

Phosphorus Recovery from MSWI Ash

Enhanced leaching with acid and base and evaluation of the developed process in an environmental perspective

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

JUAN DU
SIYANG YU

Department of Civil and Environmental Engineering
Division of Water, Environment and Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2011
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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

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ABSTRACT

Phosphorus is an essential element for human beings and ecosystem. It is a non-renewable resource and humanity is about to approach its depletion in next 100 years. Therefore, developing sustainable alternatives to compensate the depletion of phosphorus is very crucial. Municipal solid waste incineration (MSWI) ash, generated approximately 240Mtonnes per year in the world, is a P-rich residue, which can be used as P recovery source. Leaching technique is applied in this study to recover phosphorus from the MSW ash. The optimal leaching conditions with about 100% P leaching efficiency is 2M HCl, 2h leaching time and 24h sedimentation when L/S ratio is 5. In order to have a purer P product with minimum metal elements, two different acid-base enhanced leaching methods are tested. Method I using acid dissolving and base precipitating has a total P recovery efficiency about 70%. The final product contains 3% phosphorus, which can be used as fertilizer with separation of Cd or a substitute of low-grade phosphorus rock in phosphate production industry. Method II using acid washing and base dissolving has a quite low P recovery efficiency. This may due to the high Ca content in the MSWI ash. An evaluation of the developed process using LCA has been carried out and compared to the conventional production processes. The results show that the developed process has a slightly lower environmental impact than the conventional productions with the use of NaOH. However, if replaced NaOH with CaO, the developed process is more benign and economic. The results indicate that the recovery of P from MSWI ash using leaching is viable. However, further study is required for improvement of performance.

Keywords: phosphorus, recovery, acid leaching, evaluation, LCA.

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Juan Du and Siyang Yu

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1 Introduction

Phosphorus is one of the essential elements for human beings and most organisms in ecosystem due to its indispensable role in constituents of DNA, RNA and ATP, which are all vital functional units in our bodies (Shionoya 1999). It is a non-renewable resource extracted from phosphate ores and widely used in agriculture as fertilizers and industries as additives.

However, although phosphoric ore is estimated to be available for at least 100 years (Cordell, Drangert et al. 2009), the humanity may approach the peak of high grade phosphorus extraction before 2050 (Franz, 2008; Driver et al., 1999). The quality of phosphorus ore will decline ever since resulting in an irreversible trend for the increasing price of phosphorus. Furthermore, the phosphoric ores are unevenly distributed, mostly found in China, the United States, former Soviet Union and Morocco. Whereas in Europe, there is only one company- Thermphos International, located in the Netherland, who produce elemental phosphorus and only one phosphorus mine in Finland with high quality of phosphorus ore (Griffith 1973). Therefore, many countries rely on importing phosphorus, imposing costs from transportation in terms of both economic and environmental aspects.

From an environmental perspective, excess of phosphorus and nitrogen entering the aquatic system through wastewater will prompt the blooming of algae which consumes most oxygen in water. The lack of oxygen in turn leads to the death of organism and deteriorating water quality. This phenomenon is known as eutrophication. Therefore, removal of excessive phosphorus from the waste system is necessary considering the pollution caused by potential leaching.

As phosphorus is a non-renewable resource and its impact on environment, better management and countermeasures are needed. Recycling is a sustainable solution to the conservation of the resource and for pollution prevention. Not only depletion will be compensated, the pollution from excess load of phosphorus could also be eliminated. Efforts have been made to recover phosphorus from several waste streams for decades, ranging from waste water, sewage sludge to incineration ashes. As focus has mainly been put on waste water and sewage sludge, research on recovery of phosphorus from sewage sludge incineration ash is increasing while another important type of incineration ash, municipal solid waste incineration (MSWI) ash, is left out due to its relatively low concentration of phosphorus. However, if taking into consideration annual mass of MSWI ash which accounts for approximately 100 thousand tons per year in Sweden alone, the total amount of phosphorus for extraction is considerable. Moreover, waste incineration is growing rapidly worldwide. In the following years, it is expected that 240Mt solid wastes will be incinerated worldwide annually, including household waste and industrial waste (Ecoprog 2010). According to Ramboll (2006), the incineration treatment can reduce the waste mass by 85%, which means the total amount of waste ash is approximately to be 36Mt. On the other hand, 1Mt of 14Mt phosphorus used in fertilizers ends up in solid wastes annually (Cordell et al. 2009). Therefore, if all the phosphorus in the ash were recovered, about 7% of the phosphorus consumption can be compensated. In order to determine whether MSWI ash is a valuable source of phosphorus and its feasibility, a study on recovery phosphorus from MSWI ash must be carried out.

2 Aim of the thesis

The purpose of this study can be divided into two main parts. Task one is to develop a leaching method to extract phosphorus from MSWI ash, while minimizing leaching of other interfering elements like metal compounds. This task includes investigating the solubility of phosphorus and other metals in the ashes with acidic leaching agents under various conditions and to find an efficient way to leach phosphorus with less mobility of the metals which may affect the impurity and usage of phosphorus products. Task two is to explore feasible methods to recover phosphorus other than leaching. Subsequently, evaluation of the developed process will be evaluated and compared to the conventional production processes.

The research questions of this study are listed below.

For task one:

- What is the composition of MSWI ash?
- What are the optimal leaching conditions?
- How to recover phosphorus with fewer impurities?
- What are the possible utilizations of the final recovered phosphorus?

For task two:

- What kinds of methods are used or studied focusing on other types of material?
- How to evaluate the methods?
- What are the advantages and disadvantages of the methods?
- What are the resources needed for production and recovery of phosphorus and how much?
- What are the environmental performances of the developed process?

3 Scope

As this study is to exploit a new area, most of the theoretical research is based on the literature study. The ash samples are from Renova, a Swedish waste treatment company located in Gothenburg. In this study, only one type of ash, which is electrostatic filter ash, is analyzed due to the limitation in time and scope for this thesis.

A full LCA study is data intensive thus time and resource demanding. The LCA in the present study will be streamlined by using data from LCA database instead of compiling data from scratch. The comparisons of the environmental impact concentrate on normalised characterisation. Weighting will not be performed.

List of abbreviations:

CMIA Chicken manure incineration ash

FBC Fluidized bed combustor

ILCD International Reference Life Cycle Data System

LCA Life Cycle Assessment

MB Mass burn

MSW Municipal solid waste

MSWI Municipal solid waste incineration

SSA Sewage sludge ash

4 Background

This chapter contains three aspects. First part is the definition, composition and some statistics of the total amount of the MSW, together with a short introduction of two typical combustion methods and comparison of different types of ash. A brief introduction about the phosphorus production is the second part. Finally is a short review of different phosphorus recovery techniques.

4.1 MSWI ash – the phosphorus reserve

4.1.1 Municipal solid waste

Municipal solid waste, commonly known as household garbage or refuse, is one of the waste materials that can cause land pollution. Normally, the municipal solid waste contains nonhazardous garbage, rubbish, and trash from households, commercial establishments, and industrial facilities. (Encyclopedia Britannica, 2011).

In Sweden, approximately 4,700,000 tonnes of MSW was generated in 2009 (Avfall Sverige 2009). The general composition of the waste is showed in Figure 1. The data is based on the statistics of seven cities in Sweden provided by the government. Organic waste (51%) and paper, wood and textile (24%), commonly the major sources of phosphorus in the waste, together account for about three-fourth of the total volume of MSW in Sweden (RVF Utveckling, 2005). Therefore, the proportion of these parts of waste can influence the phosphorus content in the incinerated ash. High organic content results in high phosphorus present in the ash while low organic content or developed sorting system leads to low phosphorus content. This part will be discussed in 4.1.3.

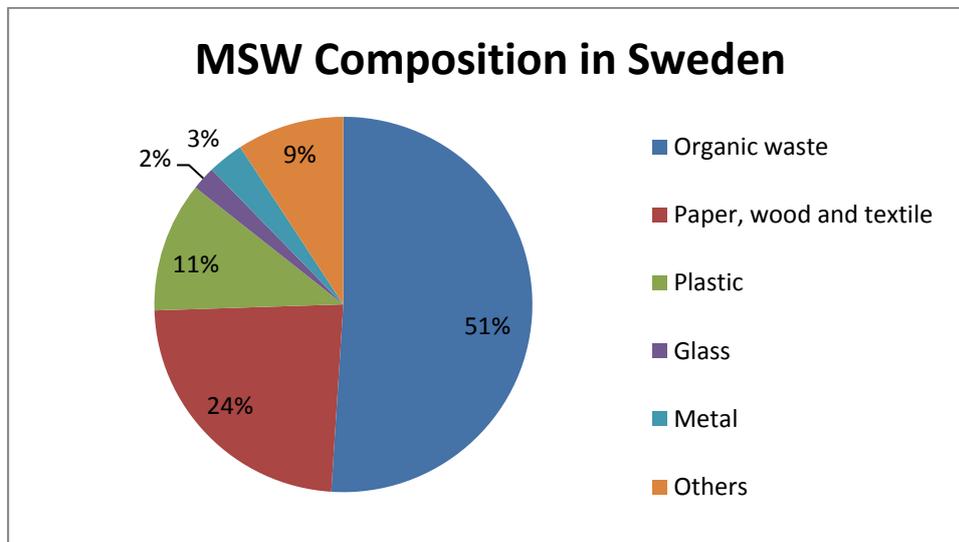


Figure 1 General composition of MSW in Sweden displayed as w%. (Source: RVF Utveckling, 2005).

Sweden is one of the countries with the highest proportion, 48%, of waste treated by incineration, whereas the average is 5% in the world (Avfall Sverige 2011). According to the study by Borgstedt and Svanäng (2011), half of the total outflow of phosphorus in Gothenburg city in Sweden ends up in MSWI ash, about the same amount in sewage sludge. Therefore, besides sewage sludge, MSWI ash also can be used as a source of phosphorus recovery due to the high content of phosphorus.

4.1.2 Combustion techniques

Waste incineration is one of the increasing strategies to treat municipal solid waste, which can minimize approximately 80-85% of the original waste mass and 95% of the volume depending on composition and recovery degree (Ramboll, 2006). In the meantime, energy is recovered in the form of heat and electric power. There are two typical combustion techniques: mass burn (MB) and fluidized bed combustion (FBC).

