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MAGNESIUM RECOVERY FROM MULTIMETAL PROCESS STREAMS

Master´s Programme in Chemical, Biochemical and Materials Engineering
Major in Chemical Engineering

Master’s thesis for the degree of Master of Science in Technology submitted for inspection, Espoo, 13 May, 2018.

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Abstract of master's thesis

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Abstract

In this study, a method to extract magnesium from multimetal component nickel sulfide process stream as struvite was developed. Recovery as struvite was chosen based on a techno-economic analysis of different alternatives. The method was tested in laboratory with 25 wt-% ammonium hydroxide and 85 wt-% phosphoric acid as the ammonium and phosphate ion source, respectively. The tests proved struvite precipitation possible from a case process stream with an abundance of Fe^{2+} and Mn^{2+} ions. Their effects to struvite recovery and purity were studied. Based on the results iron and manganese removal steps are recommended. Iron removal as iron(III)hydroxide and manganese removal as manganese(II)carbonate were used in this study and they turned out to be efficient according to the ICP -analyses of the solutions. Half of the solution's initial magnesium was recovered in the struvite recovery step with 30 % co-precipitating in iron and manganese removal steps and rest remaining in the solution. The purities of the struvite products were checked with XRD -analysis. The XRD -patterns matched very well with the reference pattern from literature.

Generic process design was done for the proposed process route. The capital investment was calculated to be around 70 M€, operational costs around 1 400 €/h and chemical costs around 10 000 €/h. Based on the laboratory results, the chemical costs can possibly be lowered down to 7 200 €/h but this needs more tests for confirmation. In case it is possible, the struvite price needs to be almost 680 €/t for a payback time of ten years. Struvite does not have a well-developed market yet but the price was estimated 386 €/t. Thus, the process is not too attractive an investment as such. To make the process feasible following areas for development were found and are recommended for further studying. First and foremost is changing the ammonium solution and phosphoric acid in struvite precipitation to diammonium phosphate. Other recommended topics are more efficient manganese recovery so that more magnesium could be recovered as struvite and utilizing the remaining sulfate and ammonium ions for ammonium sulfate fertilizer production. Finally, dehydration/hydration cycle of struvite to dittmarite and back can result in transportation savings. The possible implementation of all suggestions could bring up to 21 M€ yearly income with the current struvite market price meaning a payback time of around three and a half years for the process! In addition, other pros affecting the total process positively to the total process were found. For example, the calcium content decreased by 50 %. The sodium and sulfate contents also decreased around 20 %.

Keywords Magnesium, recovery, struvite, bioleaching

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Tiivistelmä

Tässä työssä kehitettiin menetelmä magnesiumin talteenottoon nikkelisulfidi tuotannon prosessivirroista. Magnesiumin saostaminen struviittina valikoitui tutkimuskohteeksi tekno-ekonomisen analyysin perusteella. Menetelmää testattiin laboratoriossa, jossa ammonium-ioni lähteenä käytettiin 25 p-% ammoniakkiliuosta ja fosfaatti-ioni lähteenä 85 p-% fosforihappoa. Kokeet osoittivat struviittisaostuksen olevan mahdollista case-liuoksesta, joka sisälsi suuren määrän Fe^{2+} ja Mn^{2+} -ioneja. Niiden vaikutuksia struviittisaostukseen ja tuotteen puhtauteen tutkittiin. Tuloksien perusteella molempien poistamista liuoksesta suositellaan puhtaamman tuotteen saamiseksi. Tässä tutkimuksessa rauta saostettiin rauta(III)hydroksidina ja mangaani mangaani(II)karbonaattina. Testiliuoksille tehdyt ICP-analyysit osoittivat menetelmät toimiviksi, tosin vieden mukanaan noin 30 % alkuperäisestä magnesiumista. Kaiken kaikkiaan noin puolet magnesiumista saatiin talteen struviittina viidenneksen jäätyä liuokseen. Struviittituotteille tehtiin XRD -analyysit, joiden tulokset vastasivat erittäin hyvin kirjallisuudesta löydettyä struviittikäyrää.

Ehdotetulle prosessille mitoitettiin laitteet, joiden perusteella prosessin hinnaksi laskettiin noin 70 M€. Käyttökustannuksiksi arvioitiin noin 1 400 €/h ja kemikaalikustannuksiksi noin 10 000 €/h. Kemikaalikustannukset voidaan hyvin todennäköisesti saada laskemaan noin 7 200 euroon tunnissa, mutta tämä vaatii vielä lisätutkimusta varmistukseksi. Mikäli se on mahdollista pitäisi struviitin hinnan olla noin 680 €/t, jotta prosessi maksaisi itsensä takaisin kymmenessä vuodessa. Struviitilla ei ole vielä kehittyneitä markkinoita, mutta kerätyn tiedon perusteella sen hinnaksi arvioitiin 386 €/t tässä tutkimuksessa. Prosessi ei siten näytä houkuttelevalta sijoituskohteelta sellaisenaan. Työssä löydettiin kuitenkin muutamia helposti tutkittavia kehityskohteita kannattavuuden parantamiseksi. Tärkeimpänä näistä on diammoniumfosfaatin käyttö ammoniumliuoksen ja fosforihapon sijaan struviittisaostukseen. Muita tapoja tehostaa prosessia ovat sekä mangaanin huolellisempi poisto, jotta kaikki jäljellä oleva magnesium saataisiin talteen struviittina että liuokseen jäävien ammonium- ja sulfaatti-ionien käyttö ammoniumsulfaatti lannoitteen valmistukseen. Lopuksi, struviitin muokkaamista dittmariitiksi ja takaisin suositellaan pienempien kuljetuskustannusten mahdollistamiseksi. Mikäli ehdotetut kehityskohteet on mahdollista implementoida prosessiin, toisivat ne mukanaan noin 21 M€ vuosituoton struviitin nykyisellä markkinahinnalla (386 €/t) eli prosessi maksaisi itsensä takaisin vajaassa kolmessa ja puolessa vuodessa. Tämän lisäksi prosessilla todettiin olevan muitakin hyötyjä. Esimerkiksi vesien käsittelyyn jatkavan liuoksen kalsiumpitoisuus pieneni puoleen tässä työssä tarkastellun prosessin jälkeen. Myös natrium- ja sulfaattipitoisuudet laskivat noin 20 % kumpikin.

Avainsanat Magnesium, talteenotto, struviitti, kasaliuotus

Preface

This study was carried out to fulfill the requirements for the degree of Master of Science in Technology in the School of Chemical Engineering at Aalto University. The work was done at the School of Chemical Engineering, the topic was given by Skyscape Oy and in the case part process solution from Terrafame mine was used.

I want to thank my advisors, Jari Kunnila and Kaisa Kiipula, and my supervisor, professor Pekka Oinas, for excellent support and guidance that made working with this thesis very enjoyable. Your genuine enthusiasm towards this work got – and kept – me deeply interested since the starting meeting.

Special thanks go to Aalto University's Juha-Pekka Pokki and Lasse Westerlund for helping me organize and carry out the laboratory tests. Thanks also to Terrafame's Sini Anttila and Minna Heikkinen for giving me a tour at the case process plant and analyzing the liquid samples.

I also want to address a huge thank you to my family and friends. It has been a privilege to grow with so supporting and smart people. Your input to this work is hard to measure but I can tell that without you it would not exist! Last but not least, thank you Jonna, my wife, for standing by my side for almost 10 years now and especially coping with the engineering life that I have chosen. Unless it chose me.

Vantaa, 13.5.2018

Riku Montonen

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Abbreviations

CAGR	Compound annual growth rate
HPAL	High pressure leaching plant
HSE	Health, safety and environment
ICP-OES	Inductively coupled plasma optical emission spectroscopy
IWT	Industrial water treatment
MHP	Mixed hydroxide precipitation
MSP	Mixed sulfide precipitation
PLS	Pregnant leaching solution
ROI	Return on investment
SEM	Scanning electron microscopy
WWTP	Waste water treatment plant
XRD	X-ray diffraction

1 Introduction

1.1 Background

Magnesium is the eighth most abundant element in the earth's crust although it never appears in its metallic form. It can be found in over 60 minerals and dissolved in salt waters. When recovered from either a mineral or brine magnesium is mostly used together with aluminum to form alloys. (Kramer 2010) The magnesium-aluminum alloys are used in many products that are part of our everyday life such as beverage cans, laptops and cars. The common characteristics with the products are that they need to be light without negatively impacting the strength of the product. Magnesium, with a density of two-thirds of aluminum, provides even lighter products while keeping the product strong. (Gupta and Nai 2011) Furthermore, the most common magnesium compounds such as magnesium sulfates, magnesium oxide, magnesium hydroxide and magnesium carbonates play an important role for example in steel and iron industry, healthcare and pharmaceuticals, and in fertilizers and environmental solutions.

Several processes have been developed for magnesium recovery, because magnesium is found all over the world in different minerals and salt waters. For instance, the processes for metallic magnesium range from extraction of magnesium from sea water to different electrochemical and thermal processes typically using dolomite and magnesite ores as the source of magnesium. (Neelameggham and Brown 2013)

One source that has not been utilized too well are the multimetal leaching liquors gathered from nickel sulfite ore processing. Typically, magnesium stays in the solution through metals recovery plant and is dumped into the gypsum pond together with manganese, calcium and other metals still present after the valuable metals have been recovered. However, extracting magnesium from the liquors of a 50 000 t/a nickel high pressure leaching plant (HPAL) as magnesium oxide would be enough to satisfy several percent of its world demand (Kyle 2010). Magnesium oxide could also be further processed into magnesium chloride, which then could be used in electrolytic reduction to form pure magnesium metal. Magnesium production of that size would mean a 4-6 % share of the world's magnesium production. With current market price of around 1.91 €/kg (InfoMine 2017) a magnesium production of 50 000 t/a would mean almost 100 M€ revenue per year. Hence the potential and possibilities of magnesium in multimetal leaching liquors are impressive. For example, a magnesium metal production of that size that would benefit the magnesium self-sufficiency of the EU, which currently produces under 1 % of the world's magnesium. Due to small magnesium production, EU classifies magnesium as one of the twenty-one critical materials that have a high economic importance to the union combined with a high risk associated with their supply. (Chapman et al. 2013)

In Sotkamo, Finland, magnesium appears in the black schist ore that contains, but is not limited to, the following minerals: pyrrhotite, pyrite, sphalerite, pentlandite, violarite, chalcopyrite and graphite (Riekkola-Vanhanen 2010) from which a mining company Terrafame currently produces zinc, copper and mixed nickel-cobalt sulfides. A significant amount of magnesium stays in the PLS (pregnant leaching solution) recovered from the heap bioleaching together with manganese, calcium, iron and small quantities of zinc, copper, nickel and cobalt. The amount of magnesium is similar to zinc's, which currently has a production rate of 66 000 – 80 000 t/a (Pöyry Finland Oy 2017)

1.2 Objective, scope and aims of the study

In this master's thesis, a method to extract magnesium from nickel sulfide ore bioheapleaching process waters will be designed. Due to the importance of magnesium metal and its production to the EU, it is chosen as the most important product and is given more weight in the literature study. However, methods to other products are also examined to find the most suitable way to utilize the multimetal process waters. The thesis is divided into two parts: literature study and applied part.

The objective in the literature study is to comprehensively gather information so that the different process alternatives examined can be efficiently compared in the applied part. This is done by introducing the global situation of magnesium production, examining different methods for magnesium recovery and going through market data.

In the beginning of the applied part the case process is presented and a techno-economic analysis is made for the processes studied in the literature part. The result gives the best fit for the case study. Further in the applied part, a method for extracting magnesium from the multimetal process stream of Terrafame mine is developed and tested in the laboratory. Based on the results a process is designed and the costs are calculated.

Research questions for the study are as follows:

1. Is there a feasible way to recover magnesium from multimetal process streams in laboratory conditions?
2. Can the method be feasibly scaled up into industrial operation?

1.3 Structure of the study

The first five chapters form the literature study starting with a brief introduction to the trends in global magnesium production from the last century in chapter 2. Chapter 3 summarizes the nickel production processes of today and how different metals are typically being handled during the process. Chapter 4 takes a broader look into different methods that could be utilized to recover magnesium from the multimetal process waters. In chapter 5, global markets for magnesium and the selected compounds which can be extracted according to the processes in chapter 4 are examined to form an overall picture of current and future uses, prices, top importers and exporters and biggest competitors in the market.

In the applied part, a process to recover magnesium from bioheapleaching multimetal process waters is designed. The design relies on the studies presented in the literature part. The applied part comprises of chapters 6, 7, 8, 9 and 10, which include presentation of the case process, analysis of the literature part, techno-economic evaluation of the alternative methods studied, methodology, laboratory work and its results. General process design is carried out in chapter 11 and the economic aspects are discussed in chapter 12. Finally, in chapter 13 the conclusions are drawn and recommendations are given.

LITERATURE STUDY

2 Magnesium production

The commercial production of magnesium started in the 20th century and increased to about 400,000 t/a in the first one-hundred years. The two main methods for producing magnesium metal are the electrolytic method and the metallothermic reduction method. The feed material for the electrolytic method is magnesium chloride, $MgCl_2$, which can be recovered from brines by dehydration or chlorinating magnesium oxide, MgO. Magnesium chloride is then electrolyzed to produce pure magnesium. For metallothermic reduction, an ore containing magnesium, typically dolomite, is calcined and then reduced. (Neelameggham and Brown 2013)

The electrolytic method was widely used in the western countries and was the dominant method to produce magnesium for most of the 20th century but was superseded during 1990s by the metallothermic reduction, more precisely by the Pidgeon process, that the Chinese adopted and now use to produce over 80 % of the world's magnesium. China's cheap labor and electricity together with low capital costs of the silico-thermic Pidgeon process have made it possible to use the Pidgeon process even for the smallest deposits in China resulting in low magnesium prices. (Neelameggham and Brown 2013) The change in the global magnesium production is illustrated in Figure 1.

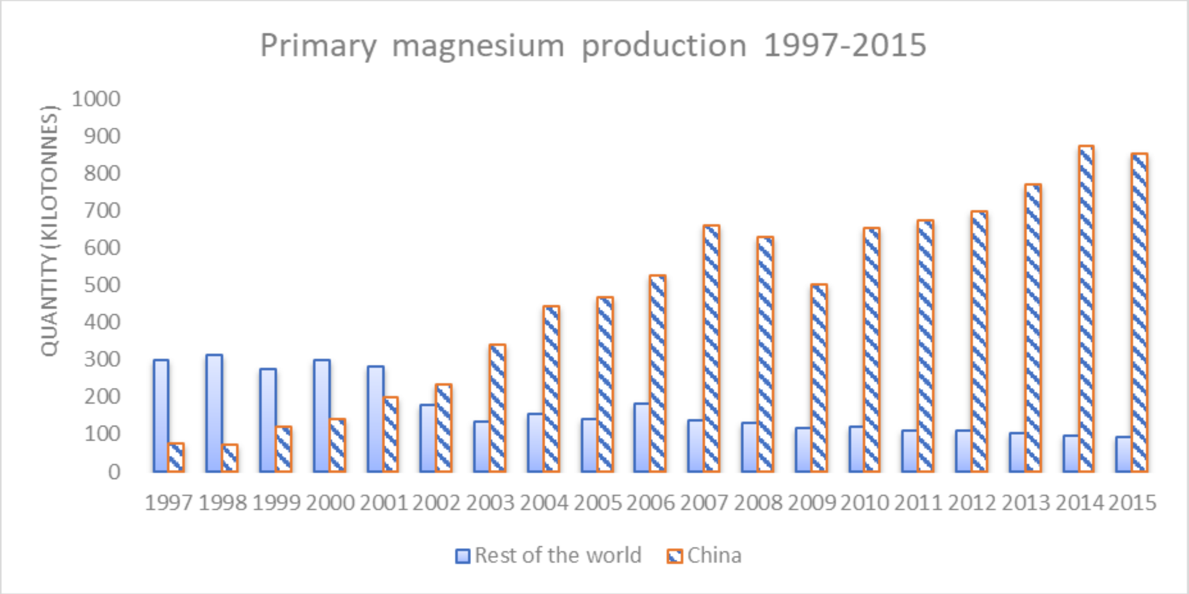

Figure 1. Primary magnesium production 1997 – 2015 (British Geological Survey 2003, British Geological Survey 2008, British Geological Survey 2013, British Geological Survey 2017)

Even though China has been dominating the markets for a while now, the production costs are forecasted to grow due to increases in the prices of both electricity and labor and even stricter environmental regulations, that will be seen in China in the very near future. (Neelameggham and Brown 2013) This might open possibilities for new players in magnesium markets. At the moment, there is magnesium production only in seven countries and just four new possible companies entering the market before 2020 according to Roskill (2016). The main primary magnesium producers in the west according to Neelameggham and Brown (2014) and the statistics from the British Geological Survey (2017) are US Magnesium in the United States, Rima Metallurgical in Brazil, Dead Sea Magnesium in Israel and Solikamsk in Russia – each having a production of under 50 000 t/a. The four new projects are situated in China, Canada, Australia and Norway with similar quantities.

However, there is no significant magnesium production currently in the EU nor are there any plans for it in the coming years. This has been noted lately in the study by Chapman et al. (2013), which states that the magnesium production in the EU is under 1 % of the global production. The negligible production has got the EU to classify magnesium as one of the twenty-one critical materials that have a high economic importance to the union combined with a high risk associated with their supply. (Chapman et al. 2013)

In the current situation, it seems that there is a need for magnesium production in the EU but the regular routes to produce magnesium are not considered feasible compared to the Chinese production. Therefore, alternative ways to produce magnesium should be considered.

3 Magnesium in nickel production

One possible source for magnesium are the leaching solutions gathered from multimetal ore leaching. Such ores are for example sulfide and laterite ores those are used in nickel production. (Mudd 2009, Eghtesad 2016). McDonald and Whittington (2008) have a table in their study that summarizes important minerals relating to nickel laterite ore processing. Serpentine mineral group defined by Faust and Fahey (1962) as $X_6Y_4O_{10}(OH)_8$, where X = mainly Mg but also Ni, Co, Mn, Fe, Zn and Y = mainly Si , can be found amongst them. Also talc, magnesite and saponite are minerals those include magnesium and are present in the table by McDonald and Whittington (2008). Magnesium is present in the minerals since it has an ionic radius similar to nickel (Monhemius 1987).

Although 60 - 75 % of the world's nickel resources are estimated to be laterite ores about half of the nickel is still produced from sulfide ores. (Sudol 2005, U.S. Geological Survey 2017) This is because the sulfide ores require less energy and chemicals and are easier to process. (Mudd 2009) Currently, the main emphasis in the research and development in nickel production seems to be in laterite processing. The leaching liquors gathered from multimetal ore heap leaching (whether laterite or sulfide source) are processed quite similarly to extract the products.

Process routes to nickel/cobalt recovery

Willis (2007) presents flowsheets for processes that have been applied to recover nickel from heap leaching leach liquors to produce intermediate products and some conceptual hybrid flowsheets. The two routes that fit into the first category of flowsheets are mixed hydroxide precipitation (MHP) and mixed sulfide precipitation (MSP). These are also the two downstream product recovery methods mentioned in a more recent study by Kyle (2010). From the two routes, HSP is more widely used according to Lewis (2010). The main difference between MHP and MSP is that MSP is selective for nickel and cobalt over magnesium, manganese, iron and chromium when MHP is selective over magnesium only (Willis 2007, Kyle 2010). Both routes are presented in brief in the following chapters.

Mixed hydroxide precipitation route

In a typical MHP process iron removal consisting of one or two stages is used after leaching to remove iron as iron(III), chromium and aluminum. Gypsum also precipitates due to acid neutralization reaction. The removal in the first stage is done in pH 2.5-3.5 and 4.4-5.0 in the second stage. (Willis 2007, Kyle 2010) In both stages 3-4 reactors in series are used. Air is injected to the first stage reactors to get rid of the carbon dioxide produced from the reactions and to oxidize Fe(II) to Fe(III). Residence times in iron removal stages are from one to three hours per stage and temperatures are around 70-90°C. (Willis 2007)

The iron removal stages are followed by two Ni/Co precipitation stages those normally have 2-4 reactors operating at 60-80°C and in pH 7.2-7.5 at first stage and 7.5-8.0 at second stage. (Willis 2007) The residence times are one to three hours per stage and magnesium oxide is most commonly used for pH control. Ni/Co product usually has impurities like aluminum, iron, chromium, copper, zinc and some manganese if they are not efficiently removed prior to precipitation. (Willis 2007, Kyle 2010)

An underflow of size 100 - 300 % of fresh precipitates from the second stages of both the iron removal and the Ni/Co precipitation are recycled back to the beginning of the process to recover the co-precipitated nickel and cobalt. Because significant loads are recycled and more than half of the manganese stays in that solution, the process can also have a manganese removal stage to prevent manganese from accumulating in the process. (Willis 2007, Kyle 2010) A typical MHP process flowsheet is presented in Figure 2.

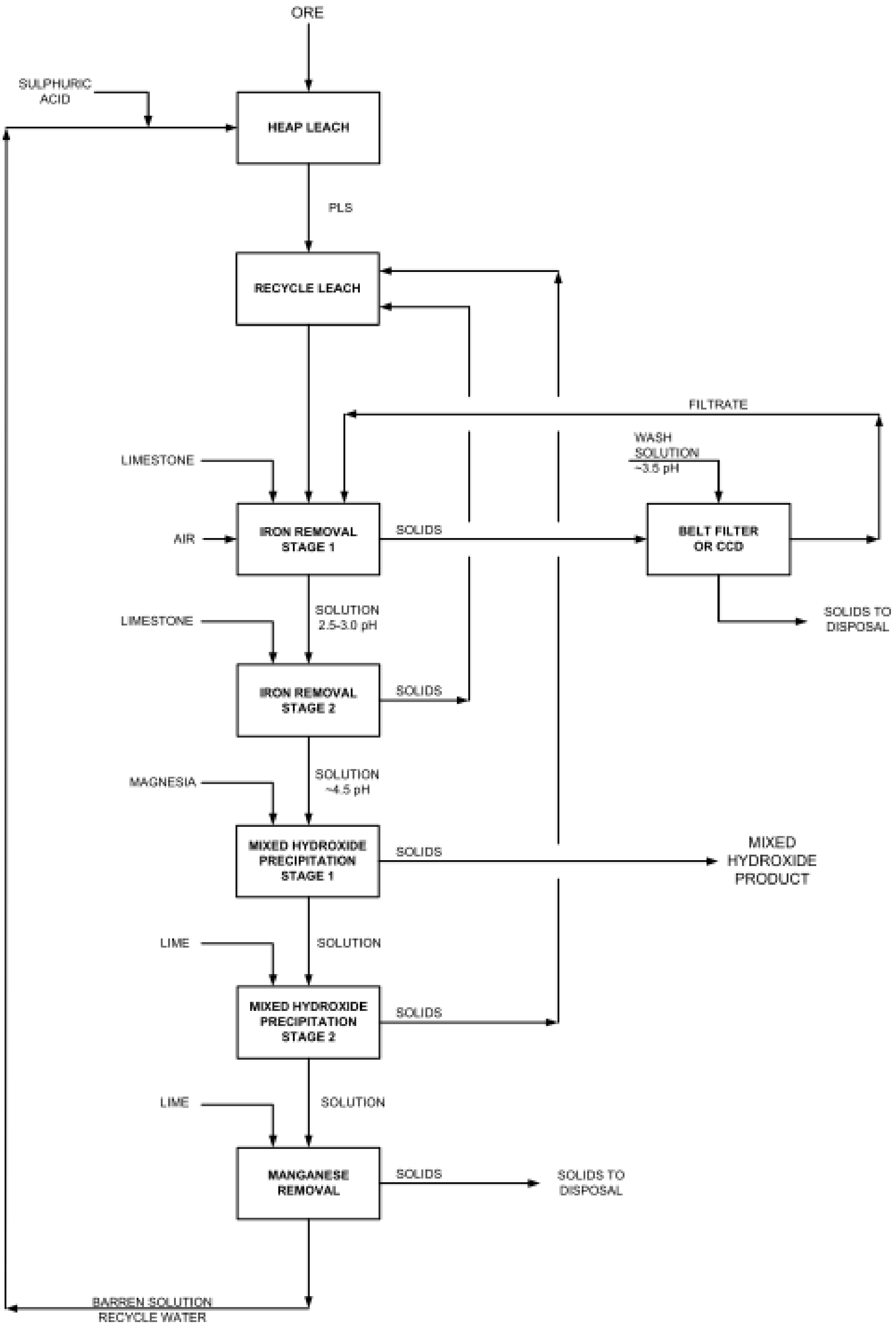

Figure 2. Typical flowsheet for MHP process (Willis 2007)

Mixed sulfide precipitation route

The MSP route has many similarities with the MHP route. They both have large recycle flows, include an iron removal stage and the precipitation of metals is very pH dependent. The main difference comes from the fact that the MSP is selective for nickel and cobalt over iron, aluminum, chromium and manganese and MHP is not. Therefore, MHP is usually selected for ores with high nickel and low iron content and the MSP route is typically chosen for ores, which are low in nickel and high in iron. (Willis 2007) This results in a different order of stages between MHP and MSP flowsheets. A typical flowsheet for MSP is shown in Figure 3.

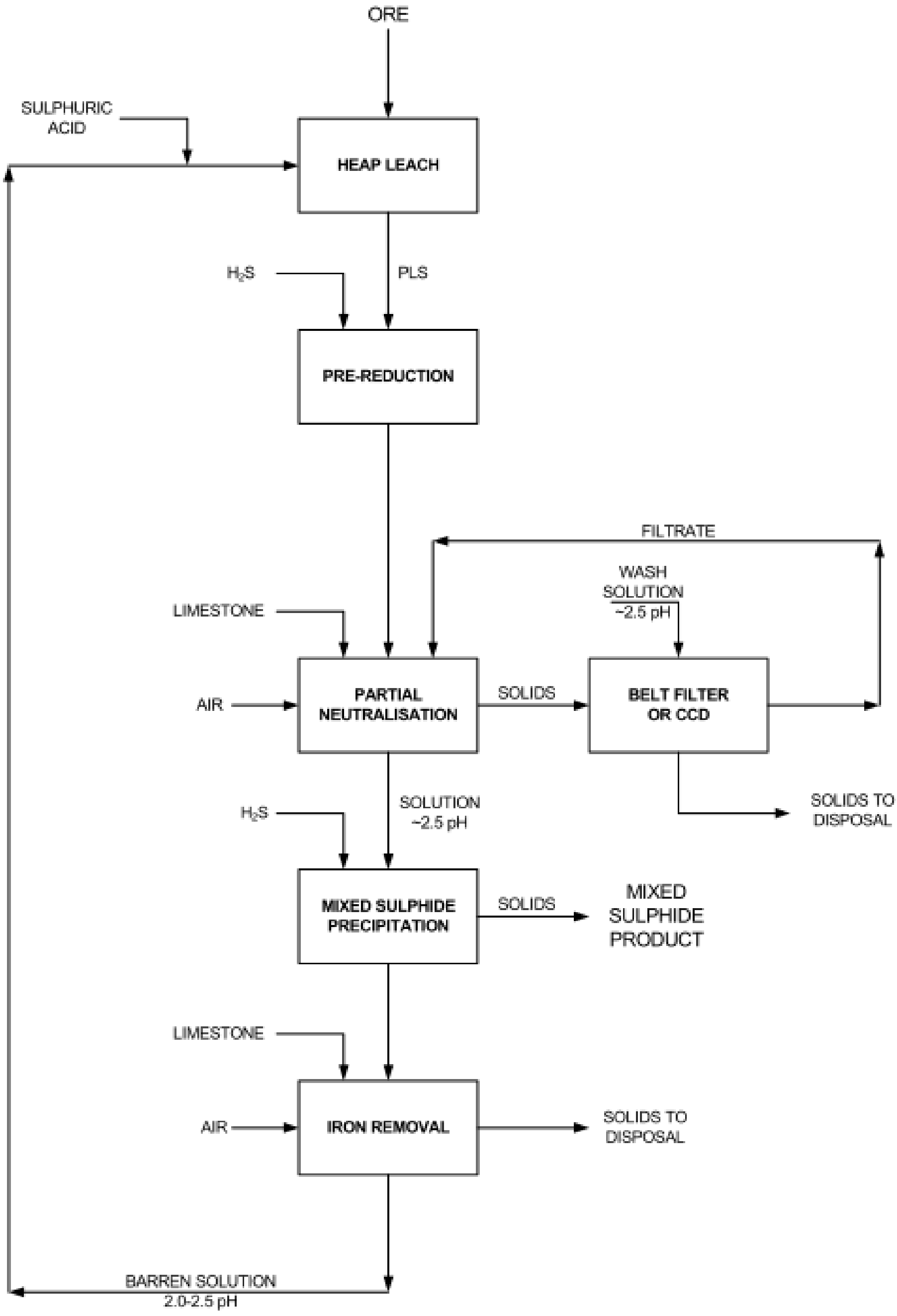

Figure 3. Mixed sulfide precipitation with pre-reduction and iron removal stages (Willis 2007)

In the pre-reduction step of MSP, Cr(VI), Mn(IV) and Fe(III) are reduced to Cr(III), Mn(II) and Fe(II). (Willis 2007, Kyle 2010) A precipitation step usually includes an autoclave or reactor vessels, a thickener and a filter. Autoclaves are faster but require higher pressure and temperature. Hydrogen sulfide gas excess in the reactors is used together with pH control to maintain conditions that are required for metal sulfides precipitation. (Willis 2007) Instead of H_2S gas, solid FeS or CaS or aqueous Na_2S, NaHS or NH_4S can be used as sulfide source (Lewis 2010). If there is a will to extract more products than one, several precipitation steps can be used in series using reactors in different pH and redox areas. The pH dependence of metal sulfide solubilities is presented in Figure 4.

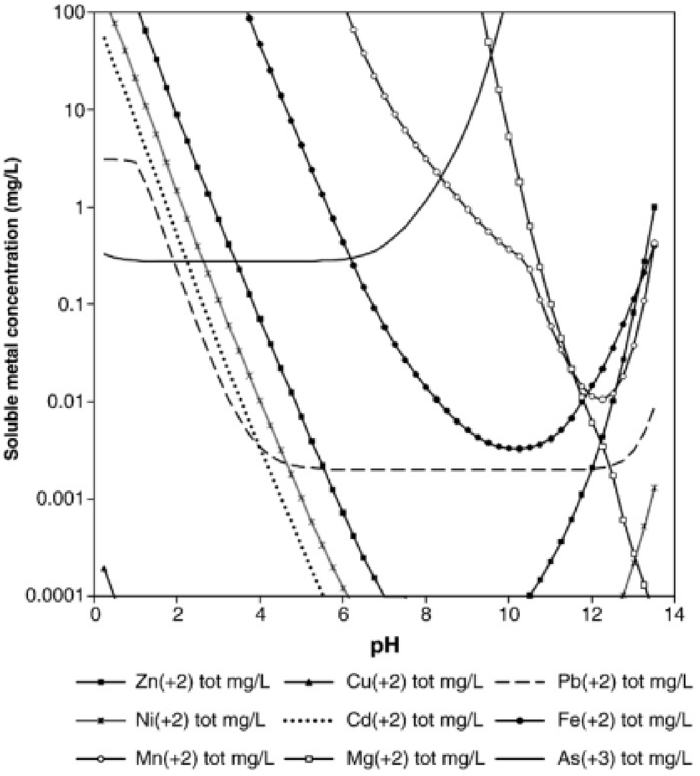

Figure 4. pH dependence of metal sulfide solubilities (Lewis 2010)

The products are usually taken away in pH < 5. Metals that remain in the solution with high concentrations are iron(II), calcium, manganese and magnesium. The solution is usually recycled back to the leaching process. According to Willis (2007), the aqueous iron can generate viscosity issues if recycled back repeatedly, which is why at least iron removal is to be considered. Willis (2007) also mentions that accumulation of magnesium and manganese will happen without removal and that lime (CaO) or calcium hydroxide ($Ca(OH)_2$) is normally used to precipitate those as hydroxides.

