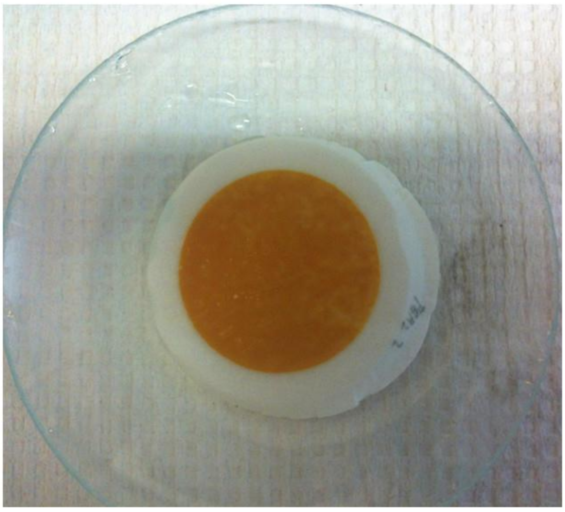
CHALMERS

Phosphorus Recovery from Sorted MSWI Bottom Ash: the acidic dissolution – precipitation method

Master of Science Thesis in the Master's Programme Environmental Measurements and Assessments

BEI GAO

Department of Civil and Environmental Engineering
Division of Water Environment Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden, 2012

Master's Thesis 2012:04

Master's Thesis 2012:04

Phosphorus Recovery from Sorted MSWI Bottom Ash: the acidic dissolution – precipitation method

Master of Science Thesis in the Master's Programme Environmental Measurements and Assessments

BEI GAO

Department of Civil and Environmental Engineering

Division of Water Environment Technology

CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden, 2012

Phosphorus Recovery from Sorted MSWI Bottom Ash: the acidic dissolution – precipitation method

Master of Science Thesis in the Master Programme Environmental Measurements and Assessments

BEI GAO

Examensarbete / Institutionen för bygg- och miljöteknik,
Chalmers tekniska högskola 2012:04

Department of Civil and Environmental Engineering
Division of Water Environment Technology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: + 46 (0)31-772 1000

Cover: Phosphorus recovery product from sorted MSWI bottom ash by the acidic dissolution – precipitation method

Printed by Chalmers Reproservice/ Department of Civil and Environmental Engineering
Göteborg, Sweden, 2012

Phosphorus Recovery from Sorted MSWI Bottom Ash: the acidic dissolution – precipitation method

Master of Science Thesis in the Master Programme Environmental Measurements and Assessments

BEI GAO

Department of Civil and Environmental Engineering
Division of Water Environmental and Technology
Chalmers University of Technology

Abstract

Phosphorus (P) is an essential non-renewable resource and is at the risk of phosphate rock depletion. Recovery from the secondary P-rich sources, sewage sludge incineration ash (SSIA) and wastewater flows has been frequently discussed. In this study an acidic dissolution – precipitation method was conducted to recover P from sorted municipal solid waste incineration bottom ash (MSWI BA). The aim of the study was to optimize the acidic dissolution – precipitation approach. The general goals with the project were to improve the P recovery efficiency and to enhance the purity of the P recovery product.

Both fresh bottom ash (FBA) and 6-month aged bottom ash (ABA) were tested. The ash samples came from a typical Mass-burn (MB) MSWI plant and were sorted to remove metal pieces. A fly ash (FA) sample was included in the study and served as a reference sample.

The experiments consisted of the maximized P leaching tests, the solid phase extraction (SPE) tests and the P recovery tests. The L/S ratio was 5, and for ash samples, duplicate experiments were performed. The P recovery tests were done by batch-leaching. Both Hach and ion chromatography (IC) methods were conducted to measure the P content (in the form of PO_4^{3-}) in the leachates. The metal contents in the leachates were analysed by ICP-MS.

The result of the maximized P leaching tests indicated that 2.5M HCl leaching without sedimentation could maximize P leaching from MSWI ash. The Hach analysis method overestimated the P content and only the IC was used for the analysis of P in the liquids from the SPE tests and the P recovery tests.

The SPE tests indicated that Empore chelating disk is effective to remove metals from the aqueous solutions and repeatedly SPE is recommended to get higher removal efficiency of the metals. Parts of metals as Al, Ca and Fe were retained in the chelating disk, which could decrease the extraction capacity of the disk. Another most important finding was the high decrease of the P concentration after the SPE. Considering that P is the element of interest to be recovered, the SPE technique was excluded from the P recovery tests.

In the P leaching tests, approximately 30–56% of P was leached in the ash leachates. In the P recovery tests, more than 90% of P in the leachates was recovered by precipitation. The P content was about 0.9% in the 1st precipitates and 0.1–2.4% in the 2nd precipitates. Aluminium, Fe, Ca, Mg and Zn were the major elements, while As, Cd, Cr, Mn, Ni, Sr and Ti were the trace elements of the P recovery product. The comparison of the metal contents between the P recovery product with low-grade phosphate rock indicated that the product cannot be used directly as the alternative of low-grade phosphate rock. The metal content of the product should be decreased before utilisation.

In order to improve the acidic dissolution – precipitation method, the P leaching step should be enhanced. A suggestion for further study is to try alkaline leaching combined with acidic pre-treatment rather than direct acidic leaching. In conclusion, the acidic dissolution – precipitation method was feasible to recover P from sorted MSWI BA. However, the leaching step requires improvements of how to concentrate P in the product as well as the implementation of the SPE technique to remove metals from the leachates before precipitation.

Keywords: phosphorus recovery, MSWI BA, acidic leaching, precipitation, SPE

Acknowledgements

The master thesis project was carried out by BEI GAO, master student in the Environmental Measurements and Assessments Program, at Water Environment Technology, Department of Civil and Environmental Engineering. It was supervised by Dr. Karin Karlfeldt Fedje, Assistant Professor Renova/Chalmers and Dr. Ann-Margret Strömvall, Associate Professor, Chalmers University of Technology.

I would like to express my truly thanks to Mona Pålsson for her kindly help in the WET lab, to Oskar Modin for his kind and patient help of IC analysis, to Jesper Knutsson and Sebastien Rauch for ICP-MS analysis, to Britt-Marie Wilen for her kindly help for the lab work, to Lars-Ove Sörman for all the help at the office.

I would like to appreciate all the students and teachers in the Water Environment Technology division for the advices to my master thesis work.

BEI GAO

Göteborg

June 2012

Table of Contents

List of abbreviations

P	Phosphorus
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
BA	Bottom ash
FA	Fly ash
FBA	Fresh bottom ash
ABA	Aged bottom ash
MB	Mass-burn
FB	Fluidized bed
WWTP	Wastewater treatment plant
SS	Sewage sludge
SSI	Sewage sludge incineration
SSIA	Sewage sludge incineration ash
HAP	Calcium hydroxyapatite
MAP	Magnesium ammonium phosphate
XRD	X-ray diffraction
ICP-MS	Inductively coupled plasma-mass spectrometry
SPE	Solid phase extraction

1 Introduction

Phosphorus (P) is an essential non-renewable resource for all living organisms but a better utilization of P is to serve as the raw material of agriculture fertilizers. However, due to the excessive mining and exploration, phosphate rock mines are being depleted. Therefore, from a sustainable point of view, it is meaningful to reuse or recover phosphorus from alternative P-rich sources.

Fortunately, research has been performed for developing P recovery techniques. A literature review showed that sewage sludge incineration ash (SSIA) (Adam et al., 2009; Blöcher et al., 2012; Honma and Utsumi, 2003; Gifu city, 2007; Kemacheevakul et al., 2011; Zimmermann and Dott, 2009) and wastewater flows (MLIT Japan, 2010; Kemacheevakul et al., 2011) are two frequently studied alternative P recovery sources in addition to sewage sludge (SS) (Blöcher et al., 2012; (Güney et al., 2008)). The results of these studies indicated that P can be recovered from P-rich sources with a relative high efficiency (SSIA: 61–100%; Wastewater: 40–86%; SS: 54%) but with a low P content in the product (SSIA: 13%; Wastewater: 7–15%).

With respect to the P flow, a large amount of P ends up in the municipal solid waste (MSW). Thus P is enriched in the municipal solid waste incineration (MSWI) ash and the latter is considered as an important P recovery source.

MSWI ash is usually grouped as bottom ash (BA) and fly ash (FA). A previous study by Du and Yu (2011) proved that it is feasible to recover P from FA. However, the weaknesses such as the low P content and the high metal content in the P recovery product, cannot be ignored. Compared to FA, larger quantities of BA (approximately 8 times more) are produced annually (Chandler et al., 1997). From an economic perspective, it is worth trying to recover P from BA instead of FA. For the chemical composition of MSWI ash, analytical results from a commercial lab (Table 1.3) revealed that the metal contents in BA were lower than in FA, which indicates a possibility of producing the P recovery product with lower toxicity from BA than from FA.

All these factors taken together indicated the importance and interests of techniques to recover P from MSWI BA.

1.1 Aim and goal

This project is a part of a series of research projects on P recovery exploring from MSWI ash. The acidic dissolution – precipitation method based on previous study by Du and Yu (2011) was conducted with several technical adjustments in this study.

The aim of the study was to optimize the acidic dissolution – precipitation approach to effectively recover P from MSWI BA.

The general goals with the project were to improve the P recovery efficiency and the purity of the P recovery product. Specific goals with the experiments were listed in Table 1.1.

Table 1.1 The specific goals with the project

Experiments	Specific goals were to	Precondition
Maximized P leaching tests	◆ find out the optimal P leaching agent by evaluating the performance of P leaching with HCl solutions in different concentrations; ◆ investigate if sedimentation of the mixture could increase P leaching by evaluating the performance of P leaching with and without 24h sedimentation.	Based on literature review, HCl solutions in three concentrations (0.5/1.5/2.5 M) were chosen for the maximized P leaching tests.
SPE tests	◆ investigate if Solid Phase Extraction (SPE) by Empore chelating disk is effective to remove metals from the leachates by evaluating the metal removal efficiency of the SPE tests; ◆ investigate if metal ions were retained in the disk after elution by evaluating the ratio of metal ions retained by Empore chelating disk; ◆ investigate whether P was adsorbed on the disk or not by evaluating the P content in the leachates remaining after the SPE tests.	Based on the results of the maximized leaching tests, the leachates for the SPE tests were produced by leaching the ash samples with 2.5M HCl without sedimentation.
P recovery tests	◆ evaluate the P recovery efficiency of the acidic dissolution – precipitation method; ◆ analyse the metal flows during the experiments; ◆ assess the P recovery product by analysing the elemental composition of the product, comparing the P recovery product with low-grade phosphate rock and estimating the toxicity of the P recovery product.	Based on the results of the SPE tests, SPE technique by Empore chelating disk was excluded in the P recovery tests.

1.2 Background

With the rapid development of economy, increasing amounts of MSW being produced and disposed every day and MSW management has become a major issue around the world. Considering waste management, incineration of MSW is the predominant treatment approach among Nordic countries (Eurostat, 2012). As mentioned before, MSWI ash is considered as alternative P-rich source in addition to SSIA, wastewater and SS. More details are introduced in chapter 1.2.1-1.2.4.

1.2.1 MSW generation

According to Eurostat data (2012), the trends in average MSW generation in the 27 nations of EU and Sweden are stated (Figure 1.1). It should be noticed that, although the bulk of MSW stream comes from households, wastes generated by small businesses and public institutions were also included.

For the 27 EU nations, MSW generation increased slightly from 474 kg/capita in 1995 to 502 kg /capita in 2010. With respect to Sweden, MSW generation kept an increasing trend and reached the peak point in 2007 (516 kg/capita) but decreased slowly from 2008 to 2010.

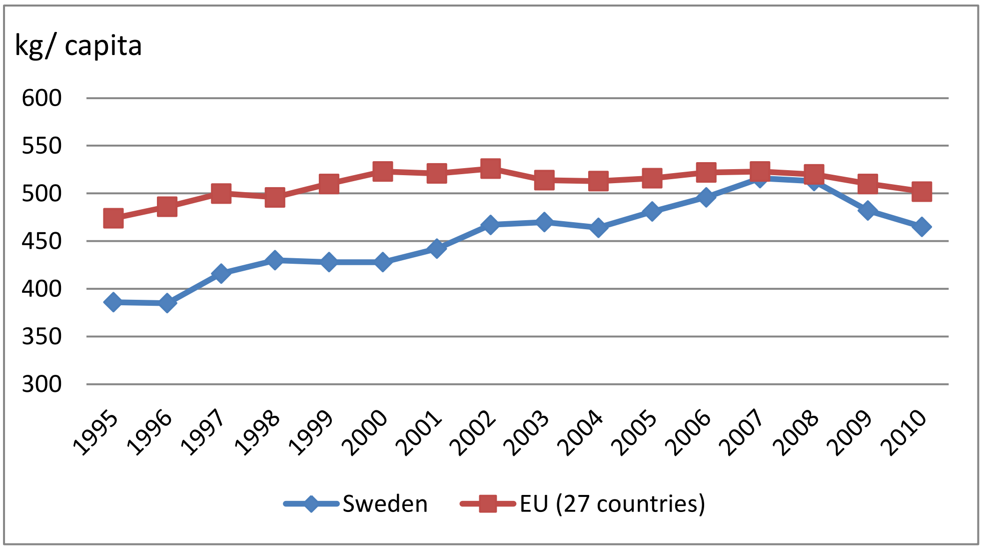


Figure 1.1. Trends in MSW generation in EU (Source: Eurostat)

1.2.2 MSW management

Figure 1.2 states the disposition of MSW by different treatment methods used in EU in 2010.

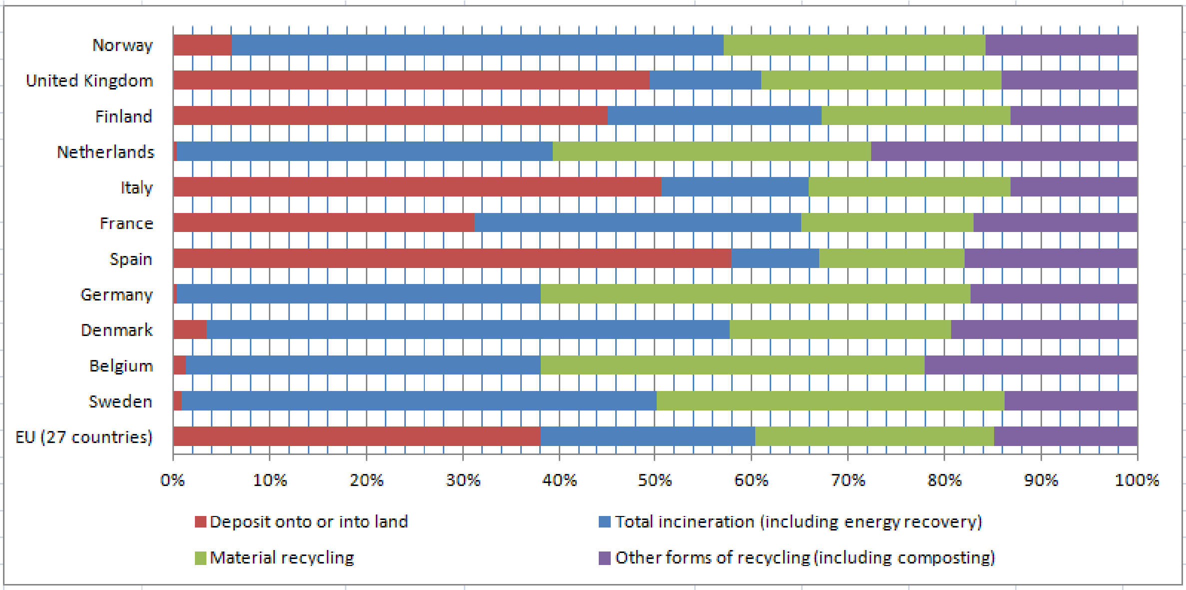


Figure 1.2. Proportion of MSW in each treatment option in 2010 (Source: Eurostat)

For the 27 EU nations, the most common way of MSW treatment was depositing onto or into land (38% of MSW were deposited onto or into land in 2010), which was deprecated or rarely used in Nordic countries, Belgium, Germany and Netherland. For Sweden, Denmark and Norway, incineration with energy recovery was the dominate way to treat waste (49%, 54%, 51%, respectively). Other European countries e.g. Spain and Norway showed an increasing trend of incinerating MSW over the past few years (the Ministry of Environment of Spain, 2008; Statistics Norway, 2012).