Mass burn combustors (MB)

In the mass burn combustors, the waste burns as fuel on a grate in the combustion chamber with excess air blown in to ensure complete combustion. The combustion temperature is normally above 1000°C. The advantages of MB combustors are easy to operation, robust and minimal demand for pre-treatment. Due to the different design of combustion chamber, there are several types of MB techniques, for instance, stationary grates, travelling grates, rotating drums grates and grate furnaces with rotary kilns (Bilitewski et al., 1995).

Mass burn incineration with a moving grate incinerator is widely used and rather mature technique has been thoroughly tested. It is capable to deal with various waste compositions (Rand, et al. 2000). In Scandinavia, this technique is most commonly used in waste to energy facilities.

Fluidized bed combustors (FBC)

In the fluidized bed combustors, the solid fuel is suspended by upward blowing air during the combustion in a fluidized bed with heated inert material, typically sand. This turbulent mixing of gas and solid provides effective chemical reactions and heat distribution. A low temperature is retained during the combustion process as 850°C, which makes it possible to minimize the formation of nitrogen oxidizes (NO_x). The fluidized bed combustors are less sensitive with variation of fuel property, like caloric value and water content compare to MB combustors. The disadvantage is that it requires pre-treatment of the waste, such as size reduction and sorting. The FBC system is categorized into two major groups, atmospheric systems and pressurized systems. The former one operates under atmospheric pressure, the other type takes place at high pressure usually ranging from one to two Mpa (Cheremisinoff, 2003).

Fluidized bed incineration is a quite new technology and hence has some limitations in its use in waste incineration as a number of characteristics still have not been proven. However, it can be a good alternative in special types of industrial waste incineration. For example, in Japan, the fluidized bed incineration is used to treat the waste from hospitals (Rand, et al. 2000).

4.1.3 Properties of MSWI ash

The composition and properties of ashes are various depending on the waste and the degree of recycling such as metal sorting. Table 1 shows different types of ashes generated in different countries. Sewage sludge ash and animals manure ash contain much more phosphorus than MSWI ash due to high content of organic compounds and less metals, except for iron and aluminium in sewage sludge ash, which are commonly used to remove phosphorus in waste water. Calcium, zinc and lead are quite high in MSWI ash and these elements can precipitate with phosphorus in various pH conditions, which may influence the recovery process as they can bond with phosphorus and prevent it from releasing or affect the purity of the recovered phosphorus when using MSWI ash. Large amount of research work relates to phosphorus recovery has been done in sewage sludge ash and animal manure ash (Levlin, et al., 2004;

Pettersson, et al., 2008; Kaikake, et al., 2009) while no study has focused on the recovery of phosphorus from MSWI ash yet. From a perspective of environmental protection and waste reuse, MSWI ash also can be treated as a resource for phosphorus recovery. In this study different leaching methods are investigated to recover phosphorus from MSWI ash.

Table 1 also presents the MSWI ash from different countries with various degree of waste sorting system. China represents the ash with less sorting or recycling food waste and papers as there is limited regulation on waste sorting system (SCIO, 2011) while Japan has fairly strict legislation (i.e. basic law for the recycling-based society and waste management law) and thorough facilities about waste sorting. Hence it can be assumed that Japan represents the ash with more or less complete sorting and recycling, i.e. without any organic waste. Sweden is somewhere in between as there is still a portion of organic waste that is not separated. As the phosphorus content decreases along with the decrease of organic waste, it indicates that the organic waste could be the largest source of phosphorus. The metal contents are various due to the industrial structure and usage of metals, and there is no clear relation to the sorting system. Therefore, if using MSWI ash as a source to recover phosphorus, it seems to be better not to separate organic waste totally from the municipal solid waste in order to have a high content of phosphorus in the ash. However, the presence of organic waste has negative effect on the incineration process, i.e. caloric value. Therefore, the percent of the organic waste needs to be considered properly.

Table 1 Element composition of different types of ashes from various countries.

Unit: g/kg ash	SSA Moraaska, Sweden ^a	CMIA, Japan ^b	MSWI ash Guangdong, China ^c	MSWI ash Fukuoka, Japan ^d	MSWI ash Sweden ^e
P	81	85	21	0.09	6
Mg	6	22	12	16	12
Ca	49	72	206	212	210
Fe	83	5	17	43	24
Cu	0.44	0.27	14	2	0.25
Zn	-	1.6	249	3	55
Pb	0.02	0.01	48	0.89	11
Cr	0.14	0.03	9	0.38	0.92
Al	218	-	39	78	30
Si	94	-	-	173	70

a: Levlin et al., 2004

b: Kaikake et al., 2009

c: Zhao et al., 2005, mass burned

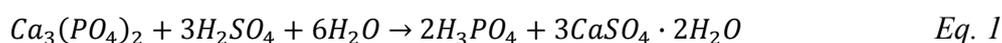
d: Wei et al., 2011, mass burned

e: Karlfeldt-Fedje, 2010, mass burned

4.2 Phosphorus production technologies

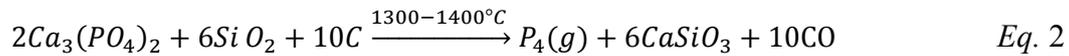
Today about 90% of phosphorus consumption (Smil, 2000) is directly linked to the production of fertilizers and the remainder is for other industrial use. Most of the phosphorus production is either via wet process or dry process (Hocking, 2005) disregarding the small fraction of recycling.

Wet process is based on the following chemical reaction to produce phosphoric acid:



This is the oldest while the least expensive process to produce phosphoric acid. During this process, the major by-product gypsum is yielded in a large quantity from 5 to 7 tons per ton of phosphoric acid and the impurities, mainly fluoride, cadmium, arsenic and uranium which present in the phosphorus ores, are also significant in the final product. Therefore, purification and concentration processes must be taken for high grade phosphoric acid.

With respect to the dry process, it is used to produce elemental phosphorus from phosphate ores. The principle involved is:



Phosphorus produced via this process can be very concentrated with a relatively low impurity. Power required to this process ranges around 12,000 to 14,000 kWh/ton, which contributes the majority of the cost of this method. But this vast energy demand can be compensated by using fossil fuel to provide the furnace temperature for the reaction to happen, since the CO produced can be circulated as fuel, suggested by Leder et al. (1985).

4.3 Literature review on P recovery from ashes

Numerous methods for recovery of phosphorus have been developed in the field of waste water treatment and can be found in reviews (Morse et al., 1998; Valsami-jones, 2004; Nieminen, 2010). However, no particular method is available for recovery P from MSWI ashes. Methods which might be feasible for recovery from MSWI ash are gathered in Table 2. Since waste water and sewage sludge are rich in phosphorus content, they could be an alternate source and some methods, namely electro-kinetic, thermo-chemical treatment and bioleaching and accumulation, are proposed targeting for sewage sludge ashes. These methods might be able to be applied in MSWI ashes due to the similar physical properties. In addition, there are several types of beneficiation methods for upgrading phosphatic ore. It is possible to adopt the underlying mechanism for MSWI ash, even though there are differences in both chemical and physical characteristics.

Table 2 Existing methods for recovery or production of P from solid phase sources

	Method	Input	Recovery efficiency	Product P %	Output	Scale	Reference
Conventional P production	Dry process	Ore	90%	99.85%	Elemental P	Production	Hocking, 2005
	Wet process	Ore	90%	22.10%	Phosphoric acid	Production	EFMA, 2000
Recovery of P	Electro-kinetic	SSA	<1%	NA	Phosphate	lab	Sturm et al., 2010
	Thermal treatment	SSA	100%	20%*	Ash	Lab	Adam et al., 2009
	Bioleaching and Bioaccumulation	SSA	61.40%	NA	Bio mass	Lab	Zimmermann and Dott, 2009
	Two step leaching with acid and base	SSA	61%**	NA	NA	Lab	Levlin et al. 2005
Upgrading of P ore	High gradient magnetic	Ore	55.6%-65.0%	13.4% - 13.8%	Upgraded ore	Lab	Shaikh & Dixit, 1993
	Rotary tribo-electrostatic	Ore	45%	13.10%	Upgraded ore	Lab	Tao and AI-Hwaiti, 2010
	Flotation	Ore	51%-83%	9.6%-14.4%	Upgraded ore	Production	Houot, 1982

* The mechanism of this method is to remove heavy metals from ash; the efficiency here indicates the concentration of P in the SSA

** Only leaching is studied thus the value represents the leaching efficiency only.

4.3.1 Electro-kinetic treatment

The Electro-kinetic method is based on the principle that positive ions are transported towards electros in an electric field. Phosphorus in the solution normally appears as four kinds of species, namely H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} . Depend on various pH, it differs which species will prevail (Figure 12). In Low pH, ($\text{pH}<2$), H_3PO_4 will be dominant while H_2PO_4^- and HPO_4^{2-} prevail at pH around 7. When in more alkaline condition, PO_4^{3-} is dominant. In the electric field, the anion and cation will move in opposite direction thereby separating the heavy metals and the phosphate. Although this method seems theoretical feasible, the recovery efficiency is however extremely low (Sturm et al., 2010), which can be seen in Table 2. Further test of condition is needed to improve the efficiency.

4.3.2 Thermal treatment

Thermal treatment of SSA takes advantage of the evaporation of heavy metals chloride under moderate temperature (1000°C). The SSA to be treated is mixed with water and CaCl_2 . After that, the ash is nudilised and dried and then transferred to the kiln for thermal treatment. After the treatment, Cd, Cu, Mo, Pb and Zn can be effectively removed from the ash. This treated ash now can be utilised as fertilizer according to some researchers (Adam et al. 2009; Mattenberger et al., 2008).

4.3.3 Bioleaching and Bioaccumulation

Zimmermann and Dott (2009) managed to recover 60% of phosphorus in the SSA using bacteria as leaching and extraction agent. The bacteria chosen for leaching oxidises the metals so that the unfavoured metals can be released prior to the extraction of phosphorus. Then, another kind of bacteria, which produces sulphuric acid, lowers the pH in the ash thereby release phosphorus from the SSA.