4 Magnesium recovery from multimetal process streams

Utilizing magnesium and manganese from the nickel plant waste streams to products like magnesium oxide (magnesia) is not very common even though their concentrations in the feed solutions can be higher than some of the products'. As Kyle (2010) notes in his study "The amount of magnesia produced from a normal 50,000 t/a nickel HPAL [high pressure acid leaching] plant would be sufficient to satisfy a large percentage of the current world demand for these magnesia products". The ways to produce magnesia and other magnesium compounds are of interest of this study, because, by utilizing the feed ore more efficiently the product portfolio can be widened, which improves the economic balance of the plant, and the effects to environment could be enhanced.

However, Kyle (2010) states two problems why that is not the current situation. The first reason is that magnesium and manganese tend to co-precipitate when using calcium oxide. The other is that the amount of magnesia produced would be so high that it might be difficult to find buyers. Also, the reagent need would be huge and bigger waste streams (gypsum slurry if using calcium oxide) would still need to be treated. Therefore, an evaluation of other methods to separate the remaining metals to produce different magnesium containing products besides magnesia is made.

The following methods are examined in this chapter: magnesium sulfate crystallization and thermal decomposition to magnesium oxide, magnesium metal production through electrolysis, magnesium carbonate precipitation, solvent extraction, oxidative precipitation and precipitation as struvite.

4.1 Magnesium sulfate crystallization and thermal decomposition to magnesium oxide

The route to produce magnesium oxide from magnesium sulfate has been known for several decades. Many inventions have been patented after the 1950s (Bailey 1959, Herbert 1969, Cross et al. 1978), which present the idea of crystallizing magnesium sulfate and then thermally decomposing the crystals to magnesium oxide, MgO, and sulfur dioxide, SO_2, those can either be recycled back to the process or taken out as products. A general flowsheet for this kind of a process (Scheidema 2015) is presented in Figure 5.

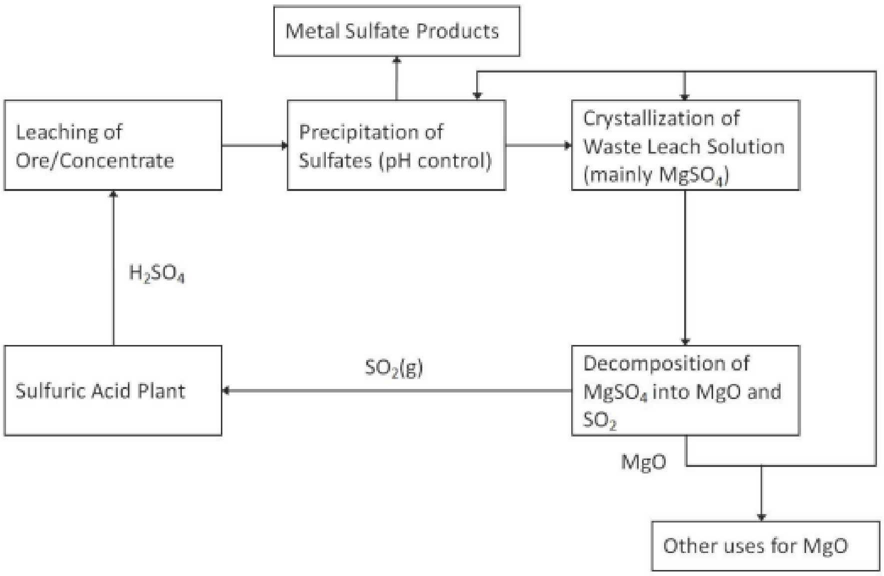

Figure 5. General flowsheet for hydrometallurgical treatment process and the recycling of magnesium oxide and sulfur to the process (Scheidema 2015)

The recirculation route is mentioned in all the patents and in the doctoral dissertation by Scheidema (2015). They all support the use of magnesium oxide as a neutralizing or precipitating agent in the process and converting the sulfur dioxide into sulfuric acid, which can be then used in the leaching step. Herbert (1969) notes that recycling magnesium oxide to the crystallization stage improves the recovery of $MgSO_4$ from the solution, thus the crystallization can be done in the lower end of the temperature range. Typical temperatures for the crystallization of $MgSO_4$ mentioned in the patents ranged from 200°C to 250°C. Herbert (1969) achieved good results when bringing the pH of the solution up to 5.2 with magnesia in 200°C.

The other patents mainly discuss about reducing the temperatures used for thermal reduction by using reducing agents. Bailey (1959) mentions, that without the reducing agent the thermal decomposition needs a temperature of around 1000-1050°C. Scheidema (2015) notes that the exact temperature depends on the atmosphere and in the calculations on the standard enthalpy chosen. The ranges Scheidema calculated for fully decomposition ranged from 993°C to 1081°C depending on the enthalpy.

Lower temperatures can be reached by using reducing agents according to the patent by Kobayashi (1980). He proposes a method to convert $MgSO_4$ to MgO by reductive calcination and claims that it can be done with 98 % conversion in 850°C with the help of boiler soot or lignite coke in nitrogen gas atmosphere. In the patent by Bailey (1959), charcoal was used as a reducing agent to recover 9.7 kilograms of MgO from 29.1 kilograms of anhydrous $MgSO_4$ in 890°C. Solid carbon or an atmosphere containing carbon monoxide gas are the main reducing agents currently used according to Schedeima (2015). Coke, charcoal and carbon monoxide were proposed to be used for the decomposition in the patent by Herbert (1969). The thermal decomposition can then be carried out in temperature range of 750-900°C.

The magnesium oxide formed in temperatures between 800-950°C is called light-burned magnesium oxide that has the highest chemical reactivity of the forms. (Kramer 2004) It has applications especially in environmental sector (Kramer 2004) but the biggest user that also supports the growth of magnesium oxide markets is the iron and steel industry (ReportsnReports 2016, IHS Markit 2017). The form most suitable for the iron and steel industry is the dead burned magnesium oxide that requires additional heating of the light-burned magnesium oxide briquettes at temperatures of about 2100°C (Zambrano 1981).

Herbert's (1969) invention is adapted for laterite ores of limonite type, those may have up to 2% and 8% of manganese and magnesia, respectively. Cross et al. (1978) did the studies with Mg-containing carbonate ore. It should be noted that, though the magnesium content mentioned in the patents by Cross et al. (1978) and Bailey (1959) was much higher than calcium and manganese, there is a need for separation of undissolved impurities before crystallization. Otherwise, the crystallized magnesium sulfate tends to contain calcium sulfate and manganese sulfate as impurities (Scheidema 2015).

An alternative route to magnesium oxide is discussed in chapter 4.3 Precipitation as magnesium carbonate .

4.2 Electrolysis of $MgCl_2$ to magnesium metal

The electrolysis of fused anhydrous magnesium chloride is an art to produce magnesium metal hydrometallurgically, that has been around since the 19th century (Kramer 2010). As it was discussed in chapter 2, this is the other commercial method that has recently been overrun by the metallothermic reduction method. However, for metallothermic reduction the feed material is typically an ore, which is why electrolytic reduction is more suitable to magnesium recovery from leaching liquor streams.

The most mature way is to use magnesium chloride as the magnesium feed to the electrolytic cells. To get large quantities of magnesium chloride Kramer (2004) presents four methods from which the only suitable method is the chlorination of magnesium oxide in the presence of carbon. The magnesium oxide can be derived from nickel sulfate leaching liquors as explained in the previous chapter. Zambrano (1981) presents that as an alternative to taking magnesium oxide out as a product it could be briquetted with carbon (for example coal). Then, the briquettes are heated in a kiln at 850°C with chlorine atmosphere to form molten anhydrous magnesium chloride, which is finally electrolyzed to form magnesium metal and chlorine gas.

Some patents (White and Berube 2000, Picard and Fournier 2014) present the idea of leaching the magnesium-containing material with hydrochloric acid. However, because leaching with hydrochloric acid is considered too distant from the case study the patents are not discussed in more detail.

4.3 Precipitation as magnesium carbonate

One method to recover the magnesium content from serpentine minerals was patented by Pundsack (1967). It proposes a route that uses ammonium bisulfate to decompose serpentine to magnesium sulfate, ammonium sulfate and silica that is recovered at the start. The solution comprising the sulfates is then treated with ammonium hydroxide to precipitate all iron as oxides in pH 8-8.5. After iron is removed from the solution, ammonium hydroxide and carbon dioxide are added to the solution to precipitate magnesium as magnesium carbonate simultaneously converting the ammonium hydroxide to ammonium sulfate. The solid magnesium carbonate separated from solution by filtration can be ignited to produce magnesium oxide with carbon dioxide and water as other reaction products

However, as discussed earlier in chapter 3, the metal in the serpentine mineral can also be manganese instead of magnesium. Therefore, and due to other minerals in nickel production, a remarkable amount of manganese is usually present in the process liquors as Willis (2007) and Kyle (2010) point out in their studies. This poses a problem, since manganese tends to co-precipitate with magnesium when calcium oxide or calcium hydroxide is used in the neutralizing step (Willis 2007).

In a study by Lin et al. (2016), a carbonate precipitation method is proposed to separate manganese from a sulfate solution including magnesium and calcium that also has similar chemical properties to Mg^{2+} and Mn^{2+} -ions. For precipitation, they used a low-cost ammonium hydrogen carbonate (NH_4HCO_3) that precipitates Mn^{2+} ions as manganese carbonate product leaving Mg^{2+} and Ca^{2+} -ions in the solution, which subsequently are used to produce an ammonium sulfate product with traces of calcium and magnesium. The manganese carbonate can be used in production of paints and fertilizers when the ammonium sulfate including calcium and magnesium can be used as fertilizer. The results from the study show that carbonate precipitation had better selectivity for manganese over magnesium and can be done in mild conditions (pH from 7 – 7,5 and temperature 40°C). In the optimal conditions the precipitation rates were 99.75 % for Mn^{2+}, 5.62 % for Ca^{2+}

and 1.43 % for Mg^{2+}. It should also be noted that this method produced only ammonium ions as impurity.

In the study by Zhang et al. (2010), four precipitation tests were carried carbonate precipitation being among them. In the test, they used Na_2CO_3 at 60°C and precipitated over 90 % of manganese together with 43.1 % of gypsum and 13.1 % of magnesium.

According to results from Lin et al. (2016) and Zhang et al. (2010) it seems that carbonate precipitation could be a potential way to purify process solutions from manganese.

4.4 Oxidative precipitation

In addition to previously mentioned carbonate precipitation study, Zhang et al. (2010) carried out two oxidative precipitations for solutions including Mn, Mg and Ca. Even though, their study focuses on manganese recovery, it is presented here since it showed some great results for purifying the solution from manganese, which could provide a solution for easier magnesium recovery. The most remarkable result from the oxidative precipitation test was collected when a system of 1.9% of SO_2 in air was used in 60°C. In one hour, they precipitated 99.5 % of Mn from the solution in the pH range of 6-7 with under 5 % of co-precipitants.

4.5 Solvent extraction

Cheng (2000) studied the use of di-2-ethylhexyl phosphoric acid (D2EHPA) in solvent extraction for synthetic laterite leach solutions. For organic phase, 10 % of D2EHPA, 5 % of tri-butyl phosphate (TBP) as modifier and 85 % short cut kerosene as diluent were used. The results showed that the cheap and stable extractant can be used to extract zinc and calcium (in pH 2-2.5) manganese and copper (in pH range 3-3.5) before mixed Ni/Co separation. Manganese was best recovered from Ni, Co and Mg at temperature 23°C with pH 3.0 with approximate 15-25 % of Mg co-precipitating. Though, the study showed that when using multiple stage extraction with 1:1 aqueous/organic ratio, Mg will stay mostly in the aqueous phase with Ni and Co in pH 3.5 with Mn and Zn crowding the organic phase. The pH-extraction isotherms of the system are presented in Figure 6.

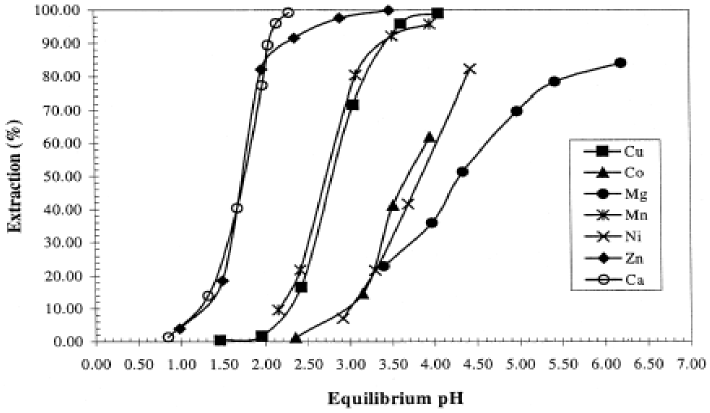

Figure 6. D2EHPA pH-extraction isotherms for selected elements at room temperature (23°C) (Cheng 2000)

In the study by Zhang et al. (2010) it is mentioned that D2EHPA could not separate manganese from calcium. Another study by Cheng et al. (2010) used Versatic 10 with LIX63 and TBP in Shellsol D70 as the organic solution. The pH isotherms for metal extraction in this system is shown in Figure 7.

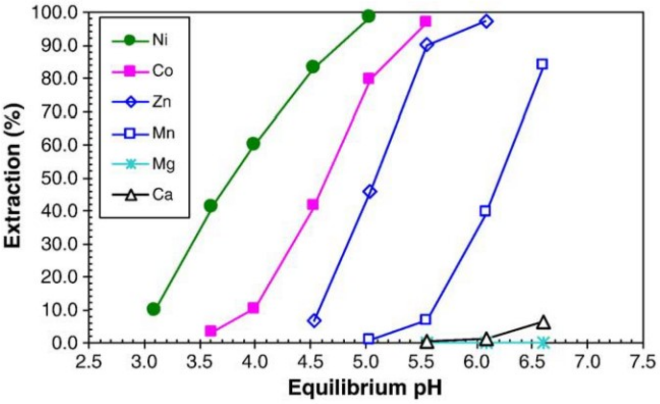

Figure 7. Metal extraction pH isotherms (0.5 M Versatic 10, 0.45 M LIX63 and 1.0 M TBP in Shellsol D70, O/A ratio 2, T=40°C (Cheng et al. 2010)

The use of D2EHPA would mean that manganese extraction should be done before the Ni/Co-extraction, which makes the use of Versatic 10 more favorable since that could be implemented after the mixed Ni/Co -sulfide precipitation in the case metal recovery plant.

4.6 Magnesium precipitation as struvite

Eghtesad (2016) proposed an interesting route to remove magnesium from nickel plant wastewater streams as struvite ($NH_4MgPO_4 \cdot 6\,H_2O$). Struvite production is also mentioned as an option in the study by Qin et al. (2009). A simplified struvite formation presented at least by Bouropoulos and Koutsoukos (2000) and Rahaman et al. (2008) is presented in equation (1). Eghtesad (2016) studied how different factors affected the precipitation using synthesized, nickel laterite plant and replicated laterite plant solutions. In the study, Eghtesad (2016) also presented a reaction mechanism for struvite formation in nickel laterite plant waste streams. It is shown in equation (2).

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O \tag{1}$$

$$MgSO_4 + 3NH_3 + H_3PO_4 + 6H_2O \rightarrow NH_4MgPO_4 \cdot 6H_2O + (NH_4)_2SO_4 \tag{2}$$

The ammonia and phosphate used in equation (2), were mixed beforehand and then added to the sulfate solution to produce struvite and ammonium sulfate, which was further treated with lime to produce gypsum and ammonia (NH_3), which was recycled to the ammonia/phosphate mixing tank.

The study presents some overwhelming results – 96.3 % of the magnesium was removed from the replicated laterite plant solution with the purity of the product 99.8 % keeping pH at 6.71 and temperature at 20 °C with residence time of just 10 minutes. Some co-precipitation of another fertilizer, Newberyite ($Mg(PO_3OH) \cdot 3H_2O$) was experienced. The effect of the most important impurities, Mn and Ca, were tested by adding them separately to the replicated solution. Addition of manganese sulfate to the solution decreased the recovery and purity. Calcium sulfate had the same effect if added in high concentration (137 mg/l) but with lower concentration (33 mg/l) it increased both the recovery and purity of the precipitate.

Struvite becomes thermally unstable at around 50 °C and starts to lose its ammonia and water molecules. However, if struvite is heated to that temperature in water, it only seems to lose its water of crystallization and forms a more stable magnesium ammonium phosphate, dittmarite ($NH_4MgPO_4 \cdot H_2O$). This on the other hand can be transformed back to struvite in excess water in room temperature. If the decomposition of struvite is carried out without excess water, it decomposes into $MgHPO_4$ in temperature of around 106 °C. $MgHPO_4$ can be further hydrated to form Newberyite in room temperature. (Sarkar 1991)

The above-mentioned decomposition/reformation cycle could be of interest if the product is to be transported. On the other hand, care with heating the product should be taken so that the ammonia is not lost from the product.

5 Magnesium and magnesium compounds

This chapter focuses on the market situation of magnesium and the possible magnesium compounds that most probably could be extracted from the case plant's PLS-stream by methods described in chapter 4. The compounds selected for the market study with magnesium metal are magnesium carbonate ($MgCO_3$), magnesium hydroxide ($MgOH$), magnesium sulfate ($MgSO_4$), magnesium oxide (MgO) and struvite ($NH_4MgPO_4{\cdot}6H_2O$). Information such as price, top exporters and importers, production quantities and main applications have been gathered if available for each compound together with the main chemical and physical properties. Each compound is examined separately.

5.1 Magnesium

Magnesium is one of the most abundant elements on the earth. It is also a very electronegative element with a standard potential of -2.4 V, which makes it a good reducing agent. Thus, it is not found as a pure metal in nature like gold and silver for instance but in over 60 minerals and dissolved in salt waters. Commercially, the most widely used magnesium sources are the minerals magnesite ($MgCO_3$), dolomite ($MgCO_3{\cdot}CaCO_3$) and carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) together with sea water. Thus, the resources for magnesium are worldwide. (Kramer 2010, King 2007, Neelameggham and Brown 2013, Avedesian and Baker 1999)

Table 1. Properties of magnesium (Dean and Lange. 1985, Kramer 2010, Gupta and Nai 2011, Neelameggham and Brown 2013, Haynes et al. 2017)

Property	**Value**	**Units**
Atomic weight	24.31	g/mol
Most common valence	2+	
Melting point	650	°C
Boiling point	1090 - 1105	°C
Hardness (Mohs scale)	2.5	
Density as solid at 25°C	1.738	g/cm3
Density as liquid at 700°C	1.584	g/cm3
Specific heat capacity at 20°C	1.025	kJ/(kg C)
Latent heat of fusion	360 – 386	kJ/kg
Latent heat of vaporization	5150 - 5502	kJ/kg
Latent heat of sublimation	6109 - 6238	kJ/kg
Viscosity at melting	1.25	cP
Solubility	Soluble in dilute acid	

In addition to its global occurrence, magnesium can also be found in many common products. As can be seen on Table 1, the density of magnesium is only 1.738 g/cm^3, which compared to aluminum and steel (2.71 g/cm^3 and 7.2 g/cm^3, respectively) provides possibilities for even lighter products. In fact, most of the magnesium is used together with aluminum to form alloys that are widely applicable within different industries such as the automotive, aerospace, electronics, food, sports and military sectors. In chemical industry, magnesium metal is used as a reducing agent for example in titanium and zirconium manufacturing. (Gupta and Nai 2011, Neelameggham and Brown 2013, Kramer 2010)

In the future, the automotive and aviation industries are predicted to be the largest ones to increase magnesium usage due to even stricter environmental concerns. (Roskill 2016, Neelameggham and Brown 2013, Gupta and Nai 2011, Cole 2016)

Production, markets, users and suppliers

As shortly discussed in chapter 2, the low-price magnesium from China has led many companies in the West to shut down their businesses. This has changed the global supply chain of magnesium drastically and has also limited the growth of the magnesium market. (Neelameggham and Brown 2013) However, a constant interest towards magnesium in the automotive and transportation sector is keeping the global market growing. Currently the size of the market is around 3183 million USD (Future Market Insights 2016b) with the compound annual growth rates (CAGR) of 3.4 % and 7.1 % given by Roskill (2016) and by Future Market Insights (2016b), respectively. Together with the increases in electricity and labor prices mentioned by Neelameggham and Brown (2014), possibilities for new players in the market might appear. The price of a magnesium ton is around 2000-2500 USD or 1930 € (InfoMine 2017) and is expected to stay in that range (Roskill 2016).

Importers and exporters

Out of the global magnesium production about half is exported. Not surprisingly, the biggest producer is also the biggest exporter of unwrought magnesium. China accounts for over half of the export, followed by the Netherlands, Germany, Israel and the USA. The countries that export over 5000 tons according to International Trade Centre (2017) and their shares of the total magnesium export are shown in Figure 8 for purities < 99.8 % and > 99.8 %.

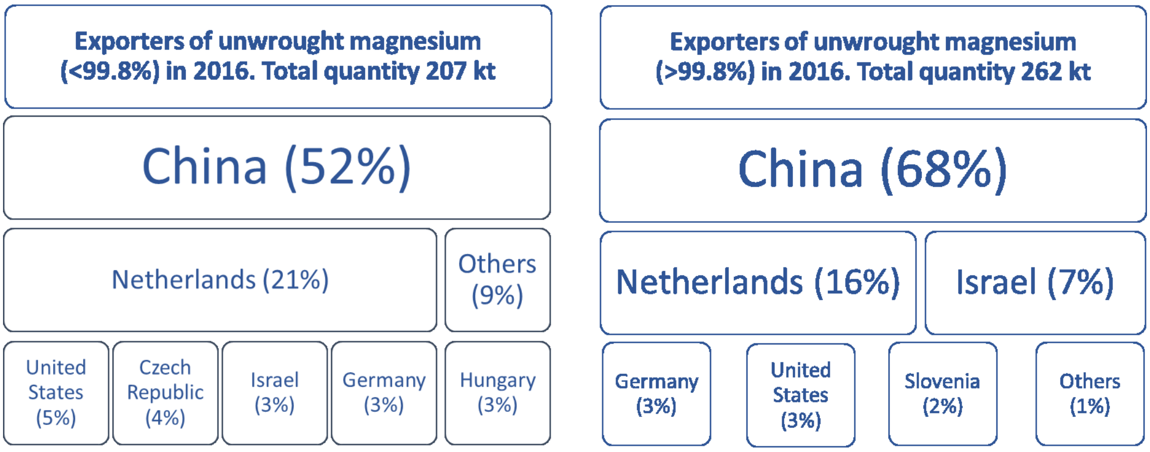

Figure 8. Exporters of unwrought magnesium in 2016.

The biggest importers, who imported over 8 000 tons in 2016 according to International Trade Centre (2017), are presented for purities < 99.8 % and > 99.8 % in Figure 9.

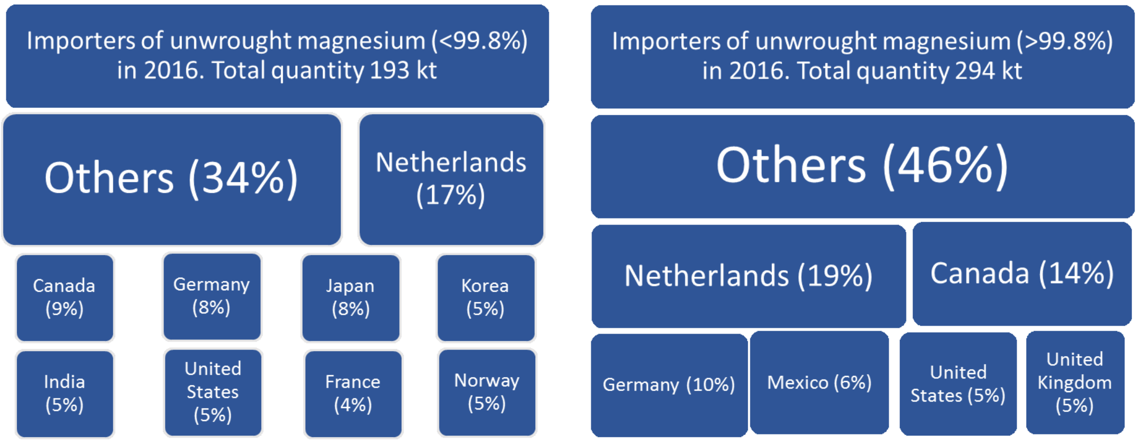

Figure 9. Importers of unwrought magnesium in 2016.

Same countries seem to import the biggest amounts of magnesium in both purities. The Netherlands have big shares both in export and import. One explanation for that could be that lots of the European marine freight is shipped to and from the big ports of the Netherlands.

5.2 Magnesium carbonate

The anhydrous form of magnesium carbonate, $MgCO_3$, also known as magnesite is the most common form of magnesium carbonate in nature. Other minerals including the $MgCO_3$ group are barringtonite ($MgCO_3 \cdot 2H_2O$), nesquehonite ($MgCO_3 \cdot 3H_2O$) and lansfordite ($MgCO_3 \cdot 5H_2O$). Some common properties for these compounds are presented in Table 2.

Table 2. Properties of magnesium carbonates (Dean and Lange 1985, Kramer 2004)

Property	$MgCO_3$	$MgCO_3 \cdot 2H_2O$	$MgCO_3 \cdot 3H_2O$	$MgCO_3 \cdot 5H_2O$	unit
Molecular weight	84.32	120.35	138.27	174.4	g/mol
Melting point	402-480	-	-	-	°C
Density	3.009	2.825	1.837	1.730	g/cm^3
Solubility product, K_{sp}	$1.0*10^{-5}$	$2.3*10^{-5}$	$8.9*10^{-6}$	-	-
Color	White	Colorless	Colorless to white	White	-
Hardness	3.5-5.0		2.5	2.5	Mohs

Magnesium carbonate can be found worldwide in earth's crust and it occurs in different purities. The typical impurity is iron but manganese and calcium can also impact the purity of magnesium carbonate. (Kramer 2004)

Production, markets, users and suppliers

Even though magnesite appears as a ready product in nature, it is also produced via synthetic routes. The natural magnesium carbonate is mostly used for the production of magnesium oxide and other magnesium compounds. Users of the high-quality magnesium carbonate are pharmaceuticals and cosmetics. It can also be found in table salt. Rubber industry uses magnesium carbonate as smoke suppressant. (Kramer 2004)

Future Market Insights (2018) has valued the market at around 230 million USD in 2017 with a CAGR of 4.3 % for the next ten years. The source justifies the growth expectations with increasing use of magnesium carbonate in magnesium oxide production. In addition, the use of magnesium carbonate in personal care and cosmetic products favors the growth.

Some of the largest manufacturers are Hebei Meishen Technology Co., Ltd., Naikai Salt Industries Co. Ltd., Celtic Chemicals Ltd., Konoshima Chemical Co.,Ltd., Lehmann&Voss&Co., Kyowa Chemical Industry Co., Ltd. and Israel Chemicals Ltd. (Future Market Insights, 2018)

Importers and exporters

According to the data from the United Nations Comtrade database (DESA/UNSD 2017), magnesium carbonate export is dominated by Finland, Turkey and South Africa who together exported over half of all the magnesium carbonate in 2016. The same source reveals India and Russia as the two major importers. The share of total quantity for the countries who imported over 7 000 kt and exported over 5 000 kt in 2016 are presented in Figure 10 and Figure 11, respectively.

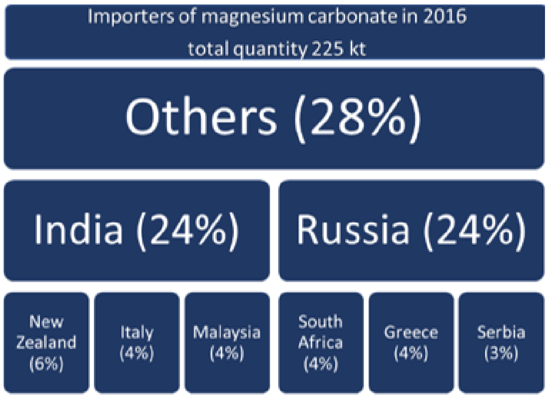

Figure 10. Importers of magnesium carbonate

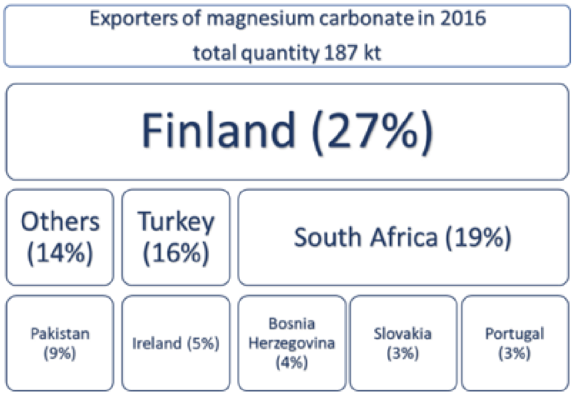

Figure 11. Exporters of magnesium carbonate

5.3 Magnesium hydroxide

Magnesium hydroxide is a white, odorless, inorganic alkaline compound. It has strong neutralizing properties and is used in the industry as a neutralizing agent as well as in pharmaceuticals as milk of magnesia to neutralize upset stomachs. (Future Market Insights 2016a) Magnesium hydroxide, $Mg(OH)_2$, can be found in nature as the mineral brucite, which is either a decomposition product of magnesium silicate or a hydrated form of periclase. (Kramer 2004)

Table 3. Properties of magnesium hydroxide (Kramer 2010, Haynes et al. 2017)

Property	**Value**	**Units**
Atomic weight	58.32	g/mol
Melting point	Begins to lose H_2O at 350	°C
Latent heat of fusion	14	kJ/mol
Hardness (Mohs scale)	2.5	
Density as solid at 25°C	2.365	g/cm^3
Solubility (25°C)	11.7	mg/l
(100°C)	4.08	mg/l
	0.00069	g/100 g
Dilute acid	Soluble	
Solubility constant K_{sp}	$5.61*10^{-12}$	

Production, markets, users and suppliers

The most common use of $Mg(OH)_2$ is in the environmental applications such as industrial water treatment (IWT), heavy-metals removal and flue gas desulfurization. Another common use is in the production of dead-burned magnesia, MgO. It is also used in pharmaceuticals, flame-retardants and as a precursor for other magnesium chemicals. (Kramer 2004)

The market was valued at 551 million USD in 2015. In the following ten years, a compound average growth rate, CAGR, of 4.6 % is expected. The growth is driven by an increasing need for more cost-efficient wastewater treatment in oil, gas and chemical industries, for which magnesium hydroxide offers a good solution and its use as a flame-retardant additive in plastics. (Future Market Insights 2016a) The biggest players in the market are Nedmag Industries Mining and Manufacturing B.V., Nabaltec AG, Huber Engineering Materials, Kyowa Chemical Industry Co. Ltd. and Xinyang Minerals Group. (Future Market Insights 2016a)

Importers and exporters

The trade data for magnesium hydroxide is grouped with magnesium peroxide in the United Nations International Trade Statistics Database which many other market databases, such as International Trade Centre, use as a source. Thus, they are presented together in this chapter as well. Total amount of exported and imported magnesium hydroxide and peroxide was quite small, only around 150 kt. The importers are presented in Figure 12. Exporters, who exported over 10 kt are presented in Figure 13. As can be seen, there are exporters in almost every continent. Data for both graphs has been gathered from (International Trade Centre 2017).