Compared to landfilling, incineration has the advantages of bulk reduction (up to 90%) and energy generation. However, due to financial constraints, only limited numbers of incinerators are served in metropolis (e.g. Hong Kong and Singapore) in Asia and no incinerator was in use in Africa and Latin America (UNEP-IETC, 2012). As a developed country, Japan is an exception in Asia, with over 70% of solid waste was treated by incineration (Cheremisinoff, 2003).

1.2.3 MSWI treatment and combustion technique

A typical MSWI treatment plant consists of waste system, storage area, combustion system, boiler and flue gas cleaning system. Other installations include air pollution control system and ash handling system (Chandler et al., 1997).

Figure 1.3 is the sketch of a generic incinerator plant designed by a Germany company. The working procedure is introduced briefly in the next section.

The wastes are transported to the incinerator by collection vehicles (1) and are dumped into the storage pit (2). The wastes are picked up by handling crane (3) and then fed into the feed hopper (4). The wastes in the feeder (5) are then mechanically pushed onto the grate (6) and passed through the incinerator slowly. Air is drawn to the undergrate air zones (8) by the forced-draft fan (7) for ventilation. Bottom Ashes (BAs) are collected in the ash bunker (11) while FAs are collected by the FA conveyor (18). The air pollution control system consists of dry scrubber (14), fabric filter baghouse (15), induced-draft fan (16) and stack (17).

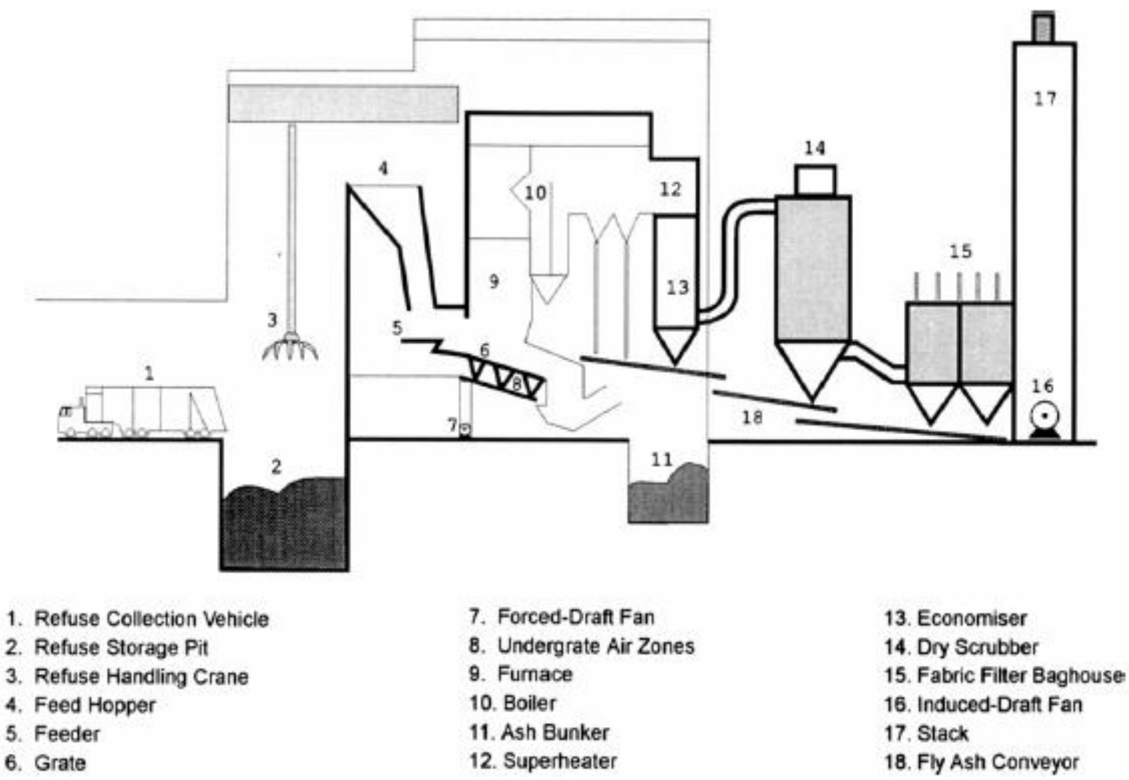


Figure 1.3.The sketch of a generic incinerator plant (courtesy Martin GmbH)

Source: Chandler et al., 1997

The choice of combustion technique is critical as it could influence the effectiveness of incineration.

Mass-burn (MB) combustion with a movable grate incinerator is a mature and easy-operated combustion technique which has been widely used in Scandinavia (UNEP-IETC, 2012). In a MB combustor, MSW is fed into the furnace directly without pretreatment and then burning on a grate (Chandler et al., 1997).

In addition to MB, an alternative technique named fluidized bed (FB) combustion was implemented among Western European countries. This is a newer technique and requires pre-treatment of the waste prior to incineration. (UNEP-IETC, 2012)

1.2.4 MSWI ash

- **Laboratory sample selection**

MSWI BA can be recycled as raw material for road construction, but BA is toxic because of high levels of toxic metals. In order to prevent heavy metal leaching, BA requires pretreatment before recycling. Natural or accelerated carbonation (aging treatment) is a common way to transfer FBA into ABA with less leachable metal content (Brecht et al., 2012).

During the ageing process, CO_2 is absorbed by alkaline materials as $Ca(OH)_2$, which do not reduce the metal content but binds them harder to ash matrix with less leaching (Meima et al., 2002) .

The chemical reactions are:

$$CaO + H_2O \rightarrow Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Polettini and Pomi (2004) indicated that mineralogical composition, acid neutralizing capacity and the leaching behavior of heavy metals of FBA varied after carbonation. It was also proved by Gerve et al. (2005) that the carbonation approach could decrease the leaching of heavy metals from BA. Besides, it is interesting to compare the elemental composition of the P recovery product to investigate if a more purified product can be retrieved from ABA than from FBA.

Concerning these factors as described above, both FBA and ABA were tested in this study. The FBA and ABA samples came from a typical MB MSWI plant belonging to a Swedish waste management company (Renova AB). Both FBA and ABA were sorted to remove metal pieces. The difference between FBA and ABA is that ABA has been laying outside for 6 months. A FA sample from the same plant was included to serve as a reference sample.

- **Chemical composition**

MSWI BA accounts for 85–90% of the total amount of MSWI ash and comprises of minerals, metal pieces, sand and glassy slag lumps (Chandler et al., 1997). Table 1.2 lists the elemental composition of MSWI BA in the same reference samples. The highest P content in BA is around 7%, which is much lower than the P content of commercial grade phosphate rock (12–17%) (Sengul et al., 2006). Elements of Si, Fe, Ca, Al, Na and K are the major elements

(>10000 mg/kg); Mg, Tl, Cl, Mn, Ba, Zn, Cu, Pb, Cr are the minor elements (1000–10000 mg/kg); Sn, Sb, V, Mo, As and Se are the trace elements (<1000mg/kg).

The elemental composition of MSWI ash samples of this study was analyzed by a commercial lab (Table 1.3).

Table 1.2. Elemental composition of MSWI BA reference samples Unit: mg/kg ash

Elements	Sweden[1] (non-sorted BA)	Netherland[2] (non-sorted BA)	Japan[3] (sorted BA)	China[4] (sorted BA)
P	4-8100	4400-8000	87-11000	11400-13500
Si	130-160000	91000-310000	170000-200000	59000-280000
Al	8000-51000	22000-73000	51000-88000	41000-99000
K	6600-39000	750-16000	7100-12400	14770-19002
Na	1500-47000	2800-42000	15000-30000	9000-94000
As	17-180	0-190	<1	26-140
Cd	0-43	0-70	1-14	1-8
Ca	22000-680000	370-1230000	120000-240000	54000-360000
Cr	50-2100	23-3200	160-440	90-1200
Cu	100-14000	190-8200	1700-3600	36-12000
Fe	46-75000	4100-150000	36000-95000	26000-62000
Pb	260-6700	100-13700	690-3500	230-19600
Mg	3400-13000	400-26000	13100-20000	6000-14000
Mn	850-8100	800-1900	620-850	410-1200
Mo	3-80	15-150	1-30	2-17
Ni	13-630	7-4200	80-220	13-1300
Zn	650-11000	610-7800	3100-5900	300-21000

Phosphorus

According to Allaska database (2011), which collects quantitative information on the properties of MSWI ash produced at Swedish combustion plants, sorted matured BA contains less P (the average value:1460 mg/kg) than non-sorted FBA (the average value: 4510 mg/kg). Due to the low leachability of P under normal temperature and pressure conditions (Batziaka et al., 2005), it is not likely that P was leached during the aging process. An explanation is that P was sorted away with the metal pieces before the aging process. For this study, the presence of high amount of P in non-sorted FBA ((3500 mg/kg) compared to sorted FBA (1800 mg/kg) could be due to ash sorting as P was sorted away with the metal pieces.

Compared to Sweden, Netherland and Japan, MSW BA generated in China contains highest amount of P (Table 1.2). This could be due to the present of high content of organic compounds in BA as sorting is weak to separate organic compounds from MSW in China.

[1] Allaska database, 2011.
[2] Chandler et al., 1997; Yang et al., 2009.
[3] Saikia et al., 2008; Wei et al., 2011; Etoh et al., 2009.
[4] Yao et al., 2010;Yao et al.,2011;Li et al., 2012; Pan et al., 2008; Liu et al., 2008.

For this study, ABA contains more P (2970 mg/kg) than FBA (1800 mg/kg) (Table 1.3). Increased content of P could be due to the release of e.g. chlorides and Na^+ in FBA during the aging process. For ABA, ash weight decreased and the P content increased. Another factor is the difference of chemical composition of the ash samples. The ABA sample was incinerated in summer when organic waste was dominated the MSW composition. The FBA sample was incinerated in winter when industrial waste is dominated the MSW composition. Compared to FBA, the higher content of organic waste in ABA leads to the higher amount of P in ABA.

Table 1.3. Elemental composition of analytical MSWI ash samples   Unit: mg/kg ash

Elements	ABA	FBA	FA
P	2970	1800	5900
Si	23800	180000	45300
Al	52900	41000	32200
K	5809	10000	54400
Na	18919	26000	58400
Sb	46	78	1900
As	13	31	460
Ba	1900	2400	400
Be	6.7	2.6	2.50
Cd	2	2.3	270
Ca	100000	100000	141000
Cr	530	940	490
Co	20	33	23
Cu	2000	8900	2000
Fe	77000	140000	19100
Pb	760	1100	4600
Mg	14400	12000	13100
Mn	7586	2000	810
Mo	16	28	36
Ni	120	230	100
Ti	5995	7100	10100
Sn	140	110	1200
V	64	70	49
Zn	2700	4900	37300

Silicon

Higher content of Si is present in FBA than in ABA (Table 1.3). Based on the low leachability of Si under normal temperature and pressure conditions (V ítkov á et al., 2010), it is not likely that Si was leached during the aging process. Besides, the release of e.g. chlorides and Na^+ in FBA during the aging process could increase the Si content.

Put these factors together, an explanation for the lower Si content in ABA could be due to the heterogeneity of ash matrix as all ash samples were taken randomly.

Metal elements

All ash samples contain considerable contents of metals as Al, K, Na, Ca, Fe and Mg. The presence of heavy metals in the ash is critical as it could contribute to the toxicity of the P recovery product. The contents of metals as Sb, As, Cd, Pb, Ti, Sn and Zn in BA are lower than in FA. Hence, it is interesting to verify if a more purified product can be produced from BA compared to the product in Du and Yu's study in 2011.

1.3 Scope and Limitation

This diploma project is a lab-based study with the aim of developing the acidic dissolution – precipitation approach for recovering P from MSWI BA.

Critical points of the experiments are to:

1. identify the optimal P leaching conditions, including the concentration of the reagent, leaching time and pH;
2. investigate the feasibility of metal removal by Empore chelating disk SPE;
3. assess the performance of the acidic dissolution – precipitation approach (P leaching efficiency, P recovery efficiency, metal flows) and the purity of the P recovery product.

2 Literature review

2.1 General literature review on P recovery techniques

Numerous experiments regarding P production/recovery were conducted during the past decades. Table 2.1 states the most common P production/recovery methods, which can be divided into three groups: conventional P production methods, methods for P recovery from solid sources and P recovery from liquid sources.

The conventional P production techniques can be classified as dry process and wet process methods.

With respect to P recovery from solid sources, the studies of recovering P from SSIA have been conducted frequently in the recent years. Methods as alkaline extraction, thermo – chemical treatment, bioleaching and bioaccumulation and the acidic dissolution– precipitation method were proved to be feasible. The P recovery efficiency was 61–100% and the P content in the product was 3.4–13%. (Gifu city, 2007; Adam et al., 2009; Zimmermann and Dott, 2009)

With respect to P recovery from liquid sources, chemical precipitation is the common way by producing P-rich solid compounds as Magnesium ammonium phosphate (MAP) and Calcium hydroxyapatite (HAP). Compared to the HAP method, the P recovery efficiency of the MAP method is higher whereas lower P content of the product was obtained (Kemacheevakul et al., 2011). A new research developed by Blöcher et al (2012) indicated that 54% of P was recovered from SS by the Low pressure wet oxidation and nano-filtration (PHOXNAN) method.

The P recovery product can be served as a substitute for phosphate rock or as raw material of fertilizers (Britton et al., 2009), detergent, food additives (Global Phosphate Forum, 2010) and livestock feed additives (Schipper and Korving, 2009). However, due to the low P content and high toxicity of the product, the P recovery techniques require improvements.

Several full-scale implementations were preformed for the commercialization of some P recovery techniques (e.g. alkaline extraction and thermo-chemical treatment).

Due to economic and technical limitations, other P recovery techniques as the acidic dissolution- precipitation method, pH adjustment and chemical precipitation were thus far only performed in lab-scale.

Table 2.1. Details of existing P production/recovery methods

P production/recovery methods		P source input/output			P recovery efficiency	P content in the product	System boundaries	References
		Input	Output					
			Solid phase	Liquid phase				
Conventional P production	Dry process	Ore	Elemental P	-	90%	99.9%	Full-scale	Hocking,2005
	Wet process	Ore	-	Phosphoric acid	90%	22%	Full-scale	EFMA,2000
P recovery from solid sources	Alkaline extraction	SSI FA	Calcium apatite	-	66%	13%	Japan, full-scale	Gifu city, 2007
	Thermo-chemical treatment	SSIA	Calcium phosphates, magnesium phosphates	-	100%	NA	Germany, lab-scale/plant-scale	Adam et al., 2009; The EU project SUSAN,2009
	Bioleaching and Bioaccumulation	SSIA	Polyphosphate	-	61%	NA	Germany, lab-scale	Zimmermann and Dott, 2009
	The acidic dissolution-acidic precipitation method[5]	MSWI FA	Phosphate precipitate	-	71%	3.4%	Sweden, lab-scale	Du and Yu, 2011
P recovery from liquid sources	pH adjustment and chemical precipitation	Human urine	MAP	-	31%	5%	Japan, lab-scale	Kemacheevakul et al., 2011
		Wastewater	MAP	-	86%	7%	Japan, lab-scale	Kemacheevakul et al., 2011
		Filtrate water	MAP	-	85%	13%	Japan, lab-scale	MLIT Japan, 2010
		Returned water	HAP	-	40%	15%	Japan, lab-scale	MLIT Japan, 2010
	PHOXNAN	SS	-	Phosphoric acid	54%	NA	Germany, lab-scale	Blöcher et al., 2012

NA-not analyzed

5 A detailed introduction of the acidic dissolution - precipitation method is stated in chapter 2.2.

2.1.1 Alkaline extraction

The alkaline extraction method aims at recovering P from SSIA. Phosphorus is recovered in the form of calcium apatite. This method has been implemented in the project of “Full scale P-recovery from sewage sludge ash” in Japan in 2007.

For “Full scale P-recovery from sewage sludge ash” project, the Gifu government expended 8.8 million U.S. dollars to build a WWTP aiming at commercialization of recovering P from SSIA. The P recovery capacity of the plant is 5 tons P/day and approximately 500 tons of calcium apatite was produced annually. The price of the product is 4992 euro/ton. The project was proved to be technically effective (66% of P was recovered) and commercially feasible. (Gifu city, 2007)

2.1.2 Thermo-chemical treatment

Adam et al. (2009) explored a thermo-chemical treatment to recover P from SSIA with a P recovery efficiency of 100%. The P recovery tests consist of two steps. The 1st step is mono-incineration. In this step, organic pollutants in SSIA were destructed. The 2nd step is thermo-chemical treatment. In this step, heavy metals in SSIA were removed by adding $MgCl_2$/$CaCl_2$ solution to transfer heavy metals into gaseous phase.