4.3.4 Two step leaching with acid and base

Levlin et al. (2005) proposed a two step leaching method for the release of phosphorus from SSA. Phosphate dissolves at high pH in the absence of calcium. If calcium is present, phosphorus will precipitate as $\text{Ca}_3(\text{PO}_4)_2$. Therefore, in order to leach out phosphorus calcium needs to be removed. The first step thus is to leach calcium at pH 4 while phosphorus remains in the ash. Subsequently the pH is raised up to release phosphate. Around 60% of phosphorus can be released from SSA using this method.

Only a few methods will be considered further due to the low efficiency or long time period required for recovery. For example, electro-kinetic exhibited an extremely low percentage of recovery, less than 1%. Though with adjustment of conditions, there is potential for increasing the efficiency drastically, this method will not be evaluated further. The sequenced bioleaching and bioaccumulation takes 11 days for a complete process which hinders the upscale to bigger capacity. The beneficiation processes basically deal with the needs for removing the carbonate and silicate contents.

4.4 Life Cycle Assessment

Life Cycle Assessment (LCA) is an analytical tool for investigating environmental impact in a holistic perspective by analyzing the inventory data, evaluating the data and interpreting the assessed results. The ISO standard ISO 14040 describes the LCA procedure as in 4 phases: goal and scope definition, inventory analysis, impact assessment and interpretation. The basic idea of LCA is to collect every environmental flow in the whole life cycle of a product and to characterise the flows according to predetermined impact categories. The environmental flows

are classified to the impact categories and further characterised using mathematical modelling, as shown in Figure 2. For example, the greenhouse gases will be calculated to CO₂ equivalent and then summed up to get the final characterised global warming result having a unit as CO₂ equivalent. Each category has different unit and meaning. Different categories' results therefore cannot be compared directly. Normalisation is then performed to solve this problem by normalising the result to a reference. The reference denotes an average value in a certain region. It also can be understood as an environmental impact experienced by one person in one year. In this way, the characterised results can be converted to a unit of time thus enable the comparison between categories. An extra procedure can be applied to include the consideration of degree of importance. The significance of each category differs. Depending on different practitioner and audience, factors may be assigned to the categories to alter the overall influence. Last step is to sum up the normalised result to form a single index indicator. The more integrated step, the more uncertainties are introduced. For this reason, the results can be interpreted in different phases depending on the objectives of the study.

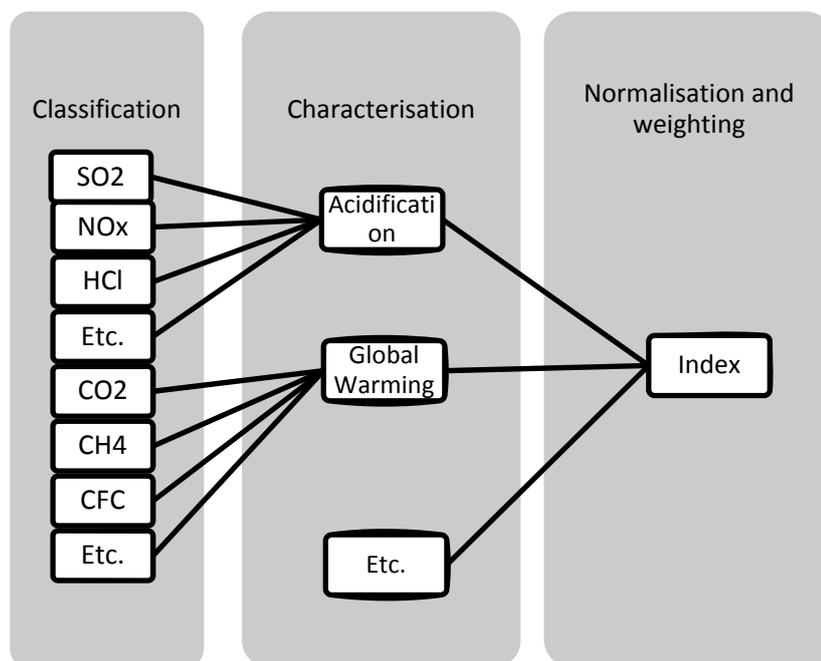


Figure 2 Stepwise impact assessment. Adapted from Baumann & Tillman, 2004

An important concept in LCA, allocation, needs to be introduced before moving to the main chapters. While gathering and calculating the environmental emissions, a problem may be encountered: manufacture of goods usually involves multiple input materials and multiple products. However, normally there is only one subject in focus in a LCA study. The environmental load should be therefore allocated between those multiple inputs and outputs. For example, in the refinery, petroleum is one of the products. When calculate the inventory of this process, the energy consumption and emission should be divided by all the products, usually taken mass in to account. Another situation that needs to consider allocation problem is open loop life cycle. For those productions use recycle materials as raw material, the environmental load from previous life cycle plays an important role in LCA study. There are several methods to deal with the problem, such as cut off, 50/50, and loss of quality and other type of methods. Depending on different requirements and rationale, practitioners may employ different methods.

5 Materials and Methods

5.1 Ash samples

The ash sample is fly ash generated by mass burn combustors from Renova. The major and trace element contents in the ash were analyzed by an accredited commercial laboratory named Eurofins AB.

5.2 Analytical methods

A pH-stat titrator was used in order to control and maintain the pH of the solution during the leaching. The phosphorus content in the leachate was measured by HACH spectrophotometer. Concentrations of major and trace elements in the leachate were determined by inductive coupled plasma mass spectrometry (ICP-MS). X-ray diffraction spectrometry (XRD) was used to qualitatively identify major crystalline compounds in the ash samples.

5.2.1 Mineralogical analysis by XRD

X-ray powder diffraction spectrometry can be used to identify the crystal structure of the components in ash sample. When an x-ray beam hits an atom at certain angles of incident (Θ), constructive interference occurs and induces a combination of scattered rays mutually reinforcing one another, which forms a diffracted beam. This situation only happens under a mathematical condition based on Bragg's law (Schiels, 2004):

$$n\lambda = 2d \sin\theta \quad (1)$$

In this equation, variable λ is the wavelength of the incident x-ray beam, and the various d is the distance between atomic layers in a crystal; n is an integer number. This principle can be utilized to identify the crystalline compounds of known structure. The result of this experiment is interpreted as a graph of the detected intensity versus the detection angle.

In this study, XRD is used to detect crystalline composition of MSWI ash. Siemens D5000 XRD with the characteristic Cu radiation and s position sensitive detector is used in this study.

5.2.2 pH-stat titrator

Metrohm SM 702 titrino has been used for keeping the pH constant. It is an automatic titrator with a long list of variables that can be set and provides an accurate titration. The titrator uses a cylindrical piston to draw in fluid and to pump out for titration. The volume it dispenses is calculated via the area of the cylindrical section and the distance the piston head has moved. The main body of the device and the pump with solution can be separated, ease for changing different titrants.

5.2.3 HACH spectrophotometer

HACH method uses a spectrophotometer to measure the transmission of the light as intensity and then gives the concentration of the detection substances, which is a quick and accurate way to detect phosphorus. It contains standard operations and uses spectrophotometry to detect phosphorus as phosphate. Spectrophotometry measures the reflection or transmission properties of a material as a function of wavelength in quantity (Allen et al. 2009). It follows the Beer-Lambert Law which relates the absorption of light to the properties of material through which the light is travelling. The transmission (T) of light through a substance, the

absorption coefficient of the substance (α) and the distance the light travels through the material (ℓ) are logarithmic relevant. The absorption coefficient also can be written as a product of a molar absorptivity of the absorber (ϵ) and the concentration of the substances in the material (c) (Ingle&Crouch, 1988). These relations are written as follow:

$$T = \frac{I}{I_0} = 10^{-\alpha\ell} = 10^{-\epsilon\ell c} \quad (2)$$

In this study, HACH DR/890 colormeter was used to measure reactive phosphorus, also called orthophosphate. The detection range is 0-2.5 mg/L PO_4^{3-} , using the standard PhosVer3 Method. Some of the samples have higher phosphorus concentration, and were diluted before measurements.

5.2.4 Elemental analysis by ICP-MS

Inductively coupled plasma mass spectrometry (ICP-MS) is widely used in elemental determinations. An ICP-MS contains two parts: a high-temperature ICP source and a mass spectrometer.

The ICP source converts the ions in the sample into gaseous atoms and then ionizes the atoms to form plasma. Once the elements are ionized, they get into the mass spectrometer through the interface cones where the centre portions of the ion beam are sampled. When the ions enter the mass spectrometer, they are separated according to their mass-to-charge ratio. The result is that the mass spectrometer is set to only allow a single mass-to-charge ratio ion to reach the detector at a given instant in time. As each element has generally unique mass-to-charge ratio, the quality and quantity of target elements can be attained by ICP-MS.

In this study, concentrations of various metal ions in filtrate from different processes were determined by ICP-MS. The samples were prepared in 10ml centrifuge tubes, consisting of 1% rhodium as include standard, nitrate acid and deionised water.

5.3 Leaching and recovery tests

The whole leaching experiment consists of three main processes. First part is to maximize phosphorus leaching and to have a general idea about acid leaching performance of the MSWI ash. The next two processes are acidic and alkaline dissolving or precipitation of phosphorus according to two different methods. The first uses acidic dissolution with consequent alkali precipitation to recover phosphorus while the other method uses acid to remove metal impurities and then dissolve phosphorus in an alkaline environment.

5.3.1 Leaching tests

The main purpose of these leaching tests is to find the optimal leaching conditions for phosphorus from ash. Influence of the acid concentration, leaching time and sedimentation time has been studied in the experiments (

Table 3). The L/S ratio of 5 is chosen based on former research by Karlfeldt Fedje (2010).

The optimal acid concentration and leaching time have been investigated as follow (

Table 3): 10g of ash samples were leached with 50ml hydrochloric acid solution of different concentrations and stirred from 2h, 4h to 24h. Each experiment setup was tested in triplicates. The leachates were filtrated with 0.45 μm type filters and the pH was measured using a pH meter. Phosphorus concentrations in the leachates were measured with HACH and selected metals were analyzed by ICP-MS.

Table 3 Testing parameters and intervals under L/S ratio of 5.