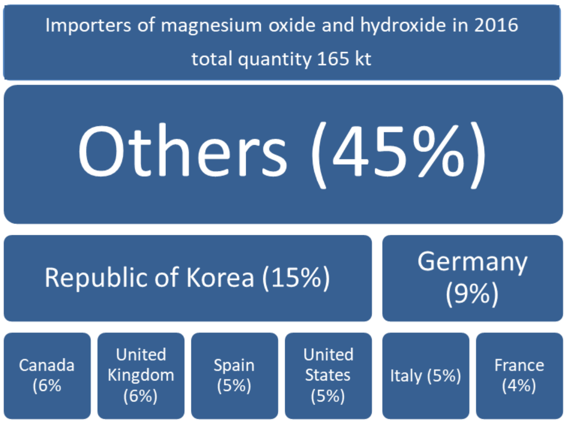

Figure 12. Importers of magnesium oxide and hydroxide

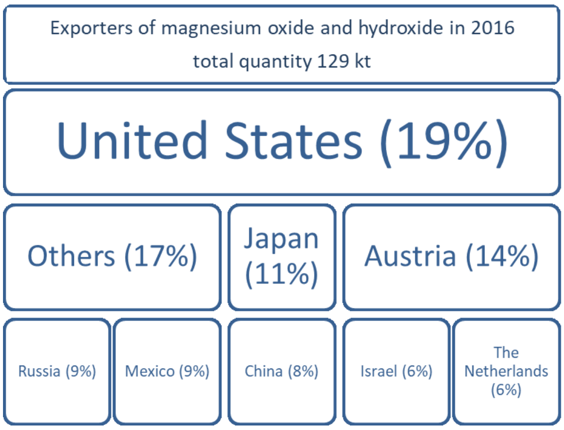

Figure 13. Exporters of magnesium oxide and hydroxide

5.4 Magnesium sulfate

Magnesium makes a strong, ionic compound with many halides and sulfates. (Neelameggham and Brown 2013) For that reason magnesium sulfate is a common compound in many double salts and hydrates. It is very soluble in water as can be seen from Table 4 and in Figure 14.

Table 4. Properties of magnesium sulfates (Kramer 2004, Haynes et al. 2017, Dean and Lange. 1985)

Property	$MgSO_4$	$MgSO_4 \cdot H_2O$	$MgSO_4 \cdot 5H_2O$	$MgSO_4 \cdot 7H_2O$	unit
Molecular weight	120.368	138.383	210.45	246.474	g/mol
Melting point	1137	150 dec		150 dec	°C
Density	2.66	2.445 – 2.57	2.908-2.93	1.67	g/cm^3
Solubility in water	35.7	35.7		35.7 (25/20) (to EtOH slightly)	g/100 g
Latent heat of fusion	14.6				kJ/mol
Electrical conductivity					
Concentration 0.5%	4.1				mS/cm
Concentration 5%	27.4				mS/cm
Concentration 10%	42.7				mS/cm
Concentration 15%	54.2				mS/cm
Concentration 20%	51.1				mS/cm
Concentration 25%	44.1				mS/cm

Magnesium sulfate can be found from the hydrates kieserite ($MgSO_4 \cdot H_2O$), starkeyite ($MgSO_4 \cdot 4H_2O$), pentahydrate ($MgSO_4 \cdot 5H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$) and epsomite ($MgSO_4 \cdot 7H_2O$) also known as Epsom salt. Some double salts containing magnesium sulfate are kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) and langbeinite ($K_2SO_4 \cdot 2MgSO_4$). (Neelameggham and Brown 2014, Kramer 2010)

A magnesium sulfate hydrate system is presented in Figure 14. Only three out of the six hydrates are stable: kieserite, hexahydrite and epsomite. Adding alkali (anything that forms $-OH^-$ ions in water) to a $MgSO_4$ solution precipitates magnesium hydroxide. Adding a soluble carbonate ($-CO_3^{2-}$) precipitates nesquehonite ($MgCO_3 \cdot 3\ H_2O$). (Kramer 2010)

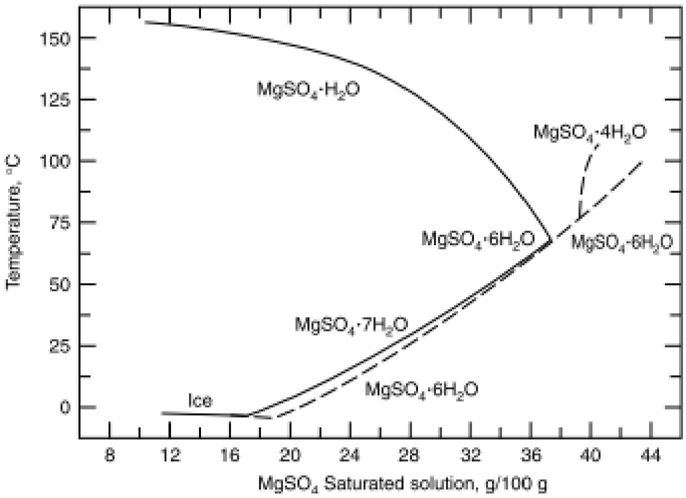

Figure 14. $MgSO_4 \cdot H_2O$ system where the dashed lines represent metastable phases (Kramer 2010)

Like magnesium, magnesium sulfate is also used in many products. The most common uses for magnesium sulfates are in food additives, pharmaceuticals and healthcare (Market Research Future 2017). In the industry, magnesium sulfate is used as a precursor, in catalyst preparation and in kraft pulp mills for oxygen delignification. Fertilizers and animal feed include magnesium sulfate and it is also used in textiles. Epsom salt can be found in mineral baths and in medicine. (Kramer 2010)

Production, markets, users and suppliers

The biggest users of magnesium sulfate are food and pharma followed by industrial and animal feed and fertilizers. Because many of the important uses of magnesium sulfates are associated with people's well-being and the world population is growing, magnesium sulfate market is expected to also grow along with a CAGR of 4.28 % per Market Research Future (2017). According to the same research, major companies in the 10,731 million USD magnesium sulfate business include companies like COMPO GmbH & Co. KG, Baymag, QinqHai Salt Lake Industry, KOLOD and Jinxing chemicals.

Importers and exporters

The biggest magnesium sulfate importers and exporters are shown in Figure 15 and 16, respectively. The data is gathered from International Trade Center (2017). The countries presented in Figure 15 imported more than 40 000 tons in year 2016. The exporting countries all exported over 30 000 tons in year 2016.

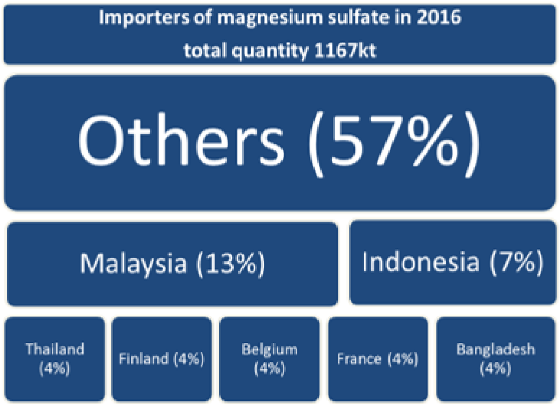

Figure 15. Importers of magnesium sulfate

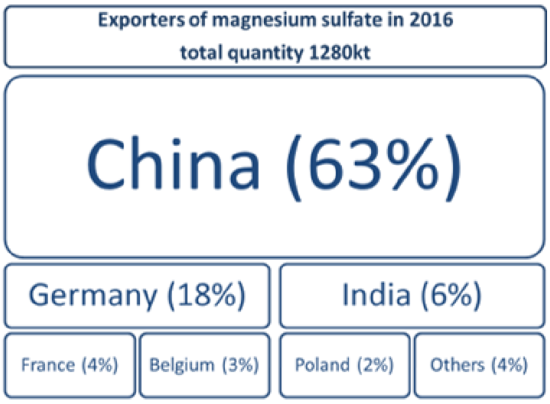

Figure 16. Exporters of magnesium sulfate

The biggest exporter of magnesium sulfate in 2016 was China with a 63 % share of the total exported magnesium sulfate. Germany was the biggest exporter in the EU with 18 % of the total 1280 kt. In addition to Germany and China, only four countries exported more than 30 kt in 2016.

Among the importers, Malaysia and Indonesia were the two biggest individual countries. The third biggest importer in terms of magnesium sulfate quantity was Finland. A quantity of 51 000 tons in 2016 was a 4 % share of world's $MgSO_4$ imports.

5.5 Magnesium oxide

Magnesium oxide or magnesia, MgO, is a weakly ionic, covalent compound. It appears in the nature as the mineral periclase. By using magnesium compounds like magnesite ore, magnesium hydroxide and magnesium chloride one can produce the main commercial forms of magnesia via thermal decomposition or chemical reactions. The commercial forms are dead-burned magnesia (periclase), caustic-calcined (light-burned magnesia), hard-burned magnesia, and calcined dolomite. Different temperatures and calcination times determine the type of magnesia product. For example, light-burned magnesia is calcinated in temperatures under 950°C when dead-burned means temperatures over 1800°C. (Kramer 2004)

Table 5. Properties of magnesium oxide (Haynes et al. 2017, Kramer 2004, Dean and Lange 1985)

Property	**Value**	**Units**
Molecular weight	40.304	g/mol
Melting point	2827 ± 30	°C
Boiling point	3260 - 3600	°C
Hardness (Mohs scale)	5.5 – 6.0	
Density as solid at 25°C	3.581	g/cm3
Specific heat capacity at 27°C	0.92885	kJ/(kg K)
Latent heat of fusion	77	kJ/kg
Aqueous solubility (20°C) **(30°C)** **EtOH**	0.00062 0.0086 insoluble	g/100 ml g/100 ml

Light-burned magnesia has a chemical reactivity from moderate to high. It readily dissolves in dilute acids, and hydrates upon exposure to moisture or water. The most reactive grades combine with moisture and carbon dioxide eventually to form basic magnesium carbonates. Hard-burned magnesia on the other hand has moderately low chemical reactivity and is readily soluble only in concentrated acids. Dead-burned magnesia's chemical reactivity is very low; thus, it reacts very slowly with strong acids. Pure-fused magnesia production is carried out at temperatures over 2750°C using an electric arc furnace. (Kramer 2004)

Production, markets, users and suppliers

Magnesium oxide has been commercially the most used, thus the most important magnesium compound in the 21st century according to Kramer (2004) and IHS Markit (2017). The market in 2015 was close to 4.3 billion euros (ReportsnReports 2016).

Steel and iron industry and cement production using refractory magnesia are the biggest consumers of magnesia. In the coming years, it is expected that the minor growth forecasted for steel production also helps refractory magnesia market to grow 1.5 % every year and the total magnesia market to have a CAGR of 0.97 % from 2017 to 2022. (ReportsnReports 2016, HIS Markit 2017)

Another form of magnesia, caustic-calcined magnesia, is used for intermediate preparation, in water treatment, as a neutralizing agent, for animal feed and in fertilizers. The market for caustic-calcined magnesia is not promising any remarkable growth. Although, as mentioned earlier in the magnesium hydroxide chapter, new water treatment solutions may replace the common lime and caustic soda. Caustic-calcined magnesia is set out to being a promising competitor to both as well as to $Mg(OH)_2$ in that field.(Kramer 2004)

Importers and exporters

Since magnesia can be handled as an ore or as fused, non-natural magnesia, and they both have their own data recorded, only the non-natural magnesia is considered in this market research. It is easily the largest one in this study as the total quantities show in Figure 17 and 18.

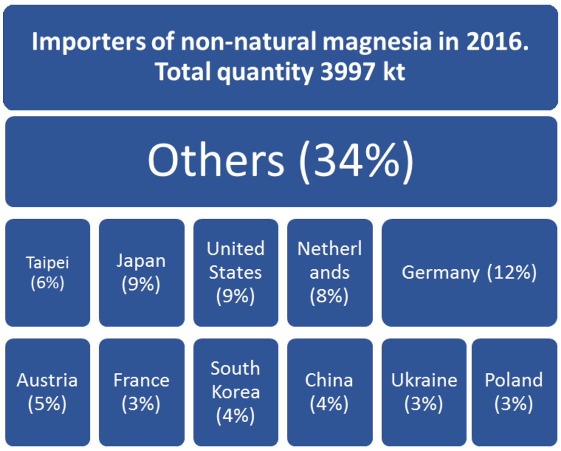

Figure 17. Importers of non-natural magnesia

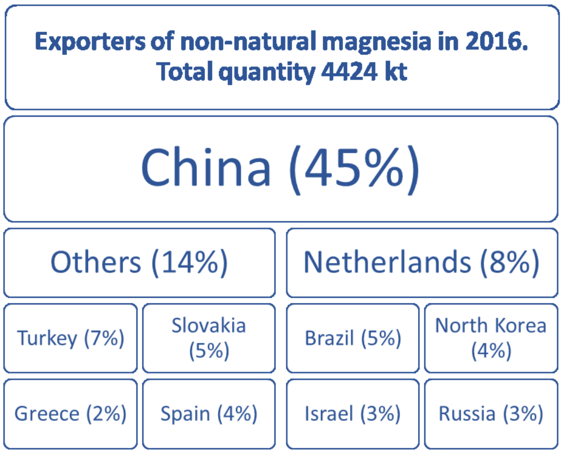

Figure 18. Exporters of non-natural magnesia

Figure 17 presents the importers with over 100 kt imports in 2016. The exports are shown in Figure 18. China is responsible for almost half of the exports with 2000 kt export quantity. The nine next biggest countries have export amounts between 100 kt - 400 kt. The data in both figures is gathered from International Trade Center (2017).

5.6 Struvite

Struvite, also known as magnesium ammonium phosphate (MAP[1]) hexahydrate, is a white crystalline substance that comprises of equal molar amounts of magnesium, ammonium and phosphate. (Rahaman et al. 2008, El Rafie et al. 2013) Many studies (Shu et al. 2006, Bhuiyan et al. 2007, Ali and Schneider 2008, El Rafie et al. 2013, Rahman et al. 2014, Ramlogan and Rouff 2016, Jia et al. 2017) suggest that struvite could be derived from wastewater treatment plant (WWTP) process waters and they seem to be the main source for struvite. Such waters have Mg^{2+}, NH_4^+ and PO_4^{3-} ions already present and at the point, when their concentrations exceed the struvite solubility limit, struvite starts to precipitate (Ohlinger et al. 1998, Bhuiyan et al. 2007). Controlled

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[1] Not to be confused with monoammonium phosphate that is also abbreviated as MAP in some sources like in the FAODATA database by Food and Agriculture Organization of the United Nations (FAO) (2017).

precipitation of struvite is favorable, because it will prevent struvite from crystallizing in the system (Ohlinger et al. 1998) and eutrophication of the receiving waters (Doyle and Parsons 2002). The amount of wastewater needed to produce 1 kg of struvite is around 100 m^3 (Shu et al. 2006). Besides WWTP streams, the potential of human urine (Tilley et al. 2008, Etter et al. 2011), landfill leachates (Prater 2015) and hydrometallurgical leach liquors (Eghtesad 2016) as the sources for struvite production have been studied.

Production, markets, users and suppliers

Struvite is not a main product of any company but a value-adding product for many and it does not have a well-developed market yet. The price for struvite can be derived from the purity of the product and the purpose that it can be used for according to Yetilmezsoy et al. (2017) or on the other hand from the prices of the chemicals that need be added to precipitate struvite according to Seymour (2009). The latter is called the “component cost” -method that can be used to determine the price for struvite through the costs of input elements to form a minimum price for the produced struvite (Seymour 2009). For example, to precipitate struvite from WWTPs an additional magnesium input is usually needed but the struvite from landfill leachate needs a magnesium and a phosphate source (Prater 2015). Thus, the prices can vary quite a lot. The prices for struvite from a website (www.alibaba.com) were about 300-400 €/ton. The sellers were mainly Chinese.

Even though struvite does not have a well-developed market yet, phosphate fertilizers have been around for years. The growth of global consumption, which has recently exceeded 45 million tons of phosphorous as P_2O_5, is illustrated in **Error! Reference source not found.**9.

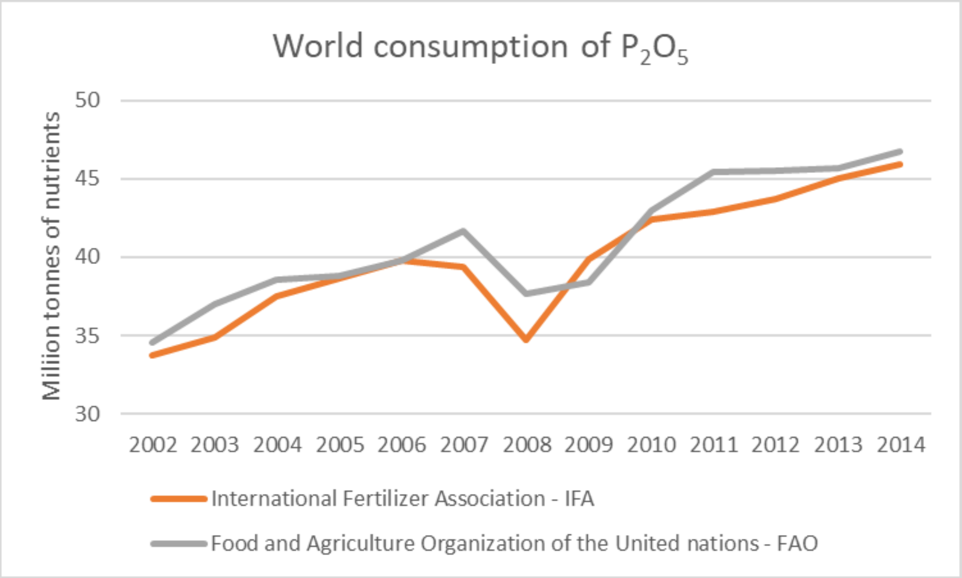


Figure 19. World consumption of phosphate fertilizers (P as P_2O_5)

The biggest players for struvite production might be the WWTPs worldwide, but even if they all started producing struvite it would only mean 0.63 million tons of P as P_2O_5, which is only a 1.5% share of the annual global use according to Shu et al. (2006). Landfill leachates do not seem to be a feasible source for struvite (Prater 2015). Hydrometallurgical leach liquors however seem very promising (Eghtesad 2016).

5.7 Market data conclusion

To make the comparison of the products easier, the main numbers for all the compounds presented have been summarized in Table 6. The chemical prices are also presented in Appendix I.

Table 6. Market data of the magnesium compounds

	Mg metal	**$MgCO_3$**	**$Mg(OH)_2$**	**$MgSO_4$**	**Struvite**	**MgO**
Approximate price	1930 €/ton (for >99.8%)	774 €/ton	887 €/ton	122 €/ton (heptahydrate) 394 €/ton (anhydrous)	386 €/ton	329 €/ton
Market size estimation 2015-2017. (1 USD = 0.9464 EUR)	2970 M€	218 M€	521 M€	10156 M€	-	4670 M€
Future growth	3.4 – 7.1 % CAGR	4.3 % CAGR	4.6 % CAGR	4.28 % CAGR	2.7 % CAGR (between years 2002-2014)(4	1-1.5 % CAGR
Total imports 2016 (biggest importers)	193 kt/294 kt(1 (Netherlands 19 %/17 %)	225 kt (India and Russia both 24%)	170 kt(2 (Korea, Rep. of 15 %)	1167 kt (Malaysia 13 %)(3	-	3997 kt (Germany 12 %)
Total exports 2016 (biggest exporter)	200 kt/270 kt(1 (China 52 %/ China 68 %)	187 kt (Finland 27%)	130 kt(2 (USA 19 %)	1280Kt (China 63 %)	-	4424 kt (China 45 %)

(1 for purities <99.8 % / for purity >99.8 %
(2 including MgO_2 import/export
(3 Finland accounted for 4 % and was the third biggest importer in 2016
(4 Calculated from phosphate fertilizer data

The greatest value per ton is for the pure magnesium metal, while the lowest market price belongs to magnesium sulfate. Struvite does not have a well-developed market yet and does not have any reliable import and export statistics available. Magnesium oxide has the biggest market size and also demand in Europe (Germany imports 12 % of all MgO). Finland is mentioned two times in the table. It is the biggest exporter of magnesium carbonate and also the third biggest importer of magnesium sulfate. All the markets are considered to grow in the coming years.

APPLIED PART

In this master's thesis, a method to extract magnesium from a bioleaching process stream will be designed. The case study in the thesis is the mining process at Terrafame mine located in Sotkamo, Finland. The metals are recovered from the process as sulfides; thus, the process is an example of an MSP process. The most suitable method to recover magnesium from the PLS is chosen from the methods presented in the literature part with a techno-economic analysis. The method chosen for the case study acts as the basis for the applied part.

6 Case process

An overview of the case process starting from open pit mining to metals recovery is presented in Figure 20. (Halinen 2015).

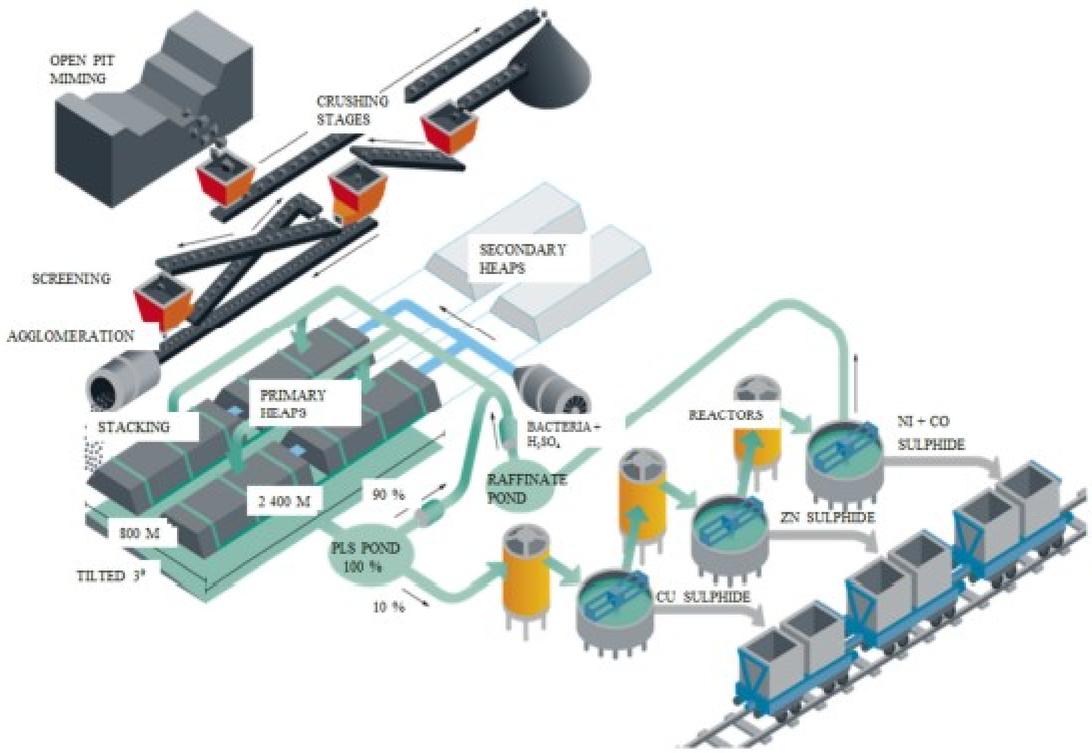


Figure 20. Schematic diagram of the Talvivaara mine (Halinen 2015)

The process starts from open pit mining where it continues to the crushing and screening stages. After the wanted screen size (80 % < 8 mm) is achieved, the ore is agglomerated and stacked on the primary heap pad. The ore is leached in the primary pad for approximately 18 months after which it is restacked onto the secondary heap pad where the leaching continues to reach the parts that have been in poor contact in the primary pad. An acidic leaching solution (sulfuric acid, H_2SO_4) is sprayed on top of the heap to keep the acidity constant and is collected after it has passed through the heap. The majority of the solution is recycled, while the rest is taken for metals recovery. In the metals recovery plant zinc, copper and a nickel/cobalt mix are precipitated as sulfides using gaseous hydrogen sulfide and pH adjustment. The metal sulfides are the products from the mine. (Riekkola-Vanhanen 2010, Riekkola-Vanhanen 2013)

Metals and metals recovery

There are two deposits with the same metal distribution, Kuusilampi and Kolmisoppi, from which the ore is mined. The main rock in Talvivaara deposits is black schist. Most common minerals in the black schist are pentlandite, chalcopyrite, sphalerite and pyrite. Violarite and graphite are also found in the ore. This combination yields a multimetal deposit containing nickel, cobalt, copper and zinc as the metals of main interest. Also, iron, aluminum, manganese, magnesium and some others are present in the minerals. (Riekkola-Vanhanen 2010, Riekkola-Vanhanen 2013)

Loukola-Ruskeeniemi and Heino (1996) have described the geochemistry of the Talvivaara deposit in more detail. The main rock, black schist, is divided into Ni-rich, Mn-rich and low Ni-Mn schists in their study. Within the black schists there are layers of black calc-silicate rocks consisting of sulfides, graphite and tremolite $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$. The magnesium content in the black calc-silicate rocks (6.78 %) is almost four times higher than in the black schists (1.78 %). Out of the black schists, the Mn-rich contains more Mg than the others. In addition to tremolite, the parent minerals for magnesium in black schists can be biotite $(K(Mg,Fe)_3(AlSi_3O_{10})(OH,F)_2$ and phlogopite $KMg_3(Si_3Al)O_{10}(F,OH)_2$, that were present in the sample examined by Bhatti et al. (2012).

Oxygen content, temperature, pH, redox-potential, total iron, ferric iron and other metal concentrations are measured from the PLS taken from the heaps. Approximately 70 % of zinc and nickel are extracted from the ore after both leaching steps have been completed. For copper and cobalt the numbers are 0-50 % and 5-40 %, respectively. The typical composition of the PLS-stream is presented in Table 7. (Pöyry Finland Oy 2017)

Table 7. Composition of the PLS -stream (Pöyry Finland Oy 2017)

Substance	Concentration (g/l)
Nickel	1.0 – 4.0
Zinc	2.0 – 10.0
Copper	~ 0.0 – 0.5
Cobalt	< 0.0 – 0.5
Iron	5.0 – 40
Manganese	3.0 – 40
Magnesium	3.0 – 10
Aluminum	3.0 – 9.0
Calcium	0.5 – 1.0
Sodium	0.1 – 2.0
Uranium	0.01 – 0.07
Arsenic, chromium, cadmium	< 0.1 each

The metals in the process are precipitated in the following order: Cu, Zn and Ni/Co. Each precipitation step includes addition of hydrogen sulfide, H_2S, after which the PLS goes to a thickener. From the thickener, the underflow containing the wanted sulfides is filtered into product. At the current capacity, the rate of production could be 66 000 – 80 000 tons of zinc, 30 000 tons of nickel, 1 500 tons of cobalt and 500 -1 500 tons of copper annually. (Pöyry Finland Oy 2017) The main reaction in precipitation is presented below.

$$MeSO_4 + H_2S \rightarrow H_2SO_4 + MeS \tag{3}$$

, where Me equals metal.

In addition to the metal precipitation steps, pre-neutralization, iron removal and total precipitation steps occur in the process. The order and additives used in each step are presented in Figure 21. Currently, magnesium is taken out from the process in the final precipitation stage together with manganese and remaining iron and gypsum. During the metal recovery, pH varies from the acidic feed conditions (pH = 1.5 – 3.0 (Pöyry Finland Oy 2017)) to the final precipitation's pH 10. (Riekkola-Vanhanen 2010, Riekkola-Vanhanen 2013)

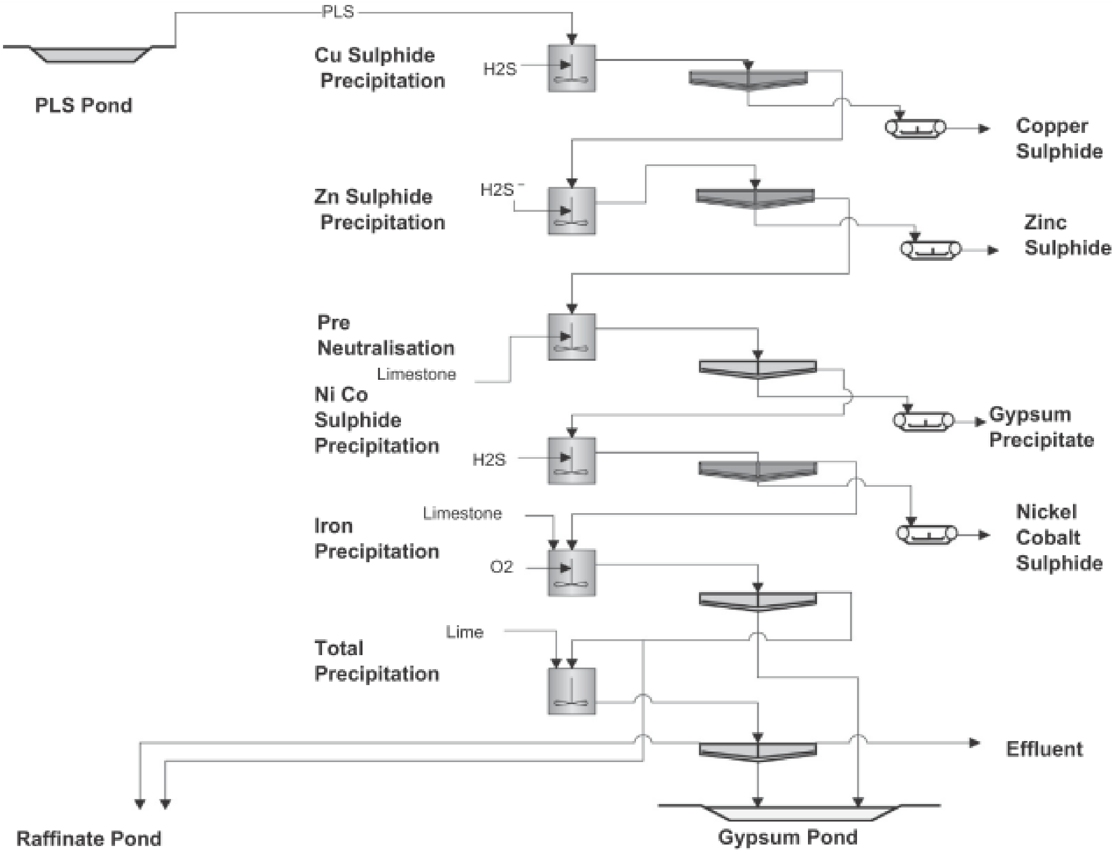


Figure 21. Metal recovery plant flow sheet (Riekkola-Vanhanen 2013)

After the metals recovery plant, part of the raffinate is recycled back to the leaching solution circulation via a raffinate pond, where the pH is first adjusted. The other part is fed into total precipitation step from which the remaining metals precipitate as hydroxides using $Ca(OH)_2$. (Pöyry Finland Oy 2017, Riekkola-Vanhanen 2013)

7 Analysis of the literature part

7.1 Techno-economic comparison of alternatives

The methods to recover magnesium from the process liquors examined in the literature part (chapter 4) were graded against different criteria to find the most promising method for the applied part. The oxidative precipitation and solvent extraction methods were not considered, because they showed potential for magnesium/manganese separation rather than providing a route to extract magnesium as a product and thus being out of the scope of this study. The criteria and weighing used in the grading process are described in Table 8.

Out of the different criteria, sustainability was given the highest weight (4.5), because health, safety and environment (HSE) questions are of great importance in a constantly developing world, where decision-makers and society have increasing interest towards the environmental effects of new industrial activities. Thus, the methods with less emissions, corrosiveness and potential hazards will benefit in the comparison table.

Economic potential was given the second highest weight, because if magnesium is to be extracted from an already well-functioning process, the value it adds to the company should be significant. Economic potential takes into account the price margin between the raw materials needed and products produced. The points given in this criterion depend on the potential of the process to be commercially viable. The weight is affected by uncertainty in product and raw material price estimations. Therefore, it is given a weight of 4.

The ease of implementation is considered under the suitability criterion. It is given a moderate weight 3. How well the graded processes fit into the hydrometallurgical plant is the main issue under this criterion.

CAPEX and OPEX were given weights 2.5 and 4, respectively, since they are not regarded as significant criteria as sustainability and economic potential, but naturally affect every decision a company makes. Operational costs were given higher importance, because they affect the profitability more in the long term.

Maturity of the processes is given a weight of 3.5. When an additional stage is added to an existing operation, it is important that the step acts as it is supposed to. The more references and data available, the more likely the process is to work from the start.