Based on the EU SUSAN Project, the research of thermo-chemical treatment was conducted since 2005. The lab-scale and plant-scale P recovery tests indicated a promising value of the thermo-chemical method with a P recovery efficiency of 100%.The implementation of the full-scale demonstration plant by ASH DEC Umwelt AG is still in the planning stage (The EU SUSAN Project, 2009).

2.1.3 Bioleaching and bioaccumulation

Zimmermann and Dott (2009) investigated a two-step biotechnology to recover P from SSIA, with a P recovery efficiency of 61%. The first step is bioleaching which is aiming at extracting heavy metals from SSIA. The second step is bioaccumulation. In the bioaccumulation process, P was accumulated and recovered in the form of polyphosphate.

2.1.4 pH adjustment and chemical precipitation

Chemcial precipiation is a feasiable way of recovering P from liquid resources (e.g. wastewater). Phosphorous can be recovered in the form of magnesium ammonium phosphate (MAP) by chemical precipitation or calcium hydroxyapatite (HAP) by crystallization. The P recovery efficiency was 31–86% and the product can be used to produce slow-release fertilizers or to serve as raw material for industry production. (Kemacheevakul et al., 2011)

2.1.5 PHOXNAN

According to Blöcher et al (2012), the PHOXNAN method combines low pressure wet oxidation (LOPROX) technique with two-step membrane-filtration was proved to be an effective way of recovering P from SS.

First, LOPROX technique was performed to remove organic pollutants in SS and leave H_3PO_4 or $H_2PO_4^-$ in the effluent. Second, ultra- membrane filtration was conducted to separate solids in the effluent. Third, nano-membrane filtration was conducted to remove heavy metals in the effluent. After the 2-step membrane-filtration was finished, the purified phosphate-containing solution was obtained and P was recovered in the form of phosphoric acid solution, with a P recovery efficiency of 54%. (Blöcher et al., 2012)

2.2 Literature review related to P recovery from MSWI ash

This chapter focuses on a study aiming to recover P from MSWI FA (Du and Yu, 2011).

2.2.1 Methodology

According to Du and Yu's study (2011), it is feasible to recover P from MSWI FA by the acidic dissolution – precipitation approach, with a P recovery efficiency of 71% and the P content of 3.4% in the product.

The acidic dissolution – precipitation approach was initially introduced by Kaikake et al. in 2009 and then was improved by Du and Yu to fit for MSWI FA in 2011. Figure 2.1 states the experimental procedure.

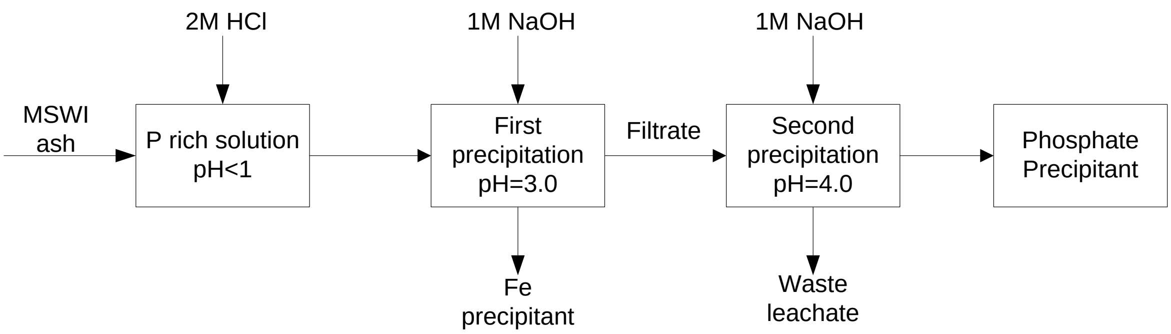


Figure 2.1. Acidic dissolution – precipitation method *Source: Du and Yu, 2011*

The P recovery experiments consist of the P leaching tests and the Precovery tests.

For the P leaching tests, MSWI FA was dissolved in 2M HCl to get the P-rich solution. The solution acted as a P feed for the P recovery tests.

The P recovery tests were performed by two-step precipitation. The aim of the 1st precipitation was to remove metals (mainly Fe) in the leachates by titrating the leachates with 1M NaOH to pH 3. When the 1st precipitation was finished, the precipitate was separated by filtration and the filtrate was reserved for the 2nd precipitation. In the 2nd precipitation, P was precipitated in the form of phosphate by titrating the filtrate with 1M NaOH to pH 4.

2.2.2 Drawbacks

The P fraction accounts for 3.4% of the product (Du and Yu, 2011), which is much lower than the P content of commercial fertilizers (7–10%) (UK fertilizers regulation,1990). Hence, in order to serve as raw material for fertilizers, further treatment is required to concentrate P in the product.

The content of Pb, Cr, Cu in the product exceed Swedish limitations (Swedish EPA, Code of Statutes 1994:2) while the content of Cd exceeds both Swedish and EU limitations (EU council directive, 86/278/EEC). The high content of heavy metals contributed to the toxicity of the product and limited its direct utilization.

3 Theoretical concepts

In this study, instruments as pH-stat titrator, HACH spectrophotometer, Ion Chromatography (IC), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and X-ray Powder Diffraction (XRD) were used in the experiments. These methods are briefly described here.

3.1 pH-Stat titration

The pH-Stat titration technique is developed to maintain constant pH of a reaction by releasing acid or base. After a constant pH value is set, a titration starts. During the titration, the pH value is measured continuously. Once pH deviation happens, reagent will be added into the reaction solution. The real time pH value, temperature and reaction rate of the solution will be measured during the titration (Fluid Management Systems Inc, 2007).

In this study, a Metrohm 665 Dosimat was used for pH adjustment of the leachates during the SPE and precipitation processes.

3.2 Hach spectrophotometer

The idea of spectrophotometry is to measure the amount of absorbed light when a light beam of a specific wave length passes through a sample. The adsorbed light is related to the concentration of interest element in the liquid samples (Blauch, 2009).

According to Beer's Law ($A = \varepsilon\ l\ c$), absorbance (A) is linear related to both cell path length (l) and analyte concentration(c), the quantity (ε) is the molar absorptivity of the absorber. Based on equation 3.1, the concentration of interest elements in the sample can be quantified.

$$A = \varepsilon\ l\ c \qquad \textit{Equation 3.1}$$

In this study, Hach DR/890 portable colorimeter was used to measure the concentration of reactive P (orthophosphate) in the leachates by the standard PhosVer3 Method. The detection range was 0–2.5 mg/L PO_4^{3-} (Hach company, 2011).

3.3 Ion chromatography (IC)

The idea of IC was first noticed by Small et al. in 1975 and has been regarded as a reliable ion-exchange liquid chromatographic method for environmental, chemical and pharmaceutical research. With the aid of IC, interest components of chemical mixtures can be isolated and detected.

First, based on ionic interactions, ionic species can be retained on the ion-exchange stationary phase with ion-exchange column. Second, convert the retained ions on the stationary phase into the mobile phase ions by elution. The ions of interest in the eluent can be measured by conductivity detector (Paul and Jackson, 1990).

In this study, DIONEX ICS-900 Starter Line IC System was used and both cation ions (Mn^{4+}, Na^{+}, K^{+}, NH_3^{4+}, Mg^{2+} and Ca^{2+}) and anion ions (Cl^{-}, CH_3COO^{-}, NO_2^{-}, NO_3^{-}, PO_4^{3-} and SO_2^{4-}) were analysed. (ICS-900 Starter Line IC System, 2012).

3.4 Inductively coupled plasma-mass spectrometry (ICP-MS)

ICP-MS is a mature technique for multi-elemental trace analysis (Beauchemin, 2006). The principle of ICP-MS is to generate positively charged ions by discharging high temperature plasma.

An ICP-MS system consists of inductively coupled plasma torch, interface and mass spectrometer. Figure 3.1 illustrates how an ICP-MS system works.

The liquid sample is pumped into the introduction system equipped with a spray chamber and nebulizer. In the introduction system, the liquid sample is present as an aero and injected into the plasma. The liquid sample will be excited as atoms and ions when passes through the heating zones of the plasma torch and then ions reach the detector. The ion detector converts the ions into electrical pulses in order to measure the magnitude of the electrical pulses. Base on the correlation between the electrical pulses magnitude and the number of ions, the ions in the samples can be quantified (Thomas, 2001).

In this study, ICP-MS was conducted to analyse the elemental composition of the samples.

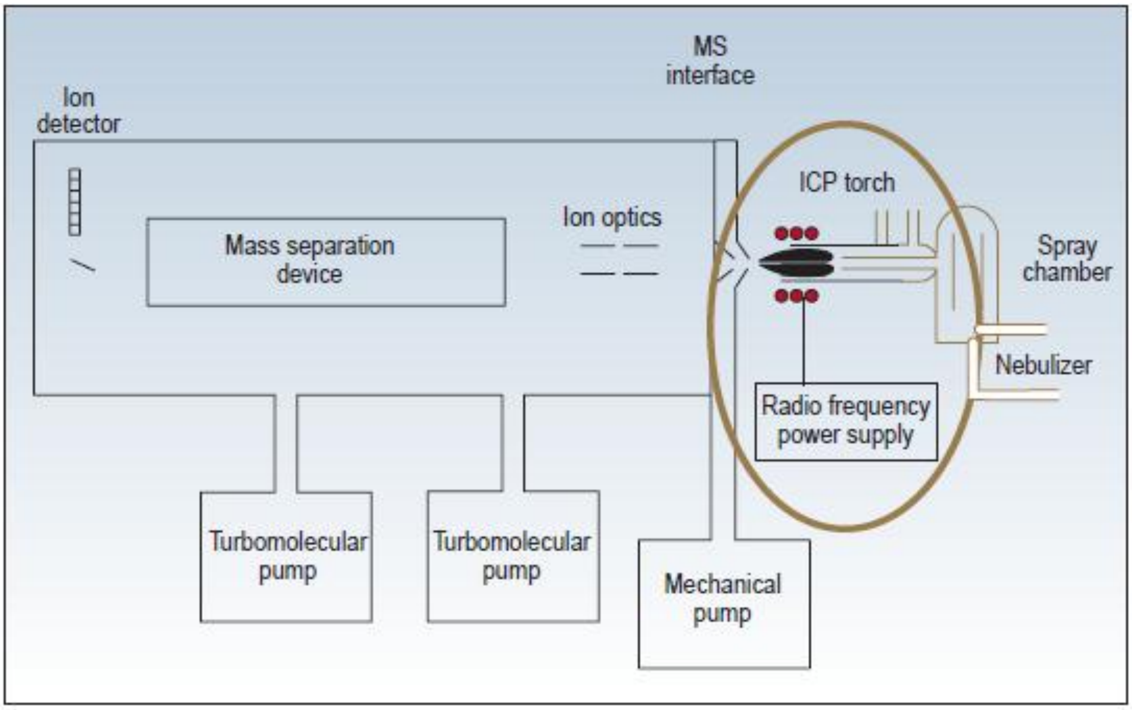


Figure 3.1. The schematic of an ICP-MS system (Source: Thomas, 2001)

3.5 X-ray diffraction (XRD)

The XRD technique can be used to analyse the crystalline compounds in the solids. The principle of XRD is introduced below.

If the angle of the X-ray beam and the detector is similar to inter-atomic distances of a specific crystalline compound, the photons will be scattered. The number of scattered photons (called Debye cones) can be recorded by a detector and present as peaks in the diffractogram (Brügemann and Gerndt, 2004). Based on Joint Committee of Powder Diffraction Standards database (Joint Committee of Powder Diffraction Standards, 2006), each compound corresponding to one or several peaks can be identified.

In this study, the crystalline compounds of the ash samples were analysed by Siemens D5000 X-ray powder diffractometer using Cu Kα radiation.

3.6 Solid phase extraction (SPE)

Solid phase extraction (SPE) is a useful technique aiming at separating one or several species from a mixture, with the advantages of fast, easy to operate, economic and eco-friendly (Sigma-Aldrich Co., 1998). Empore chelating disk, a patented ion-exchange type SPE product developed by 3M Company, has been proved to be an effective SPE product to remove metals in the liquids (3M Industrial and Consumer Sector, 1996).

Empore chelating disk comprises of 90% iminodiacetate functionalized poly (styrene-divinylbenzene) (SDB) and 10% polytetrafluoroethylene (PTFE) by weight. Based on its affinity for multivalent metal ions (e.g. Ca^{2+}, Mg^{2+}, $Fe^{3+}$and Zn^{2+}), metal ions can be removed after the solution passes through the chelating porous membrane. The pH level is crucial as the disk functions as a weak anion exchanger at pH 2 but functions as a metal cation chelater as pH increases. In order to ensure the best chelation effect, precondition of the disk is necessary. The precondition process consists of prewash, converts the disk to ammonium form, sample extraction and elution. The disk can be reused by acidic elution (3M Industrial and Consumer Sector, 1996).

In order to remove metals leached in the leachates, 47mm Empore chelating disk was chosen for the SPE tests. In order to avoid Fe precipitation at pH 3, the control pH level was set to 2.5.

4 Experimental set-up

The experiments consist of the XRD tests, the maximized P leaching tests, the SPE tests and the P recovery tests. For all ash samples, duplicate experiments were performed.

Based on literature review (Du and Yu, 2011), L/S=5 is recommended. The P leaching reactions were conducted by 2h stirring with the speed of 200rpm. In order to separate solids from the leachates, centrifugation at 3000 relative centrifugal force (RCF) was preformed. Before Hach/IC/ICP-MS analysis, liquid samples were filtrated by 0.45 μm polyethersulfone filters to remove particles. All the precipitates were separated and collected by 55mm ashless quantitative filter papers with oven drying at 80^{o}C for 12h.

Both Hach and IC analysis were conducted to measure the P content (in the form of PO_4^{3-}) in the solutions. The metals content in the solutions were measured by ICP-MS instrument. The elemental composition of the solids (precipitates generated in the P recovery tests) was identified by ICP-MS.

4.1 Maximized P leaching tests

The aim of the maximized P leaching tests was to find the optimal P leaching conditions.

According to Du and Yu's study (2011), the content of leached P from MSWI FA varied under different acid concentrations and sedimentation time, which indicated that acid concentration and sedimentation time are the two critical factors affecting the P leaching performance.

In this study, solutions of HCl in three concentrations (0.5M/1.5M/2.5M) were chosen as the P leaching agents. In order to verify if sedimentation of the mixture could increase the P leaching, the performances of P leaching with and without 24h sedimentation were evaluated. Both Hach and IC analysis were conducted to measure the P content in the leachates.

Figure 4.1 shows an overview of the whole P recovery process with the maximized leaching tests in detail.

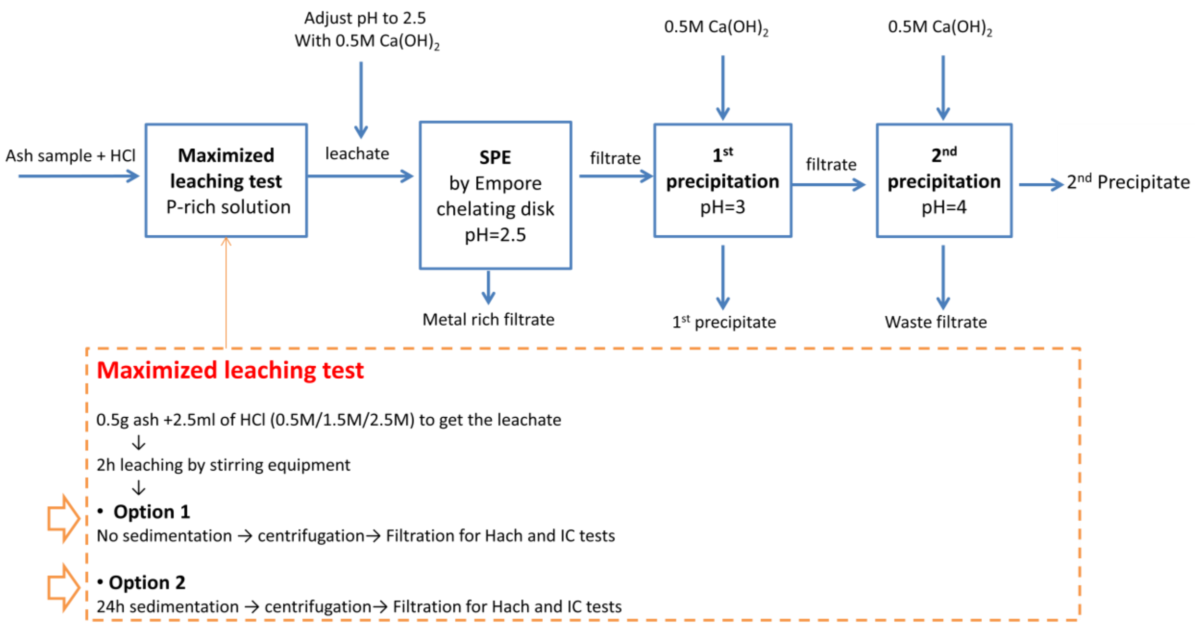


Figure 4.1. The experimental procedure of recovering P from MSWI BA with details on the maximized leaching tests

4.2 SPE tests

The aim of the SPE tests was to investigate if Empore chelating disk is effective to remove metals from the leachates without negative effects on the P recovery. Based on ICP-MS analysis, metal removal efficiencies and ratios of metals retained on the disk were quantified. In order to remove metals from the leachates effectively, SPE was performed twice.