HCl conc., mol/L	24h sedimentation			No sedimentation
	2h	4h	24h	2h
1	X	X	X	X
1.5	X			
2	X	X	X	X
2.5	X			
3	X	X	X	

X : Tested conditions

Once the optimal leaching condition is attained, a batch leachate applying these conditions and using 100g MSWI ash was prepared. This batch leachate was used in Method I. Due to the large volume of this ash-acid mixture and the difficulty of filtration, the bath leachate was only the upper clear layer of this mixture with 24h sedimentation without filtration. Only a very small amount of the batch leachate was centrifuged and filtrated for the ICP-MS measurement.

5.3.2 Recovery method I

This acid dissolution-alkali precipitation method has been introduced by Kaikake (2009) to recover phosphorus from chicken manure incineration ash (CMIA). As the CMIA and MSWI ash have similar elements composition (see Table 1), the present work is aimed to examine whether this method is feasible for phosphorus recovery from MSWI ash.

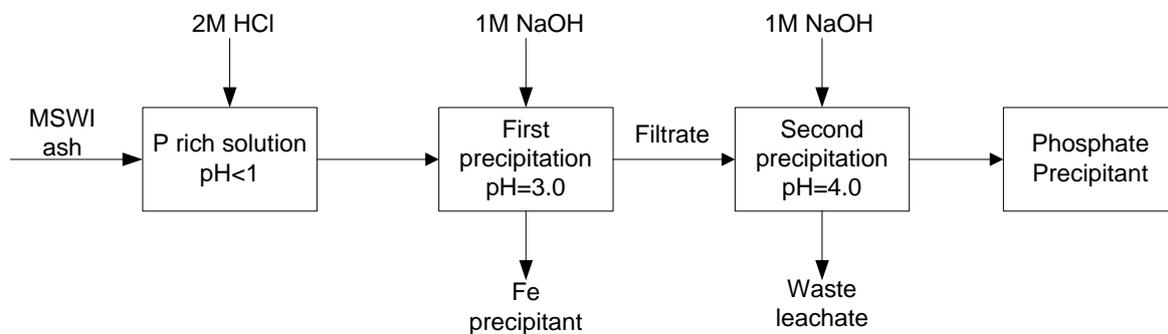


Figure 3 Acid dissolution-alkali precipitation method.

The aim of this method is to precipitate some of the impurities presenting in a P-rich leachate to reach a solid phosphorus product with fewer metals usable as for example, fertilizer. All experiments were done in triplicate at room temperature (Figure 3). The batch leachate obtained in 5.3.1 was used to perform the first precipitation. The purpose of the first precipitation is to remove mainly iron and some other metals, such as aluminium, lead and zinc. 20 ml of the P-rich leachate has been titrated dropwise to a constant pH = 3.0 with 1M sodium hydroxide solution for 1h in 500rpm stirring rate. The particles formed during this process (first precipitant) were separated by filtration using 0.45µm type filters and dried at 50°C in the oven. The first filtrate was reserved for the second precipitation. The second precipitation was performed in order to precipitate phosphorus and subsequently acquire the final product. 20 ml of the reserved filtrate and 1M sodium hydroxide was added dropwise to reach a constant pH of 4 for 5h in 400rpm stirring rate. The formed precipitant (second

precipitant) was separated by filtration using 0.45 μ m type filters and thereafter dried at 50°C in the oven.

5.3.3 Recovery method II

Alkaline leaching has been claimed to produce a phosphorus product with lower metal contamination comparing to acidic leaching. However, acidic leaching offers a higher release of phosphorus than using alkaline environment (Levlin et al., 2004). This is due to that the calcium binds the phosphate in the ash to form calcium phosphate in alkaline environment, which reduces the amount of released phosphorus. Therefore, a two steps acid-alkali leaching method has been used in order to increase the phosphorus leaching rate with alkali. The acid is used first to leach out calcium in the ash. Then alkali is used to dissolve phosphorus in the remaining ash. The basic processes and principles are showed in Figure 4. In the first step, 1M hydrochloric acid is added dropwise to the ash and the pH of the solution is controlled meticulously at 4. In this condition, Ca will dissolve into the solution but phosphorus will still remain in the ash as solid. Then the solids are separated by centrifugation and the remaining ash is used in the next step. The second step is to dissolve the phosphorus from the remaining ash by adding 1M sodium hydroxide. After the addition of sodium hydroxide, metals will react with hydroxide ions to form precipitants while the phosphorus will dissolve as phosphate. After filtration, the phosphorus is extracted from the ash to leachate with a small amount of metals' existence.

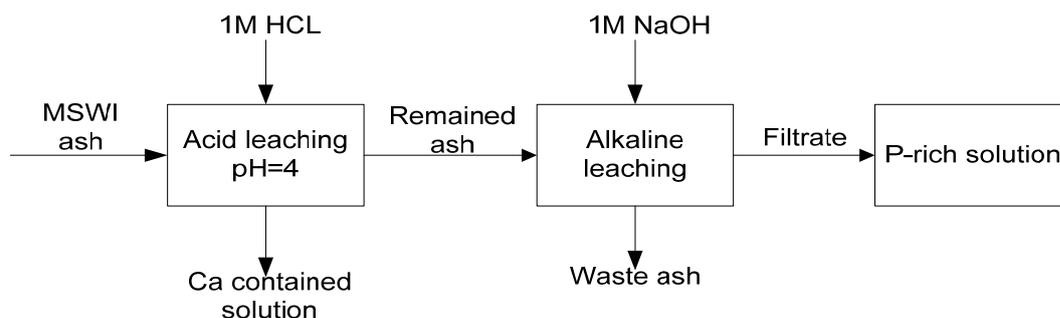


Figure 4 The two steps method to recover phosphorus from ashes. (Source: Levlin et al., 2004)

5.4 LCA procedures

The evaluation of environmental impact has been performed using the SimaPro which is LCA software combined with databases. The ecoinvent system processes database is used. In the SimaPro, process is the basic building block. It is presented as the product of the process. Therefore, for each of the processes in a life cycle of the study subject, a correspondent process should be created, except for those already present in the database. Then the processes are coupled by completing the mass and energy balance, namely, connecting to each other as input and output. Repeat this procedure and a complete life cycle should be created. This means the inventory of all the process is built. The characterised results and normalisation thus can be easily calculated after choosing the preferred impact assessment method. In this study, CML2001 is used as impact assessment method because of the emphasis on heavy metals which are important in the case of MSW ash.

The two conventional processes as well as the main chemicals used can be found in the database (full parameters are listed in Appendix D). The developed recovery process and the landfill of MSW ash have to be created based on available data. The quantities of the inputs

and outputs should be adjusted depending on their concentrations. Selection of impact categories are shown in the report. Complete result can be found in the appendix.

6 Results and discussion

This chapter presents the results of this study in two parts. The first one is the technology development which is the laboratory results about leaching processes. The second part mainly consists of evaluation of the developed process and its comparisons to the conventional production processes using LCA methodology.

6.1 Technology development

6.1.1 Ash composition

The elemental composition of the studied ash is presented in Table 4. Phosphorus content in the MSWI ash is around 0.6%, which is equivalent to 5% by weight as phosphate. High contents of heavy metals indicate the ash is a quite hazardous material, see also Table 5. There is a large amount of alkali earth metals in the MSWI ash, hence the alkalinity of the ash is high which is verified in Karlfeldt-Fedje (2010)'s research. Therefore, the capacity of the MSWI ash to buffer acid is high and it is predicted to demand a large $[H^+]$ to decrease the pH of the ash while leaching.

Table 4 *Elemental composition of MSWI ash.*

Major Elements	content, mg/kg ash	Trace Elements	content, mg/kg ash
P	5900	Ag	32
Al	32200	As	460
Ca	141000	Au	<10
Cu	2000	B	300
Fe	19100	Ba	400
K	54400	Be	<2.5
Mg	13100	Cd	270
Na	58400	Co	12
Pb	4600	Cr	490
S	64500	Hg	0.51
Sb	1900	Mo	36
Si	45300	Mn	810
Sn	1200	Ni	100
Ti	10100	Pd	<10
Zn	37300	Pt	<10
		Se	<10
		V	49

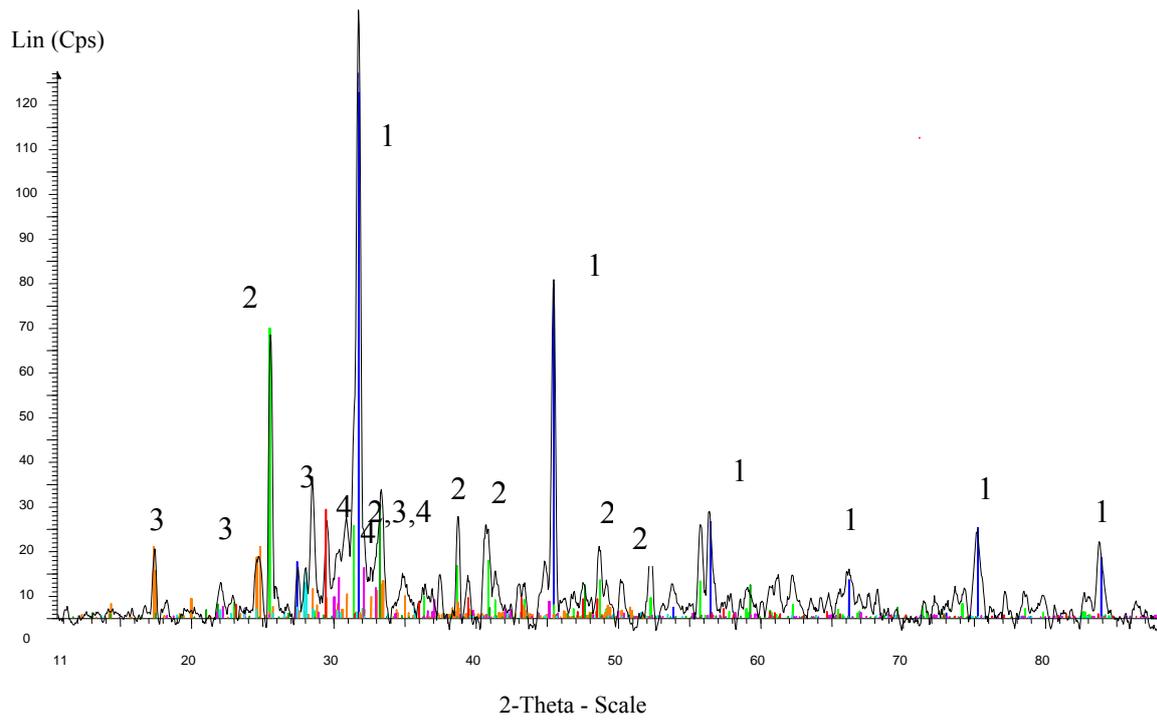
MSWI ashes are normally treated as waste products and landfilled. The major environmental concern of the disposal of these ashes is their high content of soluble salts, nutrients and heavy metals (Table 4). Leaching of these elements from the ash poses risks to surface and ground water contamination. Moreover, according to the Swedish limitation for hazardous waste in landfill, the contents of metals in this MSWI ash are too high to be deposited in the landfill in Sweden (Table 5). All the metals exceed the limit values except mercury. Hence, decrease the content of the pollutants is needed before landfill. Recovery of some valuable elements can be a promising way to reduce the risk of the ash and turn the waste into a resource.