Table 8. Clarification for used criteria

Criteria	What is considered?	Reasons for weight	Weight
Economic potential	Product – raw material price margin including yields	In search of a value-added product, money has an important role. No need to add anything to a process that works well if there is no significant benefit from it.	4
CAPEX	Amount and specialty of equipment. Comparison to the uranium project capital costs	Investment for a long-time period so the costs are probably not that much of an issue if the method shows great economic potential.	2.5
OPEX	Operating conditions, personnel need, reagents etc.	Accounts to the profitability of the process, which is why slightly more important than CAPEX.	4
Maturity	Amount of references found, scale of testing, commercial solutions available	When an additional stage is added to an existing operation, it is important that the step acts as it is supposed to. The more references and data available, the more likely the process is to work from the start.	3.5
Sustainability	Waste (solid, water), emissions, corrosivity, hazards	Increasing interest from decision-makers and society towards the HSE sector of new industrial activities play an important role in today's investments.	4.5
Suitability	Similarity to the current process equipment, product suitability to the current product portfolio	If the process is similar to current process(es) it will be easier to implement. The current personnel could operate it with only little additional training. Not too important factor.	3

The processes were given grades 1 - 5 for each criterion, 5 being the highest and 1 the poorest. The grades were then multiplied by the weight factor and summed up for total points. The bigger the total score, the better the process fit to the case study. The results from the grading are given in Table 9. In the table, magnesium oxide production only considers the thermal decomposition of magnesium sulfate crystals and magnesium electrolysis only considers the carbothermic chlorination of magnesium oxide and the electrolysis of magnesium chloride.

Table 9. Comparison table of different process alternatives

ROUTE/ PRODUCT		$MgSO_4$ Crystallization		Calcination of $MgSO_4$ to MgO & SO_2		Electrolyzing to Mg metal		Total route from $MgSO_4$ to Mg(s)		$MgCO_3$ precipitation		Struvite precipitation	
Criteria	Weight	Points	Total	Points	Total	Points	Total	Points	Total	Points	Total	Points	Total
Economic potential	4	4	16	2.5	10	4	16	3.5	14	1	4	2	8
CAPEX	2.5	2	5	2	5	2	5	2	5	4	10	4	10
OPEX	4	0.5	2	1	4	4	16	1.83	7.33	5	20	5	20
Maturity	3.5	4	14	4.5	15.8	5	17.5	4.5	15.8	3	10.5	1.5	5.25
Sustainability	4.5	3.5	15.8	2.5	11.3	2	9	2.67	12	4	18	4.5	20.3
Suitability	3	4	12	3.5	10.5	3.5	10.5	3.67	11	2	6	3	9
Total	21.5	64.75		56.5		74		65.01		68.5		72.5	
Score		**3.01**		**2.63**		**3.44**		**3.03**		**3.19**		**3.37**	

Economic potential

Prices for chemicals and the amounts needed or produced per one ton of product are tabulated and can be found in Appendices I and II. The values were used to perform the economic potential calculations, which are presented in Appendix III. The calculations consider the profit gained from the process stream in one hour and are purely based on chemical prices. The volume flow of the process was set as 350 m^3/h and the magnesium content as 15 kg/m^3. The recovery rates used for different methods are based on educated guesses. The highest profits are for magnesium sulfate and magnesium metal and they received the highest grades in this criterion. Magnesium oxide and struvite fall behind so much that they are rewarded only with two points each. Magnesium oxide was given a slightly higher score since the markets for it are considerable, which makes it easier to sell than struvite. Because magnesium carbonate precipitation can barely be considered as a profitable process, it gets the lowest score in economic potential.

CAPEX and OPEX

Struvite precipitation succeeded well within CAPEX and OPEX criteria, because fast reaction in mild environment results in reasonably sized equipment that can be manufactured from common materials. Magnesium carbonate precipitation was given the same grades in CAPEX and OPEX for similar reasons. Crystallization and especially the possible thermal decomposition of magnesium sulfate scored low in both categories. The temperature needed for the decomposition consumes a lot of energy, which is why it scored the lowest. The equipment needed to ensure the purity of magnesium sulfate increases CAPEX and results in low score in that category. Electrolysis of magnesium chloride to magnesium metal has the lowest costs in the route to magnesium metal and scores well in the OPEX category. Summary of the operational costs are presented in Table 10. For more detailed information see Appendix IV.

Table 10. Operational cost summary

Route	$MgSO_4$ Crystallization	Calcination of $MgSO_4$ to MgO & SO_2	Electrolyzing to Mg metal	Total route from $MgSO_4$ to Mg(s)	$MgCO_3$ precipitation	Struvite precipitation
Operational costs €/h	14232	1547	1082	16861	Like struvite	8.8

Maturity, suitability and sustainability

Crystallization as magnesium sulfate and thermal decomposition are amongst the three most mature processes in comparison with studies and patents from the 1950's, the most mature process being the electrolysis that has been developed in the 19th century. Struvite precipitation from sulfide leaching liquors represents a more novel approach with only a couple published studies. Interest from the case company towards struvite precipitation increases its grades both in maturity and suitability criteria. Magnesium sulfate has industrial and many other uses so it could be easier to find buyers for it. It also blends in the sulfide product group well, which results in the highest score in suitability. Magnesium carbonate was given the lowest score, because the patent studied for magnesium carbonate precipitation did not consider possible manganese in the process stream at all, which raises uncertainty of suitability. However, the studies considered in the literature study show that manganese could be precipitated also using carbonate precipitation possibly before magnesium carbonate precipitation.

The highest points in the sustainability criterion was given for struvite. The main reason behind the high score is that the major by-product, ammonium sulfate, can also be used as a fertilizer or then decomposed into ammonia and sulfuric acid those can be recycled back to the process. Also, a possible by-product Newberyite ($Mg(PO_3OH)\cdot 3H_2O$) can be used with struvite as a fertilizer. (Eghtesad, 2016) Thus, there is no need for an additional separation step. Magnesium sulfate crystallization gains high points as well, because it should only produce water as the evaporation product. Though, there is a possibility that the water needs to be treated, which lowers the score a little. The by-products and chemicals used in magnesium carbonate precipitation, thermal decomposition of magnesium sulfate and magnesium metal electrolysis result in moderate and low scores for the processes in this category.

Summary

According to the results presented in Table 9 and the calculations in Appendix IV, magnesium precipitation as struvite is the most promising method for magnesium recovery from nickel sulfide process streams and is chosen for further studying.

7.2 Methods chosen for applied part

Most of the struvite precipitation studies are based on the need of phosphate removal from wastewater treatment plant solutions. Very little, if any, is concentrated on struvite precipitation from nickel sulfide leaching liquors. Thus, a need for laboratory tests to prove whether precipitating struvite from the case plant solution is possible or not is evident. A method for laboratory tests is developed based on the results from other struvite precipitation studies about the optimal precipitation conditions, how other metals influence the precipitation, morphology and solubility of struvite etc. The goal of the laboratory tests is to gather information about the possible recovery efficiency of magnesium as well as the product purity. Due to the overwhelming results in both the magnesium recovery and the product purity, the base conditions for the struvite precipitation tests are adopted from the Eghtesad's (2016) study. Other studies are used to justify the decisions and for additional data such as iron and manganese removal. In addition to proving the precipitation concept, the laboratory tests are done to obtain data that will help in sizing the equipment, which in turn will help to develop the final struvite precipitation process.

8 Methodology

A method is developed to test whether or not struvite can be precipitated from the case plant solution. First, the differences between the case plant solution and a reference solution from the literature are discussed. Secondly, the two major factors affecting the struvite precipitation, pH and supersaturation, as well as the minor factors such as temperature and stirring speed are introduced and tackled. Lastly, taking into account all the different factors discussed, a laboratory test set-up is presented.

8.1 Metal content

The comparison between the contents of the case plant solution and the reference solution that Eghtesad (2016) used are presented in Table 11.

Table 11. Metal contents of liquors used for struvite precipitation

Metal contents of the liquors				
	Case solution		**Eghtesad (2016)**	
Metal	mol/l	x:Mg	mol/l	x:Mg
Mg	0.4941	100 %	0.0612	100 %
Fe	0.3483	70 %	-	-
Mn	0.1135	23 %	0.0001	0.2 %
Na	0.1116	23 %	0.0330	54 %
Ca	0.0161	3 %	0.0190	31 %
Ni	0.0009	0.2 %	-	-

The main differences to consider are the iron and manganese contents that are many times larger in the case solution than in the reference solution. On the other hand, sodium and calcium concentrations are notably smaller. Most of manganese and iron in the solution can be assumed to be divalent cations. The removal of iron and manganese are to be considered (and carried out) in the laboratory tests. However, since the main emphasis of this study is to develop a process for magnesium recovery as struvite, the removal of iron and manganese are to be carried out rather in an effective than optimal way.

8.1.1 Iron removal

By having a look at the metal hydroxide solubility curves (Figure 22) it seems that iron could be precipitated as hydroxide in pH values 5 - 7. Thus, a suitable method for iron removal could be hydroxide precipitation. One way to do it according to Burke and Banwart. (2002) is the oxidation of Fe(II) by oxygen as shown in equation 4.

$$O_2(aq) + 4\,Fe^{2+} + 6\,H_2O \leftrightarrow 4\,FeOOH(s) + 8\,H^+ \quad (4)$$

The equation (4) can also be divided into two pieces (Antila, 2000), where a) iron(II) first forms a hydroxide and then b) the formed iron(II)hydroxide oxidizes into iron(III)hydroxide when contacted with oxygen in the air.

$$Fe^{2+} + 2\,OH^- \leftrightarrow Fe(OH)_2 \quad (5a)$$

$$4\,Fe(OH)_2 + O_2 \leftrightarrow 4\,FeO(OH) + 2\,H_2O \quad (5b)$$

FeO(OH) is the anhydrous form of iron(III) oxide-hydroxide. In aqueous conditions it typically catches one water of crystallization and forms a monohydrate $FeO(OH) \cdot H_2O$ or $Fe(OH)_3$. The iron(III)hydroxide has a reddish-brown color. (Antila, 2000)

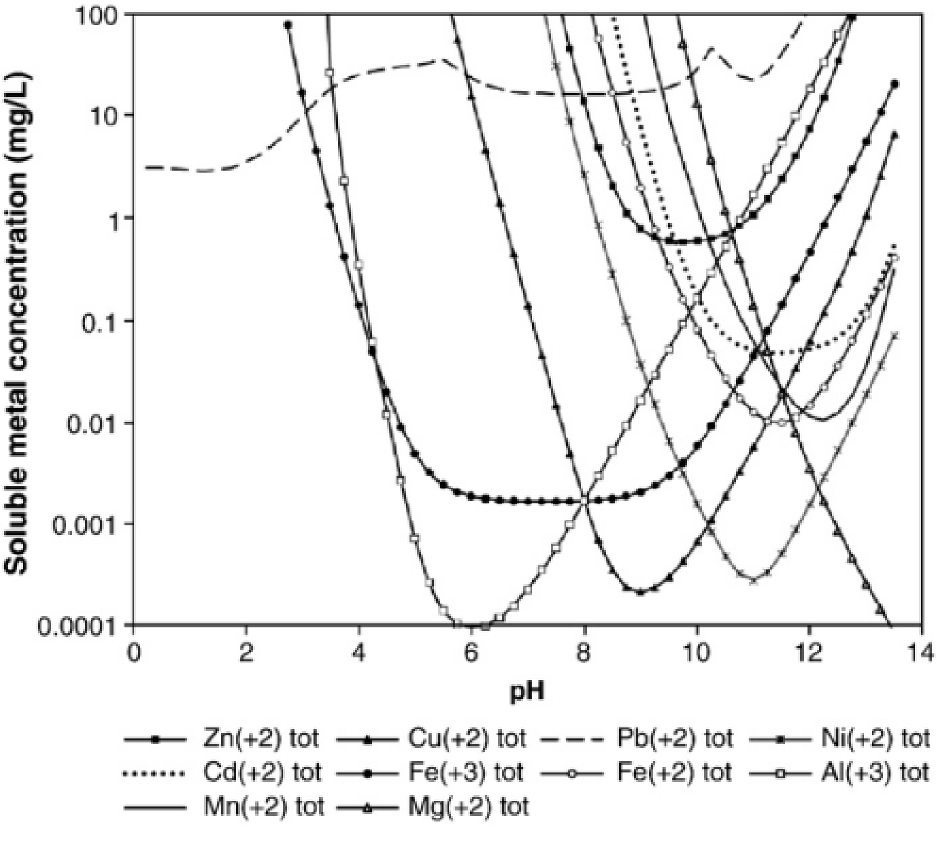


Figure 22. pH dependence of metal hydroxide solubilities (Lewis 2010)

It is mentioned in the book by Antila (2000) that in alkaline conditions the oxygen of air is enough for the oxidation. Thus, the pH level should be raised to over 7 to speed up the precipitation. The forming hydrogen atoms will lower the pH, which is why base must be added to avoid pH drop.

8.1.2 Manganese removal

Based on the metal hydroxide solubility curves (Figure 22) the solution pH should be around 9.5 in order to precipitate most of the manganese from the solution. The magnesium curve is quite close to the manganese and some co-precipitation of magnesium hydroxide might occur. However, this should be very minimal, almost nonexistent, since magnesium hydroxide tends to dissolve in ammonium-rich solutions according to Antila (2000). The same source states that manganese hydroxide precipitation might suffer from the presence of ammonium ions. Manganese hydroxide oxidizes further according to the following reactions (6a-6c) according to Antila (2000). As the manganese(II)hydroxide from the first equation is a white precipitate, the other two products are brown.

$$Mn^{2+} + 2\,OH^{-} \leftrightarrow Mn(OH)_2 \tag{6a}$$

$$4\,Mn(OH)_2 + 0_2 \leftrightarrow 4\,MnO(OH) + 2\,H_2O \tag{6b}$$

$$4\,MnO(OH) + O_2 \leftrightarrow 4\,MnO_2 + 2\,H_2O \tag{6c}$$

Other option for manganese removal is the carbonate precipitation presented in chapter 4.3 in the literature study. According to Antila (2000), manganese carbonate precipitation should work despite the presence of ammonium ions. Magnesium carbonate on the other hand should stay in the solution.

8.2 pH

One of the main factors affecting struvite precipitation is pH. The effect of pH is important, because the availability of ammonium and phosphate ions are very dependent on it. The amounts of these ions are plotted against pH in Figure 23 and Figure 24.

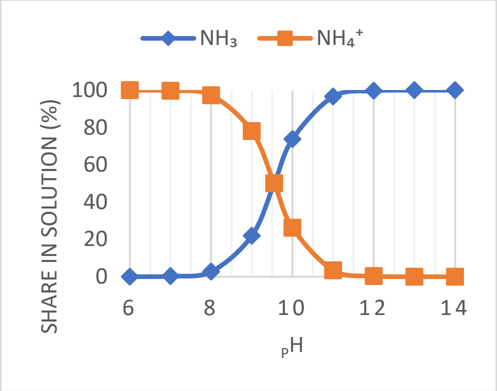


Figure 23. NH_3 vs NH_4^+ in different pH

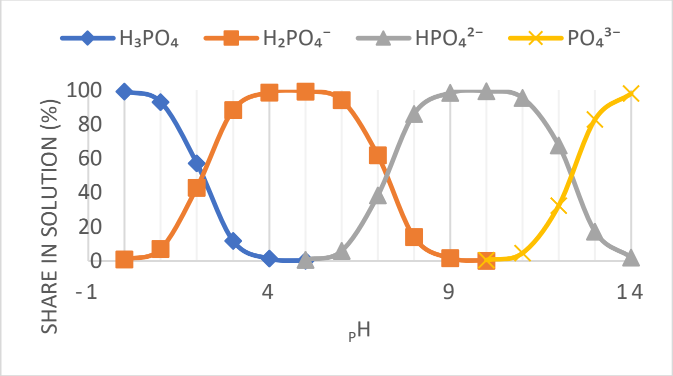


Figure 24. H_3PO_4 and its conjugate bases in different pH

As it can be seen, under pH 7 there are practically no PO_4^{3-} -ions because of the triprotic nature of phosphoric acid. On the other hand, if the pH raises to values over 11 there will only be a small amount of NH_4^+ -ions available. The dependency of pH to struvite solubility has been studied by many. Values from different studies are gathered to Table 12.

Table 12. Struvite solubility

Study	**Doyle and Parsons (2002)**	**Ali (2005)**	**Eghtesad (2016)**
Struvite solubility pH-range	7 – 11	7.5 – 11	
Minimum solubility pH	9	9 – 11	9.63

As a conclusion from the values in Table 12 it can be said that for the tests a pH range from 7.5 to 11 can be used with optimal results for struvite precipitation at pH around 9.5. If tests are to be done in different pH areas, the amount of available ammonium and phosphate ions should be considered for each case from the figures 23 and 24.

8.3 Supersaturation

Supersaturation seems to affect the homogeneity of the precipitate (Bouropoulos and Koutsoukos 2000) as well as magnesium recovery efficiency (Eghtesad 2016). Rahaman et al. (2008) noticed an increase in phosphate ion removal kinetics as the supersaturation ratio increased. Huang et al. (2006) mention that the crystal size was not affected by the supersaturation ratio.

Bouropoulos and Koutsoukos (2000) found out that at pH 8.5 and temperature of 25°C the precpipitate was not homogeneous under supersaturation ratios of 2. Above that, precipitates started to be uniform.

Eghtesad (2016) noticed that with a supersaturated solution with Mg:PO_4^{3-}:NH_4^- ratios of 1:1:1 the reaction efficiency was only around 30 %. By changing the ratio to 1:1:3 the efficiency raised to over 90 %. Eghtesad also noted that the efficiencies of the solutions in the metastable region were clearly not as good as their supersaturated correspondents. To ensure supersaturation conditions in this study's laboratory experiments, the pH control is done with ammonium hydroxide to bring the needed ammonium ions to the solution.

8.4 Minor factors

Other factors such as temperature, stirring speed, seeding and residence time do not have that big an impact on struvite precipitation. They have more to do with the size of the struvite seeds.

Temperature

Struvite precipitation is most efficient in ambient temperatures according to the study by Eghtesad (2016). Similar results are found in the study by Bhuiyan et al. (2007). The best results in both studies were in the range of 15 – 30°C. The ambient temperature of the laboratory is around 20°C, so there is no need for temperature control. Although, the temperature should be measured to find out is the reaction endo- or exothermic.

Stirring speed

Rahaman et al. (2008) and Ali (2005) mentioned that excessive stirring may cause damage to crystals but on the other hand, faster stirring promotes the nucleation of struvite. It was noted by Eghtesad (2016), that lower stirring speeds resulted as insufficient mixing and promoted simultaneous gypsum precipitation when there were impurities such as calcium in the solution.

For a synthetic feed stirring speed did not have an impact. The stirring speed of around 340 rpm was mentioned as the optimal in Eghtesad's study and should be used in the laboratory tests.

Seeding

According to Eghtesad (2016), seeding increased magnesium recovery but is not recommended due to threefold amount of seeding material compared to the expected amount of struvite. In addition, it did not seem to have any effect on the appearance of precipitates, which is what seeding is usually used for. Because no significant assets are found, no seeding is done in the laboratory tests.

Residence time

The same concept of residence time is used in this study than was in Eghtesad's (2016) meaning the time after all the ammonium and phosphate ions are added to the solution until the stirring stops. Lower residence times result in lower power consumption and prevent crystals from breaking. Even though Huang et al. (2006) mention that the crystal size increases with longer times, a short residence time of 10 minutes is chosen for the experiments of this study

8.5 Planning the laboratory tests

Based on the different aspects discussed in the previous subchapters, a laboratory set was developed and is presented in Figure 25.

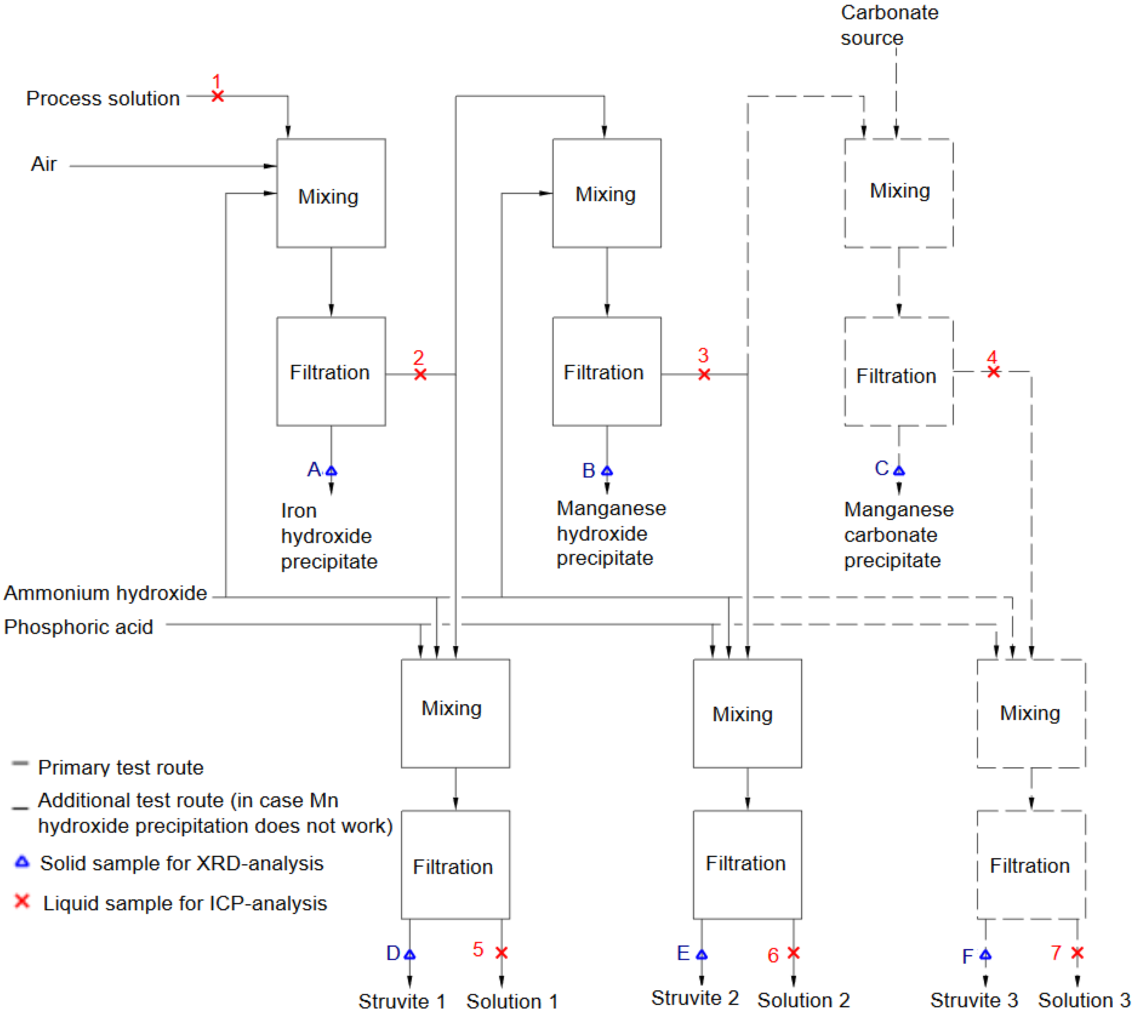


Figure 25. Block diagram for laboratory tests

The process solution is first mixed in an aeration reactor and is treated with ammonium hydroxide to raise the pH to around 8. To avoid pH drop, a sufficient amount of ammonium hydroxide is added during the oxidation. The mixing is continued until all the iron has been oxidized resulting in no more hydrogen atoms. Thus, the oxidation is considered ready when the pH stops decreasing. The mixture will then be fed to a Büchner funnel to separate the solids from the liquid. The precipitate is stored for analysis. Half of the solution will later be used for a struvite precipitation test, while the other half continues to manganese precipitation step.

The first attempt to precipitate manganese is to precipitate it as a hydroxide. The most important factor in manganese hydroxide precipitation is the pH control. A pH too high might result in magnesium co-precipitation. The goal is to keep the pH at about 9.5. An approximation of the manganese content in the solution will be made to calculate the hydroxide ion need for precipitation. After an equimolar amount of hydroxide ions is fed into the reactor as ammonium hydroxide, the mixture is stirred for 10 minutes. After that, the solids and liquid will be separated with Büchner funnel. The precipitate is stored for analysis, while the solution will later be used for a struvite precipitation test.

High ammonium ion concentration can decrease the efficiency of the manganese hydroxide precipitation. If the manganese hydroxide precipitation does not seem to purify the solution enough (to an Mn:Mg ratio of 0.2), a carbonate precipitation test is to be made. For this step, a sufficient amount of a suitable carbonate compound is diluted in distilled water. The saturated solution is then mixed in the reactor to form precipitate. After the addition, the mixture is poured into Büchner funnel to separate the solids from the liquid. The liquid is then used for a struvite precipitation test.

Struvite precipitation tests

As discussed earlier, struvite precipitation can be done in pH range 7.5 - 11. The only test solution on the edge of this range is the one gathered from the iron precipitation step. To make sure that the possible precipitating struvite does not dissolve back to the solution, the pH is raised to over 8, more preferably to around 8.5. A pH value over 8.5 can result in manganese hydroxide co-precipitation. The pH of the two manganese poor test solutions is raised to around 9.6. An approximation of the magnesium amount in the solution is made and the amount needed to precipitate all magnesium is used to calculate the need for phosphoric acid. To ensure minimum co-precipitation of other compounds only 60 % of the total amount is added to the solutions. The molar amount of ammonium ions added to the process solution before the struvite precipitation tests should be greater than is needed to precipitate all the magnesium as struvite. However, ammonium hydroxide is used for pH control.

The tests are carried out in room temperature. Struvite precipitates rapidly after the first phosphoric acid drops are introduced to the solution according to Eghtesad (2016), which is why the acid is added gradually with constant, efficient stirring to avoid partial sedimentation. A stirring rate of 300 rpm can be used. Because struvite precipitation is very rapid, the solution is only mixed 10 minutes after the last drop of phosphoric acid has been introduced to the solution.

The temperature of the mixture is to be measured during the precipitation test to find out how exo-/endothermic the reaction is.

Precipitates

The reaction yield (efficiency) can be calculated by comparing the mass of the precipitate to the theoretical mass. Since struvite comprises of equimolar amounts of Mg^{2+}, NH_4^+ and PO_4^{3-} -ions and the first two are already in the test solutions, the easiest way is to calculate the theoretical mass of precipitating struvite by assuming $n(struvite)= n(PO_4^{3-})=n(H_3PO_4)$. This way we can make an equation for yield as shown in equation (7).

$$Yield = \frac{Mass\ of\ the\ precipitate}{Theoretical\ precipitate\ mass} * 100\ \% = \frac{Mass\ of\ the\ precipitate}{n(H_3PO_4)*M(struvite)} * 100\ \% \qquad (7)$$

The color of the forming struvite precipitate gives an estimate of the purity of the product right away. Pure struvite appears as white powder. The three struvite precipitates from sample points D, E and F, and the by-product precipitates from A, B and C in Figure are dried and pulverized. The pulverized samples are analyzed by using X-ray diffraction (XRD) measurement. The results should reveal the main compounds in the samples and their purities.

Solution samples

The efficiency of each precipitation step can be calculated from the inductively coupled plasma spectroscopy (ICP) results. ICP analysis detects the metal content in the solution. When samples are taken before and after each precipitation step, it can be seen how much of each metal goes with the precipitate and how much stays in the solution. The decrease of magnesium content in the solution is compared to the theoretical amount to calculate the efficiency of the recovery. The theoretical amount of precipitating magnesium is calculated by using equation (8), where the assumption: all the phosphoric acid dissociates to PO_4^{3-}, thus $n(H_3PO_4) = n(Mg)$ is made.

$$m(theoretical\ Mg) = n(Mg) * M(Mg) = \rho(H_3PO_4) * \frac{V(H_3PO_4)}{M(H_3PO_4)} * M(Mg) \qquad (8)$$

Altogether seven solution samples are gathered. The spots are marked to Figure as red crosses.

9 Laboratory tests

Laboratory tests were carried out based on the methodology presented in chapter 8.5. The test set consists of different batch experiments: iron precipitation, manganese precipitations and struvite precipitation tests. 25 w-% ammonium hydroxide (Merck Millipore) was used for pH control and ammonium ion source and 85 w-% phosphoric acid (Merck Millipore) was used as the phosphate ion source. Ammonium hydrogen carbonate (Merck**)** was the carbonate source in the carbonate test. All the experiments were conducted at Aalto University facilities. The temperature of the room was around 21°C during the tests.

Equipment

The iron and manganese precipitation tests were done with the equipment described in Figure 26.

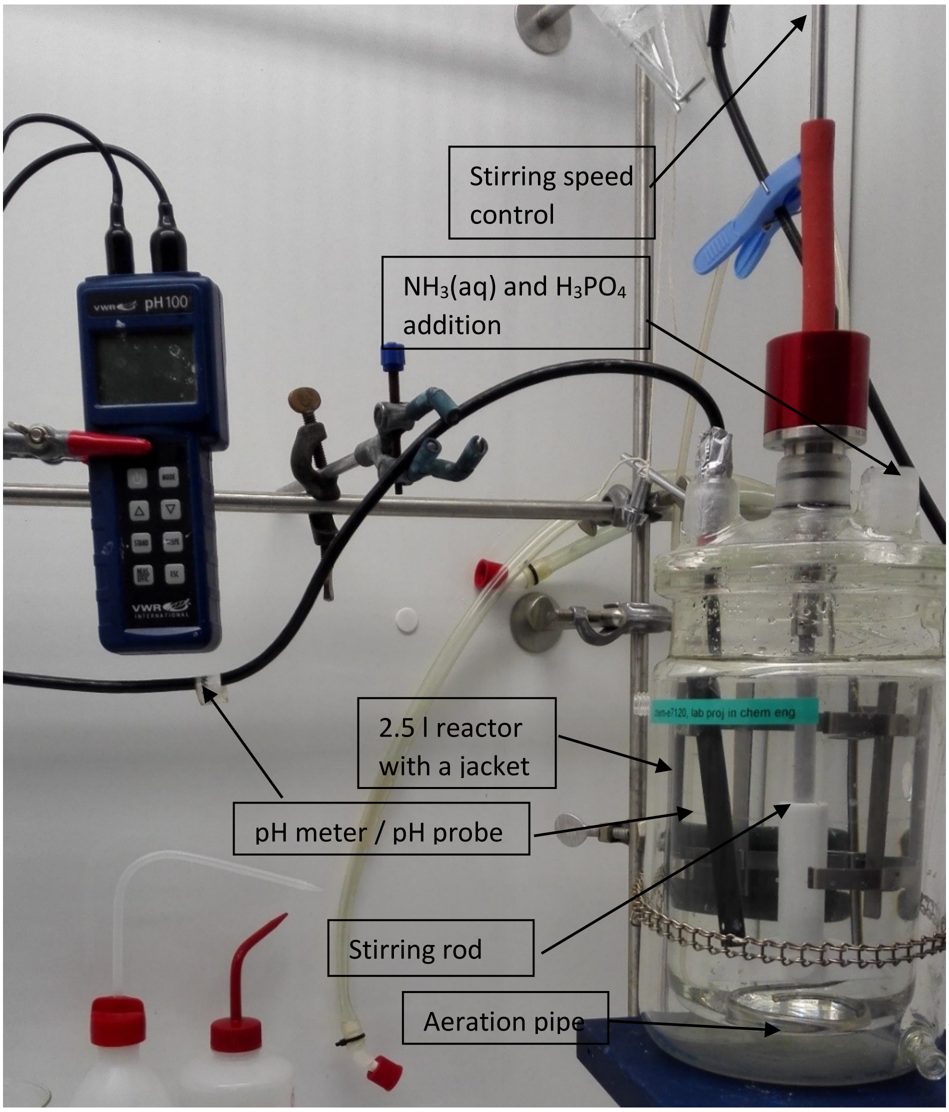


Figure 26. Batch reactor used for the precipitation tests

The reactor volume was 2.5 liters and was equipped with a speed-controlled stirring rod. Temperature and pH was measured with a VWR pH 100 pH meter. An aeration pipe was introduced to the reactor for iron precipitation. The struvite and manganese carbonate precipitation tests were made in a 200 ml beaker and the solution was stirred with a magnetic stirrer.

Iron removal

The reactor was filled with 2269 g (around 2100 ml) of the case solution. The initial pH of the solution was measured 3.29 and the solution was light green. The air feed and the stirring (300 rpm) were started and were constant during the tests. 16 ml of 25-% ammonium hydroxide was used to increase pH to alkaline area in order to make iron precipitation faster. At pH 7.75 the solution turned into dark blue/black. After 30 minutes of stirring the splashes on the top of the reactor had started to turn brownish/rusty. The mixing was continued for 7 hours. The ammonium hydroxide additions and how the pH changed during the experiment is shown in Figure 27.