Based on the results of the maximized leaching tests, the leachates for the SPE tests were produced by leaching ash samples with 2.5M HCl solution without sedimentation. The leachates were thereafter titrated to pH 2.5 by adding 0.5M $Ca(OH)_2$ and then the SPE tests were carried out.

Figure 4.2 shows an overview of the P recovery tests with the SPE tests in detail.

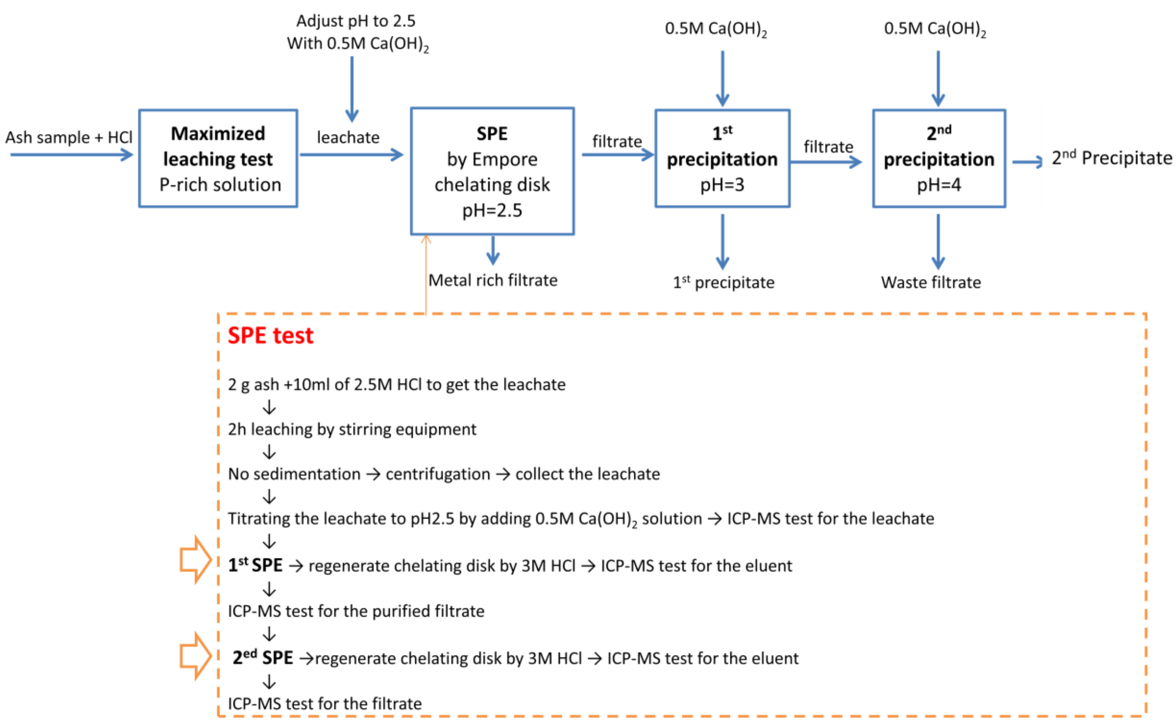


Figure 4.2. The experimental procedure of recovering P from MSWI BA with details on the SPE tests

4.3 P recovery tests

The P recovery tests were aimed at evaluating the performance of recovering P from sorted MSWI BA by the acidic dissolution – precipitation method.

Due to losses of P during the SPE process, Empore chelating disk SPE was excluded in the P recovery tests. The P leaching condition was 2.5M HCl leaching for 2h without sedimentation. Batch experiments were conducted by mixing 20g of ash samples with 100ml of 2.5M HCl solution to get the batch leachates. Based on the results of the maximized P leaching tests, only IC analysis was conducted to measure the P content (in the form of PO_4^{3-}) in the leachates. The P recovery procedure is stated in Figure 4.3.

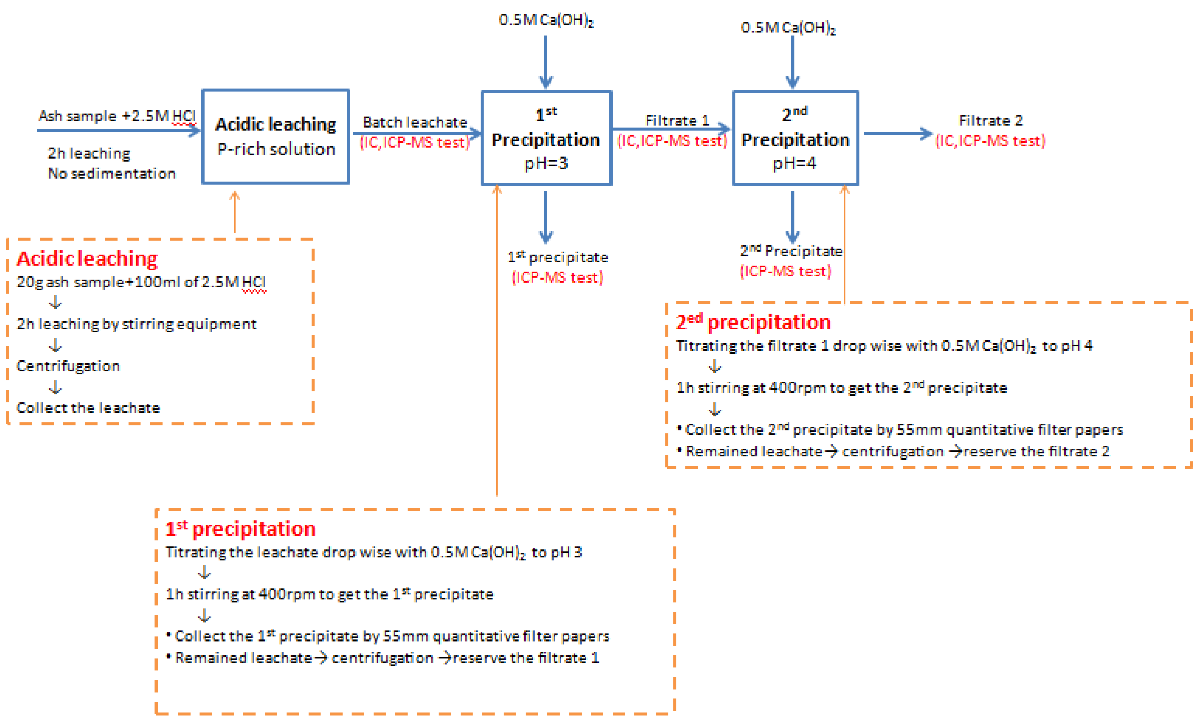


Figure 4.3. The experimental procedure of recovering P from MSWI BA with analysis techniques within brackets

5 Results and discussion

5.1 XRD analysis

The crystalline compounds of original and leached ash samples were identified by XRD analysis (Table 5.1).

Table 5.1 Crystalline compounds identified in the ash samples

<table>
<tr><th colspan="2" rowspan="2">Minerals</th><th colspan="4">Ash samples</th></tr>
<tr><th>FBA</th><th>Leached FBA</th><th>ABA</th><th>Leached ABA</th></tr>
<tr><td colspan="2">SiO_2</td><td>Major</td><td>Major</td><td>Minor</td><td>Major</td></tr>
<tr><td colspan="2">$CaCO_3$</td><td>Minor</td><td></td><td>Major</td><td></td></tr>
<tr><td colspan="2">KCl</td><td></td><td>Minor</td><td></td><td></td></tr>
<tr><td colspan="2">NaCl</td><td></td><td>Minor</td><td></td><td></td></tr>
<tr><td rowspan="5">Fe-oxides</td><td>Magnetite[6]</td><td>Minor</td><td>Minor</td><td></td><td></td></tr>
<tr><td>Iron Oxide</td><td></td><td>Minor</td><td></td><td></td></tr>
<tr><td>Hematite[7]</td><td></td><td>Minor</td><td></td><td></td></tr>
<tr><td>Maghemite-C[8]</td><td></td><td>Minor</td><td>Minor</td><td></td></tr>
<tr><td>Magnesioferrite aluminian[9]</td><td></td><td></td><td></td><td>Minor</td></tr>
<tr><td colspan="2">Anorthite[10]</td><td>Minor</td><td>Minor</td><td></td><td></td></tr>
<tr><td colspan="2">Alumoakermanite[11]</td><td>Minor</td><td></td><td></td><td></td></tr>
<tr><td colspan="2">Melilite[12]</td><td></td><td></td><td>Minor</td><td></td></tr>
<tr><td colspan="2">Diopside[13]</td><td></td><td></td><td></td><td>Minor</td></tr>
<tr><td colspan="2">$CaMg_{0.75}Fe_{0.25}Si_2O_6$</td><td></td><td></td><td></td><td>Minor</td></tr>
<tr><td colspan="2">$CaFe_3AlO_7$</td><td></td><td></td><td></td><td>Minor</td></tr>
<tr><td colspan="2">$Na_3MgAlSi_2O_8$</td><td></td><td></td><td></td><td>Minor</td></tr>
</table>

6 Magnetite: $(Mg_{0.3}Fe_{0.7})((Mg_{0.73}Fe_{1.27})O_4)$
7 Hematite: $Fe_{1.957}O_3$
8 Maghemite-C: Fe_2O_3
9 Magnesioferrite aluminian: $(MgAl_{0.74}Fe_{1.26)}O_4$
10 Anorthite: $CaAl_2Si_2O_8$
11 Alumoakermanite: $(Ca,Na)_2(Al,Mg,Fe+2)(Si_2O_7)$
12 Melilite: $Ca_2Mg_{0.25}Al_{1.5}Si_{1.25}O_7$
13 Diopside: $Ca_{0.964}Mg(Si_2O_6)$

- Phosphorus compounds

No mineral containing P compounds were detected. An explanation could be that the P contents in FBA and ABA were too low to be detected by XRD analysis. The absent of P in leached ashes may be because of large fractions of P was leached in the acidic solutions (Table 5.1).

- Quartz

Quartz (SiO_2) was identified and present as the major compound in all ashes except ABA.

Silicic acid gel is the highly porous form of SiO_2 and could be obtained by mixing hydrochloric acid with silicate. It is soluble in hydrofluoric acid and alkali at 80–100℃ but insoluble in water and ethanol (EFSA, 2009).

According to Du and Yu's study (2011), SiO_2 dissolved in hydrochloric acid was present in the form of silicic acid during the acid leaching of MSWI FA. Due to its insolubility in hydrochloric acid, silicic acid was condensed and present as yellow gel in the leachates.

The formation of silicic acid gel in the acidic leaching process is critical. During the filtration process, it was quite hard to remove particles in the gel-containing leachates by 0.45 μm polyethersulfone filter. Probably phosphate ions were concentrated in silicic acid gel rather than leached in the leachates and could affect the performance of P leaching.

- Calcium carbonate

Calcium carbonate ($CaCO_3$) was identified in FBA and ABA, but not in leached ashes because it was dissolved by hydrochloric acid. Aged bottom ash (ABA) contains more $CaCO_3$ than FBA, because $CaCO_3$ was formed during the natural aging process ($CO_2 + CaO \rightarrow CaCO_3$).

- Fe-oxides

Various Fe-oxides were identified in all ashes, especially leached FBA.

One explanation could be that Fe-oxides were formed during the leaching process. Another more likely explanation is that Fe-oxides in original ashes were hidden by more soluble compounds and could not be detected by XRD.

Iron was present in the forms of magnetite and alumoakermanite in FBA. During the acidic leaching, different kinds of Fe-oxides were formed and presented in leached FBA. Iron mainly presented as magnetite-C in ABA but presented in the forms of magnesioferrite aluminian, $CaMg_{0.75}Fe_{0.25}Si_2O_6$ and $CaFe_3AlO_7$ in leached ABA.

- Other compounds

Alkali metal chlorides (e.g. KCl and NaCl) were identified as the minor compounds in leached FBA. An explanation could be that KCl and NaCl precipitates were formed in the leaching process and then adsorbed on ash.

5.2 Maximized P leaching tests

The P leaching efficiency is related to leaching time and HCl concentration. The P leaching efficiencies under different leaching conditions were calculated. Considering that the ash matrix and the corresponding leachates are complex, and for the data accuracy, both Hach and IC analysis were conducted to measure the P content in the leachates.

5.2.1 Analysis of P leaching by Hach

- **The P leaching efficiency**

The P leaching efficiency equals to the P content in the leachates divided by the P content in the ash. The P content in the ash was calculated by multiplying the weight of the ash sample with the P fraction in reference ash (Table 1.2).

P leaching efficiency (%) = P in the batch leachates / P in the ash $\times 100$ *Equation 5.1*

The P leaching efficiencies under different leaching conditions were calculated to evaluate the P leaching performance (Appendix I, Table 1).

The calculated P leaching efficiencies were abnormal because some values were above 100%. The heterogeneity of the ash could be a reason because the P content in the reference ash could be lower than the actual P content in the ash sample. But it is not much likely as the P leaching efficiencies were so much exceeding 100%.

Although only P present in the form of phosphate was measured by Hach instrument, the P content in the leachates was still overestimated by Hach instrument. The reason for the measurement deviation could be to the complexity of the leachates. If some particles present in the leachates, the measured P content by Hach instrument would be much higher than the actual value.

- **The P content in the leachates**

Although the calculated P leaching efficiency values were abnormal, it is interesting to investigate if some trends of the P leaching can be identified. Comparisons of the P content in the leachates under different leaching conditions are stated in Figure 5.1 and 5.2.

Figure 5.1 states the P content in the leachates depending on HCl concentration.

For FA and FBA, the maximized P leaching was obtained by 2.5M HCl leaching. For ABA, more P was leached by 1.5M HCl than 2.5M HCl, but not very much.

Du and Yu’s study (2011) indicated that 2M HCl maximized the P leaching from FA and more P was leached by 2.5M HCl than 1.5M HCl. The P leaching effect was correlated to HCl concentration and 2M HCl yielded the optimal leaching performance in FA study.

From the reasons above , 2.5M is chosen as the optimal concentration of the HCl solution.

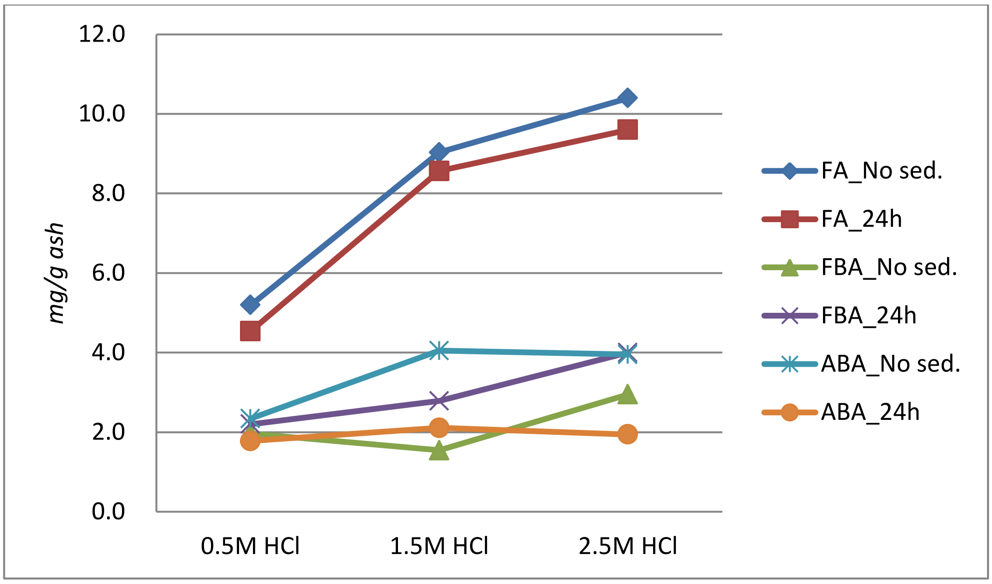


Figure 5.1. P content in the leachates depending on concentration of HCl; analysed by Hach

Figure 5.2 states the P content in the leachates depending on sedimentation time.