Table 5 Comparison of trace elements in MSWI ash and Swedish guideline value (Source: Swedish environmental protection agency code of statutes 2004:10).

	Limits for hazardous waste in landfill, Sweden (mg/kg solid)	Municipal solid waste ash Göteborg, Sweden (mg/kg ash)
Sb	5	1900
As	25	460
Pb	50	4600
Ba	300	400
Cd	5	270
Cu	100	2000
Hg	2	0.51
Cr	70	490
Mo	30	36
Ni	40	100
Se	7	<10
Zn	200	37300

The XRD result of the ash is presented in Figure 5. The patterns of several components are displayed in different colours which are NaCl, CaSO₄, K₂ZnCl₄ and KCaPO₄. The major form of phosphorus is likely to be KCaPO₄. However, as the detection limit of XRD is about 1 wt%, there could be other forms of phosphorus have a mass content less than 1% in the detected sample.

Figure 6 shows the solubility of different phosphate compounds. Calcium phosphates will dissolve when pH drops down to 4.5 while most of the iron phosphate and aluminium phosphate are unlikely to undergo substantial dissolution. When pH reaches 1, all the aluminium phosphate will become soluble and part of the iron phosphate will dissolve either. Therefore, when pH reaches the maximum phosphorus dissolution, it can be expected that large amount of calcium, aluminium and iron could also be leached out from the ash.



1- NaCl; 2-CaSO₄; 3-K₂ZnCl₄; 4- KCaPO₄

Figure 5 XRD pattern of MSWI ash.

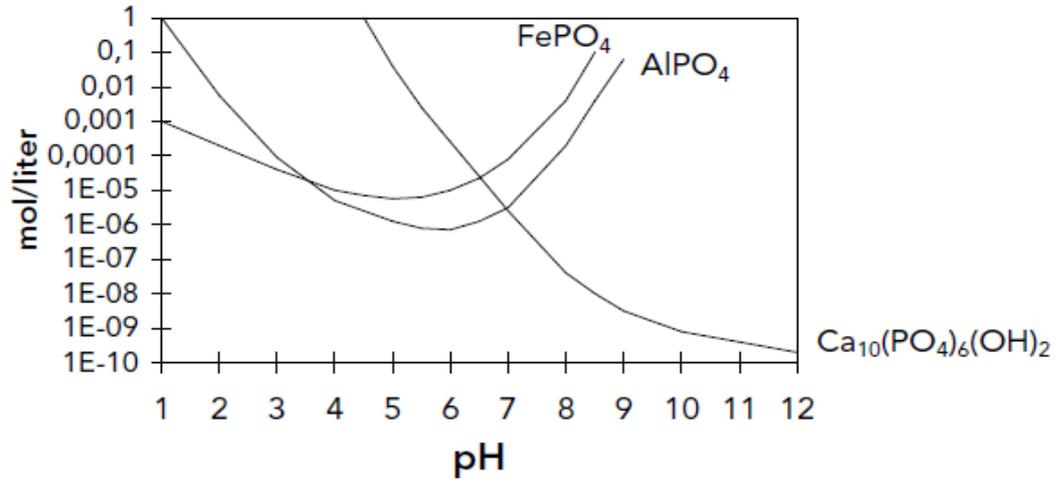


Figure 6 Solubility of different phosphate compounds. (Source: Stumm and Morgan, 1996)

6.1.2 Optimal leaching conditions

Several parameters, i.e. acid concentration, leaching time, pH, and sedimentation time, have been studied in the pilot experiments to obtain the optimal leaching conditions to have a maximum phosphorus leaching efficiency.

6.1.2.1 Acid concentration

The effect of different concentrations of hydrochloric acid is shown in Figure 7. The horizontal line corresponds to 100% leaching of phosphorus in 1kg MSWI ash, which is calculated from the P content in the MSWI ash analyzed by the accredited commercial laboratory. The other curve shows the phosphorus content in the leachate after leaching experiment using different concentrations of hydrochloric acid under 2h stirring and 24h sedimentation time.

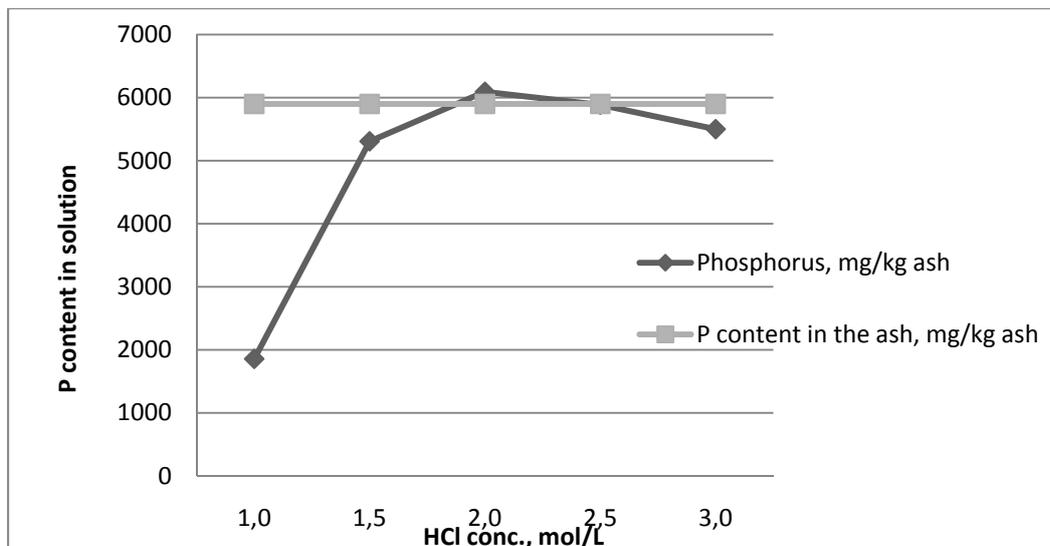


Figure 7 Influence of acid concentration on phosphorus leaching. 2h stirring time, 24h sedimentation time, L/S ratio=5.

As seen in Figure 7, there is a peak in phosphorus concentration when using 2mol/L HCl. The upward trend before the peak is mainly due to the increased release of phosphate from the phosphate compounds through the increased acid concentration. As showed in Table 6, 2mol/L HCl seems to release all of the acid-soluble phosphorus in the ash sample while there is no positive effect of phosphorus leaching efficiency with further increased acid concentration but a small decline. This phenomenon may be attributed to precipitation of phosphate with some elements with further increased acid concentration (i.e. Fe), which are released from ash matrix as a result of excessive acid. The pH of the leachate using different HCl is also shown in Table 6. It can be seen that there is a significant increase of phosphorus dissolution when pH drops below 1 compared to 3. After the pH reaches 0.2, no benefit can be gained for phosphorus dissolution by keeping decreasing the pH. The data also shows that when pH is below 0.6, the total phosphorus leaching efficiency can achieve above 90%.

The discrepancy that the phosphorus content in the ash is somewhat lower than the value calculated from the leachates can be caused by the non-evenly distribution of phosphorus in the ash. A very small amount of ash was analyzed by the accredited laboratory according to standardised methods. However, the ash is a rather heterogeneous material, which can induce this abnormal result---phosphorus in the leachate is higher than the total content in the ash. However, this anomaly will not have any significant influence on the result. It has been

concluded that 2M hydrochloric acid is the best concentration as almost 100% phosphorus leaching efficiency has been achieved. Though the P-leaching efficiency is 90% when using 1.5M hydrochloric acid, in order to guarantee the maximum phosphorus leaching, 2M hydrochloric acid is chosen instead of 1.5M. However, one important fact should be noticed that if the hydrochloric acid has a high environmental impact, the best acid concentration should be reconsidered as 1.5M which has a high leaching efficiency but a lower acid consumption.

Table 6 Phosphorus leaching efficiency depending on different acid concentration. 2h stirring time, 24h sedimentation time, L/S ratio=5.

HCl conc., mol/L	pH of the leachate	P in solution, mg/kg ash	P in the ash, mg/kg ash	P leaching efficiency %
1.0	3.0	1900	5900	31
1.5	0.6	5300	5900	90
2.0	0.2	6100	5900	100
2.5	<0.0	5900	5900	100
3.0	<0.0	5500	5900	93

6.1.2.2 Leaching time

Figure 8 shows the effect of different leaching times and hydrochloric acid concentrations on phosphorus leaching efficiency.