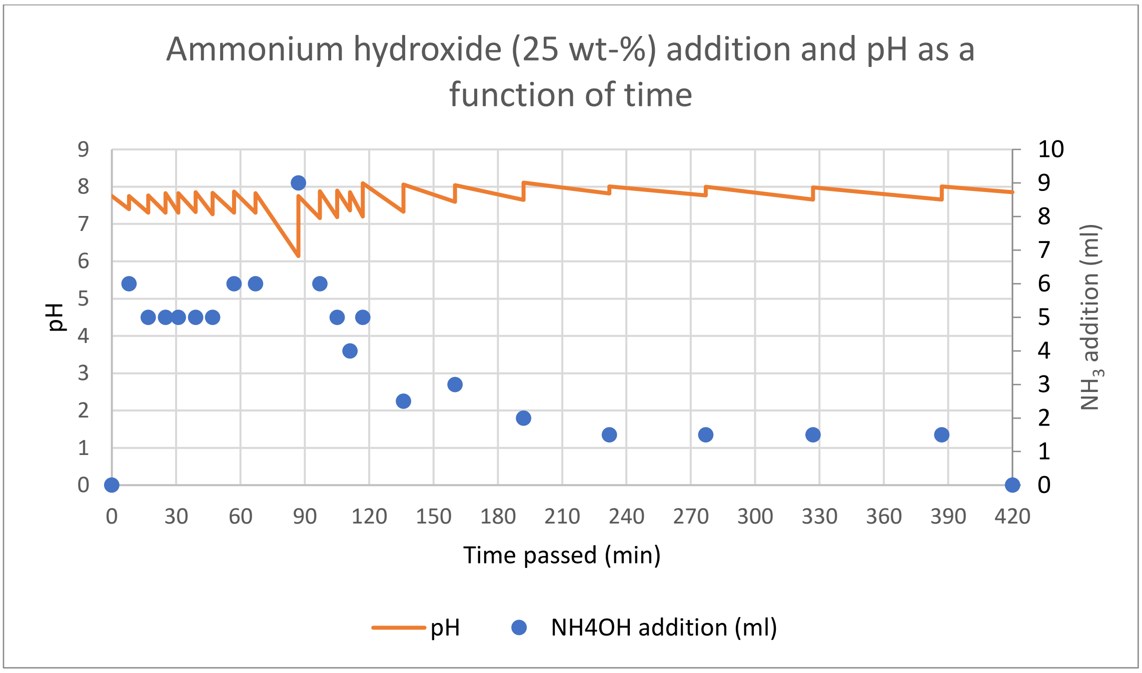


Figure 27. pH of the solution as a function of time with ammonium hydroxide addition

Aqueous ammonia was added when pH had decreased to around 7.3 during the first two hours. This happened in approximately 10-minute intervals. The volume of each addition was 4 – 6 ml. The deviation at around 90 minutes was a result from a 20-minute interval after which a 9-ml addition was needed to raise the pH to wanted level. After two hours had passed, the pH did not decrease with the same pace anymore. The time between the additions was raised to 30 minutes, 45 minutes and eventually to one hour the further the test went. The size of ammonia addition decreased to 1.5 – 2.0 ml. During the iron precipitation test a total of 85.5 ml of ammonium hydroxide was added to the reactor.

After 7 hours, the test was stopped and the black-colored solution was immediately filtered by using a Büchner funnel with filter paper. Because the solution still had a black color in it, it was collected into a glass bottle where it was left for 87 hours to settle. The solution was then filtered again. The solution now gathered was transparent and yellow/light brown. The precipitate from iron removal step was very moist and black. Altogether around 500 g of moist precipitate was collected.

The color changes of the solution during aeration, pictures of the precipitate and the purified solution can be found in Appendix V.

Manganese removal

Half of the iron-poor solution, 838.2 g, was used for manganese precipitation test. The pH had dropped from the 7.85 to 7.73. Approximately 15 ml of ammonium hydroxide was used to raise the pH to 9.5 to precipitate manganese hydroxide. The solution was stirred with 300 rpm for 10 minutes. Very small-sized brown precipitate was observed in the reactor. The solution was poured into a glass container for storage. After 30 minutes, the precipitate and the solution had separated. Because of the effects exhibited on iron precipitation, the solution was left in the storage tank overnight to let it precipitate to the full. The solution was filtered resulting in orange, transparent solution and 7.05 g of brown precipitate after 18 hours in the storage tank.

Solution handling

The solutions were not too clear after the first filtrations. They kept their orange/light brown color pointing out the presence of Fe and/or Mn ions and some precipitation occurred little by little in the storage bottles. Before continuing to struvite tests, the solutions were filtered every morning and afternoon for several days. Altogether, the poor in iron solution was filtered six times and the poor in manganese solution eight times. After the filtration cycle, the iron poor solution had become transparent and colorless. However, the manganese solution did not seem to clarify. Thus, the alternative carbonate precipitation route needed to be tested.

CO_3^{2-} precipitation pre-test

60 ml of the manganese poor solution was taken aside for the test. Sodium bicarbonate ($NaHCO_3$) was used as the carbonate source. It was made sure that all the remaining manganese will precipitate so an assumption that the manganese content was still 6000 mg/l was made. To successfully remove all manganese, an equimolar amount of sodium hydrogen carbonate was diluted in distilled water. The dilution was then added to the solution. A magnetic stirrer was used during the whole precipitation test.

After the addition, white precipitate started to form in seconds. Stirring was continued for 10 minutes after which the precipitate was left to settle for three hours after which it was filtered. The precipitate was washed with 10 ml of distilled water which was added to the solution. Just one hour afterwards the precipitate had turned from white to light-brown. The solution however was as transparent as distilled water.

A picture of the precipitate is shown in Appendix VI together with the precipitates gathered after some manganese hydroxide filtration those varied slightly from each other.

Struvite precipitation pre-tests

Even though the solutions were not clear after the first filtrations, small (40 ml) volumes of both solutions were taken aside and small amounts of phosphoric acid was added into them. The results from both tests produced light-brown precipitate. The precipitate from Mn and Fe poor solution was slightly closer to pure white color.

The solution from the carbonate precipitation pre-test was also treated with a small amount of phosphoric acid. The resulting precipitate was pure white. All the reactions were observed exothermic.

Struvite precipitation tests

After the iron and manganese solutions had been filtered several times, they were considered as pure as possible with hydroxide precipitation. From the manganese poor solution 105.6 g was taken aside and was treated with 0.9 g ammonium hydrogen carbonate diluted in 13.1 g of water to precipitate the remaining manganese as carbonate. Around 100 g of each solution was then measured to 200 ml beakers. Each of them was treated with 2 ml of phosphoric acid and the pH was controlled with ammonium hydroxide. The initial and final pH as well as the temperatures were measured. The information is tabulated in Table 13.

Table 13. Struvite precipitation test data

Measured variable	**Unit**		**Fe-poor**	**Mn-poor (hydroxide)**	**Mn-poor (carbonate)**
Weight of the solution	(g)	Initial	107.05	106.90	97.30
		Final	103.80	108.70	100.90
Weight of the precipitate	(g)	Wet	8.3	8.5	7.9
		Before drying	5.0	6.0	7.9
		After drying for 16.5h in a 45°C oven	3.8	4.1	4.3
pH	-	Initial	7.82	9.20	8.67
		Range	8.45-8.80	9.2-9.6	9.2-9.6
		Final	8.80	9.56	9.58
Ammonium hydroxide (25-%) addition to raise pH from initial to upper limit of the range	(ml)		~0.45	~2.5	~3.5
Temperature	(°C)	Initial	21.5	22.0	22.0
		Final	24.4	26.1	26.0
Stirring speed	(rpm)		300		
Phosphoric acid (85-%) addition	(ml)	Total	~2.00		
Ammonium hydroxide (25-%) needed to neutralize the hydrogen ions	(ml)	Total	~6.00	~10.00	

The tests were made in the following order: 1. Fe-poor, 2. Mn(hydroxide) and 3. Mn(carbonate). Thus, the precipitate from the Fe-poor solution got more time to dry before putting all the samples in the 45°C oven for 16.5 hours.

The phosphoric acid and ammonium hydroxide additions were done with Pasteur pipettes. One drop was assumed 0.05 ml. During the test from Fe-poor solution it was noted that to neutralize the effect of 0.05 ml of phosphoric acid, 0.15 ml of ammonium hydroxide was needed. In the manganese precipitations the amount of ammonium hydroxide was 0.25 ml per 0.05 ml of phosphoric acid. An ammonium hydroxide amount of that size brought the final weights of the manganese poor solutions higher than their initial weights. All the tests were exothermic. Images of the formed precipitates can be found in Appendix VII.

Precipitates

The precipitates from all precipitation tests including manganese carbonate test were dried and pulverized for XRD measurements. The measurements were carried out using a computer-controlled PANalytical X'pert Pro/PW 3040/60 and Cu Kα radiation with an average scanning rate of 28.75° (2θ) min^{-1}. Data were collected over a range of 4.5-120° 2θ. The data collected was analyzed with Match!3 program by CRYSTAL IMPACT using a ICDD PDF-4+ 2016 reference database.

Solution samples

The samples were sent to Terrafame laboratory for analysis. The equipment used for the analysis was an inductively coupled plasma – optical emission spectroscopy (ICP-OES) Thermo iCAP 6500 Radial.

10 Results and discussion

In this chapter, the results from the laboratory tests are presented.

Solutions

The main results from the solution samples are presented in Table 14. Full data of the analysis are found in Appendix VIII.

Table 14. Main results from ICP-OES analysis

Sample point in Figure 25	Sample name	Ca	Fe	Mg	Mn	Na
		mg/l	mg/l	mg/l	mg/l	mg/l
1	Starting solution	538	16520	11310	5798	2391
2a	Iron free solution II	537	7.26	10900	3573	2075
2b	Iron free solution FINAL	504	<0.06	10310	3457	1942
3a	Mn free solution I	505	0.09	10190	1008	1952
3b	Mn free solution FINAL	490	<0.06	9794	951	1887
4	Solution from CO_3^{2-} test	182	<0.06	8302	4.19	3682
5	Struvite test residue from iron free solution	461	<0.06	7255	1322	1880
6	Struvite test residue from Mn free solution	438	0.16	5994	280	1743
7	Solution from CO_3^{2-} struvite test	193	<0.06	3388	1.31	3320

Multiple liquid samples were taken during the iron and manganese precipitation steps. The first representative samples and the final samples from each test were sent for analysis to see if the many filtration steps had any effects to the solution purity.

There was a failure with the filtration paper during the first iron precipitate filtration, which is why the solution after the second filtration (2a) is considered as the first sample. It should be noted that the second filtration was done 87 hours after the first one giving the suspension time to settle into precipitate and liquid before filtration. The final solution from the iron precipitation (2b) that was taken after the mixture had been filtered six times. The final sample from the manganese precipitation was taken after the mixture had been filtered eight times.

The results obtained from the ICP-analysis of these samples show that the iron content had dropped down to 0.04 % of the initial during the first (successful) precipitation. By having a look at the detailed results in Appendix VIII, it can be stated that the iron precipitation also takes away the remaining aluminum, cadmium, cobalt and copper as well as most of nickel and zinc. The effect of more filtrations was mostly negative since more filtrations resulted in bigger magnesium loss. Thus, it is recommended to carry on to the manganese precipitation step with the solution from the first filtration.

Similar results were gained for the manganese hydroxide precipitation solutions. There was only a small drop in the manganese content in the solution samples taken after first and final filtration. It seems that with an ammonium ion content this high it is not possible to go much lower concentrations than 1000 mg/l with hydroxide precipitation route. Interestingly, the manganese carbonate precipitation seemed to work very well even though it also removed around 15 % of the current magnesium content.

The magnesium recovery efficiencies for each struvite precipitation test are calculated. The results are presented in Table 15. The theoretical amount is calculated from equation (8). The densities of the initial solutions were assumed to be 1.028 g/l.

$$m(theoretical\ Mg) = n(Mg) * M(Mg) = \rho(H_3PO_4) * \frac{V(H_3PO_4)}{M(H_3PO_4)} * M(Mg) \qquad (7)$$

,where $p(H_3PO_4) = 1685\ g/l$ $V(H_3PO_4) = 2\ ml\ (85\ wt\text{-}\%)$

$M(H_3PO_4) = 97.99\ g/mol$ $M(Mg) = 24.305\ g/mol$

Table 15. Magnesium recovery efficiencies

	unit	Fe-poor	Mn (hydroxide)	Mn (carbonate)
m(solution)	g	107.05	106.90	97.30
ρ(solution)	g/l	1.028		
V(solution)	ml	110.05	109.89	100.02
m(Mg, initial)	g	1.13	1.08	0.83
m(Mg, final)	g	0.726	0.599	0.339
m(difference)	g	0.38	0.42	0.49
M(theoretical)	g	0.836		
Mg recovery efficiency	%	45.64	50.81	58.44

Based on the ICP-OES results, the iron and manganese removal before struvite precipitation is justified.

Precipitates

The XRD-measurements were done to find out if the products were struvite and to check the content of the iron and manganese precipitates.

The diffraction patterns for the struvite test precipitates can be found in Appendix IX. The diffraction patterns were compared to synthetic struvite powder patterns from ICDD PDF-4+ 2016 database. One pattern for pure struvite is presented in Appendix X. The uniformity of the sample and the powder pattern is compared between different factors by the program. The factors are explained shortly in Table 16.

Table 16. How to read the XRD-results (Putz and Brandenburg, n.d.)

Entry	Entry number according to the new ICDD PDF numbering scheme.
P(Peakpos.)	Probability that the entry's pattern matches the one of the unknown sample with regard to the peak positions. The possible range of this value is 0.0 (no matching) to 1.0 (full matching).
P(I/IO)	Probability that the entry's pattern matches the one of the unknown samples with regard to the intensities of correlated peaks. Values from 0 to 1 as in P(Peakpos.)
I scale fct.	The intensities of the entry's peaks have been multiplied by this factor to obtain the best possible agreement P(I/IO) with the unknown pattern.
FoM	"Figure-of-Merit", a number which is calculated from the various measures of agreement between database and unknown pattern (e.g. P(Peakpos.), P(I/IO) etc.).

Every sample had struvite as the top match when the results were organized according to FoM column. How well the samples matched with their best match are presented in Table 17. More detailed results with more candidates can be found in Appendix XI.

Table 17. Best matches with the samples

Sample	Entry	Name	P(Peakpos.)	P(I/IO)	I scale fct.	FoM
Fe-poor	96-900-7675	Struvite	0.6144	0.9955	0.9388	0.8892
Mn(hydroxide)	96-900-7675	Struvite	0.6875	0.9974	0.958	0.9027
Mn(carbonate)	96-210-6463	Struvite	0.7217	0.9947	1.114	0.9101

The reference database contained many different struvite entries. The entries 96-900-7675 and 96-210-6463 were in top 5 matches in every case. Not surprisingly, the best match between the sample and the entry was found to be for the carbonate precipitation sample.

The iron and manganese precipitates were also analyzed with the XRD. Unfortunately, their patterns were not possible to be matched with anything due to a high level of noise caused possibly by a different zero-background disk than what was used for struvite tests. By following the changes of the iron precipitate over time it can be said that the main component was right after drying the precipitate was reddish-brown pointing out to iron(III)hydroxide. The manganese hydroxide precipitates differed very much from each other. They all were brown, some lighter some darker, but it is very hard to give an educated guess of the main component. The manganese carbonate precipitate seemed also light-brown.

All the struvite precipitates were weighed as wet and dry as shown in Table 13. The weights of the dried precipitates were compared to the theoretical struvite weight calculated with equation (6). The yields were calculated and are presented in Table 18.

Table 18. Struvite yields

	Fe-poor	Mn(hydroxide)	Mn(carbonate)
Weight (dry)	3.8	4.1	4.3
Weight (theoretical)	8.509		
Yield-%	44.66	48.18	50.53

Overall process

The results from the struvite precipitations are collected in Table 19.

Table 19. Results from struvite precipitations

	Color	Magnesium recovery efficiency (%)	Struvite yield (%)	Figure-of-merit
Fe-poor	Light-brown	45.24	44.66	0.8892
Mn(hydroxide)	Light-brown	53.55	48.18	0.9027
Mn(carbonate)	White	57.80	50.53	0.9101

It can be stated that struvite precipitation is possible from nickel sulfide leaching liquors. According to the results presented in Table 19, it is recommended to include both iron and manganese removal steps before magnesium recovery as struvite to increase the product purity. The iron removal was so efficient and produced a quite uniform precipitate that it is chosen to be used as the first step. The data to be used for iron precipitation step in the process design is gathered to Table 20.

Table 20. Data from iron removal step

	Unit	Value		
m(solution)	(g)	2269		
Ammonium hydroxide to raise pH	(ml)	16		
Ammonium hydroxide for pH control	(ml)	85.5		
Results				
m(precipitate)	(g)	Wet 638, dry 460		
m(solution)	(g)	1754		
pH		Initial 3.29	Range 7.3 – 8.0	Final 7.73

From the two manganese removal methods tested, carbonate precipitation was more efficient although it seemed to remove some of the magnesium simultaneously.

Most of the magnesium co-precipitation was probably due to a too big an addition of saturated carbonate solution. That was realized after receiving the ICP-results those showed manganese content around 951 mg/l in the solution before carbonate precipitation. Though, the carbonate solution used in the carbonate precipitation would have been enough to precipitate 6000 mg/l of manganese making the saturated carbonate solution addition almost six-fold to what actually was needed.

Because the carbonate test was also done for a solution that had already been through the manganese hydroxide step and not for a solution right after iron precipitation, one more test was needed to find out the efficiency of manganese carbonate precipitation step.

For the test, 0.57 g of ammonium hydrogen carbonate was diluted into 7.1 ml of water. This saturated solution was then added to 106.5 g of iron-free solution that had had its pH increased from 7.73 to 8.94 with 0.75 ml of ammonium hydroxide. As a result, 1.37 mg of wet precipitate that weighed 0.75 after drying in a 60 °C oven for 3 hours and 120.9 g of solution that now had a pH of 8.55 were received.

After taking a solution sample, 76 g of the solution was left for a struvite precipitation test. 3.8 ml of ammonium hydroxide was used to raise the pH to 9.46. The phosphoric acid addition was done gradually and altogether 1.7 ml of phosphoric acid was used. The pH control was done with 8.5 ml of ammonium hydroxide. After the additions, the mixture was stirred for 10 minutes. During the precipitation there definitely was a typical pungent odor of ammonia right above the beaker when it was smelled in the fume hood. White precipitate with a mass of 10.1 g as wet and 86.5 g of solution were received from the struvite precipitation test. The precipitate was dried in an oven for 22 hours in 42 °C.

The data from these two tests are collected into Table 21 and Table 22.

Table 21. Data from carbonate precipitation

	Unit	**Value**		
m($NaHCO_3$)	(g)	0.57		
V(water)	(ml)	7.1		
m(iron-free solution)	(g)	106.5		
Results				
m(precipitate)	(g)	Wet 1.37, dry 0.75		
m(solution)	(g)	120.9		
Ammonium hydroxide added	(ml)	0.75		
pH		Initial 7.73	Raised to 8.94	After 8.55

Table 22. Data from struvite precipitation

	Unit	Value		
m(solution)	(g)	76		
Ammonium hydroxide to raise pH	(ml)	3.8		
V(phosphoric acid)	(ml)	1.7		
Ammonium hydroxide for pH control	(ml)	8.5		
Results				
m(precipitate)	(g)	Wet 10.1, dry 5		
m(solution)	(g)	86.5		
pH		Initial 8.55	Range 9.2-9.5	after 9.46

A sample from the starting solution and solutions after the carbonate and struvite precipitation tests were collected and sent to Terrafame laboratory for the ICP-OES analysis. The precipitates were analyzed with XRD.

The XRD-analysis for the manganese precipitate was similar to the previous ones done for the struvite samples using PANalytical X'pert Pro/PW 3040/60 and Cu Kα radiation with an average scanning rate of 28.75° (2θ) min^{-1} with data collected over a range of 4.5-120° 2θ and the data then analyzed with Match!3 program by CRYSTAL IMPACT using a ICDD PDF-4+ 2016 reference database. For the struvite sample, the range was set to 4.5 – 75° 2θ and the scanning rate was decreased to 1.6° (2θ) min^{-1} for better results.

The pattern for the struvite matched very well with the synthetic struvite patterns of the ICDD PDF-4+ library. The top four candidates (all struvite) and how the sample corresponded to them is presented in Table 23.

Table 23. Data from struvite sample XRD-analysis

Entry	Name	P(Peakpos.)	P(I/IO)	I scale fct.	FoM
00-015-0762	Struvite, syn	0.877	0.988	0.870	0.965
04-010-2533	Struvite, syn	0.709	0.984	0.885	0.936
04-040-2894	Struvite, syn	0.702	0.986	0.889	0.935
04-009-6297	Struvite, syn	0.647	0.982	0.893	0.924

The biggest peaks of carbonate precipitate pattern were identified close to the peaks of manganese carbonate. The patterns for the struvite and manganese carbonate with the reference patterns of the best matching candidates can be found in Appendix XII and XIII, respectively.

The theoretical yield of struvite was 69.7 %.

Solution samples gathered during this carbonate route re-test were sent to Terrafame laboratory for ICP-analysis. The results are gathered to Table 24. The starting solution analysis is also shown in the table. The sulfate concentration was also measured from the new samples.

Table 24. ICP-results from carbonate route test

	Sample name	**Ca**	**Fe**	**Mg**	**Mn**	**Na**	**SO_4^{2-}**
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
I	Starting solution	538	16520	11310	5798	2391	
II	Iron free solution FINAL	488	1	10860	3739	2013	85483
III	Solution after CO_3^{2-} precipitation	330	<0.06	9517	525	2920	79246
IV	Solution after struvite precipitation	276	<0.06	1920	10	2497	63654

10.1 Mass balance

Mass balance for the process was done based on the results from the laboratory tests. The mass balance worksheet can be found as Appendix XIV. Struvite production is estimated to be around 8.5 t/h when the flow from the current process is 150 m^3/h. The flows for dry by-products are 30 t/h and 0.87 t/h for iron hydroxide and manganese carbonate, respectively. 20 % of the magnesium stays in the solution while around half is recovered as struvite and the rest 30 % co-precipitates in the iron and manganese precipitation steps.

Chemical costs and product incomes

The amounts from the mass balance for every chemical used and product produced are collected to Table 25 to calculate the economics of the process. The prices are gathered from Appendix I for ammonium hydroxide and phosphoric acid. Iron(III)hydroxide, manganese(II)carbonate and sodium hydrogen carbonate prices are estimates.

Table 25. Chemical costs and product incomes

Iron precipitation	**Amount (t/h)**	**Price (€/t)**	**Price total (€/h)**	**+/-**
Ammonium hydroxide	6.06	261.49	1584.6	-1584.6
Iron(III)hydroxide	30.32	100.00	3032.0	+3032.0
			Total	1447.4
Manganese precipitation	**Amount (t/h)**	**Price (€/t)**	**Price total (€/h)**	+/-
Ammonium hydroxide	0.75	261.49	195.1	-195.1
Sodium hydrogen carbonate	0.61	120.00	73.2	-73.2
Manganese(II)carbonate	0.87	610.00	530.7	+530.7
			Total	262.4
Struvite precipitation	**Amount (t/h)**	**Price (€/t)**	**Price total (€/h)**	+/-
Ammonium hydroxide	18.22	261.49	4764.3	-4764.3
Phosphoric acid	4.50	759.90	3419.6	-3419.6
Struvite	8.52	386.46	3292.6	+3292.6
			Total	-4891.3
			Process total	**-3180.99**

10.2 Profitability

As can be seen from Table 25, struvite precipitation is the only step that returns a negative value. The magnitude of it compared to the other two steps is so big that there is no way this process would be feasible as such. There are ways to make the process feasible like increasing the iron hydroxide product purity to increase the price, until it would lead the process into a breakeven point. But to make the process more beneficial considering only the struvite precipitation step, which still is the main object of this study, the following options could be possible to decrease the chemical use of the struvite precipitation step.

- Enhancing the struvite precipitation to recover all the remaining magnesium from the solution. This means bigger phosphoric acid uses which in turn increases the ammonium hydroxide use.
- The laboratory tests and various studies show that struvite precipitation was successful in pH’s lower than 9.6. Instead of raising the pH after manganese carbonate precipitation

step to around 9.6 and leaving it to 8.5 decreases the ammonium hydroxide use about 6 t/h. In addition, when the pH is lower the pH control takes approximately 60 % of the ammonium hydroxide needed in pH 9.6 lowering the use of ammonia another 6 t/h. Thus, the total use of ammonia in struvite step can possibly be decreased to one third of what it is in the proposed process route. However, this might result in bigger phosphoric acid demand.

- If the ammonia gas formed is possible to be kept in the struvite precipitation reactor, it could possibly protonate back to the solution decreasing the ammonium hydroxide addition even more.
- Other phosphate sources could be studied as alternatives. Changing phosphoric acid to for example ammonium dihydrogen phosphate, one can save about 25 % of the price of the phosphate source.

The profitability of the process in terms of chemical costs is analyzed in relation to different struvite prices in two cases: laboratory conditions and with a lower ammonia consumption (7.33 t/h) in struvite step. The effect is shown in Figure 28.

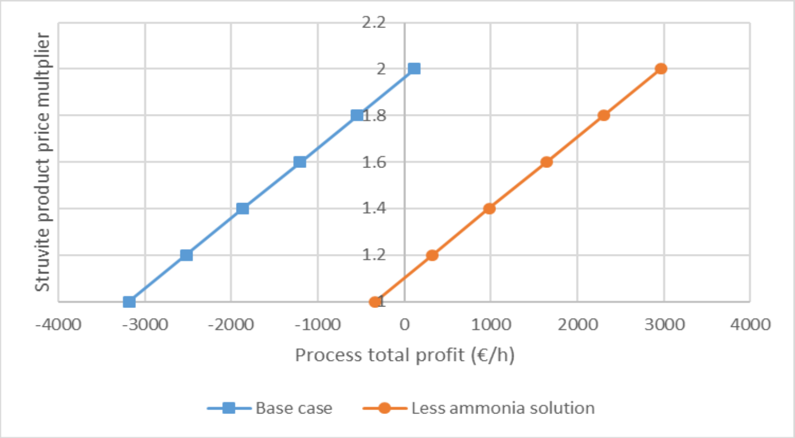


Figure 28. Effect of struvite price to the total process profit

It can be seen from Figure 28 that to get the studied process beneficial, the price of struvite should be almost two times bigger than the estimated current market price. That is most likely not going to happen, which is why the need for lower process costs such as precipitating struvite in lower pH is evident. By lowering the ammonium hydroxide need, there is only a need for 1.1 times larger (325 €/t) struvite price needed in the markets for a turnover.

Keeping the struvite price 386 €/t and increasing the iron precipitate price as was discussed above a similar graph (Figure 29) is obtained.

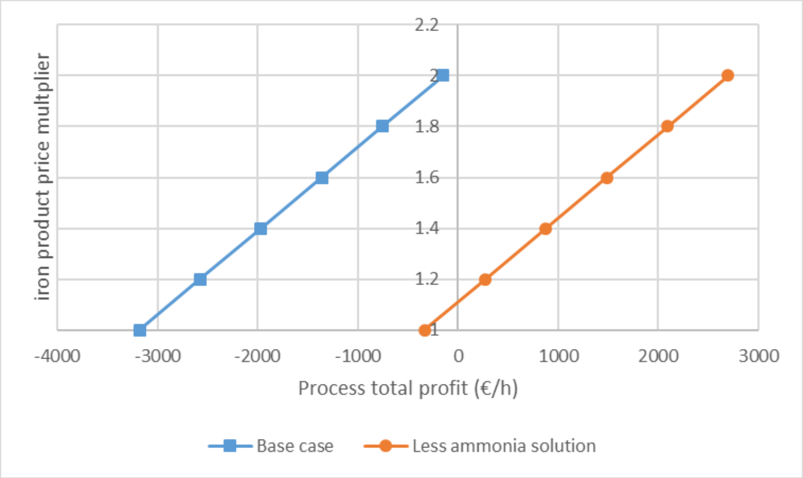


Figure 29. Effect of iron precipitate price to the total profit

According to the data in Figure 28 and Figure 29, it is proposed to study the possibilities of decreasing the ammonium hydroxide and increasing the value of the products and by-products to make the process economically feasible. Manganese(II)carbonate is not considered in these sensitivity analyses, because it has only a minor effect on total profit.

11 Process design

Generic process design is made based on the results received from the laboratory tests to see if the proposed process route is feasible. The process is designed to handle a flow of 150 m^3/h, which is the approximate outcome from one of the two process lines of the current process.

11.1 Description of the process

The process is divided into the following process areas: Iron hydroxide precipitation, manganese carbonate precipitation and struvite precipitation. In addition, a separate area is needed for feed tanks. Each process area is discussed in more detail in the following chapters.

11.1.1 Iron hydroxide precipitation

The iron hydroxide precipitation test in the laboratory took seven hours. Most of the precipitation was already complete in three hours, after which the ammonia additions decreased drastically. Considering the current iron precipitation processes in nickel production (Willis 2007), three hours of residence time is common. However, the reactors work in temperatures around 70-90°C. Thus, three hours can be considered acceptable from that perspective. The three-hour residence time makes iron precipitation the bottleneck of this process route. Because the precipitate was very sticky, batch reactors are chosen for iron hydroxide precipitation so that the reactors are easy to wash between cycles, if needed. The pipelines should also be equipped with flushing. Filters usually include a washing system in them.

The iron hydroxide precipitation area consists of six batch reactors. They are divided into three reactor pairs to ensure that the proposed process route can receive the approximated flow of 150 m^3/h all the time. Each pair of reactors is designed to handle 150 m^3 of the solution. The reactors work in cycles so that the second pair of reactors are started one hour after the first reactors and the third pair an hour after the second ones so that every hour 150 m^3 is taken into the iron precipitation step and a similar amount continues further in the process route.

The feed to the reactors is heated with heat exchangers to 80 °C. The reactors have a pH-controlled ammonium hydroxide feed and continuous air input. At start, the pH is raised from around 3.3 to alkaline conditions, preferably to around 8.0. Stirring is constant at 300 rpm and the reactors are heated with low-pressure steam. After three hours, the formed suspension is pumped to filter feed tank. Filter feed tank is needed to ensure constant flow to the filters for the best functionality. The suspension is pumped to filter(s) to separate the precipitate and convey it to a dryer. The solution is pumped to manganese carbonate precipitation feed tank.

11.1.2 Manganese carbonate precipitation

Manganese precipitation step is considered to be done in 30-minute batches. Only one reactor with a volume for 75 m^3 is needed for this to keep the process running with the required pace. The reaction seemed to work very well in temperature of 20°C. Thus, the manganese reactor needs to be a jacketed one to withstand the ambient temperature changes. Among the process solution, saturated carbonate solution and ammonium hydroxide are also fed to the reactor in the beginning of the batch. Amount of the carbonate solution is adjusted so that its mass is around 7 % of the fed process solution. The ammonium hydroxide is used to increase the pH around 8.6. Stirring is constant at 300 rpm and the reactor is heated with low-pressure steam. After the reaction, the formed suspension is pumped to filter feed tank and further to the filter(s) where the precipitate is separated and conveyed to a dryer. The solution is pumped to struvite precipitation reactor.

11.1.3 Struvite precipitation

Struvite precipitation takes also around half an hour and is done in a reactor with a volume of 75 m^3. The process solution is pumped directly from the filter(s) to the reactor. The pH is then raised to around 9.5 with ammonium hydroxide. Thereafter, phosphoric acid is being pumped into the solution with low velocity. The mass of phosphoric acid is about 4 % of the process solution. pH is constantly controlled with ammonium hydroxide and stirring is constant at 300 rpm. The forming ammonia gas is led through a vent for gas scrubbing.

After a sufficient amount of phosphoric acid has been introduced to the solution and the pH has been increased to 9.5, the mixture is pumped into a filter feed tank, where stirring is continued for 10 minutes before pumping it to the filter(s). From the filters, the precipitate is conveyed to a dryer and the solution is pumped to the already existing water treatment area.

