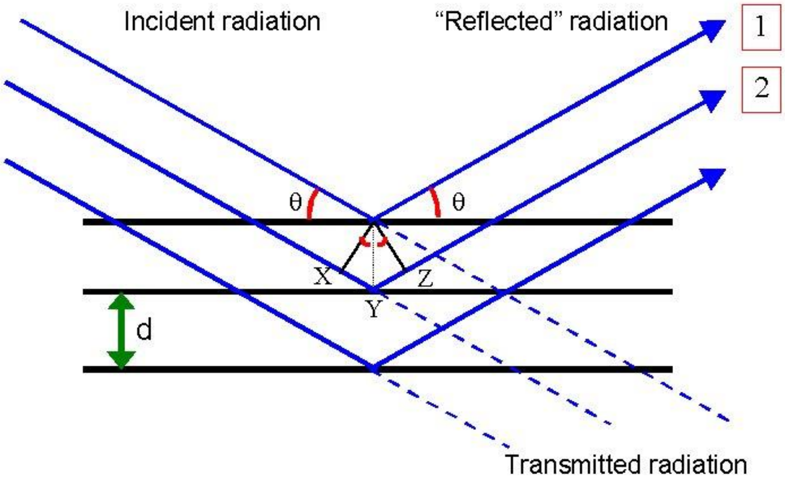
8.2 ANALYTICAL METHODS

Different analytical methods were used to evaluate the different recovering strategies and to establish the sludge composition and consistency.

8.2.1 X-RAY POWDER DIFFRACTION (XRD)

XRD is used as a chemical characterization method, where the sample is exposed to an X-ray of known wavelength. The X-ray is diffracted by the crystalline compounds in the sample and creates a specific pattern of peaks which can be used to identify the compounds. Since the wavelength is known, the distance between the atomic planes (d) in the crystal structures can be calculated, according to Bragg´s law, as shown In Figure 11. A set of distances is specific for each crystalline compound and the data can be compared with standards to be able to identify the crystalline compounds present in the sample. (Zavalij, 2005) (Joint Committee of Powder Diffraction Standard, 2010)

Prior to the analysis the sample was dried at a temperature of 105°C for one day. The specific preparation procedure can be found in Appendix I.



***Bragg´s Law;* 2d sinϑ = nλ**

d **=** distance between atomic planes
ϑ**=** incidence angle
n= the diffraction order
λ **=** wavelength

FIGURE 11 Bragg´s Law (Linneuniversitetet)

8.2.2 INDUCTIVE COUPLED PLASMA (ICP)

Inductive coupled plasma (ICP) is a technique which can be used on dissolved samples to determine the concentrations of a large number of elements. ICP with mass spectrometric detection (ICP-MS) gives very low detection limits.

FIGURE 12 shows the main parts of an ICP spectrometer. The sample is sprayed into the instrument and transported by a support gas to the plasma that is heated by a radio frequency field. When the sample reaches the plasma it will be nebulized into ions and atoms which can be detected either by their masses or by the light them exudates. (Pettersson, 2010)

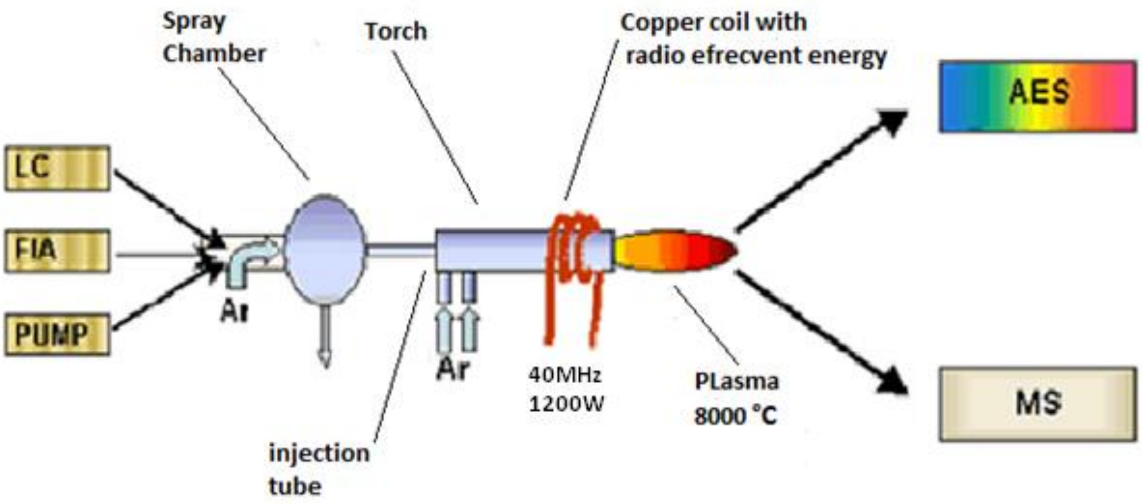


FIGURE 12 ICP (Pettersson, 2010)

The specific preparation procedure for the ICP analysis can be found in Appendix 1.

8.2.3 THE ASCORBIC ACID METHOD FOR ORTOPHOSPHATE MEASUREMENT

For the analysis of phosphate contents in the aqueous samples the ascorbic acid method was used. This method has an analytical range of 0.0 to 31, 6 mol $PO_4{}^{3-}$ / dm^3. The ascorbic acid method is a colorimetric method which detects low-level orthophosphate ($PO_4{}^{3-}$) concentrations. The solution containing the orthophosphate is mixed with a reagent, containing ammonium molybdate, antimony potassium tartrate and sulfuric acid, to form a complex which will be reduced by the ascorbic acid and form a blue-colored complex. The intensity of the color is proportional to the phosphate concentration in the sample and is measured in a colorimetric instrument, in this case a Hach portable colorimeter. (Dukart, 2006)

The instrument is calibrated with a phosphate standard of 12,6 mol $PO_4{}^{3-}$/ dm^3 prior to the analysis. (Merkanti Hach)

9 RESULTS AND INTERPRETATION OF RESULT

As it was described earlier in this report the following targets had been set up as a measure of technical and economical feasibility for the different suggested recovery methods;

I. If the method is carried out in one step a yield of at least 50 % is required
II. If the method is carried out in several steps the yield from the first step has to be at least 30 %
III. The method has to be possible to use on site in Trollhättan.

It should be noted that the environmental aspects were a core aspect when choosing the methods to be further investigated; therefore this aspect is not included within these targets.

9.1 SLUDGE COMPOSITION

The XRD analysis showed the presence of NaCl in an amorphous matrix.

The element concentrations obtained from the ICP analysis are shown in Figures 13-15. (ALS Scandinavia, 2011) The exact results from the analysis are shown in Appendix II. Three samples were taken in order to ensure good quality results.

In order to determine how the composition of the sludge changes with time, samples from three containers have been analyzed with ICP. These results are shown in Appendix II. The mean values are used in the calculations within the short-term approach for removing the unwanted substances from the sludge.