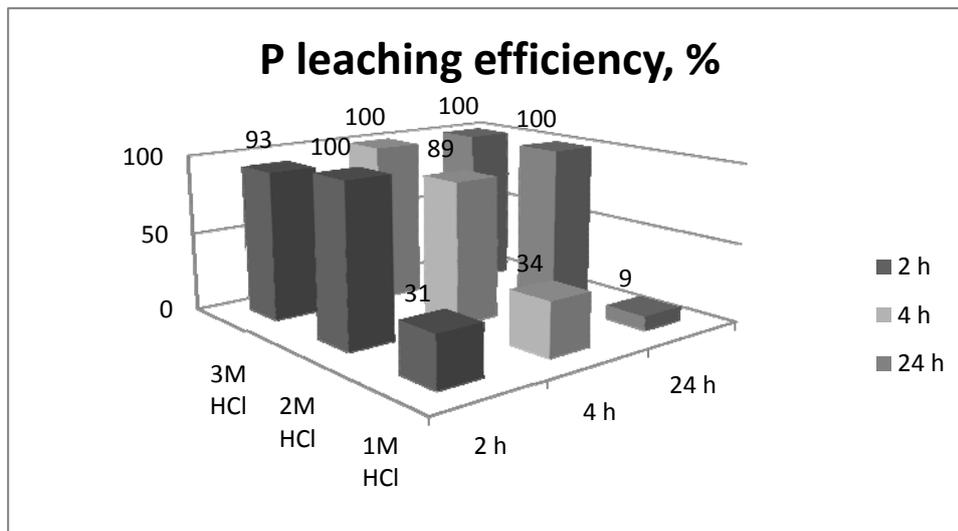


Figure 8 P leaching efficiency depending on time and HCl concentration. 24h sedimentation and L/S ratio=5.

The general tendency shows that 1M hydrochloric acid has a very low leaching efficiency compared to the higher HCl concentrations regardless that what leaching time is used. Moreover, longer leaching time (24 h) does not benefit the efficiency but decreases when 1M hydrochloric acid is used. This is probably because longer leaching time provides enough reaction time to let more metals release from the ash matrix so that phosphate can precipitate with these metal ions again therefore decreases the release of phosphorus.

There is no significant variation of phosphorus leaching efficiency with different leaching times when using 3M hydrochloric acid, which indicates that when high concentrations of

acid is used, the time of leaching become less an important factor for leaching phosphorus. Although 3M hydrochloric acid has a similar high P leaching efficiency as 2M hydrochloric acid, the acid consumption is higher comparing to 2M hydrochloric acid when having the same result. Therefore, 2M is still the optimal acid concentration under different leaching times.

While using 2M hydrochloric acid to leach, 2h and 24h have high phosphorus leaching efficiency nearly 100% (Table 7), whereas the efficiency of 4h is lower. The metal contents are shown in Figure 9. There is a relationship between phosphorus and metals release in the leachates. When there are certain amounts of metals released, there is corresponding amount of phosphorus released in the leachate. Hence, the 4h has lower phosphorus leaching efficiency and metals dissolution. This may due to some precipitation reactions that decrease the release of phosphorus and metals. Although 24h and 2h have similar high leaching efficiency, 24h leaching time gives more metal contents in the leachate than 2h leaching time. As the objective is to have maximum phosphorus leaching with minimum impurities, 2h leaching time is better than 24h.

Table 7 Phosphorus leaching efficiency depending on different time.

Acid conc., mol/L	Leaching time, 24h sed., h	P in solution, mg/kg ash	P in the ash, mg/kg ash	P leaching efficiency %
2	2	6100	5900	100
2	4	5300	5900	89
2	24	7900	5900	100

To summarize, 1M hydrochloric acid is not suitable for phosphorus leaching while 2M and 3M hydrochloric acid both have a good capacity to dissolve phosphorus. However, 2M hydrochloric acid uses less acid while phosphorus release is similar. Therefore, 2M hydrochloric acid is chosen instead of 3M hydrochloric acid. As 2h leaching time gives higher phosphorus leaching efficiency than 4h, and a lower metal content than 24h when using 2M hydrochloric acid (Figure 9), 2h is chosen to be the optimal leaching time.

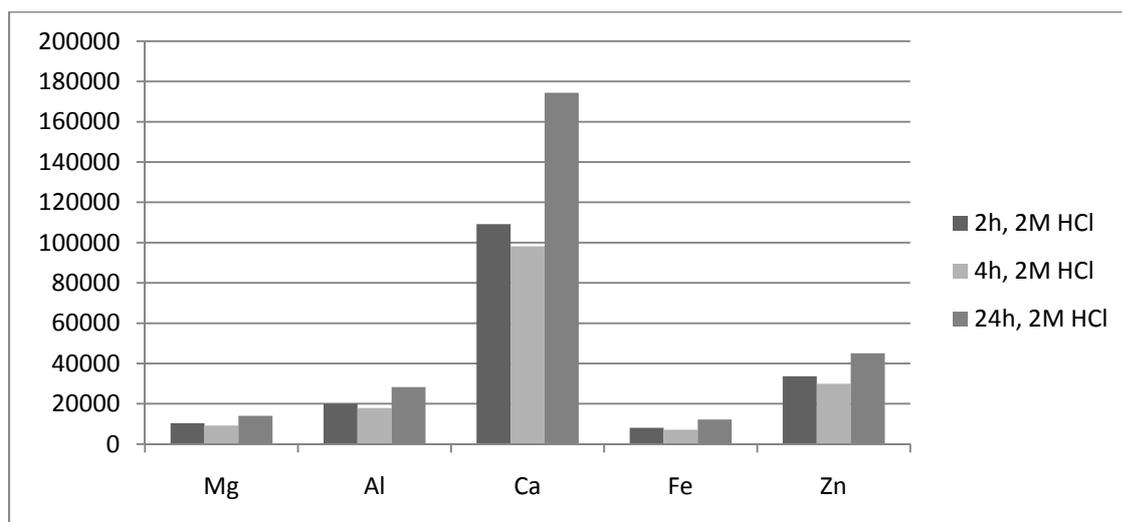


Figure 9 Metal content in the leachate after different leaching times with 2M HCl. All data are given as mg/kg ash.

The dissolution of ash matrix during leaching are also analyzed and displayed in Figure 10. There is a similar tendency when using 1M and 2M hydrochloric acid: 4h leaching time gives a least loss of ash (30 and 190 g/kg ash, respectively) while 24h leaching time gives the most losses (280 and 400 g/kg ash, respectively). The possible explanation could be that 2h leaching time dissolves many elements while 4h leaching time may give enough time to let some of the dissolved elements have precipitation reactions. When it comes to the 24h leaching time, all the formed precipitants have enough time to dissolve again and in addition to that former encapsulated compounds can be released from the ash matrix. The loss of ash rises as the leaching time increases when using 3M hydrochloric acid (20%, 29% and 48% loss of ash, respectively). As 3M hydrochloric acid provides a rather low pH environment, all the dissolved elements are unlikely to have precipitation reactions. The longer the time, the more ash matrix fraction will dissolve in such a low pH.

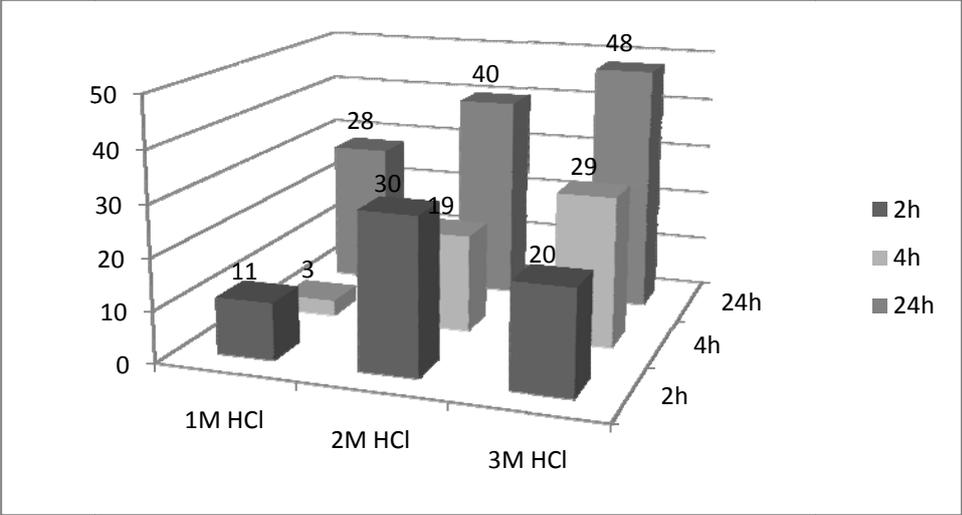


Figure 10 Ash losses during the leaching given as w%.

The dissolution of ash matrix also reflects the element contents in the leachates. It can be seen in Figure 9 and Figure 10 that high loss of ash fraction will induce high content of metals in the leachates.

6.1.2.3 Sedimentation time

Table 8 indicates that sedimentation before filtration has no significant influence on the phosphorus leaching efficiency. However, the silicon concentration in the leachates is quite different with and without sedimentation. Leachates obtained directly after the leaching with no sedimentation before filtration become jelly material in 24 hours. As shown in Table 8, the reason of this phenomenon may be the high content of silicon and the mechanism is explained in 6.1.3. Such colloidal substances will affect the further experiment when using this leachate, because the solution amount is no longer accurate when measuring the solution by volume. Therefore, 24h sedimentation has been performed after leaching to slow or even avoid gel formation in a short time.

Table 8 Si and P content in the leachate with or without sedimentation.

Unit: mg/kg ash	Si	P
2h, 2M HCl, 24h sedimentation	8970	6100
2h, 2M HCl, no sedimentation	22600	5300

Based on the results stated above, the optimal leaching conditions with 100% P leaching efficiency are presented in Table 9.

Table 9 The optimal leaching conditions (L/S ratio: 5).

HCl conc., mol/L	Time, h	Sedimentation
2	2	24h sedimentation

6.1.3 Leachate used for recovery

The batch leachate is prepared based on the optimal leaching conditions (Table 9). Due to the difficulty of the filtration, only a small amount of the leachate is filtrated to investigate the metal concentrations by the ICP-MS analysis. The filtrated leachate is a yellow solution with a pH of about 0.1 in room temperature. About 100% of phosphorus in ash is dissolved, giving a phosphorus concentration of about 6100 mg/kg.

Table 10 Metal content in leachate and ash.