There is no clear correlation between the P leaching performances with sedimentation time. For FBA, more P was leached but the added values were quite limited. For ABA and FA, the P content decreased slightly after 24h sedimentation by all concentrations of HCl leaching. As mentioned before, silicic acid gel may be formed during the leaching and parts of P may concentrate into silicic acid gel during the sedimentation. This could explain why the P content decreased slightly after 24h sedimentation because parts of P were concentrated into silicic acid gel.

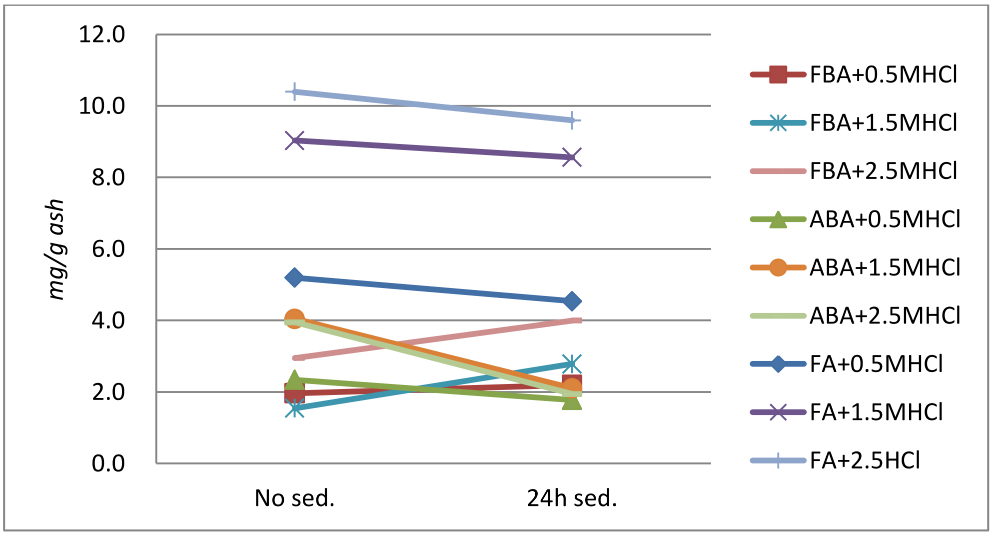


Figure 5.2. P content in the leachates depending on sedimentation time; analysed by Hach

5.2.2 Analysis of P leaching by IC

- **The P leaching efficiency**

Based on the IC results, the P leaching efficiencies were calculated (Appendix I, Table 2). Compared to the Hach results, more reasonable values were obtained by IC analysis. However, the risk that the P content in the leachates was underestimated cannot be ignored because only P in the form of phosphate was measured by the IC instrument.

❑ The P content in the leachate

Comparisons of the P content in the leachates under different leaching conditions were stated in Figure 5.3 and 5.4.

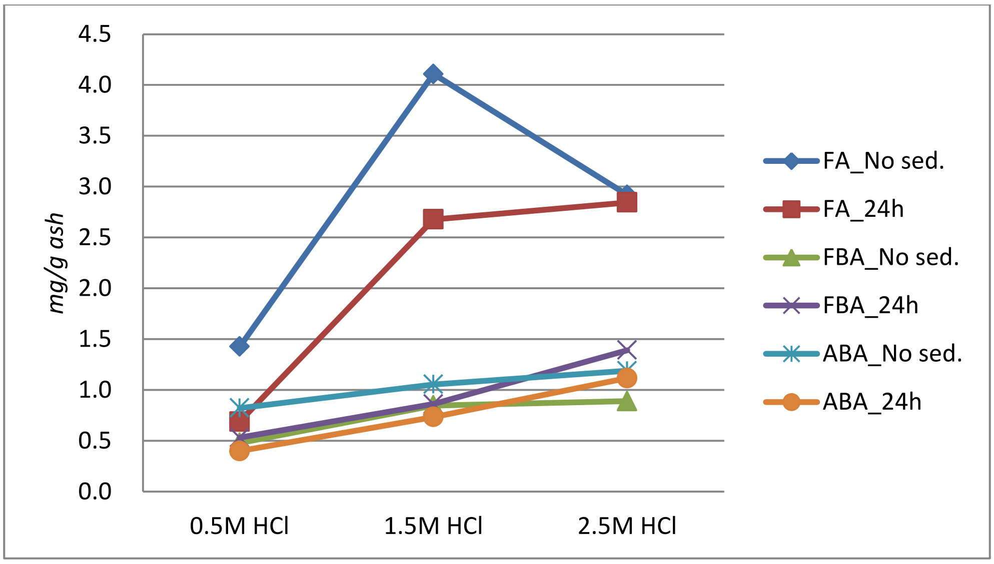


Figure 5.3. P content in the leachates depending on concentration of HCl; analysed by IC

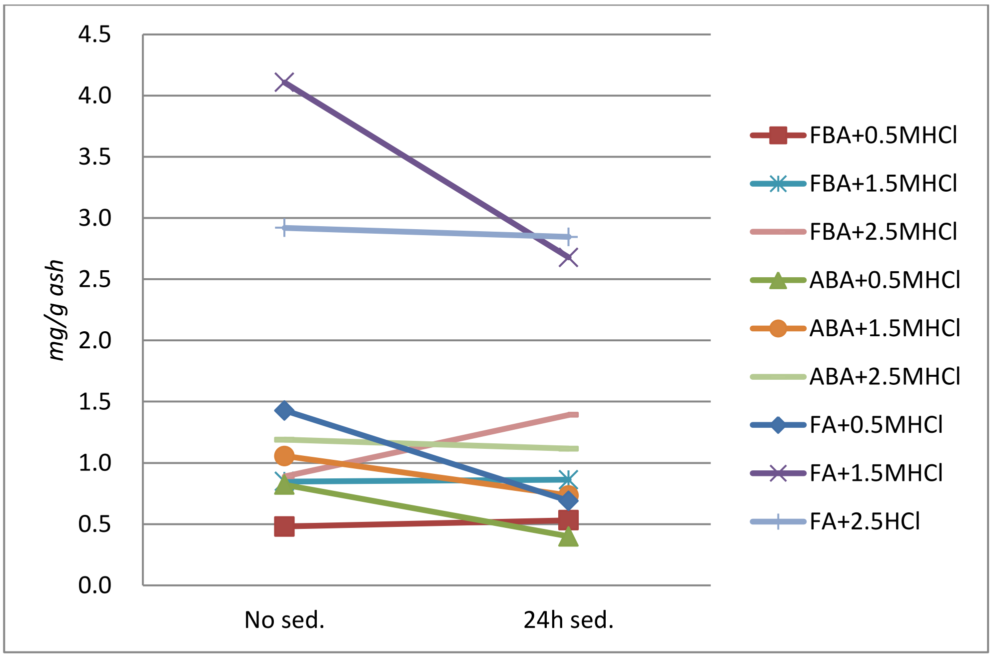


Figure 5.4. P content in the leachates depending on sedimentation time; analysed by IC

The maximized P leaching effects for FBA and ABA were obtained by leaching with 2.5M HCl (Figure 5.3), which indicates that the P leaching efficiency increases with increasing acid concentration. For FA, the maximized P leaching was obtained by leaching with 2.5M HCl and after 24h sedimentation, which confirming the results by Du and Yu (2011).

As seen in Figure 5.4, there is no obvious correlation between the P content in the leachate and the sedimentation time. For FBA, more P was leached after 24h sedimentation. For FA and ABA, the P content decreased heavily after 24h sedimentation. An explanation is that parts of P were separated from the leachate and concentrated into silicic acid gel.

5.2.3 Qualitative comparative analysis

The P content in the leachates may be overestimated by the Hach method; probably underestimated by IC analysis as only P in phosphate form is measured. Concerning that the calculated P leaching efficiency was unsecure, a qualitative assessment is more appropriate to investigate the maximized leaching conditions.

With respect to the optimal HCl concentration, similar trends were found in Hach and IC analysis. The Hach and IC results indicate that 2.5M is the optimal concentration of HCl for the P leaching and 24h sedimentation cannot improve the P leaching. A comprehensive conclusion can be drawn that 2.5M HCl leaching without sedimentation could maximize the P leaching from MSWI BA.

In order to guarantee the experimental accuracy, an inter-calibration measurement between Hach and IC measurement is suggested for further studies. As the P content was overestimated by Hach instrument, only IC measurement was conducted to measure the P content in the further SPE and the P recovery tests.

- **Gel formation**

Yellow gel occurred in the leachates (Figure 5.5) when leaching by 2.5M HCl of FA and after 24h sedimentation, while no gel occurred in FBA and ABA leachates.

According to the XRD analysis, SiO_2 was present as the major or minor crystalline compound in FBA and ABA. Silicon dioxide is the main factor for yellow gel formation (Du and Yu, 2011). The mechanism of gel formation is that Si^{4+} reaction with H^+ under strong acid condition to form silicic acid (a form of silicon dioxide), silicic acid releases water easily and leads to gel formation (ILER, 1979).

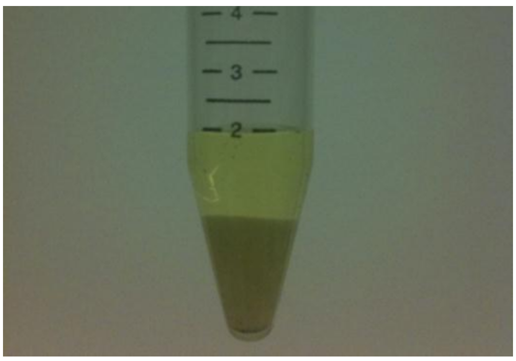


Figure 5.5. Yellow gel occurred in the leachates for FA with 2.5M HCl and 24h sed.

High content of Si is present in FBA (180000 mg/kg), but the Si contents in FA and ABA are lower (45300 mg/kg; 23800 mg/kg) (Table 1.2). For the formation of silicic acid gel, the reason is not the present of Si in the ash but how effectively Si is leached from ash. According to the XRD results (Table 5.1), the SiO_2 fraction in ABA increased after acidic leaching, which indicates that it is hard to release Si from ABA. A possible explanation for the formation of silicic acid gel only during the FA leaching could be that, SiO_2 in BA is more difficult to release than in FA. As a result, more Si released from FA to the leachates and resulted in the formation of silicic acid gel.

5.3 SPE tests

5.3.1 Metal removal analysis

The metal removal efficiencies for the SPE tests were calculated (Appendix I, Table 3). The Empore chelating disk showed a high affinity for Zn, Cu and Pb ions, with removal efficiencies of over 82%. The removal efficiencies of Ca, Mg, Li and Ni ions of the 1st SPE were low, under 30%. By repeatedly SPE, the metal removal efficiencies increased effectively except for Cu ions (Figure 5.6 – 5.8). All the Cu ions were removed from the leachates after the 1st SPE.

A conclusion can be drawn that Empore chelating disk is effective to remove metals from aqueous solutions. In order to get higher removal efficiency, repeatedly SPE is recommended.

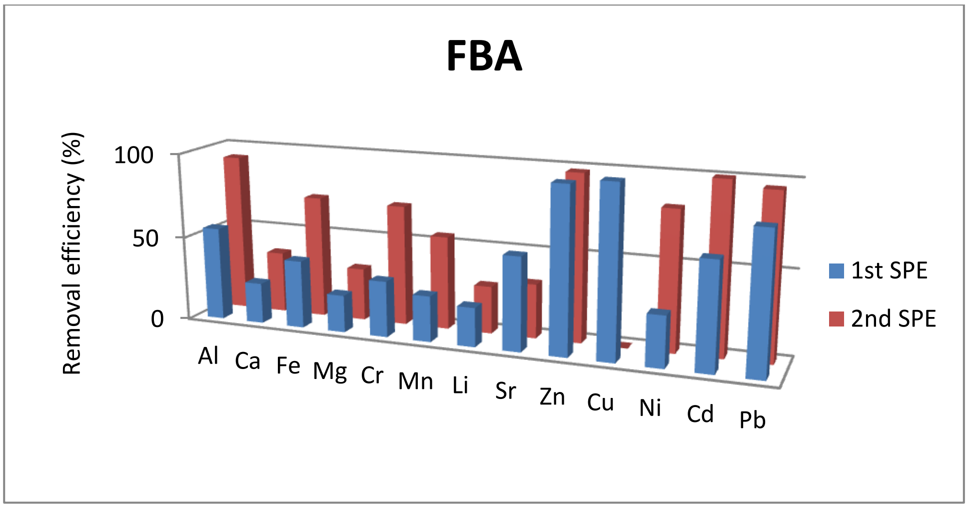


Figure 5.6. Comparison of metal removal efficiency by the SPE, FBA

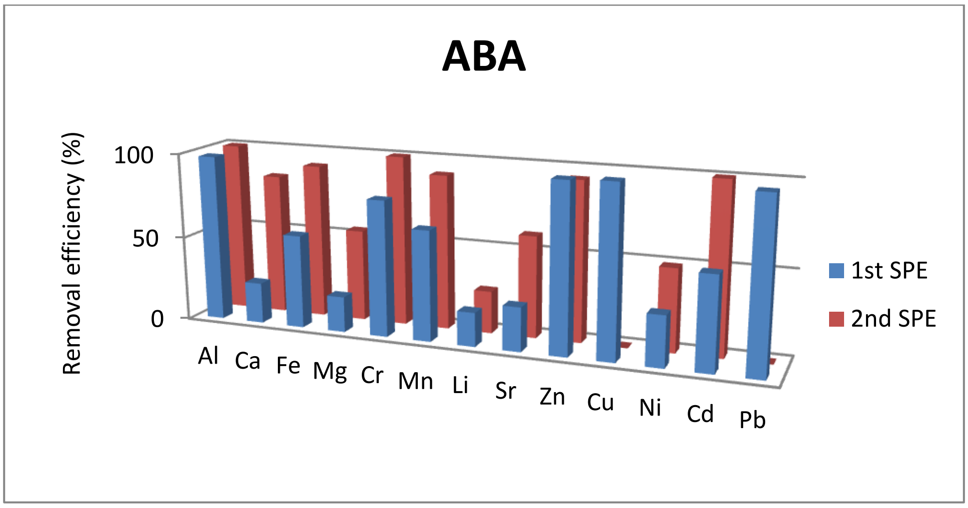


Figure 5.7. Comparison of metal removal efficiency by the SPE, ABA

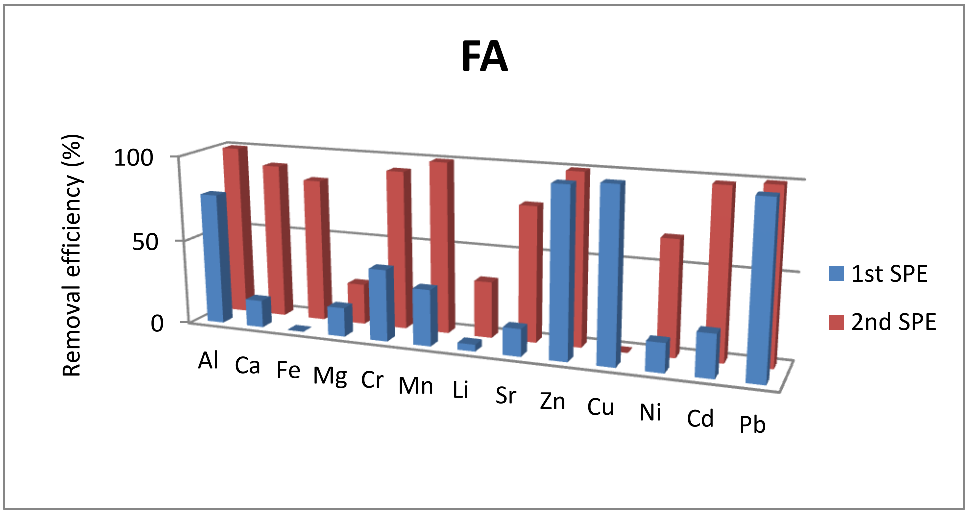


Figure 5.8. Comparison of metal removal efficiency by the SPE, FA

5.3.2 Analysis of metals retained by Empore chelating disk

The function of Empore chelating disk is to adsorb positively charged metal ions by chelating them in the disk and elution is necessary to remove the metal ions adsorbed in the disk before reusing it (3M Industrial and Consumer Sector, 1996). However, as a result of incomplete elution, parts of adsorbed metal ions could be retained in the disk. Therefore, it is worth exploring if any metal ions were retained in the disk after elution. Based on material balance (Figure 5.9, Equation 5.2–5.4), the ratios of metals retained by Empore chelating disk were calculated (Table 5.2).