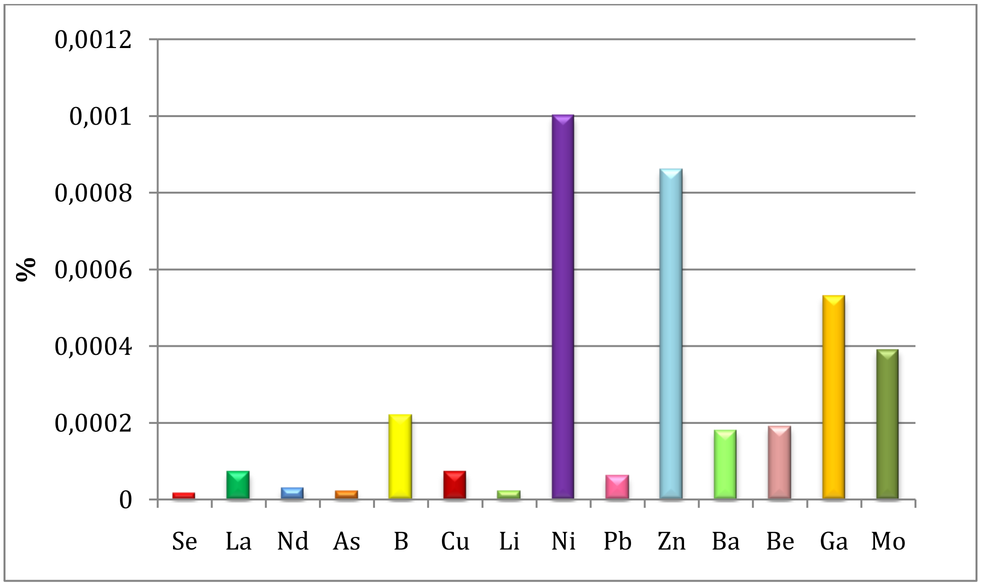


FIGURE 13 Elements in sludge < 0, 01 %

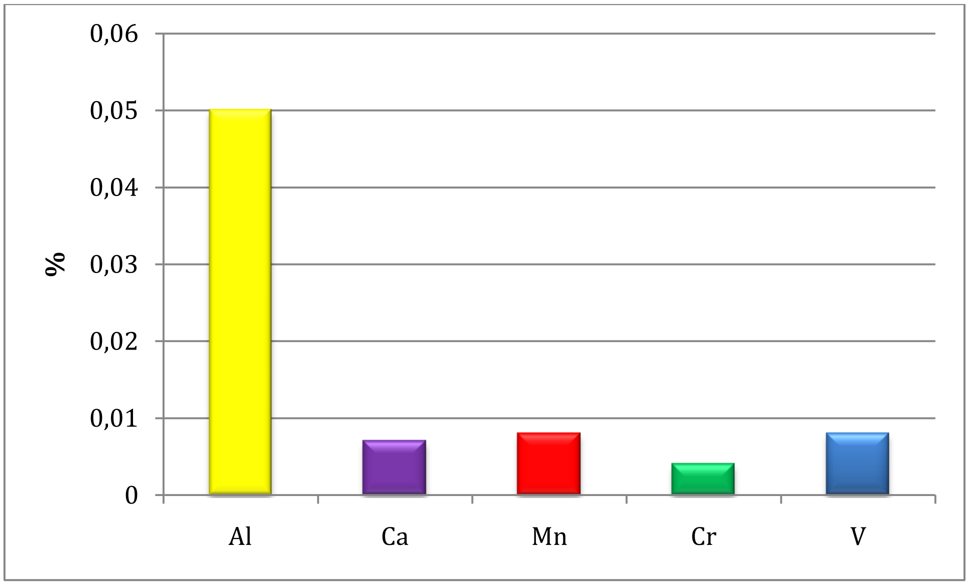


FIGURE 14 Elements in sludge < 1 %

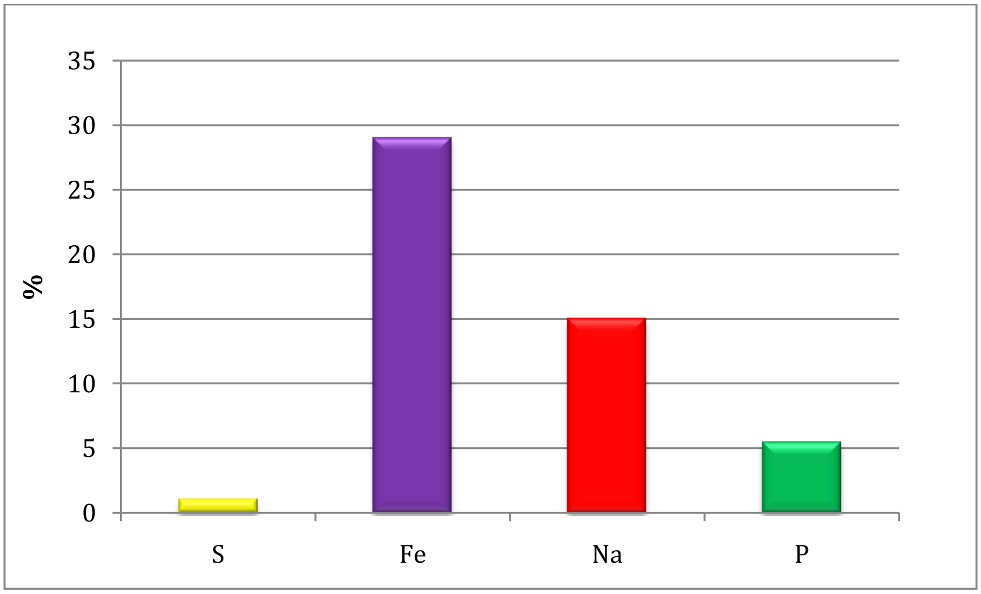


FIGURE 15 Elements in sludge > 1%

9.2 SHORT-TERM AND LONG-TERM APPROACHES TO RECOVER PHOSPHOROUS

9.2.1 SHORT-TERM APPROACHES

9.2.1.1 Dissolution with HCl and NaOH

Both these approaches gave an insufficient yield of PO_4^{3-} (<50%) in the solvent compared to the starting concentration in the sludge. However, several aspects, like chemical costs, working environment, treatment to recover phosphates from the solution etc should also be taken into account. The results from the washing steps with 0.1 M HCl and 0.01 M NaOH are shown below in Figure 16-18. All diagrams are results from a combination of different samples and experiments, in order to ensure qualitative results. In order to illustrate this in best possible way the results are shown in three different diagrams, where the red line illustrates the target to reach of 50 % efficiency. The possibility of making the experiment in several steps was discussed as an attempt to increase the yield. However since the yield in the first experiments was not meeting the requirements for target II, this was not investigated further.