Elements	Total content, mg/kg ash	Leachate, mg/kg ash	Leaching efficiency, %	Elements	Total content, mg/kg ash	Leachate, mg/kg ash	Leaching efficiency, %
Na	58400	62000	100	Cd	270	280	100
Mg	13100	9500	73	Ba	400	10	3
Al	32200	19800	61	Ni	100	98	98
K	54400	53600	99	Cr	490	200	41
Ca	141000	44700	32	Cu	2000	1600	80
Fe	19100	8000	42	Zn	37300	27400	73
Mn	810	710	88	Pb	4600	4100	89
Co	23	15	65				

The profiles of the metal concentrations in ash and in the leachates are provided in Table 10. Large fractions of the metals are leached out from ash into acidic solution. Generally, the macronutrients (Na and K) are dissolved to a larger extent than the metals, and nearly approach 100% leaching efficiency. This is due to that these elements are unlikely to form insoluble components under low pH circumstance. The amounts of metals in the leachate are lower than in the ash. Cadmium and nickel are the only exceptions, having concentrations approximately similar to that in the ash. In addition, some of the heavy metals also have a relatively high leaching efficiency, like aluminium, manganese, nickel, copper, zinc, lead and cobalt. Element contents in the ash are dramatically decreased, which means this leaching treatment makes the MSWI ash less hazardous. However, these heavy metals in the leachate may be a problem considering the purity of the final product of phosphorus, thus influence the usage. As a result of the high toxic metal contents, the leachate should be carefully treated and these metals need to be taken care of during the whole phosphorus recovery processes.

A lot of the toxic metals are leached out from the ash. The remaining parts are phosphorus free acid-insoluble compounds, which can be utilized as raw materials in construction or cement production industry. Therefore, the major fraction of the MSWI ash may be reused rather than disposed after this teaching treatment, which can decrease the impact of environment and the demanded area needed for landfills. However, this has to be further studied.



Figure 11 The picture of the gel.

As discussed before, gel formation in the leachates was a problem (

Figure 11). In order to avoid this phenomenon, leachates were left to have sedimentation for 24h. However, in some leachates this is not enough to avoid gel formation, which happened after 4 days. The detailed information is provided in Table 11. It can be seen that not all of the leachates formed gel, but only under certain conditions, the leachates will become colloidal (marked yellow). Very low and very high acid concentration will not favour the gel formation no matter how long the leaching time is while if the acid concentration is around 1.5 to 2, the shorter leaching time can benefit the gel formation. Moreover, without sedimentation before filtration, the leachate is easier to become jelly than with 24h sedimentation.

Table 11 The gel formation of the leachates.

HCl concentration, mol/L	Time, h			Note
	2	4	24	
1				24h sedimentation
1.5		-----	-----	
2				
2.5		-----	-----	
3				
1		no sedimentation		
2		no sedimentation		

 with gel formation

----- no sample tested under such condition

The mechanism of this phenomenon is probably that silicate ions can react with hydrogen ions to form silicic acid in acidic solution. Silicic acid is inherently unstable, and will condense and grow to forms silica gel, a hard and glassy substance (Hauser, 1955). The silicon concentration and pH of the leachate during different leaching conditions are summarized in Table 12. It certifies the theory that the silicon is the main factor. As shown in

the table, silicon content is much higher in the colloidal samples than in the normal samples. Hence, it is very likely that the colloidal material is the silicic acid which is produced under high concentrations of silicon in an acidic environment.

Table 12 Si concentration and pH of the leachates. The bold rows are the colloidal leachates.

	Si, mg/kg ash	pH
1M, 2h, sed.	2300	3
1M, 4h, sed.	3050	2.6
1M, 24h, sed.	600	3.1
1.5M, 2h, sed.	20300	0.6
2M, 2h, sed.	8970	0.2
2M, 4h, sed.	18300	0
2M, 24h, sed.	1470	0
2.5M, 2h, sed.	710	0
3M, 2h, sed.	<1	0
3M, 4h, sed.	<1	0
3M, 24h, sed.	<1	0
1M, 2h, no sed.	15900	2.6
2M, 2h, no sed.	22600	0

6.1.4 Recovery of phosphorus from method I

Method I can be divided into two main processes after obtaining the P-rich solution---the first precipitation giving iron solid compounds and the second precipitation giving the P-rich product. The results of these processes are presented below.

6.1.4.1 Precipitation of iron

The recovery of elements in the first precipitation is shown in Table 13. The data is the average of triplicate analyses. A very small amount of phosphorus is removed during the first precipitation (less than 1% based on the phosphorus content in the precipitant). Other elements have removing efficiencies around 15% except iron, which is 56%.

The problem that the contents of some of the metals (i.e. Mg, Ca, Fe, Zn, Pb) in the first filtrates are higher than the batch leachate can possibly be the different treatments between the representative leachate sample for measurement and the leachate used to do the recovery experiment. As mentioned in 5.3.1, the leachate sample for ICP-MS measurement is centrifuged and filtrated while as the leachate for the experiment is without centrifugation and filtration due to the difficulty of filtration. Because the centrifugation and filtration treatments can remove most of the solids which can adsorbed various metal elements, the representative leachate sample with centrifugation and filtration contains less amount of metals than the first filtrate.

Table 13 *Removed elements during the first precipitant.*

Elements	Leachate, mg/kg ash	First filtrate, mg/kg ash	First precipitant, mg/kg ash	Remove efficiency , %
P	6092	4425	58	<1
Mg	9500	10500	1200	13
Al	19800	19100	3500	18
Ca	44700	47500	5400	12
Mn	710	700	100	14
Fe	8000	8500	4500	56
Co	15	16	3	20
Cu	1600	1507	200	13
Zn	27400	30544	3300	12
Cd	280	280	40	14
Pb	4100	5800	750	18

Overall, the results suggest that the precipitation at pH 3 is quite suitable for removing some of the metals especially iron from the leachate to eliminate subsequent contamination in final product with a low loss of phosphorus. However, metal concentrations in the remaining filtrate are still high.

6.1.4.2 The second precipitation

During the second precipitation, 71% of phosphorus is precipitated and recovered from the original leachate, which is provided in Table 14. Due to the distinct decreases of aluminium, magnesium, calcium, lead, zinc and iron in the second filtrate compared to the first filtrate, it can be expected that the precipitant mainly consisted of phosphorus and these metals, in addition to other major elements like O, C, H, S, Si which are not measured in this case.

The abnormal value about concentration of iron in the second precipitation may be caused by interfering in the measurement or contamination during the process.

Table 14 *Recovery elements during the second precipitant*

Elements	Leachate, mg/kg ash	First filtrate, mg/kg ash	Second filtrate, mg/kg ash	Second precipitant, mg/kg ash	Recovery efficiency , %
P	6092	4425	134	4331	71
Mg	9500	10500	9200	1400	15
Al	19800	19100	3800	5900	30
Ca	44700	47500	41800	7800	17
Mn	710	700	640	180	25
Fe	8000	8500	2900	17200	215
Co	15	16	14	7	48
Cu	1600	1507	1250	360	23
Zn	27400	30544	27000	2500	9
Cd	280	280	250	100	36
Pb	4100	5800	4660	600	15

In order to understand the mechanism of P precipitation reactions, the stability constants of different phosphorus species are displayed in Figure 12. The dominant species is H_3PO_4 when pH is 0. As the pH rises, H_3PO_4 begins to transform to $H_2PO_4^-$. Then $H_2PO_4^-$ reaches its peak when the pH rises to 4. After that HPO_4^{2-} begins to form. There are large amount of iron, magnesium, and calcium in the first filtrate and with these metals the following reactions could probably happen at pH 4 to form the P precipitant product.



Furthermore, although there is an addition of alkali after that pH achieves to 4, the raise in pH is not observed. This can be explained by that the hydroxide is consumed to produce HPO_4^{2-} (Eq. 3) which forms precipitants with different metal ions (Eq. 4, 5 and 6).

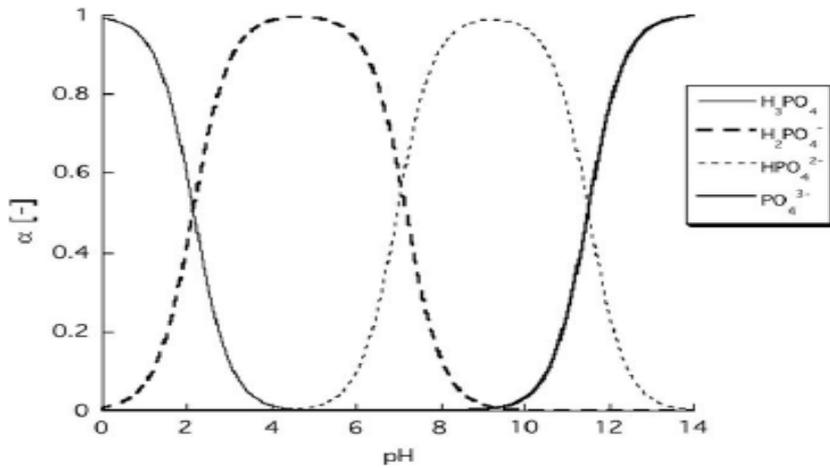


Figure 12 Equilibrium distribution of phosphorus species as a function of pH. (Source: William & Siegfried, 1954)

During the experiments, a noticeable phenomenon is stratification in the second leachate (Figure 13). The leachate was a rusty colour solution directly after filtration (left sample in Figure 13). After few days, the rusty colour begins to settle down to the bottom of the container while the upper layer becomes clear and transparent (middle sample in Figure 13). The rusty coloured layer could be colloid of some elements and the compositions of the left sample and the upper layer of the middle sample are shown in Table 15. A significant difference of iron content between the two samples suggests that the rusty colour sedimentation is mainly iron colloids. This iron colloids may be another reason leads to the extremely high value of iron in the second precipitant as mentioned before.