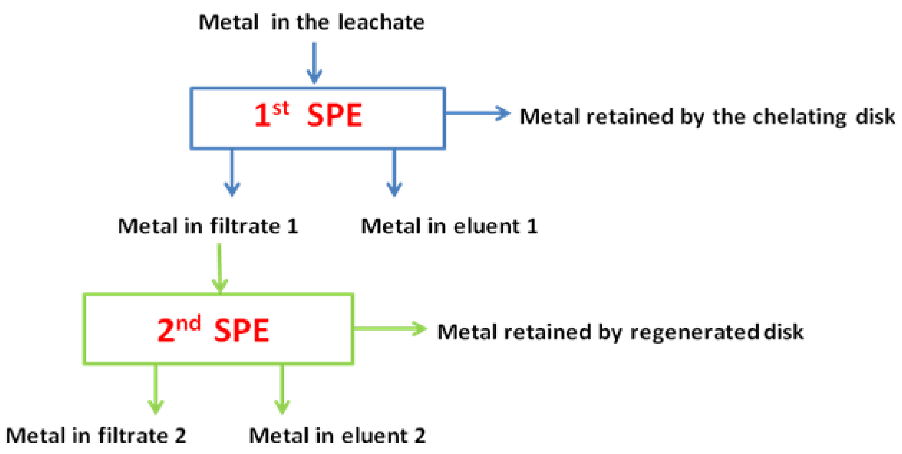


Figure 5.9. A sketch of material balance

- A general material balance equation is,

$$\text{Mass}_{\text{In}} = \text{Mass}_{\text{Out}} + \text{Mass}_{\text{retained}} \qquad \textit{Equation 5.2}$$

- For the 1st SPE tests, the material balance equation is,

Metal in the leachate = Metal in filtrate 1 + Metal in eluent 1 + Metal retained by the chelating disk

Equation 5.3

- For the 2nd SPE tests, the material balance equation is,

Metal in filtrate 1 = Metal in filtrate 2 + Metal in eluent 2 + Metal retained by the regenerated disk

Equation 5.4

Table 5.2. Metals retained by Empore chelating disk

Leachate types	SPE steps	Ratios of metals retained by Empore chelating disk (%)												
		Al	Ca	Fe	Mg	Cr	Mn	Li	Sr	Zn	Cu	Ni	Cd	Pb
FA leachate	1st SPE	16	7	45	0	0	0	0	6	32	0	84	0	0
	2nd SPE	100	35	100	11	0	8	0	0	0	0	100	0	0
FBA leachate	1st SPE	45	0	0	0	0	0	0	2	0	0	17	0	0
	2nd SPE	100	44	84	57	0	33	0	37	100	0	100	100	0
ABA leachate	1st SPE	39	15	0	13	0	49	0	14	0	0	16	0	0
	2nd SPE	100	54	100	43	0	0	0	41	0	0	100	90	0

During the SPE procedure, metals like Al, Ca, Fe, Mg, Mn, Sr, Zn, Ni and Cd were retained by Empore chelating disk while no Cr, Li, Cu or Pb were retained. This could affect the chelating capacity and the metal removal efficiency of the disk. Because Empore chelating disk is expensive, reuse of the disk is necessary. Therefore, in order to ensure the metal removal capacity, eluting metal ions from the disk completely is important. According to the specification of Empore chelating disk (3M Industrial and Consumer Sector, 1996), elution by 3M HCl was conducted twice. In order to ensure complete elution, a suggestion is to let HCl solution to soak for 10 minute instead of 1 minute.

5.3.3 Analysis of the P content

The P content in the leachates remaining after the SPE tests were measured by IC instrument for investigating whether P was adsorbed on the disk or not.

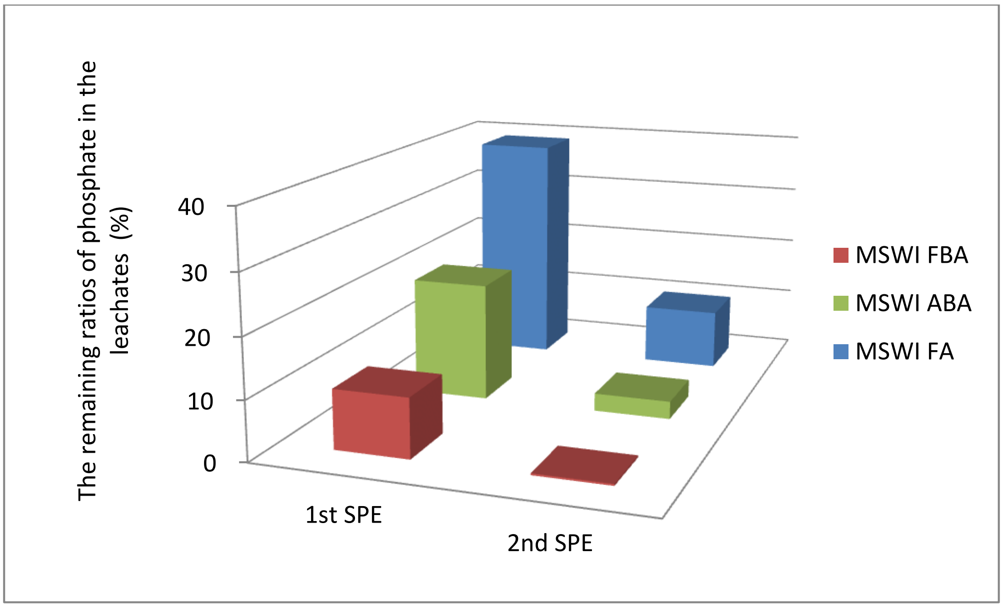


Figure 5.10. The remaining ratios of phosphate in the leachates after the SPE tests

The IC result shows that the P content decreased heavily after the SPE tests. Concerning FBA leachates, 61% phosphate was removed in the 1st SPE and only 10% phosphate remained after the 2nd SPE (Figure 5.10). For ABA and FA, the remaining ratios of phosphate in the leachates were even lower than in the FBA leachates. The high decrease of P after the SPE indicates that parts of P were remained by Empore chelating disk. An explanation could be that phosphate attached to metal ions which were attached to the chelating ligand.

Combining chapter 5.3.1–5.3.3 together, although the SPE method turns out to be an effective way to purify the leachates by removing metal ions, large amounts of P was removed in the meanwhile. Considering P is the element of interest to be recovered, the SPE method was excluded in the further P recovery tests.

5.4 P recovery tests

5.4.1 P recovery efficiency by IC

Based on mass balance (equation 5.5–5.6) and calculation equations (equation 5.7–5.8), the P leaching efficiencies and the P recovery efficiencies were calculated (Table 5.3).

- P in the batch leachate = P in the 1st precipitate + P in the filtrate 1 *Equation 5.5*
- P in the filtrate 1= P in the 2nd precipitate + P in the filtrate 2 *Equation 5.6*
- P recovery efficiency based on P content in the ash =

  (P in the 1st precipitate+ P in the 2nd precipitate) / P in the ash *Equation 5.7*
- P recovery efficiency based on P content in the leachate =

  (P in the 1st precipitate+ P in the 2nd precipitate) / P in the leachate *Equation 5.8*

Table 5.3. P content, leaching and recovery efficiency of the P recovery tests

Ashes	P content (mg/kg ash)						P leaching efficiency (%)	P recovery efficiency (%)	
	In the ash[14]	Batch leachate	Filtrate1	1st precipitate	Filtrate2	2nd precipitate		Based on P content in the ash	Based on P content in the leachate
FBA	1800	851	42	810	35	6	47	45	96
ABA	2970	1675	146	1529	2.7	143	56	56	99
FA	5900	1773	378	1395	172	206	30	27	90

The P leaching efficiencies of all ashes was 30–56%, which was consistent with the values retrieved from the maximized P leaching tests (40–49%).

Larger fractions of P were present in the 1st precipitates than in the 2nd precipitates. Du and Yu's study (2011) indicated that large amounts of P in FA were recovered during the 2nd precipitation. However, for this study, large fractions of P were recovered during the 1st precipitation (Table 5.3). One factor could be that different concentrations of HCl were used for the leaching tests. In this study, 2.5M HCl was used while 2M HCl was used in Du and Yu's study. Leaching with a higher concentration of HCl gave a higher P release and led to co-precipitation with P during the 1st precipitation.

Du and Yu's study (2011) indicated that the precipitation of P compounds could be prevented effectively at pH 3. However, the P recovery tests results of this study did not confirm their conclusion and most of P was precipitated at pH 3. An explanation could be that different titrating solutions were implemented. For environmental and economic considerations, 0.5M $Ca(OH)_2$ solution was recommended for this study instead of 1M NaOH solution which has

[14] analytical data of ash samples supplied by Eurofins

been implemented in Du and Yu's study (2011). The phosphate ions form insoluble precipitates as $Ca_3(PO_4)_2$ with calcium ions in the liquids. As a result, most of P was precipitated during the 1st precipitation.

According to the experimental set-up, the major precipitates at pH 3 should be Fe compounds. However, elemental analysis of the P recovery products (Table 5.4) indicates that P and Fe compounds were formed simultaneously during the 1st and the 2nd precipitation. Hence, the P recovery tests could be more efficient by simplifying the precipitation steps to precipitate P at one time at pH 4.

Based on the P content in the leachates, the P recovery efficiency was calculated. Higher amounts of P were recovered by precipitation in this study (over 90%, both the 1st and the 2nd precipitates were included) than Du and Yu's study (71%, only the 2nd precipitates were included). Therefore, in order to increase the P recovery efficiency of the whole process, the P leaching step should be improved. According to Petzet et al., (2012), neither direct acidic leaching nor alkaline leaching can get a satisfactory P leaching efficiency. Petzet et al., (2012) proved that alkaline leaching (1M NaOH solution) combined with acidic pre-treatment (HCl solution of different concentrations) could maximize the P leaching from SSIA. In order to improve the P leaching step, a suggestion is to try alkaline leaching combined with acidic pre-treatment instead of direct acidic leaching which was tried by Du and Yu but must do more experiments to investigate the proper pH.

5.4.2 Analysis of the metal content

The metal content could contribute to the toxicity of the product. The metal content in the leachates could indirectly demonstrate the metal flows. The variation trends of the metal content are listed below; see Figure 5.11–5.13. For all ashes, the metal content in the leachates decreased heavily after the 1st precipitation while less metal fraction was lost during the 2nd precipitation. Those metals were precipitated as a part of the products.

A conclusion can be drawn that, metals like Al, As, Cu, Cr and Zn were precipitated during the 1st precipitation while large parts of P were recovered in the meanwhile. If the metal content of the product exceed limitations, the product cannot be used directly. Toxicity analysis of the product will be introduced in the following chapter.

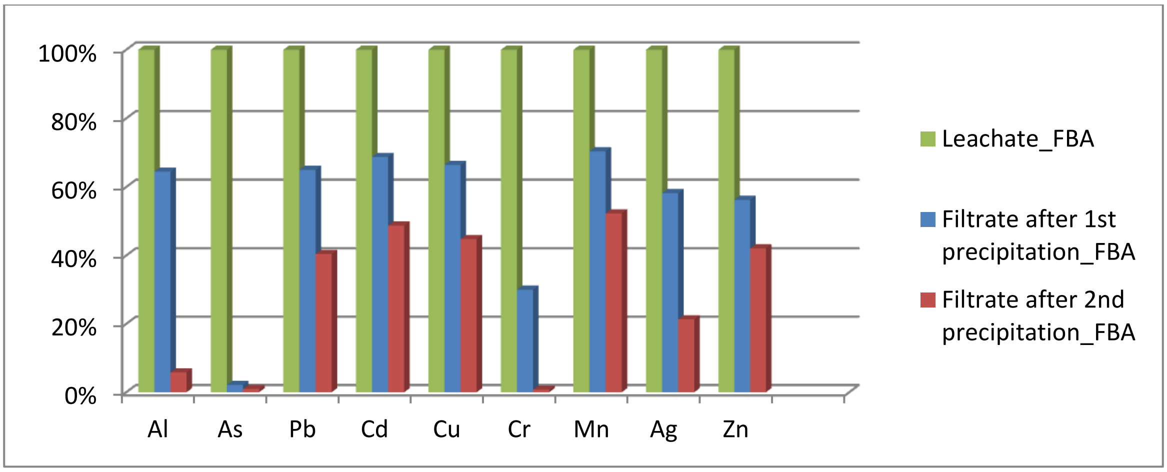


Figure 5.11. Variation of metal content during the P recovery tests, FBA

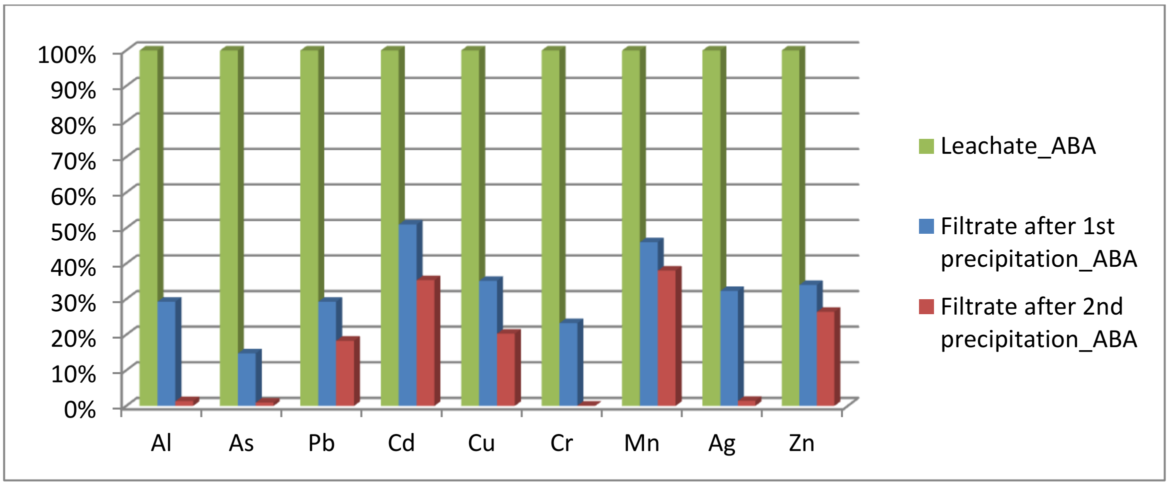


Figure 5.12. Variation of metal content during the P recovery tests, ABA

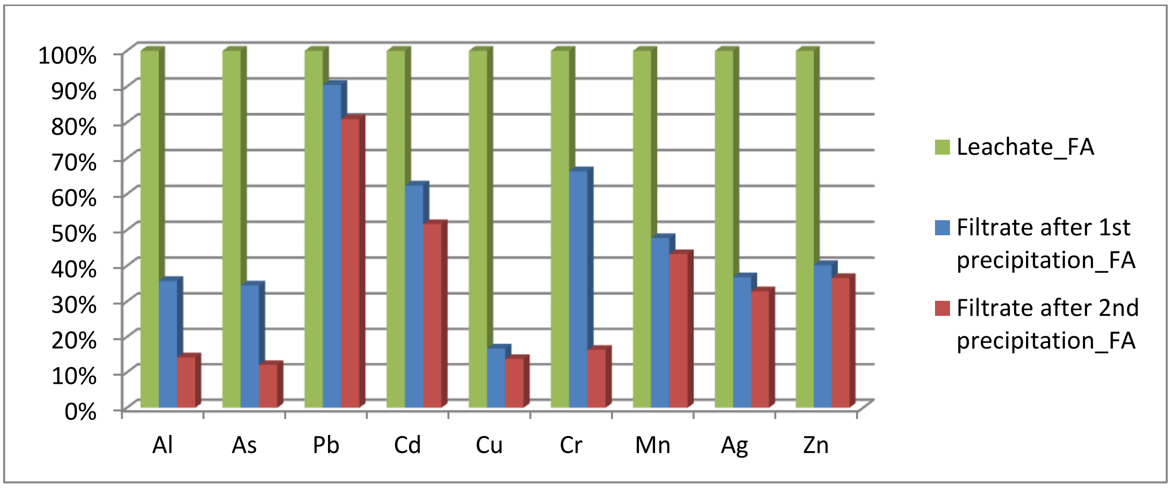


Figure 5.13. Variation of metal content during the P recovery tests, FA

5.4.3 The P recovery products

- **Elemental composition**

Elemental composition of the P recovery products are given in Table 5.4 and Figure 5.14–5.16. For FBA and ABA, both the 1st and the 2nd precipitates after complete digestion were analysed by ICP–MS instrument. For FA, only the 2nd precipitates was analysed because the amount of the 1st precipitates was not enough for ICP-MS analysis.