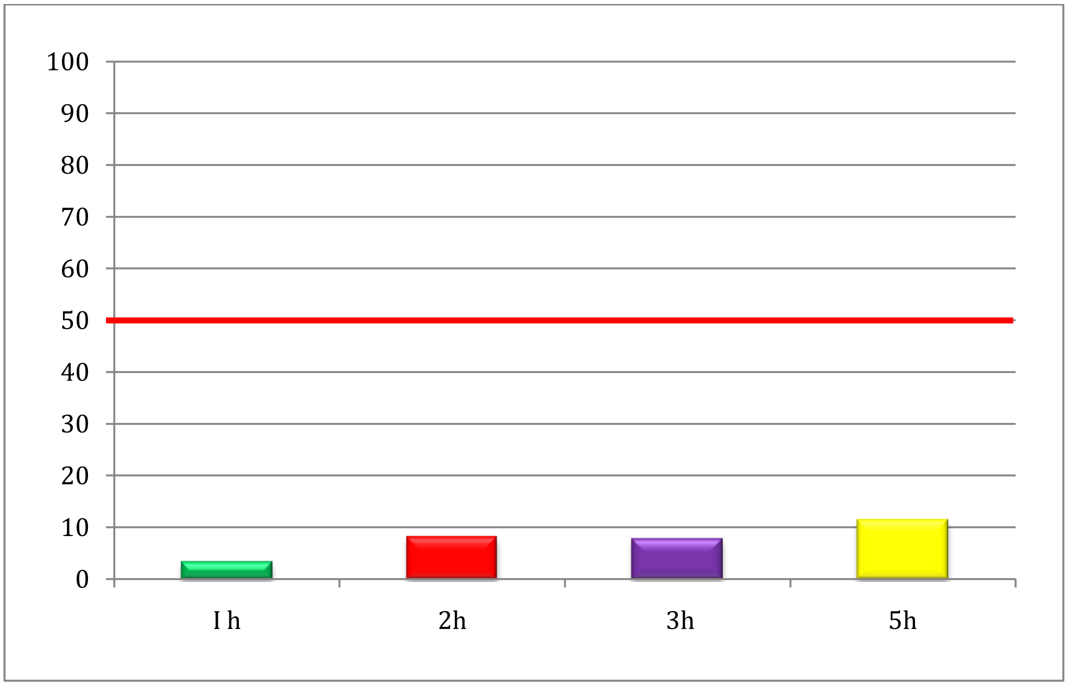


FIGURE 16 Yield in % from experiment with 0, 1 M HCL

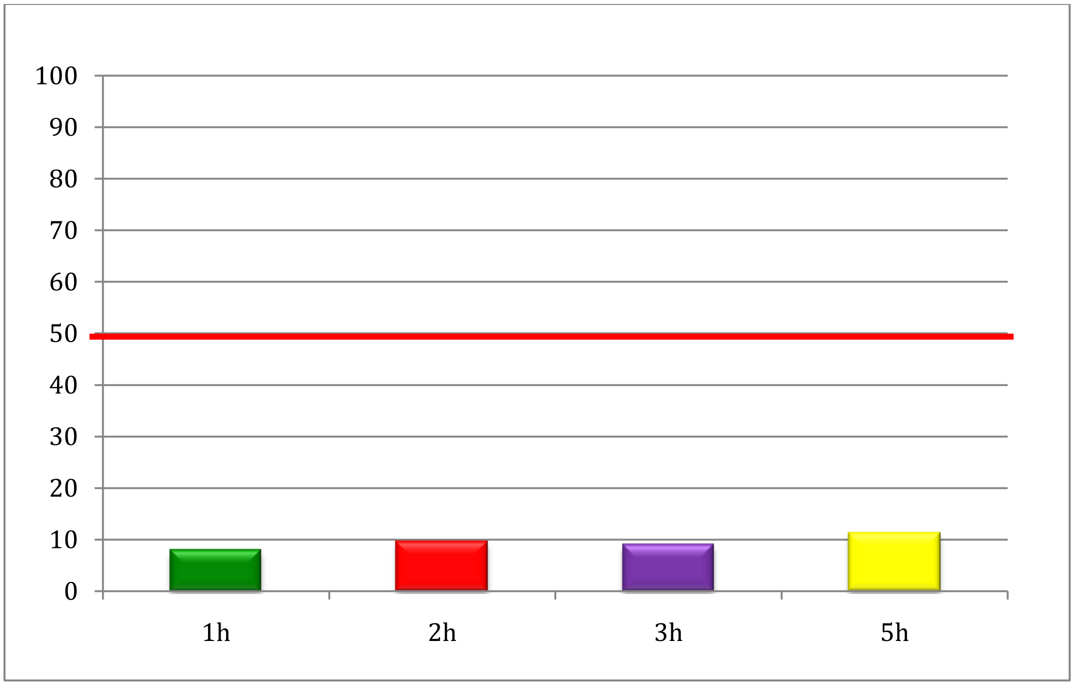


FIGURE 17 Yield in % from experiment with NaOH and no heating

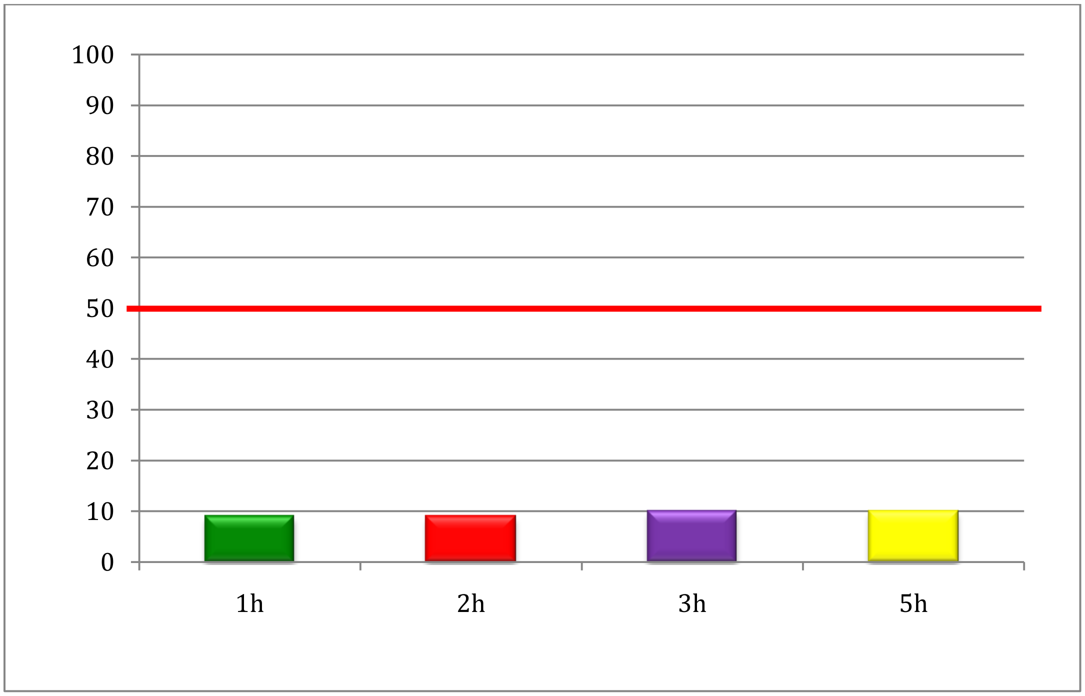


FIGURE 18 Yield in % from experiment with NaOH, with heating

In summary, it can be concluded from the figures above that these two approaches are not recommendable as phosphorous recovering methods. Even if both methods comply with target III, the more important targets I and II could not been reached.

9.2.1.2 Removal of unwanted substances from the sludge

The variations in composition of the sludge as well as the composition of the solvents have been taken into consideration within the experiments, since these parameters appeared to influence the result. Therefore, the solutions used in this experiment were analyzed as well as the weekly samples taken of the sludge. Double sample was taken in order to ensure results of a quality. The results from these analyses were then used to correct the yield achieved from the first analysis. The results from the elemental removal by acid and hydroxide washing steps are illustrated in Figure 18-19, Table 4 -5.