11.1.4 Feed tank area

The storage or feed tanks for 25 wt-% ammonium hydroxide, 85 wt-% phosphoric acid and process solution as well as the preparation of the saturated carbonate solution all belong to this area. The tank for the process solution is designed to act as a buffer and has a volume ~ 900 m^3.

The freezing point of the process solution is around 0°C, which is why also this tank needs to have a jacket for heating or placed inside a heated warehouse.

The carbonate solution preparation includes a carbonate feed tank, from which the solid carbonate is fed to two preparation reactors with a weigh belt feeder. The tanks are designed for 30 m^3 of solution, which means that one batch is enough for 4 hours. The tanks are used by turns.

The acid and base tanks need to be separated from each other for safety purposes. To make sure that a phosphoric acid delivery is not needed more than twice per month, a volume of 1000 m^3 is chosen for the tank. The tank needs to be at temperatures above 20 °C to prevent it from crystallizing.

The ammonium hydroxide use is about ten times bigger than phosphoric acid, which means a consumption over 650 m^3 per day. Two tanks with volumes around 3400 m^3 each are used for storage. The freezing point of ammonium hydroxide (25 wt-%) is at -57.5 °C so no additional heating is needed for the tanks.

11.2 Equipment

Rough sizing is done for the main equipment. Tank and reactor sizing was justified in the process description part. The conveyors are given lengths of 50 m each. The methods to calculate the sizes of filters, dryers and pumps are described herein.

Filters

Very rough sizing was done for filters using equation (8) from a manual by Sandgren et al. (2015).

$$Filter\ volume = \frac{V(dry\ solids\ in\ dm^3)}{Cycles\ per\ hour} \tag{8}$$

The data used for calculations and the calculated volumes are presented in Table 26.

Table 26. Filter sizing

Filter	Volume flow of dry solids (m^3/h)	Cycle time (min)	Filter volume (dm^3)	Filter volume (m^3)
Iron precipitation	7.13	20	2378	2.38
Manganese precipitation	0.23	20	78	0.08
Struvite precipitation	4.98	20	1659	1.66

Dryers

The dryers chosen in this generic process design are direct contact. Sizes for the dryers were guessed based on the following assumptions 1) the cycle time is 60 minutes 2) the moisture content of the cakes is 10 % in every case and 3) cake thickness is 50 mm. The volumes of the cakes were divided with the thickness to get an area needed for drying. This is a very rough estimation that does not consider thermal properties of the products nor the heat transfer. The sizes for the dryers are shown in Table 27.

Table 27. Dryer sizing

Dryer	**Flow (m^3/h)**	**Cake thickness (m)**	**Area (m^2)**
Iron hydroxide	7.84	0.05	157
Manganese carbonate	0.26	0.05	5.2
Struvite	5.5	0.05	110

Pumps

All the pumps in the process are considered centrifugal. The capacities for the pumps around iron precipitation step are chosen 1400 l/min each, which corresponds to 84 m^3/h. The pumps of the main process line after iron precipitation all have a capacity of 1000 l/min. There are two pumps working side-by-side with a shared stand-by pump at each pumping point. The ammonium hydroxide feed pump has a capacity of 30 m^3/h that translates to 500 l/min. For phosphate feed a pump with a capacity of 60 l/min is sufficient. The carbonate solution transfer can be done with a 150 l/min pump. All the smaller pumps also have a stand-by pump in case of emergency.

Process equipment summary

The equipment are collected to Table 28. The sizes for each one like length for conveyors and volume for reactors are presented together with chosen materials. The material selection is based on a Chemical Compatibility Chart by Industrial Specialties Mfg. (2018)

Table 28. Process equipment

Equipment	**Size**	**Design factor**	**Final size**	**Material**
Reactors				
Iron precipitation	6 x 75 m^3	1.2	6 x 90 m^3	All tanks are 304 Stainless steel
Manganese precipitation	75 m^3	1.2	90 m^3	
Struvite precipitation	75 m^3	1.2	90 m^3	
Carbonate solution	2 x 8.5 m^3	1.2	10.2 m^3	
Tanks				
Feed tank	1 x 2700 m^3	1.2	3240 m^3	304 stainless steel
Ammonium hydroxide tank	2 x 3400 m^3	1.2	4080 m^3	316 stainless steel
Phosphoric acid tank	1000 m^3	1.2	1200 m^3	Hastelloy®-C
Plate and frame filters				
Iron precipitation	1 x 2.38 m^3,	1.2	1 x 2.86 m^3,	
Manganese precipitation	1 x 0.08 m^3,	1.2	1 x 0.096 m^3,	
Struvite precipitation	1 x 1.66 m^3	1.2	1 x 1.99 m^3	
Direct contact rotary dryers				
Iron precipitation	1 x 157 m^2,		1 x 157 m^2,	
Manganese precipitation	1 x 5.2 m^2,		1 x 5.2 m^2,	
Struvite precipitation	1 x 110 m^2		1 x 110 m^2	
Pumps				
Iron precipitation	6 x 1400 l/min,		6 x 1400 l/min,	All pumps are PTFE lined
Mn-precipitation	6 x 1000 l/min		6 x 1000 l/min,	
Struvite precipitation	6 x 1000 l/min,		6 x 1000 l/min,	
Struvite step to WWTP	3 x 1000 l/min		3 x 1000 l/min	
Carbonate solution pump	2 x 150 l/min,		2 x 150 l/min,	
Ammonia pump	2 x 500 l/min,		2 x 500 l/min,	
Phosphoric acid pump	2 x 60 l/min		2 x 60 l/min	
Conveyors				
Conveyors from filters to dryers	3 x 25 m		3 x 25 m	
Conveyors from dryers to packing	3 x 50 m		3 x 50 m	

12 Economical aspects

12.1 Capital costs

The equipment costs are estimated using equation 11 and correlations from Towler and Sinnott (2013).

$$C_e = a + bS^n \tag{11}$$

Where C_e is the purchased equipment cost (in January 2010 in USD for carbon steel product), a and b are cost constants, S is a size parameter (for example driver power for agitator or length for a conveyor) and n is an exponent for that type of equipment. All the values are given in the book by Towler and Sinnott (2013) and the ones associated with this study are gathered to Table 29.

Table 29. Values for equipment cost calculations

Equipment	**Units for S**	**S_{lower}**	**S_{upper}**	**a**	**b**	**n**
Propeller	Drive power, kW	5.0	75	17 000	1 130	1.05
Conveyor belt 1.0 m wide	Length, m	10	500	46 000	1 320	1.0
Jacketed, agitated reactor	Volume, m^3	0.5	100	61 500	32 500	0.8
Tank with a cone roof	Capacity, m^3	10	4 000	5 800	1 600	0.7
Centrifugal pump	Flow, liters/s	0.2	126	8 000	240	0.9
Plate and frame filter	Capacity, m^3	0.4	1.4	128 000	89 000	0.5
Direct contact rotary dryer	Area, m^2	11	180	15 000	10 500	0.9

Because the prices from equation 11 are in USD for carbon steel products in 2010 they must be multiplied by material factor and converted into current value. The value conversion is done by using equation (12) presented in a process design guide distributed over a plant design course in the university by Oinas and Sarwar (2016). The material factors are also taken from the same manual and are presented in Table 30.

$$C = C_e\left(\frac{I}{I_O}\right) \tag{12}$$

,where I is the current index and I_0 is the base index. The 2010 index (base index) is taken from the design manual by Oinas and Sarwar (2016) and it is 550.8. The latest one is approximated 563.4 based on the information found on internet (Jenkins, 2017; Jenkins, 2018) Thus, the prices are multiplied with 1.023 to bring them to this day. The conversion 1 USD = 0.8588 EUR is used for the equipment prices as was used for the chemical prices.

Table 30. Material factors

Material	Pumps, blowers, etc.	Other equipment
All carbon steel	1.0	1.0
Stainless steel 316	1.8	1.6
Stainless steel 304	1.7	1.5
Rubber lined steel	1.4	1.25
Hastelloy®-C	4	4

A material factor of 4.4 for Hastelloy®-C was found from internet (Engineering Toolbox, 2007) and was rounded to 4. The costs for each equipment can be found in Appendix XV with USD prices in 2010. The total sums for each equipment category converted to euros and brought to this day are presented in Table 31.

Table 31. Equipment cost

Category	Cost (M€)
Reactors	12.97
Tanks	2.94
Filters	0.93
Dryers	1.55
Conveyors	0.50
Pumps	0.28
Total	**19.2**

It can be seen from Table 31, that the cost for the main equipment is 19 M€. The price includes the equipment itself but no installation nor engineering. The total plant capital cost can be approximated using different multipliers. The two most commonly used factors are developed by Lang and Hand (Towler and Sinnott, 2013). Here, a Lang factor of 3.63 for mixed fluids-solids processing plant is used. Thus, the total plant capital cost approximation is 19.2 M€ x 3.63 = 69.7 M€.

12.2 Operational costs

The amounts of electricity and steam are calculated as they take the biggest shares of the operating costs. Labor is also taken into account.

Electricity

Most of the electricity is used for pumping. The pump delivery power (kW) is estimated with equation 13 (Vogel, 2011).

$$P = \frac{\dot{V} * H * \rho * g}{3600 * 10^3 * \eta_{tot}} \tag{13}$$

,where $\dot{V}$ is the normal feed flow (m^3/h), H delivery head (m), ρ density (1028 kg/m^3), g gravitational acceleration (9.81 m/s^2) and η_{tot} overall efficiency (assumed 0.75).

The tops of the reactors are at around 10 m from the ground level. The delivery heads are given a value of 20 m to overcome the pressure losses of piping and fittings as well as the kinetic and static pressure differences.

Steam

Steam is used for heating the iron precipitation feed and the reactors as well as to heat the air entering the dryers. The heat transfer coefficient is considered negligible in the calculations. Thus, the equation (14) can be used to approximate steam need.

$$Q_{solution} = Q_{steam} \rightarrow \dot{m}_{solution} C_{p,solution} \Delta T = \dot{m}_{steam} \lambda_{steam} \tag{14}$$

, where the heat capacity, C_p, of solution in any point of the process is assumed 4.187 kJ/kg/°C (as for water). The heat of vaporization, λ, is dependent on the steam pressure.

The following assumptions for the process are made: 1) initial temperature of the feed from the current process is 15°C. The solution is heated in the iron precipitation step to 80°C. 2) The process pipes are insulated to minimize heat transfer with the ambient conditions. 3) There is a need for a 5°C temperature raise in the manganese precipitation step. 4) Struvite precipitation is exothermic and the heat recovered during the year neglects the heating needs, so no steam is calculated for that step.

The iron precipitation requires a lot of heating, which is why a 10-bar steam is used for that purpose. Lower, 4 bar steam can be used in manganese precipitation.

Steam need for dryers is estimated by calculating the water mass in the cake ($\dot{m}_{water}$) and how much energy is needed to evaporate that amount at specific temperature (λ_{water}). Thus, equation (14) is slightly modified to equation (15). The results are collected to Table 32.

$$\dot{m}_{water} * \lambda_{water} = \dot{m}_{steam} * \lambda_{vaporization} \tag{15}$$

Table 32. Steam consumption

Reactor	**Q** (kW)	$\boldsymbol{P_{steam}}$ (bar)	$\boldsymbol{\lambda_{steam}}$(kJ/kg)	$\boldsymbol{\dot{m}_{steam}}$ (kg/h)
Iron precipitation	12120	10	2013.56	21 660
Manganese precipitation	695	4	2132.95	1 172
Dryer	**Q** (kW)	$\boldsymbol{P_{steam}}$ (bar)	$\boldsymbol{\lambda_{steam}}$(kJ/kg)	$\boldsymbol{\dot{m}_{steam}}$ (kg/h)
Iron hydroxide	2703	4	2132.95	4 563
Manganese carbonate	107	4	2132.95	180
Struvite	1173	4	2132.95	1 980

Labor

For the proposed process route, three operators are recommended to work simultaneously with 1 supervisor. There are 5 shifts so salaries for 15 operators and 5 supervisors are taken into account in fixed labor cost calculations. The operators are paid 50 000 €/a, the supervisors 75 000 €/a. Total salary per year would then be 1 125 000 €.

Operational costs

The prices for the utilities are calculated in Table 33. The price for electricity is taken from Tilastokeskus (2018). Price for low-pressure steam is found on a master's thesis (Almgrén, 2012). It was compared to steam prices found online (Intratec, no year). They seemed to fit, and 43.09 €/t was considered a reasonable price if steam is to be purchased.

Table 33. Operational costs

Utility	**Consumption**	**Price**	**Cost**	**Yearly cost**
Electricity	73 kWh	0.08 €/kWh	5.8 €/h	50 k€
Low-pressure steam	1 172 kg/h	43 €/t	340 €/h	2 940 k€
Mid-pressure steam	21 661 kg/h	43 €/t	930 €/h	8 060 k€
Labor			130 €/h	1 130 k€
		TOTAL	1400 € /h	12 180 k€

12.3 Profitability

For the process to break-even the prices for either iron product or struvite must be almost 1.7 times as high as was estimated in Table 25 for the low ammonia use case. Other options are to lower the operational costs or to find cheaper chemicals.

The payback time for the whole process is estimated with equation (16).

$$Payback\ time = \frac{total\ investment}{annual\ profit} \tag{16}$$

For a payback time of 5 to 10 years the prices would need to raise as shown in Table 34.

Table 34. Struvite product price needed for different payback times

Payback time (years)	5	6	7	8	9	10
Total investment (M€)	69					
Annual profit (M€)	13.8	11.5	9.9	8.6	7.7	6.9
Operating hours (h/a)	8640					
Profit needed (€/h)	1597	1331	1141	998	887	799
Operational costs (€/h)	1400					
Product value – raw material margin (€/h)	2997	2731	2541	2398	2287	2199
Struvite product price needed for the margin (€/ton)	773	742	720	703	690	680
OR						
Iron product price needed for the margin (€/ton)	201	193	187	183	180	177

Few things should be noted while looking through the data in Table 34. The product prices are calculated assuming that struvite precipitation can be done in lower pH than was tested in the laboratory. However, the operational and capital costs are calculated for the process route tested in the laboratory, thus, the ammonia pumps are sized and their electricity use is approximated according to bigger flows. This most likely has only a minor effect to capital and operational costs and was not calculated again.

13 Conclusions and recommendations

In this study, a method to extract magnesium from multimetal component nickel sulfide process stream as struvite was developed. Recovery as struvite was chosen based on a techno-economic analysis of different alternatives. The method was tested in laboratory, which proved struvite precipitation possible from a case process stream with an abundance of Fe^{2+} and Mn^{2+} -ions. Their effects to struvite recovery and purity were studied. Based on the results iron and manganese removal steps are recommended. Iron removal as iron(III)hydroxide and manganese removal as manganese(II)carbonate were used in this study and they turned out to be efficient according to the ICP -analyses of the solutions. Approximately 30 % of the initial magnesium co-precipitated in iron and manganese precipitations, while 50 % of the initial magnesium was taken away as struvite. The remaining 20 % stayed in the solution after theoretical amount of phosphoric acid had been added to the solution. This refers to reactions between phosphate and other compounds such as manganese, sodium and ammonium whose amounts in the solution decreased during struvite precipitation. The amount of the impurities as well as the purity of the struvite product were not measured within the time limit of this work. However, the XRD-pattern of the sample matched very well with the literature reference pattern and was considered very pure.

The laboratory test results were used as a basis for generic process design. The total capital investment for the process route including iron, manganese and struvite precipitations is estimated to be 70 M€ with operational costs around 1 400 €/h and chemical costs of 10 000 €/h. The route used in the laboratory tests turned out not feasible with estimated product prices of 384 €/t for struvite and 100 €/t for $Fe(OH)_3$.

Struvite precipitation seemed to work in lower pH value than what was used in the proposed process route. This result could possibly lower the ammonia consumption and decrease the total chemical costs from 10 000 €/h to around 7 200 €/h. In that case, the product prices should be either 680 €/t or 177 €/t for struvite and iron hydroxide, respectively, to achieve a hardly acceptable payback time of 10 years.

In conclusion, magnesium precipitation as struvite from nickel sulfide process liquor was proved possible, rather simple and easy to implement. The precipitation can be done in mild conditions and it is rapid that results in reasonably sized equipment even for process streams with large volumes. Because struvite starts to precipitate at pH 8, precipitation should be carried out after the recovery of the primary metals. Hence, this precipitation does not disturb the current metal recovery of the plant.

The struvite precipitation step studied did not turn out feasible. However, there are several ways to improve it. First, the manganese precipitation step should be carried out more carefully to prevent manganese co-precipitation in struvite step leaving all the phosphate for struvite formation. This would increase the amount of precipitating struvite from 8.5 t/h to around 12 t/h (48 kmol/h).

Secondly, ammonium dihydrogen phosphate ($NH_4H_2PO_4$) or diammonium phosphate ($(NH_4)_2HPO_4$) are recommended to be studied as the source for both ammonium and phosphate ions instead of ammonium hydroxide and phosphoric acid to save chemical costs. The potential savings are shown in Table 35.

Table 35. Ammonium and phosphate ion source price comparison

	$NH_4H_2PO_4$	$(NH_4)_2HPO_4$	NH_4OH (25 %) + H_3PO_4 (85 %)
Approximate price (€/ton)	585	295	261 + 760
Theoretical tons needed to precipitate 48 kmol of struvite	5.5	6.4	1.7 + 4.7
Approximate price for ammonium/phosphate ion source(s) (€)	3 200	1 900	4 015
Struvite production (t)	11.8		
Price for produced struvite, when price 386 €/t	4 550 €		

According to the data in Table 35 both alternative compounds provide cheaper chemical costs than ammonium hydroxide and phosphoric acid combination. Here, it shows economic potential for the studied precipitation method as well but one should remember that this does not include pH control costs, which are also needed for ammonium dihydrogen and diammonium phosphates. However, the most promising option in the table, diammonium phosphate, only releases one hydrogen to the solution when diluted, and so, it will consume only half the amount of the pH control solution used in the studied struvite precipitation step.

Third option to improve the feasibility of the process is in the remaining solution. The sulfate and ammonium content are very high and show potential for another product, ammonium sulfate, which is a common fertilizer sold for around 100 €/t. Based on the laboratory test results there is potential for around 11 t/h ammonium sulfate production for extra profit.

By implementing all the three improvements, struvite recovery may turn into a very profitable process. Leaving ammonium sulfate aside from the calculations and subtracting the operational costs the total income from the now improved proposed process route per hour would be roughly 2 000 € meaning a payback time of under five years and 21 M€ annual income afterwards!

In addition, the laboratory test results show the whole method has features that can affect the overall profitability of the plant. For example, calcium content decreased by 50 %, which lowers the precipitation of gypsum in the water treatment step and results in lower waste amounts. The sulfate and sodium amounts decreased along the process route as well.

Based on the observations made throughout this study the following recommendations are given to make the proposed process route feasible.

- Struvite precipitation
    - Further studies on struvite precipitation at pH 8.6 - 8.8 from iron and manganese poor solution.
    - Studying the use of diammonium phosphate as the ammonium and phosphate ion source.
- Removal of manganese
    - Purification of the solution of manganese prior to prevent co-precipitation of manganese compound in struvite precipitation so that more magnesium could be recovered as struvite.
    - Finding an alternative for sodium hydrogen carbonate to further reduce the sodium content in the remaining solution.
- Other potential options
    - Study on ammonium phosphate recovery from the remaining solution.
    - Hydration/dehydration cycle of struvite for lower transportation costs of the product.

References

Ali, M.I., 2005, *Struvite crystallization from nutrient rich wastewater,* James Cook University.

Ali, M.I. and Schneider, P.A., 2008. “An approach of estimating struvite growth kinetic incorporating thermodynamic and solution chemistry, kinetic and process description”, *Chemical Engineering Science,* vol. 63, no. 13, pp. 3514-3525, https://doi.org/10.1016/j.ces.2008.04.023.

Almgrén, M, 2012, *Prosessihöyryn tuotannon kustannusoptimointi*, available from: http://urn.fi/URN:NBN:fi-fe201210029312.

Antila, A., Koskentalo, T., Toivonen, J. and Yliruokanen, I., 2000. *Analyyttisen kemian harjoitustyöt : ionien reaktioita.*11. korj. p. ed. Helsinki: Otatieto ISBN 951-672-298-9.

Avedesian, M. and Baker, H., 1999. *Magnesium and magnesium alloys.* Materials Park (OH): ASM International.

Bailey, R.P., Quebec Metallurgical Industries Ltd., 1959. *Method for extracting nickel from laterite ores.* U.S. Patent 2,899,300.

Bhatti, T.M., Vuorinen, A.and Tuovinen, O.H., 2012. ”Dissolution of non-sulfide phases during the chemical and bacterial leaching of a sulfidic black schist”, *Hydrometallurgy*, vol. 117-118, pp. 32-35, https://doi.org/10.1016/j.hydromet.2012.01.008.

Bhuiyan, M.I.H., Mavinic, D.S. and Beckie, R.D., 2007. A solubility and thermodynamic study of struvite. *Environmental Technology*, vol. 28, no. 9, pp. 1015-1026. http://dx.doi.org/10.1080/09593332808618857

Bouropoulos, N.C. and Koutsoukos, P.G., 2000. *“*Spontaneous precipitation of struvite from aqueous solutions*”*, *Journal of Crystal Growth,* vol. 213, no. 3-4, pp. 381-388, https://doi.org/10.1016/S0022-0248(00)00351-1.

British Geological Survey, 2017. *World Mineral Production 2011-2015.* Keyworth, Nottingham: British Geological Survey ISBN 978-0-85272-868-0.

British Geological Survey, 2013. *World mineral production 2007-2011.* Keyworth, Nottingham: British Geological Survey ISBN 978-0-85272-757-7.

British Geological Survey, 2008. *World mineral production 2002-06.* Keyworth, Nottingham: British Geological Survey ISBN 978-0-85272-615-0.

British Geological Survey., 2003. *World Mineral Statistics 1997-2001: production: exports: imports.* Keyworth, Nottingham: British Geological Survey ISBN 0-85272-451-9.

Burke, S.P. and Banwart, S.A., 2002. *“*A geochemical model for removal of iron(II)(aq) from mine water discharges*”*, *Applied Geochemistry,* vol. 17, no. 4, pp. 431-443, https://doi.org/10.1016/S0883-2927(01)00092-0.

Chapman, A., Arendorf, J., Castella, T., Thompson, P., Willis, P., Espinoza, L.T., Klug, S. and Wichmann, E., 2013, *Study on Critical Raw Materials at EU level*, Dec 16 2013.

Cheng, C.Y., Boddy, G., Zhang, W., Godfrey, M., Robinson, D.J., Pranolo, Y., Zhu, Z. and Wang, W., 2010. “Recovery of nickel and cobalt from laterite leach solutions using direct solvent extraction: Part 1-selection of a synergistic SX system*”*, *Hydrometallurgy*, vol. 104, no. 1, pp. 45-52. https://doi.org/10.1016/j.hydromet.2010.04.009.

Cheng, C.Y., 2000. “Purification of synthetic laterite leach solution by solvent extraction using D2EHPA”, *Hydrometallurgy,* vol. 56, no. 3, pp. 369-368, https://doi.org/10.1016/S0304-386X(00)00095-5.

Cole, G.S., 2016. Summary of “Magnesium Vision 2020: A North American Automotive Strategic Vision for Magnesium”. In: S.N. Mathaudu, A.A. Luo, N.R. Neelameggham, E.A. Nyberg and W.H. Sillekens eds., *Essential Readings in Magnesium Technology* Cham: Springer International Publishing, pp. 35-40 ISBN 978-3-319-48099-2. https://doi.org/10.1007/978-3-319-48099-2_5.

Cross, H.E., Krieger, W., Anschutz, E., Reh, L. and Hirsch, M., GEA Group AG, 1978. *Process of producing magnesia with sulfuric acid recycle*, U.S. Patent 4,096,235.

Dean, J.A. and Lange, N.A., 1985. *Lange's handbook of chemistry.* 13. ed ed. New York: McGraw-Hill ISBN 0-07-016192-5.

DESA/UNSD., 2017. *United Nations Comtrade database,* https://comtrade.un.org/.

Doyle, J.D. and Parsons, S.A., 2002. “Struvite formation, control and recovery”, *Water Research,* vol. 36, no. 16, pp. 3925-3940, https://doi.org/10.1016/S0043-1354(02)00126-4.

Eghtesad, M., 2016. *Optimization of magnesium removal from hydrometallurgical leach liquors by struvite formation.* University of British Columbia.

El Rafie, S., Hawash, S. and Shalaby, M.S., 2013. Evaluation of struvite precipitated from chemical fertilizer industrial effluents. *Adv.Appl.Sci.Res*, vol. 4, no. 1, pp. 113-123.

Engineering ToolBox, (2007). Piping Materials and Cost Ratios. Available at: https://www.engineeringtoolbox.com/piping-materials-cost-ratios-d_864.html [Accessed 20.2.2018].

Etter, B., Tilley, E., Khadka, R.and Udert, K.M., 2011.“Low-cost struvite production using source-separated urine in Nepal”, *Water Research*, vol. 45, no. 2, pp. 852-862, https://doi.org/10.1016/j.watres.2010.10.007.

Faust, G.T. and Fahey, J.J., 1962. The serpentine-group minerals, U.S. Government Printing Office, Washington.

Food and Agriculture Organization of the United Nations, (FAO), 2017. *FAOSTAT.* Nov 2, Available from: http://www.fao.org/faostat/en/#data/RF.

Future Market Insights, 2018. *Magnesium Carbonate Market: Global Industry Analysis (2012 - 2016) and Opportunity Assessment (2017 - 2027).* Jan 29 2018, [viewed Jan 20, 2018] Abstract only. Available through: https://www.futuremarketinsights.com/reports/magnesium-carbonate-market.

Future Market Insights, 2016a. *Magnesium Hydroxide Market: Global Industry Analysis and Opportunity Assessment 2016 – 2026,* June 9 2016, [viewed Sep 20, 2017], Abstract only. Available through: https://www.futuremarketinsights.com/reports/magnesium-hydroxide-market.

Future Market Insights, 2016b. *Magnesium Metal Market: Global Industry Analysis and Opportunity Assessment 2016 - 2026.* May 26 2016, [viewed Jan 31, 2018], Abstract only. Available through: https://www.futuremarketinsights.com/reports/magnesium-metal-market.

Gupta, M. and Nai, M.L.S., 2011. *Magnesium, Magnesium Alloys, and Magnesium Composites.* Hoboken: Wiley Available from: http://ebookcentral.proquest.com/lib/aalto-ebooks/detail.action?docID=675046 ISBN 9780470905081.

Halinen, A., 2015. *Heap Bioleaching of Low-grade Multimetal Sulphidic Ore in Boreal Conditions.* Tampere University of Technology ISBN 978-952-15-3630-4.

Haynes, W, Lide, D, & Bruno, T 2017, *CRC Handbook Of Chemistry And Physics, 97Th Edition*, Boca Raton, Florida: CRC Press, eBook Collection (EBSCOhost), EBSCO*host*, [viewed 13 Sep 2017].

Herbert, K., American Metal Climax Inc., 1969, *Treatment of nickeliferous oxidic materials for the recovery of nickel values.* U.S. Patent 3,466,144

Huang, H., Mavinic, D.S., Lo, K.V. and Koch, F.A., 2006. Production and Basic Morphology of Struvite Crystals from a Pilot-Scale Crystallization Process. *Environmental Technology*, vol. 27, no. 3, pp. 233-245. https://doi.org/10.1080/09593332708618637

IHS Markit, 2017. *Magnesium Oxide and Other Magnesium Chemicals.* June 2017, [viewed Sep 20, 2017], Abstract only. Available through: https://www.ihs.com/products/magnesium-oxide-chemical-economics-handbook.html.

Industrial Specialities Mfg., 2018, Chemical Compatibility Chart, Version 11, available from: https://www.industrialspec.com/resources/chemical-compatibility.

InfoMine, 2017. *Historical Magnesium Prices and Price Chart.* May 31, [viewed Sep 19, 2017]. Available from: http://www.infomine.com/investment/metal-prices/magnesium/all/.

International Trade Centre. *Trade Map*, https://trademap.org/Index.aspx.

Intratec, no year, Steam Price History & Forecast, available from: https://www.intratec.us/chemical-markets/steam-prices

Jenkins, S., 2018. *2017 CEPCI updates: Dec. (prelim.) and Nov. (final).* Feb 20, Available from: http://www.chemengonline.com/2017-cepci-updates-dec-prelim-and-nov-final/.

Jenkins, S., 2017. *Current economic trends: CEPCI January (prelim) and December (final).* Mar 17, Available from: http://www.chemengonline.com/current-economic-trends-cepci-january-prelim-and-december-final/.

Jia, G., Zhang, H., Krampe, J., Muster, T., Gao, B., Zhu, N.and Jin, B., 2017. “Applying a chemical equilibrium model for optimizing struvite precipitation for ammonium recovery from anaerobic digester effluent”, *Journal of Cleaner Production,* vol. 147, pp. 297-305, https://doi.org/10.1016/j.jclepro.2017.01.116.

Kobayashi, S., Idemitsu Kosan Co. Ltd., 1980. *Process for reductive calcining of magnesium sulfate.* U.S. Patent 4,225,573

Kramer, D.A., 2010. Magnesium and Magnesium Alloys. In Kirk-Othmer Encyclopedia of Chemical Technology, (Ed.). doi:10.1002/0471238961.1301071423091219.a01.pub3

Kramer, D.A., 2004. Magnesium Compounds. In Kirk-Othmer Encyclopedia of Chemical Technology, (Ed.). doi:10.1002/0471238961.1301071410010311.a01.pub3

Kyle, J., 2010, Nickel laterite processing technologies – where to next? In: *ALTA 2010 Nickel/Cobalt/Copper Conference,* 24 – 27 May, Perth, Western Australia.

Lewis, A.E., 2010. Review of metal sulphide precipitation. *Hydrometallurgy*, vol. 104, no. 2, pp. 222-234. https://doi.org/10.1016/j.hydromet.2010.06.010.

Lin, Q., Gu, G., Wang, H., Wang, C., Liu, Y., Zhu, R.and Fu, J., 2016. "Separation of manganese from calcium and magnesium in sulfate solutions via carbonate precipitation”, *Transactions of Nonferrous Metals Society of China,* vol. 26, no. 4, pp. 1118-1125, https://doi.org/10.1016/S1003-6326(16)64210-3.

Loukola-Ruskeeniemi, K. and Heino, T., 1996. ”Geochemistry and genesis of the black shale-hosted Ni-Cu-Zn deposit at Talvivaara, Finland”, *Economic Geology*, vol. 91, no 1, pp. 80-110, http://dx.doi.org/10.2113/gsecongeo.91.1.80

Market Research Future., 2017. *Global Magnesium Sulphate Market Research Report- Forecast to 2027.* Feb 2017, [viewed Dec 11, 2017] Abstract only. Available through: https://www.marketresearchfuture.com/reports/magnesium-sulphate-market-2282.

McDonald, R.G. and Whittington, B.I., 2008. “Atmospheric acid leaching of nickel laterites review: Part I. Sulphuric acid technologies”, *Hydrometallurgy*, vol. 91, no. 1-4, pp. 35-55, https://doi.org/10.1016/j.hydromet.2007.11.009.

Monhemius, A.J., 1987. Treatment of laterite ores of nickel to produce ferronickel, matte or precipitated sulphide. *Extractive Metallurgy of Nickel*, pp. 51-75.

Mudd, G.M., 2009, Nickel sulfide versus laterite: the hard sustainability challenge remains. In: *Proc. 48th Annual Conference of Metallurgists, Canadian Metallurgical Society,* Sudbury, Ontario, Canada, 23–26 August 2009.

Neelameggham, N. R. and Brown, B. (2013). Magnesium. In *Critical Metals Handbook*, G. Gunn (Ed.). doi:10.1002/9781118755341.ch11

Ohlinger, K.N., Young, T.M.and Schroeder, E.D., 1998. “Predicting struvite formation in digestion”, *Water Research,* vol. 32, no. 12, pp. 3607-3614, https://doi.org/10.1016/S0043-1354(98)00123-7.