Table 5.4. Elemental composition of the P recovery products

Elements	units	FBA		ABA		FA
		1st precipitate	2nd precipitate	1st precipitate	2nd precipitate	2nd precipitate
P	g/kg	8.5	1	9.4	7	24
Al	g/kg	19	110	32	120	63
Fe	g/kg	40	47	22	44	13
Ca	g/kg	110	79	130	72	43
K	g/kg	1.5	1.2	2.1	1.1	13
Mg	g/kg	3.2	3.1	4.6	6.9	2.2
Sb	mg/kg	130	< 18	66	32	3900
As	mg/kg	50	< 18	22	31	1500
Ba	mg/kg	25	20	21	23	23
Pb	mg/kg	440	570	440	1300	4500
Cd	mg/kg	0.85	< 1.4	2	3.5	50
Cu	mg/kg	2300	3100	1500	6900	490
Cr	mg/kg	150	350	78	230	570
Hg	mg/kg	< 0.05	< 0.18	< 0.05	< 0.13	< 0.12
Mn	mg/kg	430	300	410	710	120
Mo	mg/kg	50	< 7.1	11	8	54
Na	mg/kg	3800	2700	4200	2100	12000
Ni	mg/kg	79	170	44	140	9.6
Sr	mg/kg	130	86	130	65	69
S	mg/kg	5200	23000	4400	20000	7200
Ti	mg/kg	2700	240	2000	930	2000
V	mg/kg	110	13	52	42	150
Zn	mg/kg	3200	3500	2200	8500	6500

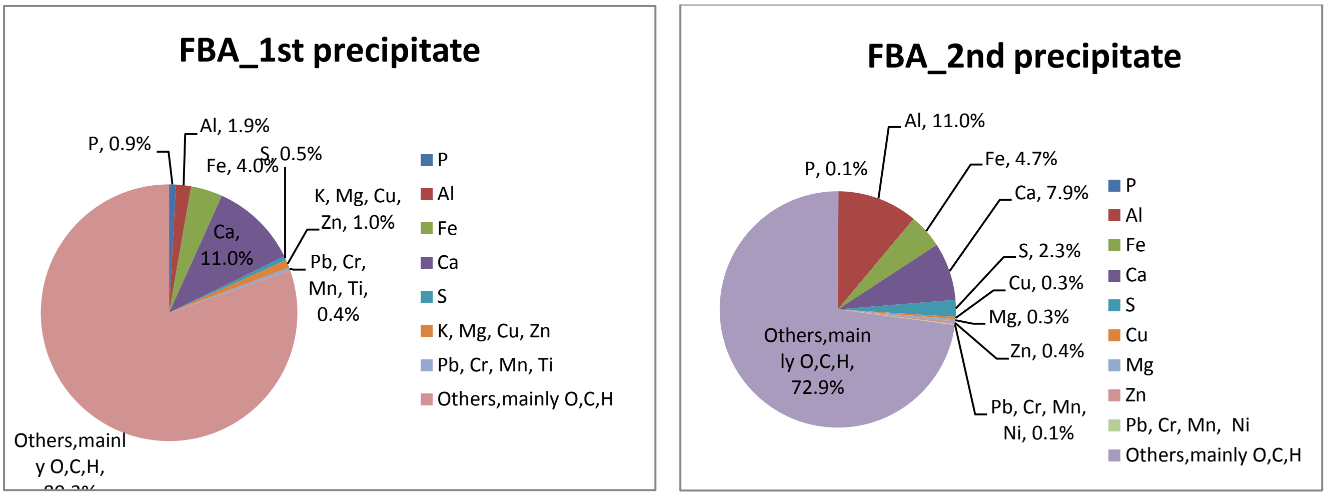


Figure 5.14. Elemental composition of the 1st and 2nd precipitates, FBA

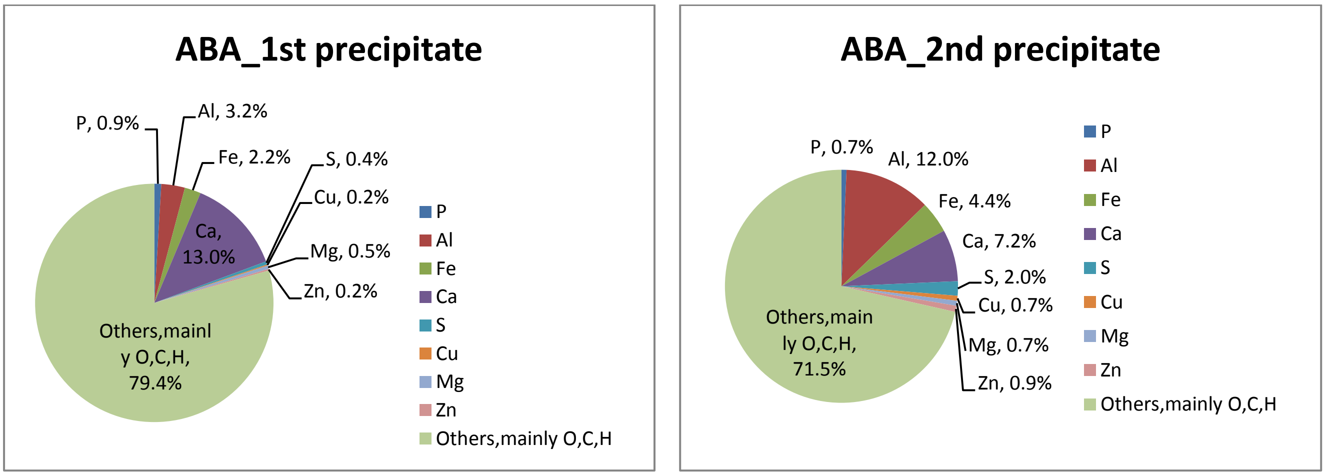


Figure 5.15. Elemental composition of the 1st and 2nd precipitates, ABA

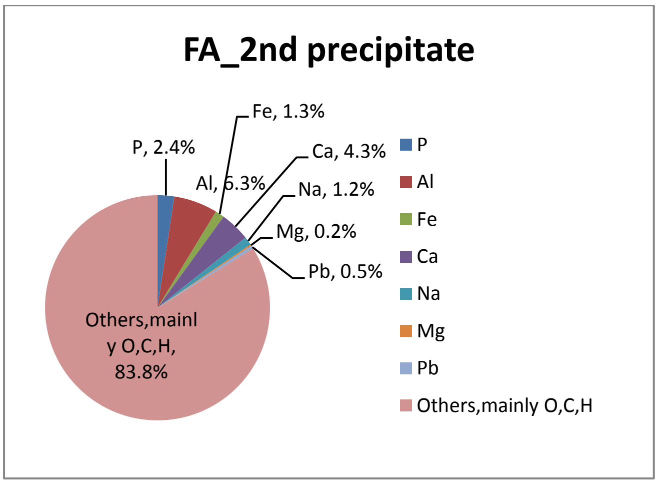


Figure 5.16. Elemental composition of the 2nd precipitate, FA

For FBA, P accounts for 0.9% of the 1st precipitate and 0.1% of the 2nd precipitate. For ABA, P accounts for 0.9% of the 1st precipitate and 0.7% of the 2nd precipitate. For FA, P accounts for 2.4% of the 2nd precipitate, which is lower than Du and Yu's result (3.4%). Concerning metal elements, for all the precipitates, Al, Fe, Ca, Mg and Zn were present as the major elements while As, Cd, Cr, Mn, Ni, Sr and Ti were present as the trace elements.

❑ Comparison between the P recovery products with raw materials

As mentioned in chapter 2.1, an application of the product is to serve as a substitute for phosphate rock (Britton et al., 2009). Considering the low P content of the P recovery product, a comparison between the element contents of the product with low–grade phosphate rock was preformed. The elemental composition of low-grade phosphate rock and the P recovery products were listed in Table 5.5.

Table 5.5. Elemental composition of low-grade phosphate rock and the P recovery products Unit: %

Elements	Low-grade phosphate rock		FBA		ABA		FA
	Iran[15]	Turkey[16]	1st precipitates	2nd precipitates	1st precipitates	2nd precipitates	2nd precipitates
P	2.2	2.4	0.9	0.1	0.9	0.7	2.4
Ca	34.6	36.6	11	7.9	13	7.2	4.3
Al	1.3	0.6	1.9	11	3.2	12	6.3
Fe	1.6	0.7	4	4.7	2.2	4.4	1.3
Mg	0.3	0.8	0.3	0.3	0.5	0.7	0.2

The P contents in FBA and ABA products were lower than low-grade phosphate rock (2.2–2.4%), which indicates that the P recovery product cannot be used directly as the alternative for low–grade phosphate rock. For FA, the P content in the product was similar with the P content in low–grade phosphate rock.

For all ashes, the Ca content of the product was much lower than in the low–grade phosphate rock while more Al and Fe were present in the P recovery product than low–grade phosphate rock. The Mg content in the P recovery product was similar with the content of low–grade phosphate rock. The present of heavy metals is critical as high metal content contributes to high toxicity of the P recovery product. Toxicity analysis of the P recovery product is introduced below.

❑ Toxicity analysis

Another utilization of the P recovery product is to serve as raw material of agriculture fertilizers (Britton et al., 2009). Concerning that a maximum of 22 kg P_2O_5 per hectare per year a regulated in the legislations will be served as fertilizers, the trace metal contents supplied by the products were calculated (Table 5.6). Reference to this is the legislations below, EPA and EU.

---

15 Mohammadkhani et al., 2011

16 Keles at al., 2010

Table 5.6. Metal content in P-sources as [g/(ha, year)] calculated on a P-supply of 22 kg / (ha, year)

Guideline values and P recovery products		Metal contents, g/(ha, year)				
		Cd	Pb	Cr	Cu	Ni
Swedish limits[17]		*0.75*	*25*	*40*	*300*	*25*
EU limits[18]		*150*	*15000*	*15000*	*12000*	*300*
FBA	1st precipitate	**1**	**500**	**170**	**2600**	**90**
	2nd precipitate	**13**	**5500**	**3400**	**30000**	**1600**
ABA	1st precipitate	**2**	**450**	**80**	**1500**	**50**
	2nd precipitate	**5**	**1800**	**300**	**9400**	**200**
FA	2nd precipitate	**20**	**1800**	**230**	200	4

Values in bold exceed the Swedish limits.

According to Table 5.6, for all the products, Cd, Pb and Cr exceed Swedish guidelines but fall below EU guidelines. The Cu and Ni contents in FBA and ABA products exceed Swedish guidelines but were below EU guidelines. For FA, the Cu and Ni contents were below Swedish guidelines.

According to EU Council directive (1986), the products are allowed to be spread in Europe. However, from an environmental perspective, we do not recommend serving the products as fertilizers directly but to remove metals in the product before the utilisation.

17 Swedish Environmental Protection Agency, Code of statutes 1994:2(changed 1998:4 and 2001:5)

18 EU Council directive,86/278/EEC, 1986

6 Conclusions and recommendations

- The XRD analysis indicated that SiO_2 was identified and present as the major compound in all ashes except ABA. Silicon dioxide could form silicic acid gel and cause problems in the leachates; Various Fe–oxides were identified in all ashes, especially in leached FBA.
- The P content in the leachates was overestimated by Hach method whereas underestimated by IC instrument. Despite of the inconsistent result of Hach and IC analysis, similar trends were found. The qualitative assessment of the results indicated that 2.5M HCl leaching without sedimentation could maximize the P leaching from MSWI ash. In order to guarantee the experimental accuracy, an inter-calibration measurement between Hach and IC measurement is suggested for further studies.
- The SPE tests indicated that Empore chelating disk is effective to remove metals from aqueous solutions and repeatedly SPE is recommended to get even higher removal efficiency. Metals as Al, Ca and Fe retained by Empore chelating disk could decrease the extraction capacity of the disk. A suggestion is to elute the disk repeatedly by 3M HCl soaking for 10 minute. Another finding is the high decrease of P in the leachates after the SPE. Considering P is the element of interest to be recovered, SPE was excluded in further P recovery tests.
- In the P recovery tests, more than 90 percents of P were recovered from the leachates by precipitation. The P leaching efficiencies was 30–56%. In order to improve the whole recovery process, the leaching step should be enhanced. A suggestion for further studies is to try alkaline leaching combined with acidic pre–treatment instead of direct acidic leaching.
- Larger amounts of P and metals were present in the 1st precipitates than in the 2nd precipitates. The P content was about 0.9% in the 1st precipitates and 0.1–2.4% in the 2nd precipitates. Aluminium, Fe, Ca, Mg and Zn were present as the major elements while As, Cd, Cr, Mn, Ni, Sr and Ti were the trace elements of the P recovery product. The elemental comparison between the P recovery products with low-grade phosphate rock indicated that the P recovery products cannot be used directly as the alternative of low–grade phosphate rock.
- The present of metals in the P recovery product is critical as high metal content contributes to high toxicity. For toxicity analysis of the products, although the products are allowed to be spread in Europe according to EU guidelines, we do not recommend serving the product as fertilizers directly but removal of metals in the product before the utilisation.

In conclusion, the acidic dissolution – precipitation method was feasible to recover P from sorted MSWI BA. However, the leaching step requires improvements. How to concentrate P in the product and to remove metals in the leachates without negative effects are the two critical questions for further studies.

7 References

3M Industrial and Consumer Sector. (1996). *General Guidelines for Applications Empore Extraction Disks with Chelating Resin.* St.Paul: 3M Company.

Adam, C. et al. (2009). Thermochemical treatment of sewage sludge ashes for phosphorus recovery. *Waste Management 29* , 1122-1128.

ALLASKA Database. (2012). Retrieved February 27, 2012, from Värmeforsk (Thermal Engineering Research Association): http://www.varmeforsk.se/allaska-en

Bakker, M., and Berkers, E. (1995). Technique at disscusion. In H. Lintsen, M. Bakker, E. Homburg, D. Lente, J. S. Van, & G. Verbong, *Technique in the Netherlands* (pp. 1800-1890). Zutphen: Walburg Pers.

Batziaka, V.et al. (2005). Leaching of Nitrogen, Phosphorus,TOC and COD from the biosolids of the Municipal Wastewater Treatment Plant of THESSALONIKI. *Proceedings of the 9th International Conference on Environmental Science and Technology.* Rhodes island.

Beauchemin, D. (2006, June 15). Inductively Coupled Plasma Mass Spectrometry. *Analytical chemistry Vol.78* , pp. 4111-4136.

Björkman, J. et al. (2011). *Risk acceptance and ethics in decision making-A literature review.* Gothenburg.

Blöcher, C. et al. (2012). Phosphorus recovery from sewage sludge with a hybrid process of low pressure wet oxidation and nanofiltration. *Water Research* , 2009-2019.

Brecht, A. V. et al. (2012). *Innovative and BREF proven material recycling of bottom ashes.* Stochholm: Ash 2012.

Britton, A. et al. (2009). Pilot testing and economic evaluation of struvite recovery from dewatering centrate at HRSD's Nansemond WWTP. *International Conference on Nutrient Recovery from Wastewater Streams Vancouver.* London: IWA Publishing.

Brügemann, L., and Gerndt, K. E. (2004). Detectors for X-ray diffraction and scattering: a user's overview. *Nuclear Instruments and Methods in Physics Research,Volume 531*, , 292-301.

Chandler, A. J. et al. (1997). *Municipal Solid Waste Incinerator Residues.* Amsterdam;New York: Elsevier.