TABLE 4 ICP result from removing the unwanted substances from the sludge with 0, 01 M NaOH

Substance	µg/l	Contribution from NaOH	Corrected result of NaOH	Results from analysis of HCl (µg/l)	% Yield
Ni	6.3	0.9	7.2	<600	-
Zn	5.2	-	-	<400	-
Ti	140	6.3	146	0.9	0.6 %
Na	90 000	229 000	31 900	267 000	84 %
S	6160	-	-	5290	86 %
Al	300	428	728	394	54 %
Cr	22	-	-	5.3	24 %
Pb	0,69				
Hg	-	-	-	-	-

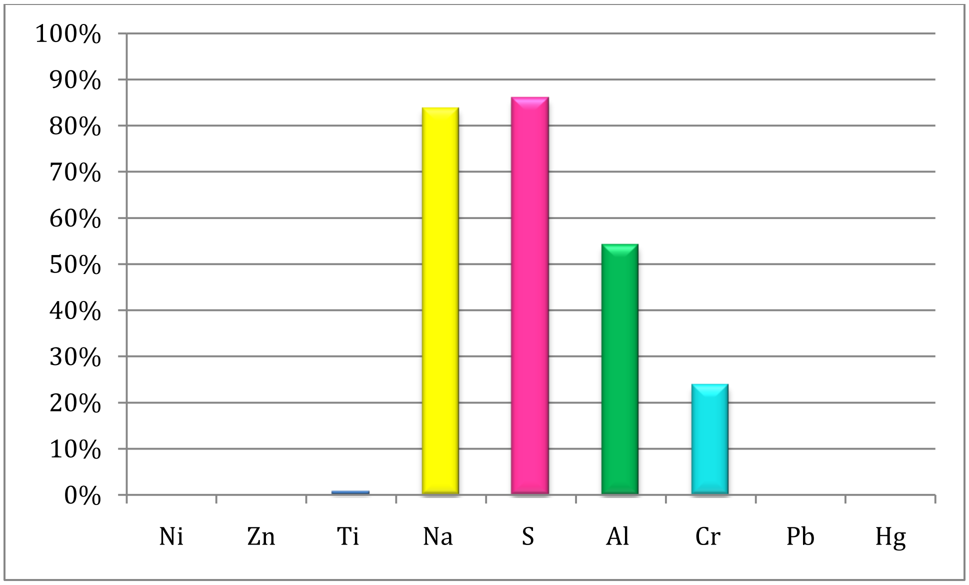


FIGURE 19 Yield from using NaOH to eliminate unwanted substances

Table 5 ICP- OES/MS results from removing the unwanted substances from the sludge with 0,1 M HCl

Substance	µg/l	Contribution from HCl	Corrected result of HCL	Results from analyze of HCl (µg/l)	% Yield
Ni	43.5	0.8	44.3	21.1	47 %
Zn	36.1	32.4	6.75	87.4	129 %*
Ti	141	0,68	142	63.2	44 %
Na	630 000	-	-	363 000	58 %
S	43 200	-	-	23 200	54 %
Al	2 100	-	-	1340	7 %
Cr	157	-	-	68,5	44 %
Pb	4.5	-	-	-	-
Hg	-	-	-	-	-

* Due to variation in the composition of the sludge, this is discussed more in chapter 10 of this report.

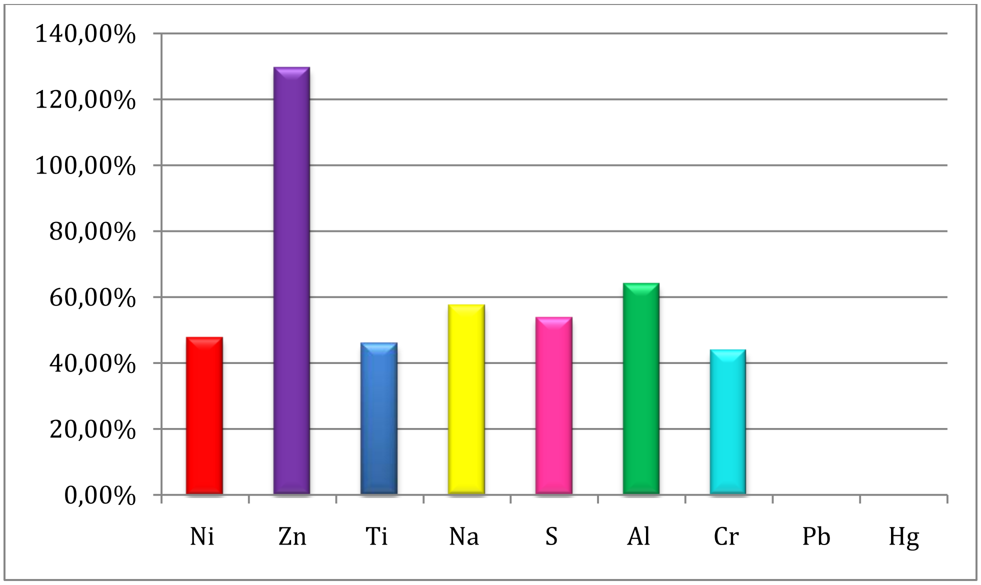


FIGURE 20 Yield from using HCl to eliminate unwanted substances

Both experiments with NaOH and HCl as solvents for removing unwanted substances from the sludge gave satisfying results, but the removal of trace metals was more effective in the acid leaching than in the alkaline leaching. The sodium (Na) illustrated in the diagrams above is assumed to be a measure of chlorides (Cl) as well since most probably Na and Cl are present as a salt (NaCl) within the sludge. Probably the best results will be achieved if the sludge is cleaned with both NaOH and HCl in a two step process.

In Table 6 the maximum amount of heavy metals used in ecological cultivation is compared to the content of the same parameters within the sludge after the sludge has been cleaned with HCl. The pesticide will require 10–25 kg/ha to be spread on arable lands, in order for the substance to be effective. (Swedish Board of Agriculture, 2008) However in for example the substance “Snigel Fritt” only about 1% of the active substance iron (III) phosphate is needed for the product to be effective. This means that only 0, 1-0, 25 kg of iron (III) phosphate will be added per hectare.

TABLE 6 comparison of cleaned sludge and the limits of heavy metals within ecological agriculture (www.krav.se)

	Limit g/Ha/year	mg/kg sludge Cleaned with HCL	g/Ha/year based on 0.25 kg Iron(II)phosphate from sludge
Pb	50	0.6	0.2
Cd	0,75	>0,01	
Cu	500	0.7	0.2
Cr	50	21	5.3
Hg	1	> 0.05	
Ni	50	5.4	1.4
Zn	700	0	0

In summary, both approaches of removing unwanted substances from the sludge reach all three of the targets. The overall efficiency is over 30 % when using HCl as a solvent to remove unwanted substances from the sludge and NaOH can be used in a second cleaning step in order to reach even higher cleaning efficiency. Since both HCl and NaOH are used within the process today, this method will also reach target number III. Thereby this method is recommended in order to recover FePO4 and then using it in agriculture applications.