Oinas, P. and Sarwar, G., 2016, Process Design Guide, *CHEM-E7200 Design Project in Chemical Engineering*, Aalto University, unpublished.

Picard, F. and Fournier, J., Alliance Magnésium, 2014. *Process for treating magnesium-bearing ores.* WO Patent 2014/029031(A1).

Pöyry Finland Oy, 2017. *Terrafame Oy. Ympäristövaikutusten arviointiselostus 18.8.2017.*

Prater, J., 2015. “Improved production of magnesium ammonium phosphate (struvite) from landfill leachate 2014 - Final report”, *College of Natural Resources University of Wisconsin-Stevens Point*, University of System Solid Waste Research Program. [viewed 2.11.2017] Available from: https://www.semanticscholar.org/paper/Improved-Production-of-Magnesium-Ammonium-Phosphate/9e7824b3f1ddf92ab781f3830c291440516a3b1b?tab=abstract

Pundsack, F.L., Johns Manville Corp., 1967. *Recovery of silica, iron oxide and magnesium carbonate from the treatment of serpentine with ammonium bisulfate.* U.S. Patent 3,338,667

Putz, H. and Brandenburg, K., No year, *Match! - Phase Identification from Powder Diffraction, Crystal Impact, Candidate List basics.* Available from: http://www.crystalimpact.com/match/help/idh_candidate_list_basics.htm.

Qin, W., Zhen, S., Yan, Z., Campbell, M., Wang, J., Liu, K.and Zhang, Y., 2009. ”Heap bioleaching of a low-grade nickel-bearing sulfide ore containing high levels of magnesium as olivine, chlorite and antigorite”, *Hydrometallurgy*, vol. 98, no. 1-2, pp. 58-65, https://doi.org/10.1016/j.hydromet.2009.03.017.

Rahaman, M.S., Ellis, N. and Mavinic, D.S., 2008. Effects of various process parameters on struvite precipitation kinetics and subsequent determination of rate constants. *Water Sci Technol*, vol. 57, no. 5, pp. 647. https://doi.org/10.2166/wst.2008.022.

Rahman, M.M., Salleh, M.A.M., Rashid, U., Ahsan, A., Hossain, M.M.and RA, C.S., 2014. “Production of slow release crystal fertilizer from wastewaters through struvite crystallization – A review”, *Arabian Journal of Chemistry,* vol. 7, no. 7, pp. 139-155, https://doi.org/10.1016/j.arabjc.2013.10.007.

Ramlogan, M.V. and Rouff, A.A., 2016. An investigation of the thermal behavior of magnesium ammonium phosphate hexahydrate. *Journal of Thermal Analysis and Calorimetry*, vol. 123, no. 1, pp. 145-152, https://doi.org/10.1007/s10973-015-4860-1.

ReportsnReports, 2016. *Global Magnesium Oxide Industry 2016 market Research Report.* QYResearch Group, Nov 2016, [viewed Sep 20, 2017], Abstract only. Available through: http://www.reportsnreports.com/reports/460272-global-magnesium-oxide-industry-2016-market-research-report.html

Riekkola-Vanhanen, M., 2013. Talvivaara mining company – From a project to a mine. *Minerals Engineering*, vol. 48, pp. 2-9. https://doi.org/10.1016/j.mineng.2013.04.018.

Riekkola-Vanhanen, M., 2010. Talvivaara Sotkamo mine-bioleaching of a polymetallic nickel ore in subarctic climate. *Nova Biotechnol*, vol. 10, no. 1, pp. 7-14.

Roskill, 2016. *Magnesium Metal: Global Industry Markets.* July 6 2016, [viewed Sep 20, 2017], Abstract only. Available through: https://roskill.com/product/magnesium-metal-global-industry-markets-outlook/.

Sangren, P., Berglind, B., Modich, S., 2015, *Basics in Minerals Processing*, 10th edition, available from: http://www.metso.com/miningandconstruction/mm_segments.nsf/WebWID/WTB-041213-2256F-43973?OpenDocument#.WqLMxug_-00

Sarkar, A.K., 1991. “Hydration/dehydration characteristics of struvite and dittmarite pertaining to magnesium ammonium phosphate cement systems”, *Journal of Materials Science*, vol. 26, no. 9, pp. 2514-2518. https://doi.org/10.1007/BF01130204.

Scheidema, M., 2015. *The reaction mechanism and operating window for the decomposition of hydrated magnesium sulfate under reducing conditions.* Aalto University, Available from: http://urn.fi/URN:ISBN:978-952-60-6347-8[urn] Aaltodoc. ISBN 9789-526063478(ELECTRONIC).

Seymour, D., 2009. Can nutrient recovery be a financially sustainable development objective. *Kennedy/Jenks Consultants*.

Shu, L., Schneider, P., Jegatheesan, V.and Johnson, J., 2006, “An economic evaluation of phosphorus recovery as struvite from digester supernatant”, *Bioresource Technology*, vol. 97, no. 17, pp. 2211-2216. https://doi.org/10.1016/j.biortech.2005.11.005.

Sudol, S., 2005. *The Thunder from Down Under.* Aug 1, [viewed Oct 2, 2017]. Available from: http://www.canadianminingjournal.com/features/the-thunder-from-down-under/.

Tilastokeskus, 2018, *Tilasto:Energian hinnat. ISSN=1799-7984. 4. Vuosineljännes 2016, Liitekuvio 5. Sähkön hinta kuluttajatyypeittäin.* Available from: http://www.stat.fi/til/ehi/2016/04/ehi_2016_04_2017-03-08_kuv_005_fi.html

Tilley, E., Atwater, J. and Mavinic, D., 2008, "Recovery of struvite from stored human urine", *Environmental Technology*, vol. 29, no. 7, pp. 797-806. http://dx.doi.org/10.1080/09593330801987129

Towler, G. and Sinnott, R.K., 2013, *Chemical Engineering Design - Principles, Practice and Economics of Plant and Process Design (2nd Edition).* eISBN 978-0-08-096660-1 Available from: https://app.knovel.com/hotlink/toc/id:kpCEDPPEP4/chemical-engineering/chemical-engineering

U.S. Geological Survey, 2017. *Mineral commodity summaries 2017.* Reston, Virginia: U.S. Geological Survey, Available through: https://minerals.usgs.gov/minerals/pubs/mcs/.

Vogel, G. H., 2013. Process Development, 2. Evaluation. In Ullmann's Encyclopedia of Industrial Chemistry, (Ed.). doi:10.1002/14356007.o22_o01

White, C. and Berube, M., Noranda Inc., 2000. *Method for the production of a high-purity concentrated magnesium chloride solution by acid leaching and neutralization.* WO Patent 2000/017408(A1)

Willis, B., 2007, Downstream processing options for nickel laterite heap leach liquors. In: *ALTA 2007 Nickel/Cobalt 12 Conference*, ALTA Metallurgical Services Perth, Australia

Yetilmezsoy, K., Ilhna, F., Kocak, E.and Akbin, H.M., 2017. "Feasibility of struvite recovery process for fertilizer industry: A study of financial and economic analysis", *Journal of Cleaner Production*, vol. 152, pp. 88-102, https://doi.org/10.1016/j.jclepro.2017.03.106.

Zambrano, A.R., Hanna Mining Co., 1981. *Production of high purity and high surface area magnesium oxide.* U.S. Patent 4,298,379A.

Zhang, W., Cheng, C. and Pranolo, Y., 2010. Investigation of methods for removal and recovery of manganese in hydrometallurgical processes. *Hydrometallurgy*, vol. 101, no. 1-2, pp. 58-63, https://doi.org/10.1016/j.hydromet.2009.11.018.

APPENDIX I – Chemical prices

		prices from 2016	0.0139	prices from 2017	0.8588		NOTES
Compound name	**Chemical formula**	**Price per kg INR**	**Price per kg EUR**	**Price per kg USD**	**Price per kg EUR**	**Average price**	
-	-	www.zauba.com	1 INR = 0.0139 EUR	www.alibaba.com	1 USD = 0.8588 EUR	EUR / ton	
Ammonia	NH_3 *(anhydrous)*	14.00	0.19	0.25	0.21	204.65	anhydrous
Ammonium bisulfate	$(NH_4)HSO_4$		0.00		0.00	0.00	
Ammonium dihydrogen phosphate	$NH_4H_2PO_4$	41.00	0.57	0.70	0.60	585.53	also known as MAP
Ammonium hydroxide	NH_4OH	16.00	0.22	0.35	0.30	261.49	sold as 25% solution
Ammonium sulfate	$(NH_4)_2SO_4$	10.00	0.14	0.13	0.11	123.18	
Carbon dioxide	CO_2		0.00		0.00	0.00	
Chlorine	Cl_2		0.00		0.00	0.00	
Magnesium	Mg (s)	157.00	2.18	2.20	1.89	1930.00	>99.8 Purity ingot
Magnesium carbonate	$MgCO_3$	65.00	0.90	0.75	0.64	773.80	
Magnesium hydroxide	$Mg(OH)_2$	35.00	0.49	1.50	1.29	887.35	
Magnesium oxide	MgO	35.00	0.49	0.20	0.17	329.13	
Magnesium sulfate	$MgSO_4$	32.00	0.44	0.40	0.34	394.16	anhydrous
Magnesium sulfate	$MgSO_4 \cdot 7\ H_2O$	12.00	0.17	0.09	0.08	122.05	heptahydrate
Phosphoric acid	H_3PO_4	63.00	0.88	0.75	0.64	759.90	sold as 85% solution
Struvite	$MgNH_4PO_4 \cdot 6\ H_2O$		0.00	0.45	0.39	386.46	
Sulfur dioxide	SO_2		0.00		0.00	0.00	
Sulfuric acid	H_2SO_4	2.00	0.03	0.10	0.09	56.84	
Oxygen	O_2						
Water	H_2O		0.00		0.00	0.00	
Carbon source	C						

APPENDIX II – Amounts of raw materials and by-products per one ton of product

Compound name	**Chemical formula**	**Molar mass**	**Kilograms needed for 1 ton of**					**Kilograms produced per 1 ton of**				
-	-	g/mol	Struvite	MgCO3	Mg(s)	MgO	MgSO4	Struvite	MgCO3	Mg(s)	MgO	MgSO4
Ammonia	NH_3 *(anhydrous)*	17.03	208.20									
Ammonium bisulfate	$(NH_4)HSO_4$	115.11										
Ammonium dihydrogen phosphate (MAP)	$NH_4H_2PO_4$	115.03										
Ammonium hydroxide	NH_4OH	35.04		831.18								
Ammonium sulfate	$(NH_4)_2SO_4$	132.20						538.68	1567.89			
Carbon dioxide	CO_2	44.01		521.98								
Chlorine	Cl_2	70.91			2917.34					2917.34		
Magnesium (>99.8%)	Mg (s)	24.31										
Magnesium carbonate	$MgCO_3$	84.31							1000.00			
Magnesium hydroxide	$Mg(OH)_2$	58.32										
Magnesium oxide	MgO	40.30			1658.28							
Magnesium sulfate (anhydrous)	$MgSO_4$	120.37	490.48	1427.59	4952.31	2986.42						
Magnesium sulfate (heptahydrate)	$MgSO_4 \cdot 7\ H_2O$	246.48										
Phosphoric acid	H_3PO_4	97.99	399.31									
Struvite	$MgNH_4PO_4 \cdot 6\ H_2O$	245.41						1000.00				
Sulfur dioxide	SO_2	64.07									1589.55	
Sulfuric acid	H_2SO_4	98.10										
Oxygen	O_2	32.00									396.98	
Water	H_2O	18.02	440.46						213.67			
Carbon source	C	12.01			494.14							

APPENDIX III – Economic potential calculations

ECONOMIC POTENTIAL

	MgSO4 in solution
Magnesium content (g/l)	15
MgSO4 content	15/24.305*70.56664
g of MgSO4 / l	43.55
,which is times Mg	2.90
volume flow m3/h	350
magnesium sulfate kg/h	15242.74

	$MgSO_4$ (aq)	to	$MgSO_4$ (s)
m	15242.74	recovery rate	12194.19
M	120.37	80.00 %	120.37
n	126.63	profit	101.31
price	already in solution	4806.46	4806.46

	$MgSO_4$ (s)	to	MgO(s)	SO_2(g)	1/2 O_2 (g)
m	12194.19	recovery rate	3674.37	5841.60	1458.81
M	120.37	90.00 %	40.30	64.07	32.00
n	101.31	profit	91.18	91.18	45.59
	gathered from previous step	1209.34	1209.34	0.00	0.00

	MgO (s)	C	Cl_2(g)	to	Mg(s)	Cl_2(g)	CO_2(g)
m	3674.37	1095.02	6465.24	recovery rate	2216.47	6465.24	4012.63
M	40.30	12.01	70.91	90.00 %	24.31	70.91	44.01
n	91.18	91.18	91.18	profit	91.18	91.18	91.18
price	gathered from previous step		recirculated	4277.79	4277.79	recirculated	

	$MgSO_4$ (aq)	CO_2 (g)	2 NH_4OH	to	MgCO3	$(NH_4)_2SO_4$	H_2O
m	15242.74	5573.09	8874.40	recovery rate	9608.74	15066.72	2053.72
M	120.37	44.01	35.04	90.00 %	84.31	132.20	18.02
n	126.63	126.63	253.26	profit	113.97	113.97	113.97
price	already in solution		9282.27	8.82	7435.24	1855.84	

	$MgSO_4$ (aq)	3 NH_3	H_3PO_4	6 H_2O	to	Struvite	$(NH_4)_2SO_4$
m	15242.74	6469.65	12408.71	13691.50	recovery rate	29523.02	15903.76
M	120.37	17.03	97.99	18.02	95.00 %	245.41	132.20
n	126.63	379.90	126.63	759.79	profit per hour	120.30	120.30
price	already in solution	1324.01	11093.39	already in solution	951.01	11409.46	1958.95

APPENDIX IV – Operational costs

STRUVITE ROUTE

PROFIT IF MAGNESIUM IONS IN LIQUID TO STRUVITE			COSTS IF MAGNESIUM IONS IN LIQUID CONVERTED TO STRUVITE		
Volume flow	350	m3/h	Ammonia needed	6470.2	kg/hour
Mg content	15	g/dm3	Phosphoric acid need	12409.6	kg/hour
Mg content per hour in the flow (kg)	5250	kg/h			
Magnesium sulfate in solution	15242.7	kg/h	Phosphoric acid sold as 85% liquid		
			The exact need is then the phosphoric acid need divided by 0.85.		
MgSO4 + 3 NH3 + H3PO4 + 6 H2O --> Struvite + (NH4)2SO4			kg of 85% H3PO4 solution	14599.6	
Recovery efficiency	95.00 %		Prices		
			Ammonia	1324.1	€/hour
Struvite recovery	29523.6	kg	Phosphoric acid	11094.2	€/hour
	11409.7	€/hour			
			total		
Ammonium sulfate recovery	15903.7	kg	profit per hour	950.3	€
	1958.9	€/hour	profit per year	8.3	M€

$MgCO_3$ ROUTE

PROFIT IF MAGNESIUM IONS IN LIQUID TO MAGNESIUM CARBONATE			COSTS IF MAGESIUM IONS IN LIQUID CONVERTED TO MAGNESIUM CARBONATE		
Volume flow	350	m3/h	Ammonium hydroxide need	8874.7	
Mg content	15	g/dm3	Carbon dioxide need	5573.3	
content per hour in the flow (kg)	5250	kg			
Magnesium sulfate in solution	15242.7	kg/h	Ammonium hydroxide price for tonne of 25% solution.		
2 NH4OH + CO2(g) + MgSO4 --> MgCO3 + (NH4)2SO4 + H20			The exact need is then four-times the 100% ammonium hydroxide need		
			kg of 25% NH4OH solution	35498.8	
Recovery efficiency	90.00 %				
			Prices		
Magnesium carbonate recovery	9609.5	kg	25% NH4OH solution	9282.6	€/hour
	7435.8	€/hour	Carbon dioxide	-	€/hour
			total		
Ammonium sulfate recovery	15066.6	kg	profit per hour	9.1	€
	1855.8	€/hour	profit per year	0.1	M€

$MgSO_4$ CRYSTALLIZATION

Volume flow	350	m3/h	HEATING OF SOLUTION		
Density of solution	1000	kg/dm3	Temperature change from 10-100 C	90	C
Mass flow	350000	kg/h	Energy needed for heating the solution	113049000.0	kJ
Magnesium content in solution	15	g/l		31.4	MWh
Magnesium mass in solution	5250	kg	EVAPORATION		
Magnesium sulfate in solution	15242.7	kg/h	Energy needed to evaporate water	677100000	kJ
Assumption for water to be evaporated	300000.0	kg/h		188.1	MWh
Cp of water dominant	4.187	kJ/kg			
Latent heat of evaporation	2257	kJ/kg	total energy need	219.5	MWh
			cost of electricity	64.84	€/Mwh
Recovery rate	90.00 %		price	14231.5	€/hour
			total		
Magnesium sulfate crystal recovery	13718.5	kg/hour	profit per hour (heptahydrate)	-12557.2	€
if as heptahydrate	1674.3	€/hour	profite per hour (anhydrous)	-8824.2	€
if as anhydrous	5407.3	€/hour	profit per year (anhydrous)	-77.3	M€

APPENDIX IV – Operational costs

Thermal decomposition of MgSO4 to MgO

Volume flow	350	m3/h
Mass flow	350000	kg/h
Magnesium sulfate in solution	15242.7	kg
Recovery rate	90.00 %	
Mass of crystals (anhydrous)	13718.46838	kg
MgSO4 moles	113973.0	mol
Standard enthalpy of formation ΔH°f	-1284.9	kJ/mol

Solid phase heat capacity

$C_p^\circ = A + B*t + C*t^2 + D*t^3 + E/t^2$

A	75.83207
B	111.722
C	-39.68842
D	5.129835
E	-0.83257

http://webbook.nist.gov/cgi/cbook.cgi?ID=C7487889&Mask=2&Type=JANAFS&Plot=on#JANAFS

Calculating the heating of MgSO4 crystals. It is assumed that the temperature is 200C in the beginning and they are heated to 1100 (decomposition temperature)

C	K	t (K/1000)	J/mol*K	Cp	kJ
200	473.15	0.47315	116.63	120.95	1378456.7
300	573.15	0.57315	125.26	129.02	1470480.7
400	673.15	0.67315	132.78	136.12	1551427.0
500	773.15	0.77315	139.46	142.46	1623604.9
600	873.15	0.87315	145.45	148.13	1688303.4
700	973.15	0.97315	150.82	153.23	1746369.8
800	1073.15	1.07315	155.64	157.80	1798437.6
900	1173.15	1.17315	159.95	161.88	1845028.8
1000	1273.15	1.27315	163.81	165.53	1886602.2
1100	1373.15	1.37315	167.25	**total**	14988711.1

	kJ
Calculating the energy needed for MgSO4 crystal decomposition. The energy needed is the additive inverse of the standard enthalpy of formation.	146443846.5

Magnesium oxide recovery rate	90.00 %	
Magnesium oxide recovered from crystals	4134.3	kg/hour
	1360.7	€/hour

total energy need	161432557.6	kJ
	44.8	MWh
cost of eletricity	64.8	€/MWh
total cost	2907.6	€/hour
total		
profit per hour	-1546.9	€/hour
profit per year	-13.6	M€/year

MAGNESIUM ROUTE

PROFIT IF MAGNESIUM IONS IN LIQUID TO MAGNESIUM METAL

Volume flow	350	m3/h
Mg content	15	g/dm3
Mg content per hour in the flow (kg)	5250.0	kg
Magnesium sulfate in solution	15242.7	kg
MgSO4-->MgO-->MgCl2-->Mg(s)		
MgO recovery from first step (100% eff.)	5104.0	kg
Mg(s) recovery from second step (100%)	3077.9	kg
MgSO4 crystallization efficiency	90.00 %	
MgSO4 --> MgO conversion eff.	90.00 %	
MgO to MgCl2 to Mg efficiency	90.00 %	
	72.90 %	
Mg (s) recovery	2243.8	kg
	4330.5	€/hour

COSTS IF MAGNESIUM IONS IN LIQUID CONVERTED TO MAGNESIUM METAL

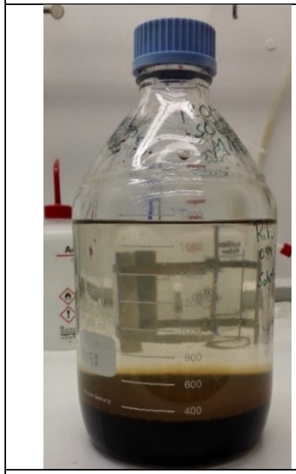
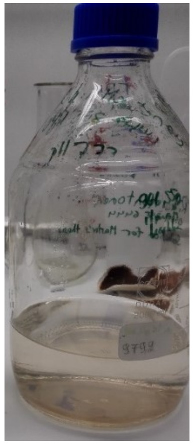
Electrolysis		
Actual potential	2.7	V
Cell efficiency	80.00 %	
n(Mg2+)	92318.09	mol
F	96485	As/mol
t	3600	s
z	2.00	
I	4948506.14	A
P	13360966.57	W / hour
Actual P	16.70	MWh
Cost of electricity	64.84	€/MWh
cost of electrolysis	1082.91	€/hour
total		
	-13891.4	€ /hour
	-121.7	M€/year

MgSO4 crystallization	-14231.5	€(hour
MgSO4 thermal decomposition	-2907.6	€/hour
MgO conversion to MgCl2	-	€/hour
Mg (s) electrolysis	-1082.9	€/hour
total	-18221.9	€/hour

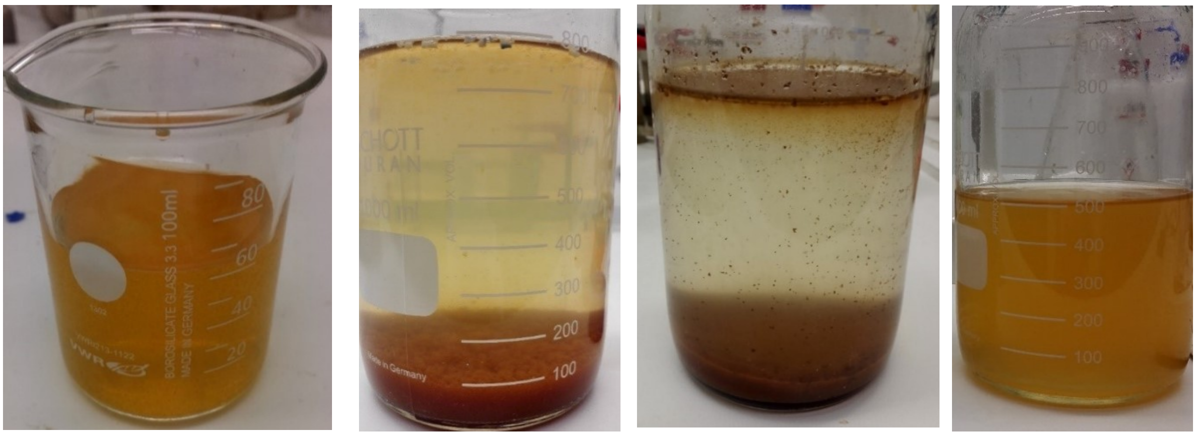
OTHER COSTS

Sulfur dioxide gas treatment	-	€/hour
Carbon source	-	€/hour
Chloride recirculation	-	€/hour
Carbon monoxide treatment	-	€/hour
total	0	

APPENDIX V – Pictures of the case solution during and after the iron precipitation step

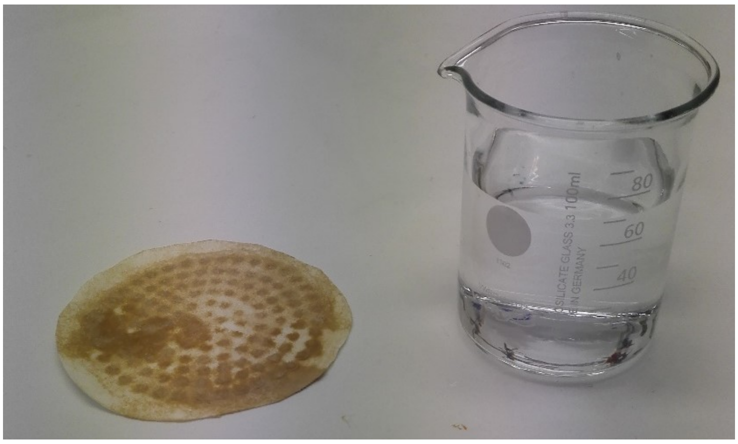
			
At the beginning (pH 3.29)	After raising pH to 7.75	30 minutes at pH 7.75	Wet precipitate gathered from the solution
			
Solution 87 hours after the reaction and one (failed) filtration	Solution from filtration of the 87 hour solution	Solution after all (six) the filtration cycles	Precipitate after drying

APPENDIX VI – Pictures from manganese precipitations



Pictures from left to right: 1. Manganese hydroxide precipitation underway, 2. Solution in the storage bottle after 30 minutes, 3. Solution in the strorage bottle after 20 hours, 4. Solution in the storage bottle after final (eighth) precipitation

Precipitates from left to right: 1. Precipitate from the first filtration, 2. Precipitate from the second filtration, 3. Precipitate from the fifth filtration, 4. Precipitate from the final (eighth) precipitation.



Precipitate and solution from the carbonate precipitation test.

APPENDIX VII – Pictures from struvite precipitations

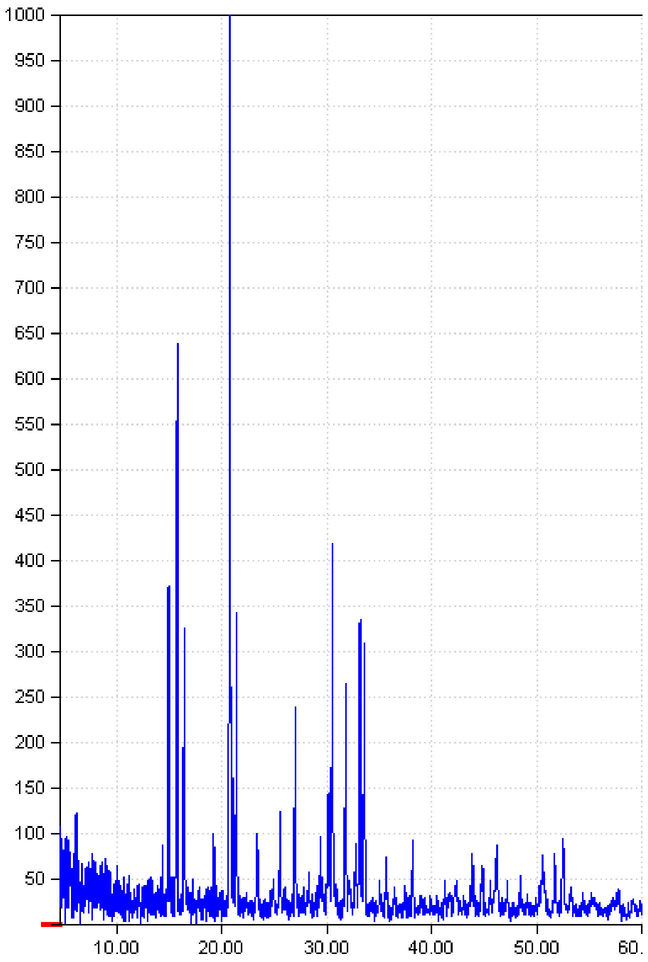
Struvite products after being on the table of the laboratory overnight. On the left, struvite produced from Fe-poor solution, struvite produced from Mn-hydroxide solution in the middle and on the right, struvite produced from Mn-carbonate solution.

Struvite products after drying in 45°C in VWR Dry-line oven for 16.5 hours. On the left, struvite produced from Fe-poor solution, struvite produced from Mn-hydroxide solution in the middle and on the right, struvite produced from Mn-carbonate solution.