Cheremisinoff, N. P. (2003). *Handbook of solid waste management and waste minimization technologies.* Elsevier Science.

De Geer, H., and Trollestad. (2009). *Etik i arbetsliv och affärer.* Stockholm: SNS Förlag.

Du, J., and Yu, S. (2011). Phosphorus recovery from MSWI Ash:enhanced leaching with acid and base and evaluation of the developed process in an environmental perspective. Gothenburg: Chalmers University of Technology.

EFMA. (2000). *Production of phosphoric acid.* Brussels.

Etoh, J. et al. (2009). Hhdrothermal treatment of MSWI bottom ash forming acid-resistant material. *Waste Management,Volume 29,Issue 3* , 1048-1057.

EU council directive. (1986). EU council directive of 12 June 1986, 86/178/EEC.

EU Council directive,86/278/EEC. (1986, June 12).

European Environmental Agency. (n.d.). *The European environment – state and outlook 2010 :Waste(Spain)*. Retrieved May 18, 2012, from European Environmental Agency: http://www.eea.europa.eu/soer/countries/es/soertopic_view?topic=waste

European Food Safety Authority. (2009). Calcium silicate and silicon dioxide/silicic acid gel added for nutrional purposes to food supplements. *The EFSA Journal 1132* , 1-24.

Fluid Management Systems Inc. (2007, February 7). *Sample Preparation: Titra-Stat/pH-Stat titration system*. Retrieved February 8, 2012, from Fluid Management Systems: http://www.fmspharmaceutical.com/phdes.htm

Gerve, T. V. et al. (2005). Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling. *Waste Management,Volume 25, Issue 3* , 291–300.

Global Phosphate Forum. (2010). Perspectives for phosphates in detergents. *Phosphates 2010 International Conference.* Brussels.

Gori, M. et al. (2011). Effect of short-term natural weathering on MSWI and wood waste bottom ash leaching behaviour. *Journal of Hazardous Materials (189)* , 435-443.

Güney, K. et al. (2008). Phosphorus recovery from digested sewage sludge as MAP by the help of metal ion separation. *Water Research* , pp. 4692-4698.

Hocking, B. M. (2005). *Phosphorus and Phosphoric:Handbook of Chemical Technology and Pollution Control(Third Edition).* San Diego: Academic Press.

Honma, S., and Utsumi, M. (2003). Investigation on development of phosphorus recovery technology from sludge burned ash. *Bureau Sewerage Tokyo Metro. Gov. Annu.2003*, (pp. 389-401).

ILER, R. K. (1979). *The Chemistry of Silica.* New York: Wiley.

Jasinsk, S. M. (2012, January). *Phosphate rock.* Retrieved February 2012, from U.S. Geological Survey:Mineral Commodity Summarie: http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/mcs-2012-phosp.pdf

Joint Committee of Powder Diffraction Standards. (2006). JCPDS-ICCD:PDF-4 release 2006. Philadelphia, USA.

K.Lam H Charles, et al. (2010). Use of Incineraton MSW Ash:A Review. Sustainability, 1943-1968.

Kaikake, K. et al. (2009). Phosphate recovery from phosphorus-rich solution obtained from chicken manure incineration ash. *Waste Management 29* , pp. 1084-1088.

Keleş, E. et al. (2010, April). Removal of Pb2+ from aqueous solutions by rock phosphate (low-grade). *Desalination* , pp. 124-128.

Kemacheevakul, P. et al. (2011). Phosphorus recovery from human urine and anaerobically treated wastewater through pH adjustment and chemical precipitation. *Environmental Technology,32:7* , 693-698.

Li, G. X. et al. (2012). Utilization of municipal solid waste incineration bottom ash in blended cement. *Journal of Cleaner Production, Volume 32* , 96-100.

Liu, S. Y. et al.(2008). Leaching behavior of heavy metals and PAHs from MSWI bottom ash in a long-term static immersing experiment. *Waste Management,Volume 28,Issue 7* , 1126-1136.

Meima, J. A. et al. (2002). Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum. *Applied Geochemistry,Volume 17, Issue 12,* , 1503–1513.

MLIT Japan. (2010). Guide to Phosphorus Recycle in Sewerage System. Tokyo, Japan.

Mohammadkhani, M. et al. (2011). Double reserse flotation of a very low grade sedimentary phosphate rock, rich in carbonate and silicate. *International Journal of Mineral Processing* . Elsevier.

NakakuboToyohiko et al. (2012). Comparative assessment of technological systems for recycling sludge and food waste aimed at greenhouse gas emissions reduction and phosphorus recovery. Journal of Cleaner Production 32, 157-172.

NGK Insulators, Gifu city. (2007). Technical report on phosphorus recovery technology from sewage sludge burned ash. *Working Papers on LOTUS Project* . Tokyo, Japan.

Pan, J. R. et al. (2008). Recycling MSWI bottom and fly ash as raw material for Portland cement. *Waste Management,Volume 28,Issue 7* , 1113-1118.

Pettersson, A. et al. (2008). Leaching of ashes from co-combustion of sewage sludge and wood. *Biomass and Bioenergy 2008 32(3)* , 236-244.

Petzet, S. et al. (2012, August). On wet chemical phosphorus recovery from sewage sludge ash by acidic or alkaline leaching and an optimized combination of both. *Water Research* , pp. 3769–3780.

Polettini, A. and Pomi, R. (2004). The leaching behavior of incinerator bottom ash as affected by accelerated ageing. *Journal of Hazardous Materials,Volume 113, Issues 1–3* , 209-215.

Renova AB. (2011, April). Analyse report of MSWI ash. Gothenburg.

Saikia, N. et al. (2008). Assessment of Pb-slag, MSWI bottom ash and boiler and fly ash for using as a fine aggregate in cement mortar. *Journal of Hazardous Materials (154)* , 766-777.

Sapporo city. (2010). Annual Report on Operation and Maintenance of Sapporo City Sewerage System 2009. Sapporo, Japan.

Schipper, J. W. and Korving, L. (2009). Full-scale plant test using sewage sludge ash as raw material for phosphorus production. *International Conference on Nutrient Recovery from Wastewater Streams Vancouver.* London: IWA Publishing,.

Sengul, H. et al. (2006). Beneficiation of Mardin-Mazida˘gi (Turkey) calcareous phosphate rock using dilute acetic acid solutions. *Chemical Engineering,Volume 122,Issue 3* , 135-140.

Sigma-Aldrich Co. (n.d.). *Guide to Solid Phase Extraction.* Retrieved March 1, 2012, from http://www.sigmaaldrich.com/Graphics/Supelco/objects/4600/4538.pdf

Statistics Norway. (2012). Norway Shows Large Increase in Waste Incineration. *EU-Recycling* , 28-30.

Stewart, W. M. (2002, February). Commercial Phosphorus Fertilizer. Norcross: Potash & Phosphate Institute.

Swedish EPA. (n.d.). Code of statutes 1994:2(changed 1998:4 and 2001:5).

Swedish EPA. (1994,1998 and 2001). Code of Statutes SNFS (in Swedish) 1994:2, ISSN: 0347-5301, changed 1998:4, ISSN:1102-3007 and 2001:5.

The EU SUSAN Project. (2009). *Sustainable and Safe Re-use of Municipal Sewage Sludge for Nutrient Recovery* . Contract Number 016079.

The Ministry of Environment of Spain. (2008). *The National Integrated Waste Plan (PNIR) 2008-2015.* the Ministry of Environment of Spain.

The Swedish water & Wastewater Association. (2000). *Facts on water supply and sanitation in Sweden.* The Swedish Water & Wastewater Association.

Thomas, R. (2001). A beginner's guide to ICP-MS. *Spectroscopy* .

UNEP-IETC. (2012). *The project "International Source Book on Environmentally Sound Technologies (ESTs) for Municipal Solid Waste Management (MSWM)".* Retrieved May 29, 2012, from United Nations Environment Programme(UNEP): http://www.unep.or.jp/ietc/estdir/pub/msw/

University of Hawai'i. (2012). *Fertilizer Material*. Retrieved Feburary 13, 2012, from Soil nutrient management for Maui County: http://www.ctahr.hawaii.edu/mauisoil/c_material.aspx

V ĺkov á, M., Ettler, V., Hyks, J., & Astrup, T. (2010). Assessment of the leaching behaviour of fly ash from a cobalt smelter,Zambia. *Proceedings Venice 2010, Third International Symposium on Energy from Biomass and Waste.* Venice.

Wei, Y. et al. (2011). Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases. *Journal of Hazardous Materials,Volume 187,Issues 1-3* , 534-543.

Yang, Y. et al. (2009). Thermal behaviour of ESP ash from municipal solid waste incinerators. *Journal of Hazardous Materials,Volume 166,Issue 1* , 567-575.

Yao, J. et al. (2010). Content,mobility and transfer behavior of heavy metals in MSWI bottom ash in Zhejiang province,China. *Fuel 89* , 616-622.

Yao,Jun et al. (2011). Investigation of Cu leaching from municipal solid waste incinerator bottom ash with a comprehensive approach. Energy 5(3), 340-348.

Zimmermann, J., and Dott, W. (2009). Sequenced bioleaching and bioaccumulation of phosphorus from sludge combustion – A new way of resource reclaiming. *Biohydrometallurgy Vols.71-73* , 625-628.

Zwaard, W. (2007). Kroniek van de Nederlandse veiligheid. *Van kinderarbeid en wassend water tot ontploffend vuurwerk.* Arnhem: Syntax Media.

Appendix I – Detailed Experimental Data

Table 1. P leaching efficiency depending on sedimentation time and concentration of HCl; analysed by Hach

MSWI Ash	Sedimentation time	P leaching efficiency (%)		
		0.5M HCl	1.5M HCl	2.5M HCl
FA	-	88	>100	>100
	24h	77	>100	>100
FBA	-	>100	86	>100
	24h	>100	>100	>200
ABA	-	79	>100	>100
	24h	60	71	65

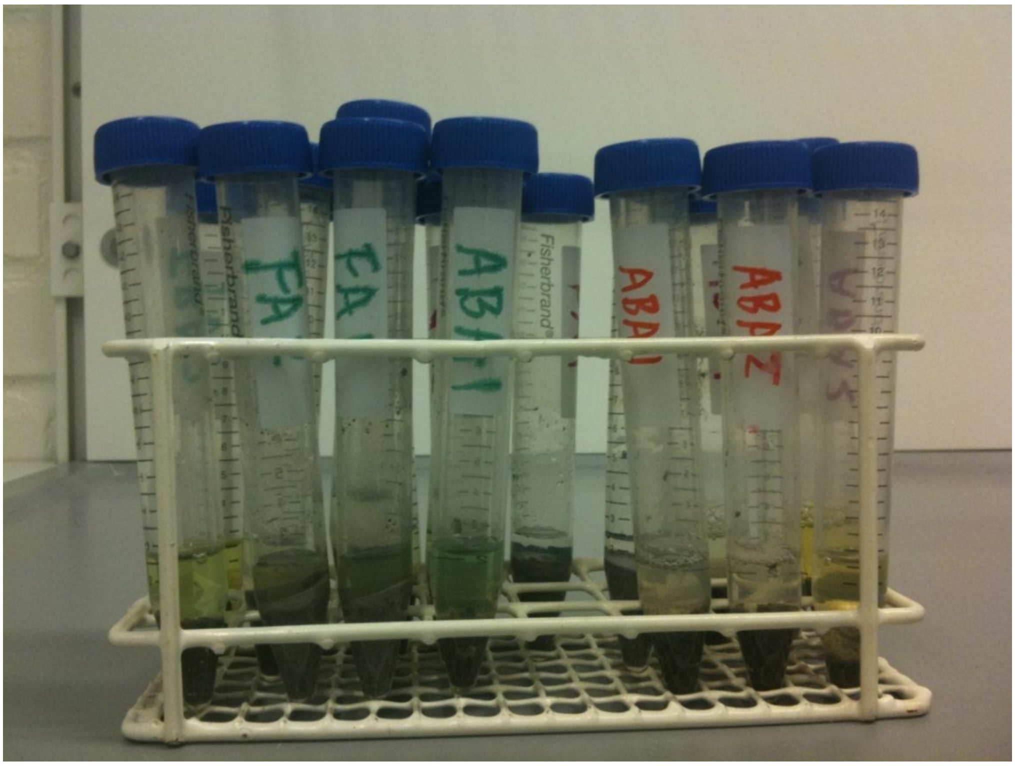
Table 2. P leaching efficiency depending on sedimentation time and concentration of HCl ; analysed by IC

MSWI Ash	Sedimentation time	P leaching efficiency (%)		
		0.5M HCl	1.5M HCl	2.5M HCl
FA	-	24	70	49
	24h	12	45	48
FBA	-	27	47	49
	24h	30	48	77
ABA	-	28	36	40
	24h	13	25	38

Table 3. Metal removal efficiency of the SPE; analysed by ICP-MS

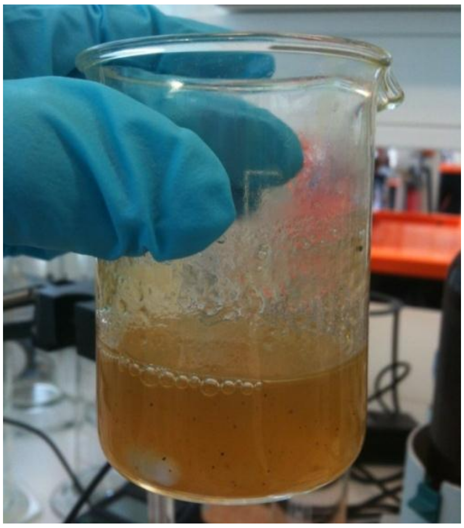
MSWI Ash	SPE steps	Removal efficiency of metal ions (%)												
		Al	Ca	Fe	Mg	Cr	Mn	Li	Sr	Zn	Cu	Ni	Cd	Pb
FA	1st SPE	77	16	0	17	42	33	4	16	98	100	17	25	99
	2nd SPE	100	91	84	24	93	100	33	79	100	0	67	98	100
FBA	1st SPE	55	24	40	22	33	27	23	55	97	100	30	63	82
	2nd SPE	93	36	72	31	71	55	28	32	98	0	82	100	96
ABA	1st SPE	98	24	55	21	80	65	20	26	99	100	30	55	100
	2nd SPE	100	83	91	54	100	91	25	60	94	0	49	100	0

Appendix II – Experimental Photos



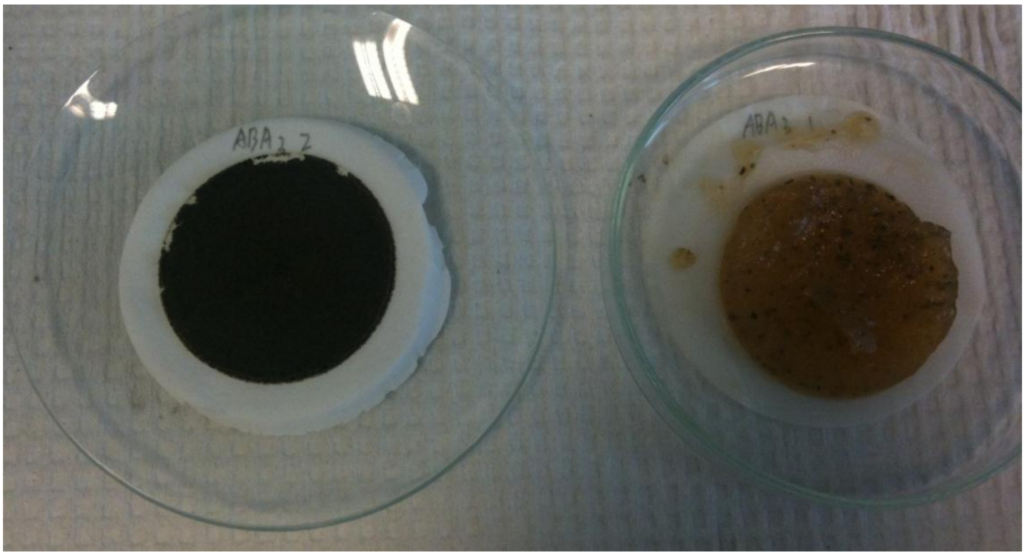
The maximized P leaching tests

The SPE tests by Empore chelating disk



1st precipitation, FBA **2nd precipitation, FBA**

The filter cakes of the 1st precipitate (left) and 2nd precipitate (right), FBA



The filter cakes of the1st precipitate (right) and 2nd precipitate (left), ABA