9.2.2 LONG-TERM APPROACHES

9.2.2.1 *Solvent extraction with amine, without oxidation of the process water*

The results which can be seen in Table 7TABLE 7 illustrates that the solvent extraction was unsuccessful in that sense that all the phosphorous is still present in the water phase. This is illustrated by a yield around 0 % for all three experiments. So, in order to achieve an acceptable yield, the method has been slightly modified.

TABLE 7 ICP results from solvent extraction

	Yield
Solvent extraction 1	0 %
Solvent extraction 2	0.3%
Solvent extraction 3	0%

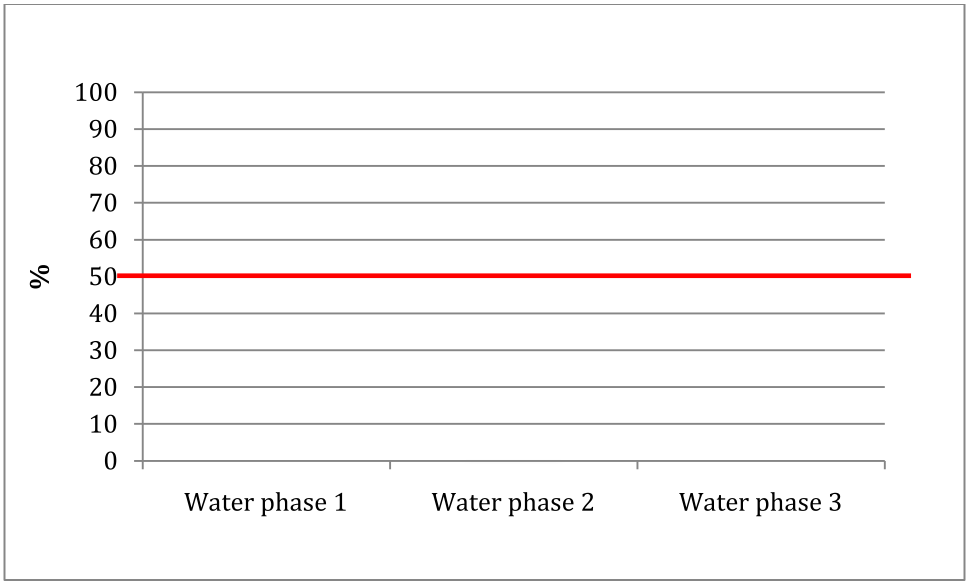


FIGURE 21 results in yield % from solvent extraction without oxidation of water

9.2.2.2 Solvent extraction with amine, with oxidation of the process water

An oxidation of the phosphates prior the solvent extraction process was added due to the poor results from the first series of experiments, which can be seen in section 9. From these results it was concluded that the extraction cannot be done without oxidizing the phosphorous species in the water into orto phosphates (PO_4^{3-}) first. The results from these experiments can be seen in Table 8 and figure 22 which illustrates that the solvent extraction in this case was successful since almost all phosphates has been moved from the water phase into the organic phase.

TABLE 8 ICP results from solvent extraction, with oxidation of the water

	Yield
Process water	
Solvent extraction 1	98 %
Solvent extraction 2	99 %

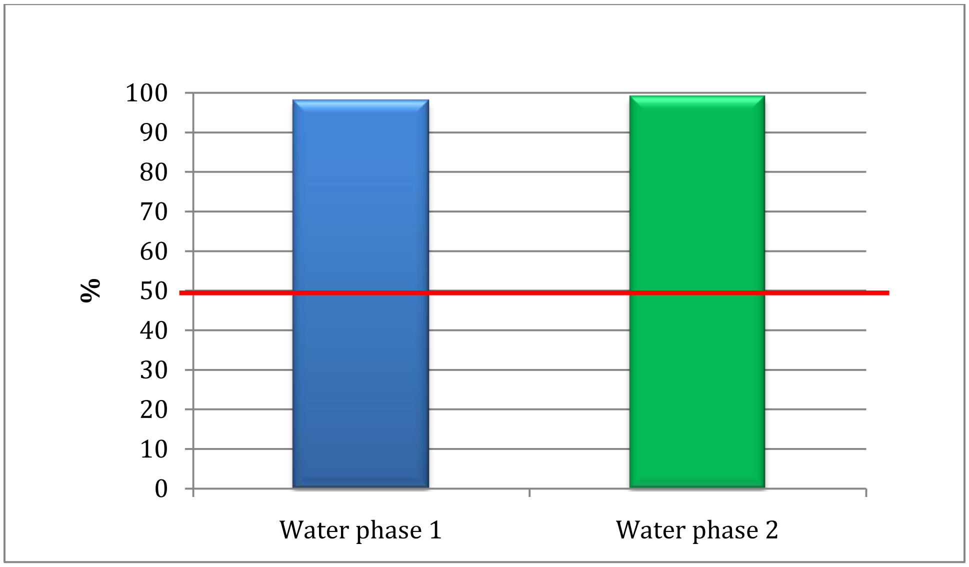


FIGURE 22 results in yield % from solvent extraction with oxidation

In summary, solvent extraction with pre-oxidation of the water reaches all the desired three targets since the overall efficiency is over 50 % (illustrated by the red line in the figures) and the method is technically feasible. Therefore this method is recommended as a long-term approach to the company.

10 DISCUSSION

All experiments have been performed only on a lab scale, therefore it is important to study these methods on a larger scale in order to find possible limitations. Furthermore all the experiments have been performed on representative sludge samples; however, sludge composition shows an internal variation and yield results might therefore differ. The calculations presented in this report were based on average values from these samples. The variations in composition are generally small which can be seen in Table 11. The exact values for all investigated elements within the sludge can be seen in Appendix II. The variation in composition can be the answer to the high value in table 5 and its corresponding experiment when trying to remove unwanted elements from the sludge. Due to limiting in time, this could not be deeper investigated.

Table 9 Overview of composition of sludge

Element	Sludge 1	Sludge 2	Sludge 3	Mean value
	mg/Dry weight	mg/Dry weight	mg/Dry weight	mg/Dry weight
Al	486	471	545	500
Ca	57	91	54	68
Fe	299000	286000	293000	293000
K	<100	329	390	359
Na	145000	157000	150000	150700
P	56200	48600	55700	53500
Cr	36	36	40	37
V	78	76	84	80
S	9650	11200	9980	10276
Ni	10	11	10	10

In this thesis project both short-term and long-term approaches to creating a product from the phosphorous rich process water were proposed and tested experimentally. Both types of treatment methods would generate a much more sustainable waste management strategy than the one used today. Application of a short-term method may be quite straight forward, started while moving towards the long term approach with the aim of preventing the waste. For the short term approaches removing unwanted substances from the sludge is the only method which has shown enough satisfying results to be a potential method to be implemented at site. Using it as raw material for the manufacturing substances to prevent snails is one alternative. Another alternative market for the iron (III) phosphate sludge is to use the iron (III) phosphate sludge as a fertilizer; however this alternative needs some further investigations. Within the long-term approach there are two possible alternatives in order to reach the goal of waste prevention rather than waste treatment. Within this report, the approach of liquid extraction to recover phosphorous has been investigated with experimental attempts while the alternative of changing the precipitant only has been given as an alternative. Both these alternatives will eliminate the waste sludge, which is generated today. Instead of going through several of steps to generate a sludge including a sparingly soluble phosphate compound and then trying to recover it, the solvent extraction approach will recover the phosphorous directly from the process water. From a sustainable waste management point of view this would be the best option. However other facts such as economy and efficiency also have to be taken into account while choosing the best alternative for the plant at Eka Chemicals.