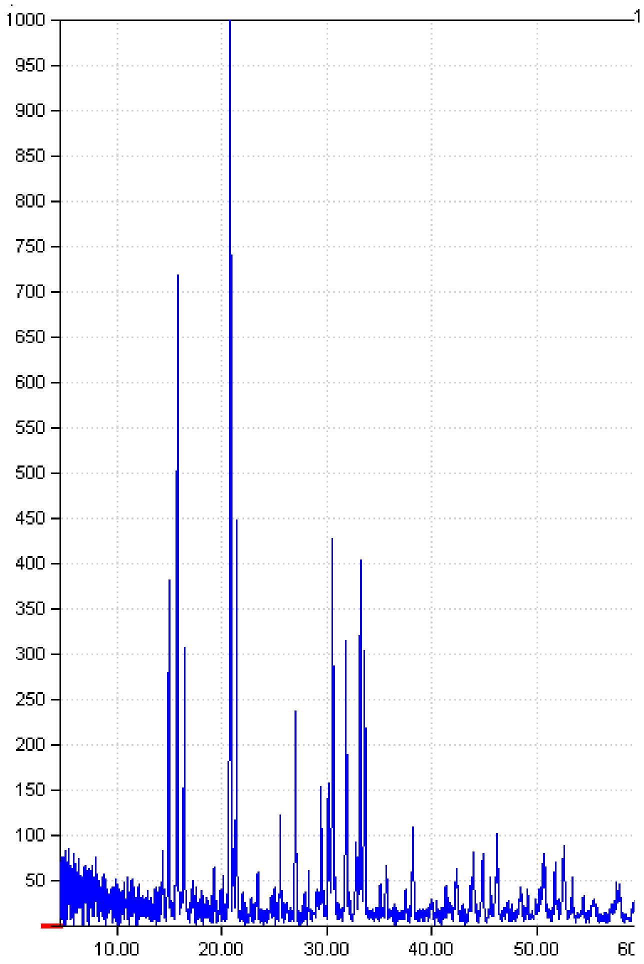
APPENDIX VIII – ICP-OES results

Sample number in Figure 25	**Sample name**	**Al**	**Ca**	**Cd**	**Co**	**Cu**	**Fe**	**Mg**	**Mn**	**Na**	**Ni**	**Zn**	**Magnesium left from the starting solution**
		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	
1	Starting solution	33.3	538	<0,2	0.79	<0,6	16520	11310	5798	2391	57.8	4.05	**100 %**
2a	Iron free solution II	<0,14	537	<0,02	<0,03	<0,06	7.26	10900	3573	2075	3.87	0.23	**96 %**
2b	Iron free solution FINAL	<0,14	504	<0,02	<0,03	0.2	<0,06	10310	3457	1942	3.87	0.05	**91 %**
5	Struvite test residue from iron free solution	<0,14	461	<0,02	<0,03	0.2	<0,06	7255	1322	1880	3.19	<0,03	**64 %**
3a	Mn free solution I	<0,14	505	<0,02	<0,03	0.33	0.09	10190	1008	1952	3.75	<0,03	**90 %**
3b	Mn free solution FINAL	<0,14	490	<0,02	<0,03	0.37	<0,06	9794	951	1887	3.56	<0,03	**87 %**
6	Struvite test residue from Mn free solution	<0,14	438	<0,02	<0,03	0.38	0.16	5994	280	1743	3.24	0.07	**53 %**
4	Solution from CO32- test	<0,14	182	<0,02	<0,03	0.33	<0,06	8302	4.19	3682	3.11	<0,03	**73 %**
7	Solution from CO32- struvite test	<0,14	193	<0,02	<0,03	0.32	<0,06	3388	1.31	3320	2.66	0.06	**30 %**

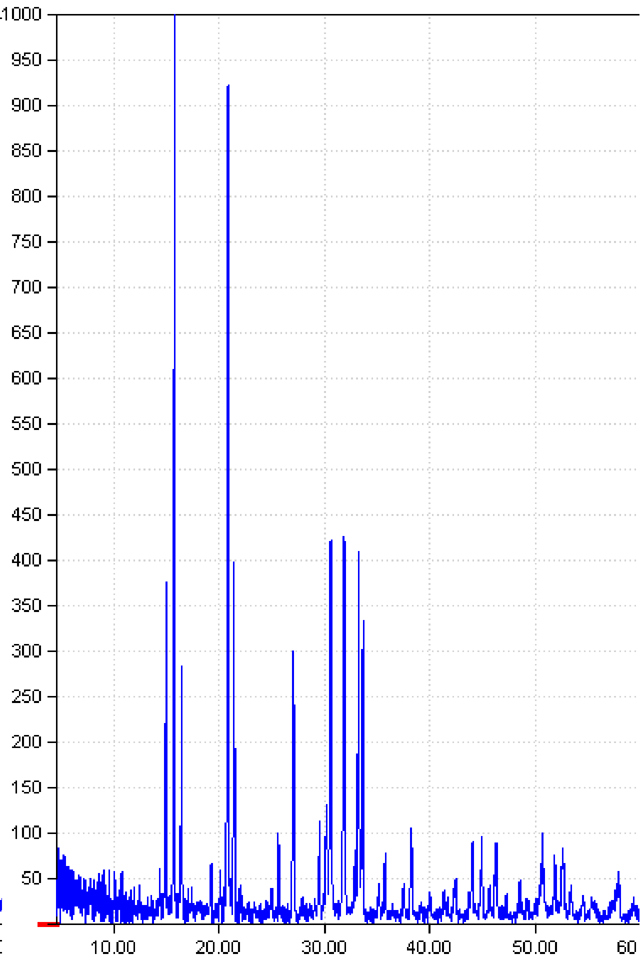
APPENDIX IX – XRD-patterns



Fe-poor



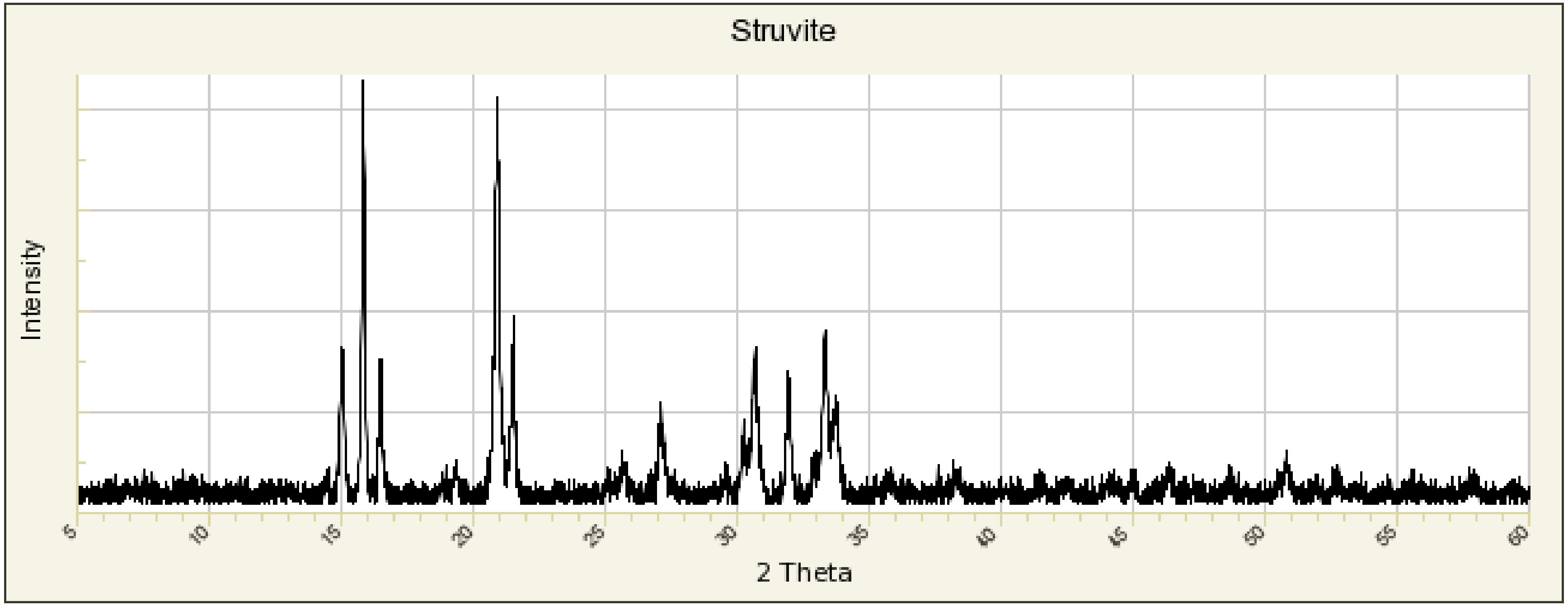
Mn(hydroxide)



Mn(carbonate)

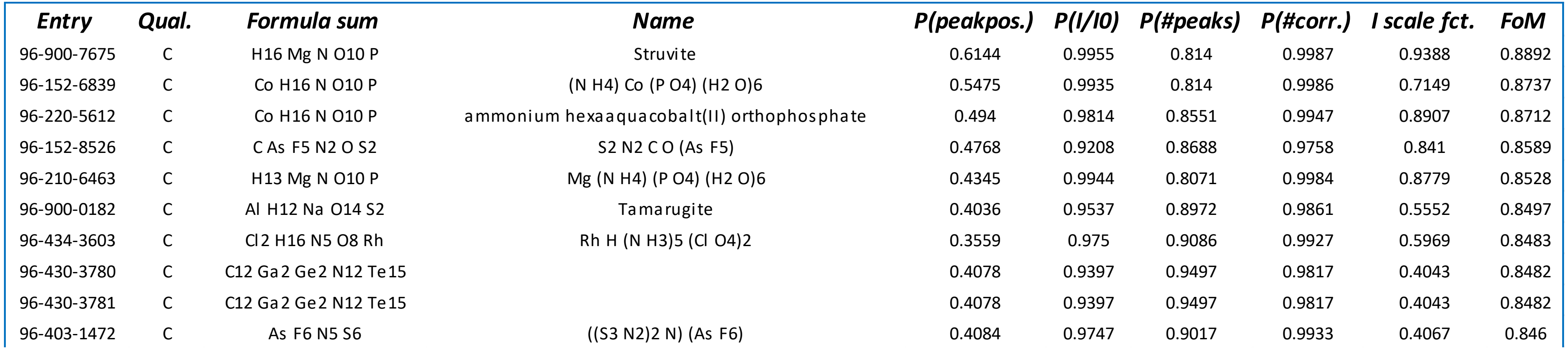
APPENDIX X – XRD-pattern of pure struvite

The pattern below for pure struvite is from the RRUFF^{TM} database. (http://rruff.info/struvite/display=default/R050511)



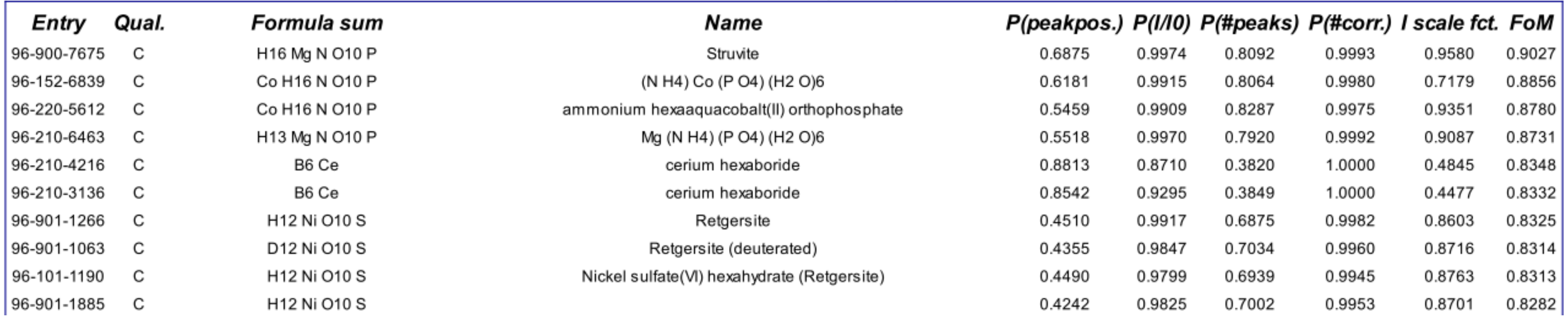
APPENDIX XI – Candidate lists for struvite samples

Candidate list of sample Fe-poor



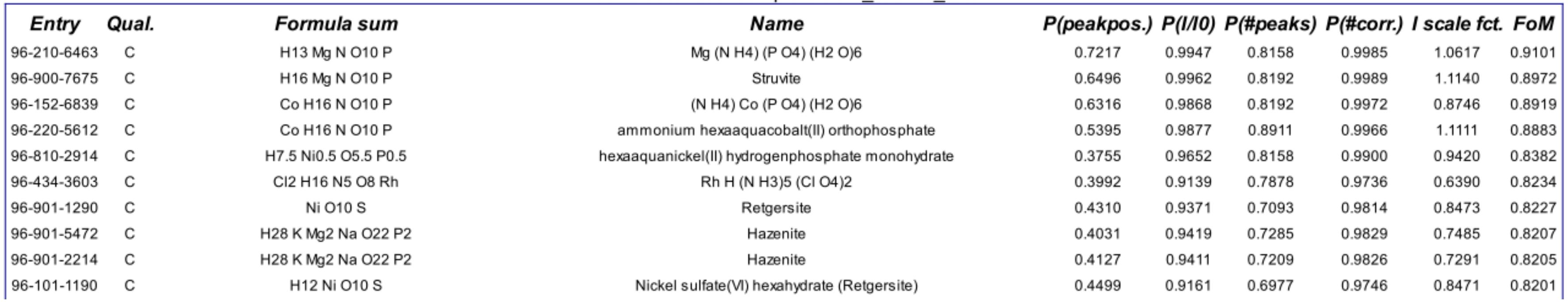
Entry	Qual.	Formula sum	Name	P(peakpos.)	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	FoM
96-900-7675	C	H16 Mg N O10 P	Struvite	0.6144	0.9955	0.814	0.9987	0.9388	0.8892
96-152-6839	C	Co H16 N O10 P	(N H4) Co (P O4) (H2 O)6	0.5475	0.9935	0.814	0.9986	0.7149	0.8737
96-220-5612	C	Co H16 N O10 P	ammonium hexaaquacobalt(II) orthophosphate	0.494	0.9814	0.8551	0.9947	0.8907	0.8712
96-152-8526	C	C As F5 N2 O S2	S2 N2 C O (As F5)	0.4768	0.9208	0.8688	0.9758	0.841	0.8589
96-210-6463	C	H13 Mg N O10 P	Mg (N H4) (P O4) (H2 O)6	0.4345	0.9944	0.8071	0.9984	0.8779	0.8528
96-900-0182	C	Al H12 Na O14 S2	Tamarugite	0.4036	0.9537	0.8972	0.9861	0.5552	0.8497
96-434-3603	C	Cl2 H16 N5 O8 Rh	Rh H (N H3)5 (Cl O4)2	0.3559	0.975	0.9086	0.9927	0.5969	0.8483
96-430-3780	C	C12 Ga2 Ge2 N12 Te15		0.4078	0.9397	0.9497	0.9817	0.4043	0.8482
96-430-3781	C	C12 Ga2 Ge2 N12 Te15		0.4078	0.9397	0.9497	0.9817	0.4043	0.8482
96-403-1472	C	As F6 N5 S6	((S3 N2)2 N) (As F6)	0.4084	0.9747	0.9017	0.9933	0.4067	0.846

Candidate list of sample Mn-poor



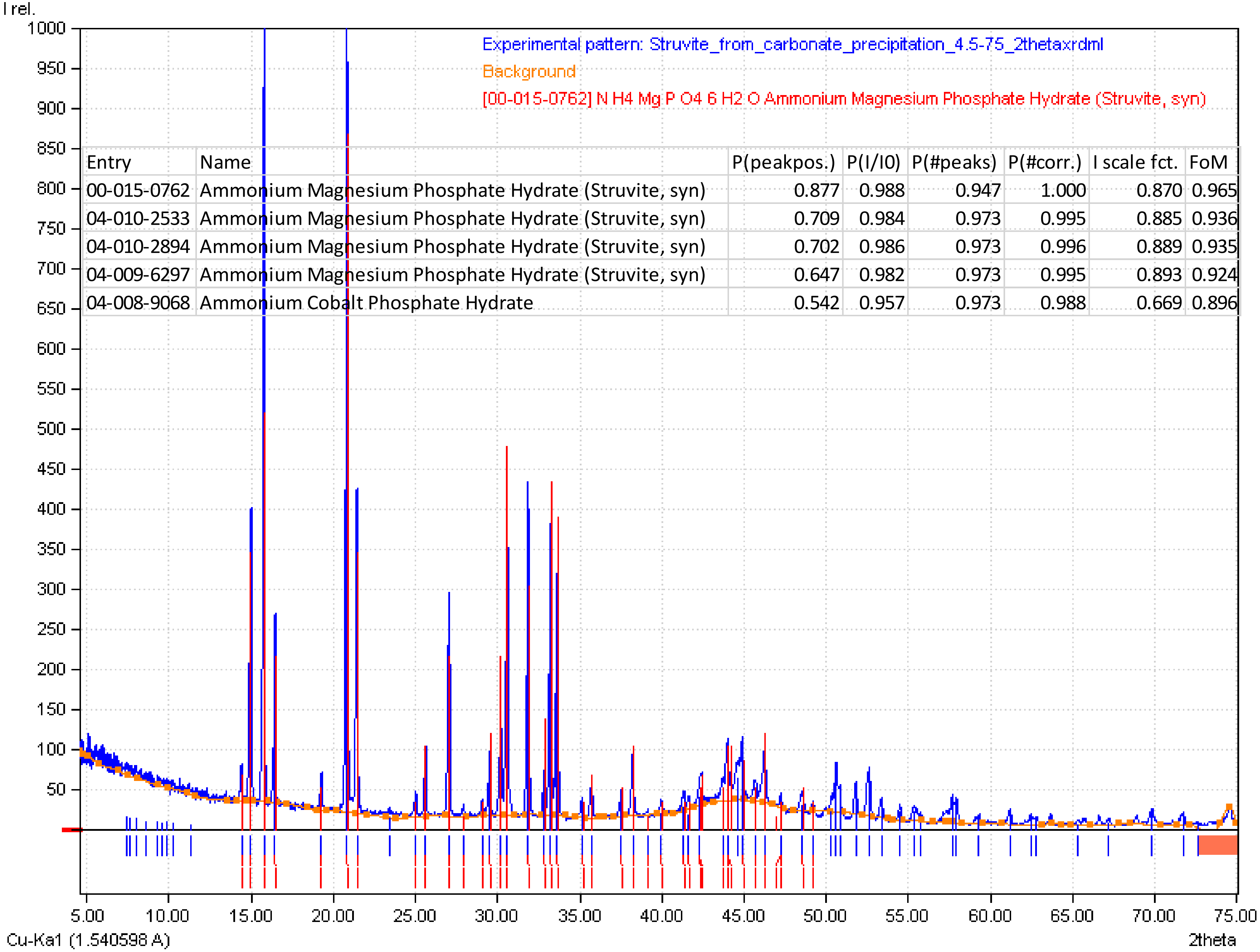
Entry	Qual.	Formula sum	Name	P(peakpos.)	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	FoM
96-900-7675	C	H16 Mg N O10 P	Struvite	0.6875	0.9974	0.8092	0.9993	0.9580	0.9027
96-152-6839	C	Co H16 N O10 P	(N H4) Co (P O4) (H2 O)6	0.6181	0.9915	0.8064	0.9980	0.7179	0.8856
96-220-5612	C	Co H16 N O10 P	ammonium hexaaquacobalt(II) orthophosphate	0.5459	0.9909	0.8287	0.9975	0.9351	0.8780
96-210-6463	C	H13 Mg N O10 P	Mg (N H4) (P O4) (H2 O)6	0.5518	0.9970	0.7920	0.9992	0.9087	0.8731
96-210-4216	C	B6 Ce	cerium hexaboride	0.8813	0.8710	0.3820	1.0000	0.4845	0.8348
96-210-3136	C	B6 Ce	cerium hexaboride	0.8542	0.9295	0.3849	1.0000	0.4477	0.8332
96-901-1266	C	H12 Ni O10 S	Retgersite	0.4510	0.9917	0.6875	0.9982	0.8603	0.8325
96-901-1063	C	D12 Ni O10 S	Retgersite (deuterated)	0.4355	0.9847	0.7034	0.9960	0.8716	0.8314
96-101-1190	C	H12 Ni O10 S	Nickel sulfate(VI) hexahydrate (Retgersite)	0.4490	0.9799	0.6939	0.9945	0.8763	0.8313
96-901-1885	C	H12 Ni O10 S		0.4242	0.9825	0.7002	0.9953	0.8701	0.8282

Candidate list of sample CO32-_struvite_test



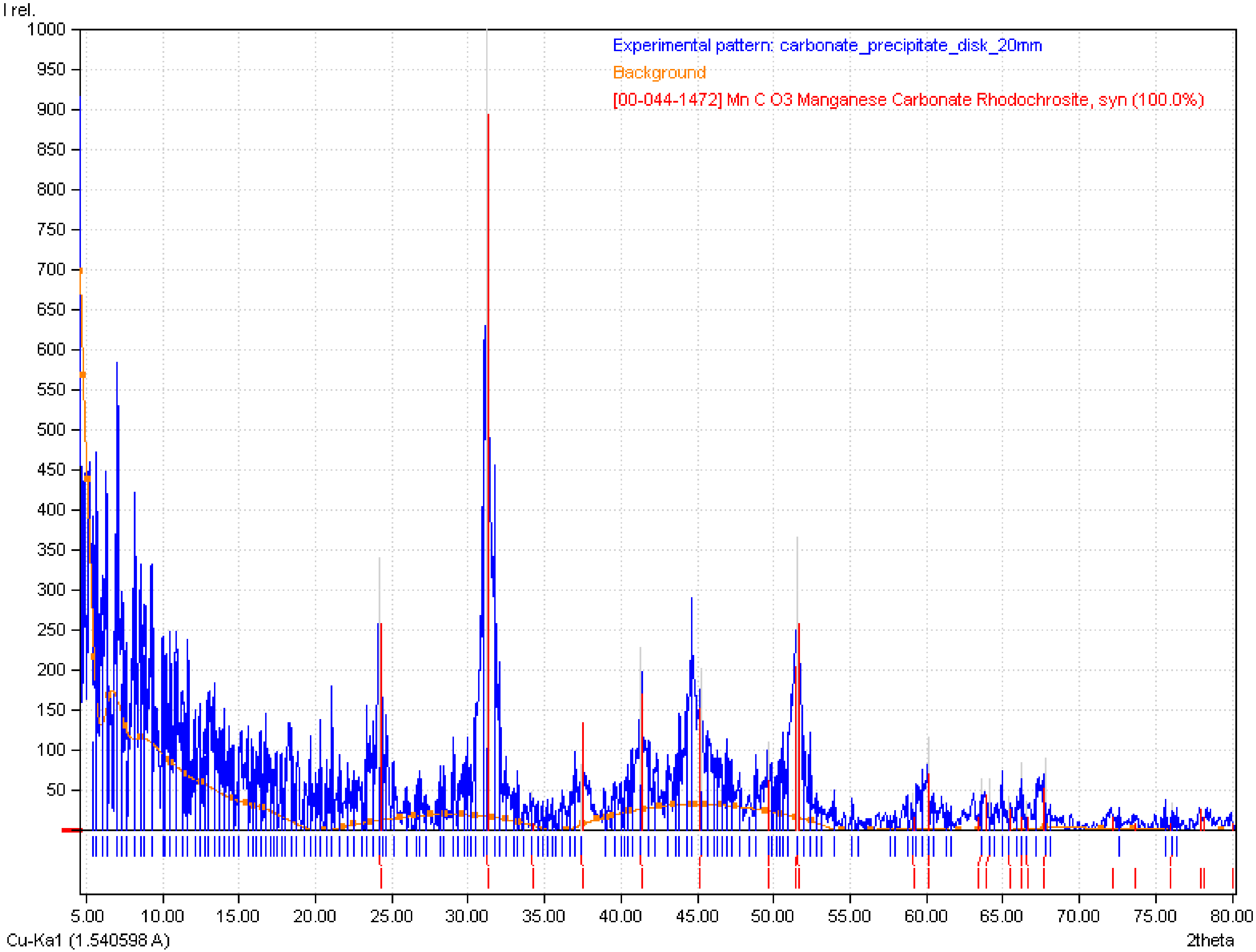
Entry	Qual.	Formula sum	Name	P(peakpos.)	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	FoM
96-210-6463	C	H13 Mg N O10 P	Mg (N H4) (P O4) (H2 O)6	0.7217	0.9947	0.8158	0.9985	1.0617	0.9101
96-900-7675	C	H16 Mg N O10 P	Struvite	0.6496	0.9962	0.8192	0.9989	1.1140	0.8972
96-152-6839	C	Co H16 N O10 P	(N H4) Co (P O4) (H2 O)6	0.6316	0.9868	0.8192	0.9972	0.8746	0.8919
96-220-5612	C	Co H16 N O10 P	ammonium hexaaquacobalt(II) orthophosphate	0.5395	0.9877	0.8911	0.9966	1.1111	0.8883
96-810-2914	C	H7.5 Ni0.5 O5.5 P0.5	hexaaquanickel(II) hydrogenphosphate monohydrate	0.3755	0.9652	0.8158	0.9900	0.9420	0.8382
96-434-3603	C	Cl2 H16 N5 O8 Rh	Rh H (N H3)5 (Cl O4)2	0.3992	0.9139	0.7878	0.9736	0.6390	0.8234
96-901-1290	C	Ni O10 S	Retgersite	0.4310	0.9371	0.7093	0.9814	0.8473	0.8227
96-901-5472	C	H28 K Mg2 Na O22 P2	Hazenite	0.4031	0.9419	0.7285	0.9829	0.7485	0.8207
96-901-2214	C	H28 K Mg2 Na O22 P2	Hazenite	0.4127	0.9411	0.7209	0.9826	0.7291	0.8205
96-101-1190	C	H12 Ni O10 S	Nickel sulfate(VI) hexahydrate (Retgersite)	0.4499	0.9161	0.6977	0.9746	0.8471	0.8201

APPENDIX XII – XRD-pattern for struvite sample

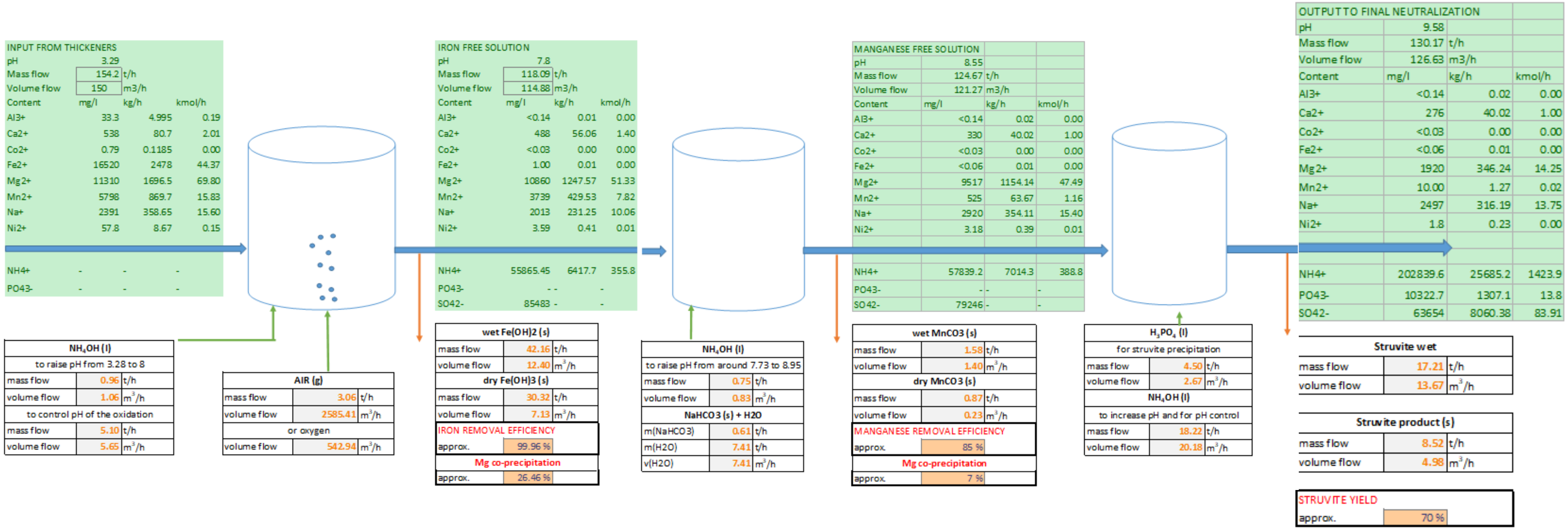


Entry	Name	P(peakpos.)	P(I/I0)	P(#peaks)	P(#corr.)	I scale fct.	FoM
00-015-0762	Ammonium Magnesium Phosphate Hydrate (Struvite, syn)	0.877	0.988	0.947	1.000	0.870	0.965
04-010-2533	Ammonium Magnesium Phosphate Hydrate (Struvite, syn)	0.709	0.984	0.973	0.995	0.885	0.936
04-010-2894	Ammonium Magnesium Phosphate Hydrate (Struvite, syn)	0.702	0.986	0.973	0.996	0.889	0.935
04-009-6297	Ammonium Magnesium Phosphate Hydrate (Struvite, syn)	0.647	0.982	0.973	0.995	0.893	0.924
04-008-9068	Ammonium Cobalt Phosphate Hydrate	0.542	0.957	0.973	0.988	0.669	0.896

APPENDIX XIII – XRD-pattern for manganese carbonate sample



APPENDIX XIV – Mass balance



INPUT FROM THICKENERS			
pH	3.29		
Mass flow	154.2	t/h	
Volume flow	150	m3/h	
Content	mg/l	kg/h	kmol/h
Al3+	33.3	4.995	0.19
Ca2+	538	80.7	2.01
Co2+	0.79	0.1185	0.00
Fe2+	16520	2478	44.37
Mg2+	11310	1696.5	69.80
Mn2+	5798	869.7	15.83
Na+	2391	358.65	15.60
Ni2+	57.8	8.67	0.15
NH4+	-	-	-
PO43-	-	-	-

NH_4OH (l)		
to raise pH from 3.28 to 8		
mass flow	0.96	t/h
volume flow	1.06	m^3/h
to control pH of the oxidation		
mass flow	5.10	t/h
volume flow	5.65	m^3/h

AIR (g)		
mass flow	3.06	t/h
volume flow	2585.41	m^3/h
or oxygen		
volume flow	542.94	m^3/h

IRON FREE SOLUTION			
pH	7.8		
Mass flow	118.09	t/h	
Volume flow	114.88	m3/h	
Content	mg/l	kg/h	kmol/h
Al3+	<0.14	0.01	0.00
Ca2+	488	56.06	1.40
Co2+	<0.03	0.00	0.00
Fe2+	1.00	0.01	0.00
Mg2+	10860	1247.57	51.33
Mn2+	3739	429.53	7.82
Na+	2013	231.25	10.06
Ni2+	3.59	0.41	0.01
NH4+	55865.45	6417.7	355.8
PO43-	-	-	-
SO42-	85483	-	-

wet Fe(OH)2 (s)		
mass flow	42.16	t/h
volume flow	12.40	m^3/h
dry Fe(OH)3 (s)		
mass flow	30.32	t/h
volume flow	7.13	m^3/h
IRON REMOVAL EFFICIENCY		
approx.	99.96 %	
Mg co-precipitation		
approx.	26.46 %	

NH_4OH (l)		
to raise pH from around 7.73 to 8.95		
mass flow	0.75	t/h
volume flow	0.83	m^3/h
NaHCO3 (s) + H2O		
m(NaHCO3)	0.61	t/h
m(H2O)	7.41	t/h
v(H2O)	7.41	m^3/h

MANGANESE FREE SOLUTION			
pH	8.55		
Mass flow	124.67	t/h	
Volume flow	121.27	m3/h	
Content	mg/l	kg/h	kmol/h
Al3+	<0.14	0.02	0.00
Ca2+	330	40.02	1.00
Co2+	<0.03	0.00	0.00
Fe2+	<0.06	0.01	0.00
Mg2+	9517	1154.14	47.49
Mn2+	525	63.67	1.16
Na+	2920	354.11	15.40
Ni2+	3.18	0.39	0.01
NH4+	57839.2	7014.3	388.8
PO43-	-	-	-
SO42-	79246	-	-

wet MnCO3 (s)		
mass flow	1.58	t/h
volume flow	1.40	m^3/h
dry MnCO3 (s)		
mass flow	0.87	t/h
volume flow	0.23	m^3/h
MANGANESE REMOVAL EFFICIENCY		
approx.	85 %	
Mg co-precipitation		
approx.	7 %	

H_3PO_4 (l)		
for struvite precipitation		
mass flow	4.50	t/h
volume flow	2.67	m^3/h
NH_4OH (l)		
to increase pH and for pH control		
mass flow	18.22	t/h
volume flow	20.18	m^3/h

OUTPUT TO FINAL NEUTRALIZATION			
pH	9.58		
Mass flow	130.17	t/h	
Volume flow	126.63	m3/h	
Content	mg/l	kg/h	kmol/h
Al3+	<0.14	0.02	0.00
Ca2+	276	40.02	1.00
Co2+	<0.03	0.00	0.00
Fe2+	<0.06	0.01	0.00
Mg2+	1920	346.24	14.25
Mn2+	10.00	1.27	0.02
Na+	2497	316.19	13.75
Ni2+	1.8	0.23	0.00
NH4+	202839.6	25685.2	1423.9
PO43-	10322.7	1307.1	13.8
SO42-	63654	8060.38	83.91

Struvite wet		
mass flow	17.21	t/h
volume flow	13.67	m^3/h

Struvite product (s)		
mass flow	8.52	t/h
volume flow	4.98	m^3/h

STRUVITE YIELD	
approx.	70 %

APPENDIX XV – Equipment costs (USD) in 2010

Equipment	**Size**	**Design factor**	**Final size**	**Material**	**material factor**	**each**	**total**
Reactors							
Iron precipitation	6 x 75 m^3	1.2	6 x 90 m^3	All reactors are 304 stainless steel	1.5	1845392	11072354
Manganese precipitation	75 m^3	1.2	90 m^3		1.5	1845392	1845392
Struvite precipitation	75 m^3	1.2	90 m^3		1.5	1845392	1845392
Carbonate solution	2 x 7.4 m^3	1.2	9 m3		1.5	344228	688456
Tanks							14763138
Feed tank	1 x 2700 m^3	1.2	1 x 3240 m^3	304 stainless steel	1.5	693807	693807
Ammonia solution tank	2 x 3400 m^3	1.2	4080 m^3	316 stainless steel	1.6	868187	1736374
Phosphoric acid tank	1000 m^3	1.2	1200 m^3	Hastelloy®-C or Duplex (for example Outokumpu 2205)	4	921191	921191
Plate and frame filters							3351372
Iron precipitation	2 x 1.2 m^3,	1.2	2 x 1.44 m^3,			234800	469600
Manganese precipitation	1 x 0.08 m^3,	1.2	1 x 0.096 m^3,			155576	155576
Struvite precipitation	2 x 0.84 m^3	1.2	2 x 1.01 m^3			217444	434888
Directly heated rotary dryers							1060063
Iron precipitation	1 x 157 m^2,		1 x 157 m^2,			1009258	1009258
Manganese precipitation	1 x 0.08 m^2,		1 x 0.08 m^2,			16081	16081
Struvite precipitation	1 x 110 m^2		1 x 110 m^2			736843	736843
Pumps							1762182
Feed pumps, iron precipitation	6 x 1400 l/min,		6 x 23.5 l/s	All pumps are PTFE lined	1.4	13758	82550
Feed pumps, manganese and struvite precipitation	15 x 1000 l/min,		15 x 16.7 l/s		1.4	12234	183515
Carbonate solution pump	2 x 150 l/min,		2 x 2 l/s		1.4	8627	17254
Ammonia pump	2 x 500 l/min,		2 x 8.35 l/s		1.4	10269	20538
Phosphoric acid pump	2 x 60 l/min		2 x 1 l/s		1.4	8336	16672
Conveyors							320529
From filters to dryers	3 x 25 m		3 x 25 m			79000	237000
From dryers to packing	3 x 50 m		3 x 50 m			112000	336000
							573000