11 CONCLUSIONS & RECOMMENDATIONS

11.1 CONCLUSIONS

- ✓ Suitable short-term approaches to recover phosphorous;

The suggested method to dissolve the iron (III) phosphate with acid as well as with sodium hydroxide turned out to give insufficient yield of recovered phosphorous.

The best alternative within the short-term approach is to remove the unwanted substances from the sludge in order to use it as a raw material in the manufacturing of snail preventing substances or other agriculture applications. This is also the only method within the short-term approaches which reached all of the targets which was put up as references in the beginning of chapter 9.

- ✓ Suitable long-term approaches to recover phosphorous;

Both solvent extraction of PO_4^{3-} for phosphate recovery, as well as changing the precipitation method are possible methods to use within the plant in Trollhättan. However, only the solvent extraction was investigated further in this work and gave good results.

11.2 RECOMMENDATIONS & FUTURE WORK

It is recommended to further investigate the possibility of changing the precipitation method, and use alternatives instead of using iron chloride to generate the sludge.

It is also recommended to make thorough economical calculations around the solvent extraction process in order to achieve a clear view if this method is beneficial. A scaled up investigation is also recommended.

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12 REFERENCES

(1987). Retrieved 03 08, 2011, from World Commission on Environment and Development: http://www.un-documents.net/ocf-02.htm#I

Akzo Nobel . (2011, January). *Akzo Nobel Pulp & Paper Chemicals Eka*. Retrieved January 2011, from www.akzonobel.com: http://www.akzonobel.com/eka/aboutus/this_is_eka/

Akzo Nobel . (2011). *Operational Eco Efficiency program.*

Akzo Nobel. (2009). *Akzo Nobel Report 2009.* Retrieved 05 06, 2011, from Managing our values: http://report.akzonobel.com/2009/sustainability/managingourvalues.html?cat=m

Akzo Nobel Corporate. (2011). *Akzo Nobel Corporate-Sustainability Strategy*. Retrieved 04 24, 2011, from Akzo Nobel Corporate-Sustainability Strategy: http://www.akzonobel.com/sustainability/managing_sustainability/strategy/

Akzo Nobel. (2011). *Our policies Sustainability & Health safety and environment*. Retrieved 03 07, 2011, from Akzo Nobel pulp and paper chamicals, eka: http://www.akzonobel.com/eka/sustainability/hse/hse_policies.aspx

Akzo Nobel. (2009). *Sustainability Report 2009 - Sustainability Framework.* Akzo Nobel.

Akzo Nobel Sverige. (2011). *AkzoNobel Sverige*. Retrieved 04 19, 2011, from AkzoNobel Sverige - Om Akzo Nobel: http://www.akzonobel.com/se/om_oss/om_akzonobel/index.aspx

ALS Scandinavia. (2011). *ALS Scandinavia*. Retrieved from ALS Scandinavia: www.analytica.se

Basu, R. (2004). *Implementing Quality: A Practical Guide to Tools and Techniques.* Intl Thomson Business.

Bulsuk, K. G. (2009, 02 02). *Karn G. Bulsuk: Full Speed Ahead*. Retrieved 05 13, 2011, from http://blog.bulsuk.com/2009/02/taking-first-step-with-pdca.html#axzz1MEO2G33B

Camerani, C. (2011, 05 06). Waste management at Eka Chemicals. (C. Bergquist, Interviewer)

Choppin, J. R. (2004). *Solvent Extraction Principles and Practice.* USA: Marcel Dekker.

Clement, M. v. (2005). 2nd IWA leading-edge conference on water and waste water treatement technologies . *2nd IWA leading-edge conference on water and waste water treatement technologies* (p. 326). IWA Publishing.

Development, I. I. (2011). *International Institute for Sustainable Development - What is Sustainable Development* . Retrieved 05 04, 2011, from International Institute for Sustainable Development: http://www.iisd.org/

Driver, J. (1998). Phosphorus recovery. *Phosphorus & Potassium Issue No 216* .

Dukart, M. E. (2006). *Standard Operating Procedure – VUSP – O Ortho-Phosphate, USEPA by Discrete Analysis.* Oak Brook, Illinois: Systea Scientific, LLC.

Eka Chemicals. (2011). AKD Process. *AKD Process* . Trolhättan, Sverige: Eka Chemicals AB.

Eka Chemicals. (2008, 03 12). Grundläggande karakterisering av avfall som ska deponeras. *Grundläggande karakterisering av avfall som ska deponeras* . Trolhättan, Västra Götalandslän , Sverige: Eka Chemicals AB.

Elliott, J. A. (2006). *An introduction to sustainable development.* New York: Routledge.

EU- DIRECTIVE 2008/98/EC. (2008, 10 19). DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL. *DIRECTIVE 2008/98/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL* . DIRECTIVE 2008/98/EC.

Eubusiness.com. (2011, 04 30). *Eubusiness.* Retrieved 05 06, 2011, from Eubusiness: http://www.eubusiness.com/topics/environ/waste-framework

Fagan, R. (2009, 03 09). *earth911.com*. Retrieved 03 08, 2011, from Waste Hierarchy: Who's on Top in the Game of Trash?: http://earth911.com/news/2009/03/09/waste-hierarchy-whos-on-top-in-the-game-of-trash/

Hasselström, J. (2001). *Fosfor utvinning ur slam.* Stockholm: Kungliga Tekniska Högskolan.

Henze, H. a. (2002). *Wastewater treatment: biological and chemical processes.* Springer.

Hill, A. L. (2010). *Life Cycle Assessment of Municipal Waste Management: Improving on the Waste Hierarchy.* Aalborg : Aalborg University.

Jiang, O. N.-Q. (2010). A Trial of Using Solvent Extraction for phosphorus Recovery. *Journal od Water Resource and Protection* , 820-838.

Joint Committee of Powder Diffraction Standard. (2010). Joint Committee of Powder Diffraction Standards, JCPDS-ICCD: PDF-4 release . *Joint Committee of Powder Diffraction Standards, JCPDS-ICCD: PDF-4 release* . Philadelphia, USA.

KTH. (2011). *Inorganic Chemistry KTH*. Retrieved 07 2011, from www.kemi.kth.se: www.kemi.kth.se

Lancaster, M. (2002). *Green Chemistry an introductory text.* Chambridge: The Royal society of Chemistry .

Lemann, M. F. (2008). *Waste Management.* Peter Lang AG.

Linneuniversitetet. (n.d.). *Linneuniversitetet*. Retrieved 02 15, 2011, from Våglängdsdispersiv spektroskopi: http://w3.msi.vxu.se/~pku/Rontgen/Wavelength_dispersive.html

Marten, R. K. (2007). Sustainable development: how to manage something that is subjective and never can be achieved? *Sustainability; Science, Practice and policy* .

MEAB. (2010). *MEAB - Products*. Retrieved 03 11, 2011, from Industrial Solvent Extraction Process Equipment : http://www.meab-mx.se/pages/products/index.html

Merkanti Hach. Analyshandbok dr/700. In M. Hach, *Analyshandbok dr/700.*

MIljöcenter. (2008). *Safety Data Sheet- Ferramol Snigel Effekt.* Arlöv: MIljöcenter.

Nationalencyklopedin . (2011). *Nationalencyklopedin* . Retrieved 04 20, 2011, from Nationalencyklopedin - Dimer: http://www.ne.se/dimer

Naturvårdsverket. *Fosfor – resurser, tillgång, kvalitet.* Naturvårdsverket.

Nieminen, L. H. (2011). Recycled iron phosphate as fertlizer raw material for tree stands on drained boreal peatlands. *Forest Ecologu and Management* .

Pettersson, J. (2010, 04 16). *Jean Pettersson*. Retrieved 02 15, 2011, from Uppsala universitet- Analytisk kemi: http://www.analytisk.kemi.uu.se/sve/information/personal/pettersson_jean/index.shtm

Puigdomenech, I. (2008). *http://www.kemi.kth.se/medusa/*. Retrieved 03 2011, from Chemical Equilibrium Diagrams: http://www.kemi.kth.se/medusa/

Spoolman, G. T. (2009). *Living in the environment .* Yolands Cossio.

Steenari, B.-M. (2011, 02). (C. Bergquist, Interviewer)

Ström, K. (1999). *Grundläggande Separationsteknik.* Göteborg.

Suschaka, J. (2001). *Phosphates recovery from iron phosphate sludge.* Poland: Technical univeristy of Lodz .

Swedish Board of Agriculture. (2008). *Bekämpning av sniglari lantbruk och yrkesmässig trädgårdsodling.* Jönköping: Swedish Board of AgricultureV.

Swedish Environmental Protecting Agency . (1997). *Fosfor och energi ur avloppsslam.* Stockholm: Swedish Environmental Protecting Agency .

SWEDISH ENVIRONMENTAL PROTECTION AGENCY. (2010). *Uppdatering av "Aktionsplan för återföring av fosfor ur avlopp".* Stockholm: SWEDISH ENVIRONMENTAL PROTECTION AGENCY.

Swedish EPA. (2002). *Aktionsplan för återföring av fosfor ur avlopp.* Stockholm: Naturvårdsvereket.

Swedish EPA. (2002). *Aktionsplan för återföring av fosfor ur avlopp.* Stockholm: Swedish EPA.

Taylor, H. E. (2001). Inductively Coupled Plasma-Mass Spectrometry. In H. E. Taylor, *Inductively Coupled Plasma-Mass Spectrometry* (pp. 1-5).

TutorVista.com. (2010). *X-Ray Study of Crystals* . Retrieved 02 15, 2011, from TutorVista.com: http://www.tutorvista.com/content/chemistry/chemistry-iv/solid-state/x-ray-crystals.php

US EPA. (2010). *Iron (Ferric) Phosphate (034903) Fact Sheet*. Retrieved 02 01, 2011, from Environmental Protection Agency: http://www.epa.gov/oppbppd1/biopesticides/ingredients/factsheets/factsheet_034903.htm

Valsami-Jones, E. (2004). *Phosphorus in Environmental Technologies.* UK: IWA Publishing.

www.Krav.se. (2011, 01). Retrieved 05 16, 2011, from 12.5 Begränsa tillförseln av tungmetaller: http://www.krav.se/KravsRegler/12/5/

Zavalij, V. P. (2005). *Fundamentals of Powder Diffraction and Structural Characterization of Materials* . Boston: SpringerLink.

APPENDIX I SPECIFIC PREPARATION PROCEDURES

i) Specific preparation procedure for ICP

Sample from washing the sludge with NaOH (ALS Scandinavia, 2011)

Dissolution and analysis of water sample, 12 ml sample and 1.2 ml HNO3 (suprapur) have been treated in a microwave oven alternatively in an autoclave.

In case of Ag determination the dissolution has been carried out with HCl in a microwave oven.

For Se the dissolution has been carried out with HCl in an autoclave at 120°C for 30 minutes.
Analyses were carried out according to USEPA Methods 200.7 (ICP-AES) and 200.8 (ICP-SFMS) respectively. The AFS analyses were carried out according to SS-EN ISO 17852:2008

Sample from washing the sludge with HCL (ALS Scandinavia, 2011)

Dissolution and analysis of water sample, 12 ml sample and 1.2 ml HNO3 (suprapur) have been treated in a microwave oven alternatively in an autoclave.

In case of Ag determination the dissolution has been carried out with HCl in a microwave oven.

For Se the dissolution has been carried out with HCl in an autoclave at 120°C for 30 minutes.
Analyses were carried out according to USEPA Methods 200.7 (ICP-AES) and 200.8 (ICP-SFMS) respectively. The AFS analyses were carried out according to SS-EN ISO 17852:2008

Sludge characterization **(PG0)**

The sample has been dried at 105 C according to SS 028113.
0.1 g sample has been melted with 0.375 g LiBO2 and dissolved in HNO3.
0.2 LOI (loss on ignition) is performed during a temperature of 1000°C.
The analysis has been performed by EPA – methods (modified) 200.7(ICP-AES) and 200.8 (ICP-QMS).

Sludge characterization (**V3B)**
Dissolution and analysis of water sample, 12 ml sample and 1.2 ml HNO3(suprapur) has been treated in a microwave oven alternatively in an autoclave.

In case of Ag determination the dissolution has been carried out with HCl in a microwave oven.

For Se the dissolution has been carried out with HCl in an autoclave at 120°C for 30 minutes.
Analyses were carried out according to USEPA Methods 200.7 (ICP-AES) and 200.8 (ICP-SFMS) respectively. The AFS analyses were carried out according to SS-EN ISO 17852:2008

Sludge Characterization (**PM2-SM)**

The sample has been dried with a temperature of 105°C according to the Swedish standard SS028113. The analyze sample has been dried with a temperature of 50°C and the elementary substances has been corrected for dry weight.

The dissolution has been performed in a microwave oven in a sealed Teflon container with HNO3/water; 1; 1. The analysis has been performed according to the EPA –methods (modified) 200.7 (ICP-AES) and 200.8 (ICP-SFMS).

Solvent extraction with amine (water phase 1-3 and process water)

Analysis of water samples without previous dissolution. The samples are acidified with 1 ml ultra high-purity nitric acid per 100 ml of sample. This does not pertain to samples that are acidified before they are received by the laboratory.
For Se the sample has been digested with hydrochloride acid in autoclave (120°C, 30 minutes). For W the sample has not been acidified. For Ag the samples are preserved with HCl.
The ICP-AES and ICP-SFMS analyses were carried out according to USEPA Methods 200.7 (modified) and 200.8(modified) respectively. The AFS analyses for Hg was carried out according to SS-EN ISO 17852:2008

ii) Specific preparation procedure for XRD

The sludge was dried in an oven during a temperature of 105 °C. When the sample was completely dry it was grinded in a pounder to achieve small even dry particles. The dry and grinded sample was transferred to the XRD sample container and distributed randomly onto the plate of the container with a piece of glass.

APPENDIX II RESULTS FROM THE CHARACTERIZATION OF SLUDGE

In this Appendix the raw data from the characterization are illustrated. Some concentrations in the tables are given as >X and this is when the concentration is below the minimum concentration needed to be reported. Different analysis methods within ICP have been used, in order to be able to detect as many elements as possible. The analytical method that has been used can be seen within the parenthesis in the table description. The specific sample preparation procedures for each analysis can be seen in Appendix I.

Table 10 Results from ICP analysis (PG0) Performed by ALS Scandinavia

Substance	**Si**	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**P**	**Ti**
(mg/kg Dry weight)	424	585	90.1	344000	810	<50	96.1	139000	61700	42
Substance	**Ba**	**Be**	**Co**	**Cr**	**Ga**	**Ge**	**Hf**	**Mo**	**Nb**	**Rb**
(mg/kg Dry weight)	<2	0.748	5.46	40.9	6.12	<10	<0.1	<2	<0.2	2.49
Substance	**Sc**	**Sr**	**Ta**	**Th**	**U**	**V**	**W**	**Y**	**Zr**	
(mg/kg Dry weight)	<1	<2	0.177	<0.1	0.0506	53.2	0.388	0.5	<2	

Table 11 Results from ICP ANALYZIS (PM2-SM) performed by ALS Scandinavia

Substance	**As**	**B**	**Bi**	**Cd**	**Cs**	**Cu**	**Hg**	**In**	**Li**	**Ni**
mg/kg Dry weight)	0.309	<2	0.0224	<0.01	<0.1	0.824	0.115	<0.04	0.651	9.5
Substance	**Pb**	**S**	**Tl**	**Zn**						
mg/kg Dry weight)	1.71	10000	0.0511	6.54						

Table 12 Results from ICP analysis (PG5) Performed by ALS Scandinavia

Substance	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**
(mg/kg Dry weight)	<0.1	3.88	<1	0.345	<0.3	<0.04	<0.3	<0.1	<0.09	<0.07
Substance	**Er**	**Tm**	**Yb**	**Lu**						
(mg/kg Dry weight)	<0.1	<0.1	<0.2	<0.03						

Table 13 Results from ICP analysis performed by ALS Scandinavia

Element	Sludge 1	Sludge 2	Sludge 3	Mean value
	mg/Dry weight	mg/Dry weight	mg/Dry weight	mg/Dry weight
TS	60.1	63.1	55.1	59.43
Ag	<0.3	<0.3	<0.3	<0.3
Au	<0.1	<0.1	<0.1	<0.1
Ir	<0.01	<0.01	<0.01	<0.01
Pd	<0.05	<0.05	<0.05	<0.05
Pt	<0.01	<0.01	<0.01	<0.01
Re	<0.01	<0.01	<0.01	<0.01
Rh	<0.05	<0.05	<0.05	<0.05
Ru	<0.05	<0.05	<0.05	<0.05
Sb	0.0941	<0.05	<0.05	<0.05
Se	0.138	0.142	0.156	0.145
Sn	<0.3	<0.3	<0.3	<0.3
Te	<0.3	<0.3	<0.3	<0.3

Table 14 Results from ICP analysis performed by ALS Scandinavia

Element	Sludge 1	Sludge 2	Sludge 3	Mean value
	mg/Dry weight	mg/Dry weight	mg/Dry weight	mg/Dry weight
La	1.13	0.517	0.492	0.713
Ce	<0.06	<0.06	<0.06	<0.06
Pr	<1	<1	<1	<1
Nd	0.331	0.237	0.316	0.295
Sm	<0.3	<0.3	<0.3	<0.3
Eu	<0.04	<0.04	<0.04	<0.04
Gd	<0.3	<0.3	<0.3	<0.3
Tb	<0.1	<0.1	<0.1	<0.1
Dy	<0.09	<0.09	<0.09	<0.09
Ho	<0.06	<0.06	<0.06	<0.06
Er	<0.1	<0.1	<0.1	<0.1
Tm	<0.1	<0.1	<0.1	<0.1
Yb	<0.2	<0.2	<0.2	<0.2
Lu	<0.03	<0.03	<0.03	<0.03

Table 15 Results from ICP analysis performed by ALS Scandinavia

Element	Sludge 1	Sludge 2	Sludge 3	Mean value
	mg/Dry weight	mg/Dry weight	mg/Dry weight	mg/Dry weight
TS	60.1	63.1	55.1	59.43
As	0.215	0.206	0.187	0.203
B	1.3	4.43	1.04	2.256
Bi	0.0247	<0.02	<0.02	<0.02
Cd	<0.01	<0.01	<0.01	<0.01
Cs	<0.1	<0.1	<0.1	<0.1
Cu	1.14	0. 38	0.376	0.718
Hg	<0.05	0.0545	0.0484	<0.05
In	<0.05	<0.05	<0.05	<0.05
Li	0.204	0.227	0.239	0.22
Ni	10.5	10.9	9.94	10.45
Pb	0.597	0.626	0.62	0.61
S	9650	11200	9980	1 027
Tl	<0.05	<0.05	<0.05	<0.05
Zn	8.62	8.96	8.17	8.58

Table 16 Results from ICP analysis performed by ALS Scandinavia

Element	Sludge 1	Sludge 2	Sludge 3	Mean value
	mg/Dry weight	mg/Dry weight	mg/Dry weight	mg/Dry weight
Si	<100	135	<100	
Al	486	471	545	500
Ca	57.7	91.3	54	67
Fe	299000	286000	293000	292 666
K	<100	329	389	359
Mg	<50	55.5	<50	50
Mn	82.1	92.2	78.2	84.17
Na	145000	157000	150000	150 666
P	56200	48600	55700	53500
Ti	32.4	32.4	36	33.6
Ba	1.87	1.87	1.58	1.77
Be	2.02	1.83	1.72	1.86
Co	<5	<5	<5	<5
Cr	36	36.5	39.6	37.37
Ga	5.49	4.44	5.92	5.283
Ge	<10	<10	<10	<10
Hf	<0.1	<0.1	<0.1	<0.1

Table 17 Results from ICP analysis performed by ALS Scandinavia

Element	Sludge 1	Sludge 2	Sludge 3	Mean value
	mg/Dry weight	mg/Dry weight	mg/Dry weight	mg/Dry weight
Mo	3.63	4.09	4.07	3.93
Nb	<0.2	<0.2	<0.2	<0.2
Rb	<2	<2	<2	<2
Sc	<1	<1	<1	<1
Sr	<2	<2	<2	<2
Ta	<0.05	<0.05	<0.05	<0.05
Th	<0.1	<0.1	<0,1	<0,1
U	0.0424	0.0374	0.0367	0.039
V	78.3	76.1	84	79.47
W	<50	<50	<50	<50
Y	<2	<2	<2	<2
Zr	<2	<2	<2	<2

Phosphorous recovery from iron (III) phosphate sludge

-A suggestion on how to recycle phosphorous in order to reach a more sustainable waste management strategy

Master's Thesis in the Master's program Industrial Ecology
CAMILLA BERGQUIST

Master's Thesis
Department of Chemical and Biological Engineering
Division of Environmental Inorganic Chemistry and Industrial Materials Recycling
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: + 46 (0)31-772 1000

Cover:
The recycle symbol illustrates the aim of recycling Phosphorous with the chemical symbol P.
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