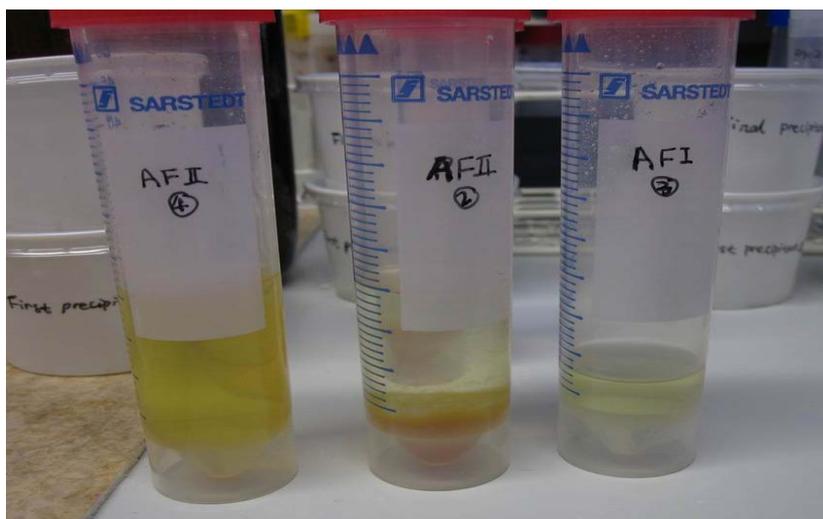


Figure 13 The picture of the stratification. The left one is the well mixed second filtrate, the middle one is the second filtrate after 2-3days, the right one is the first filtrate.

The first precipitation and the second filtrate contain a lot of valuable metals, like Al, Fe, Cu, Mg etc. They can be used as raw materials for heavy metals recovery. For instance, Karlfeldt-Fedje (2010) states that copper can be recovered from MSWI ash leachates using solvent extraction reagents based on oximes.

Table 15 Elements contents in the upper layer and mixed second filtrate.

Elements	Mg	Al	Ca	Cr	Mn	Fe	Co	Cu	Zn	Cd	Pb
Second filtrate upper without colloid, mg/kg ash	9200	3500	41400	18	630	1800	14	1230	26700	250	4580
Second filtrate well mixed, mg/kg ash	9200	3800	41800	20	640	2900	14	1250	27000	250	4660

6.1.4.3 The purity and usages of the phosphorus product

The overall efficiency of phosphorus recovery from MSWI ash is approximately 71%. The composition of the phosphorus product is presented in Figure 14. The phosphorus accounts for 3% of the final product calculated as element P, 10% as phosphate. Comparing to the phosphorus content in the ash, the percentage is magnified 5 times. There is a large proportion of other elements which accounts for 70% of the total amount. These unknown elements could be C, O, H, S and Si as components of the precipitants.

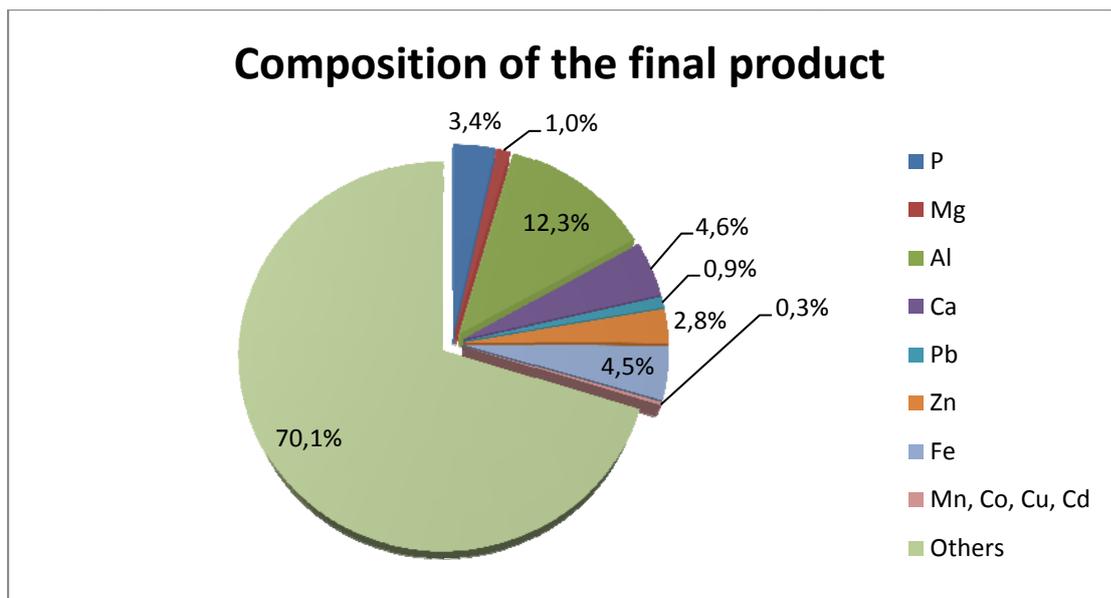


Figure 14 Composition of the final phosphorus product.

The normal commercial fertilizers known as superphosphate contain 7%-10% of phosphorus elements in weight (UK fertilizers regulation, 1990). Therefore the phosphorus rich product is not suitable to use directly as the phosphorus fertilizers. Additional purification techniques are needed to increase the phosphorus content in the product and to reduce the impurities content. However, if this P-rich product were to be used directly as a low quality phosphorus fertilizer on agriculture land, high content of some trace elements may be a limiting factor. Normally, the phosphorus demand for one hectare farmland for a year is 22kg (Pettersson, et al., 2008). Table 16 shows the limitations of trace elements calculated on a P-supply of 22 kg P/(ha, year). All the trace elements exceed the Swedish limitation while only cadmium exceeds the EU limitation for using this product as other type of fertilizer. Hence, the P rich product may be used as fertilizer in some of the European countries after separation of cadmium.

Table 16 Trace elements concentration in P-sources as g/(ha, year) calculated on a P-supply of 22 kg P/(ha, year).

Trace elements, g/(ha, year)	Cd	Pb	Cr	Cu
Swedish limits	0.75	25	40	300
EU limits	150	12000	15000	12000
Phosphorus product	500	3000	100	1800

(Source: Swedish EPA and EU council directive)

Another use of the product is to use as a substitute of phosphate rock. Phosphate rocks, the raw materials for the fertilizers production industry, can be divided in to three categories in the terms of qualities: low-grade phosphate rock (12–16% P_2O_5), intermediate-grade phosphate rock (17–25% P_2O_5), and high-grade phosphate rock (26–35% P_2O_5). The commercial grade phosphate ores are 28%-38%, which is considered to be economic to mine and for production (Sengul, et al., 2006). As the high quality phosphate ores are about to approach the exhaustion in next few years, the utilisation of low phosphate contained sources becomes important.

Table 17 Composition of the low-grade phosphate rock and the product in the study.

Unit: %wt	Low grade phosphate rock (Iran) ^a	Low grade phosphate rock (Turkey) ^b	Phosphorus product from MSWI ash
P	2.2	2.4	3.4
Ca	34.6	36.6	4.6
Al	1.3	0.6	12.3
Fe	1.6	0.7	4.5
Mg	0.3	0.8	1

a: Mohammadkhani, et al., 2011.

b: Keles, Özer and Yörük, 2009.

The phosphorus product from the study contains about 3% phosphorus while some low-grade phosphate rocks consist of 2-3% phosphorus, which can be found, for example, in Iran and Turkey. In Table 17, phosphorus content in phosphorus product from MSWI ash is even higher than low-grade phosphate rocks. Therefore, the phosphorus product in this study is possible to use as low-grade phosphorus materials to produce fertilizers in a near future.

There are several studies about the techniques to produce high phosphate content products using low-grade phosphate rocks. One common technique is using flotation to optimize the phosphorus content. According to Mohammadkhani (2011), the content of P₂O₅ can be increased from less than 5% to 22% and the total recovery efficiency is 66% after three anionic-cationic reverse phosphate flotation stages. Another method is using thermal technique. Heating the ores for a certain time can increase the concentration of P₂O₅ to 29-32%, corresponding to recovery efficiency as 80-84% (Zafar, et al., 1995).

6.1.5 Recovery of phosphorus from method II

Method II can be divided into two processes: acid washing is used to decrease the calcium content in the ash without mobilizing phosphorus. The second process is alkali dissolution to dissolve phosphorus from the ash with low impurities content.

6.1.5.1 Acid washing

The elemental removal efficiencies are displayed in Table 18. The removal percentages of the nutrients (Na and K) from the ash are especially high (above 90%) as these nutrients have high solubility in acid. Some contamination metals like cadmium and zinc also have good removal efficiencies. Especially cadmium has about 100% removal efficiency in this acid washing process. As cadmium has a high toxicity for the ecosystem, the high release rate can benefit the phosphorus product with less hazardous elements.

Table 18 Removal efficiency of metals in acid washing process.

Unit: mg/kg ash	Na	Mg	Al	K	Ca	Zn	Cd	Pb	P
Acid washing, pH=4	54973	4186	1196	58084	13096	20772	279	1344	10
Ash contained	58400	13100	32200	54400	141000	37300	270	4600	5900
Remove percentage, %	94	32	4	100	9	56	100	29	<1

The main purpose of this process is to remove calcium because calcium can precipitate with phosphorus in the next step, which will decrease the phosphorus content in the final P-rich

solution. According to the figures in Table 18, the removal rate of calcium is rather low, less than 10%. There is still a large proportion of calcium in the ash and it may affect the phosphorus dissolution in next step. The possible reason for the low removal efficiency of calcium may be due to that the total content of the calcium in the ash is so high that only one acid washing process is not enough to remove much of it. Several washing steps may improve the release fraction of calcium. However, this has not been studied.

6.1.5.2 Alkaline dissolution

In order to find the best alkaline dissolution pH to dissolve P, three different pH conditions were tested. The results can be seen in Table 19. The best dissolution pH among the tests is 12, which has a phosphorus concentration of 2.1mg/kg. The overall phosphorus recovery efficiency of this method is very low and the highest percentage is only 0.04%. The phosphorus loss in acid washing process is small which accounts for 0.18% of the total phosphorus in the ash. Therefore, most of the phosphorus still remains in the ash.

Table 19 Phosphorus recovery efficiency.

Sample pH	P in acid washing leachate, mg/kg	P in alkaline dissolution filtrate, mg/kg	P percentage, %
pH=4	10.6	----	0.18
pH=11	----	0.1	0
pH=12	----	2.1	0.04
pH=13	----	1	0.02

When pH of the solution reaches 12, many metal phosphates dissolve into solution (Figure 6), except from the calcium phosphates. Although acid washing can reduce the calcium content, the ash still contains 13% of calcium whereas the content of phosphorus is about 0.6%. According to Stendahl and Jäfverström (2003), when using hydroxide sodium to leach, 90% of phosphorus can be released with 3% calcium content while only 65% phosphorus is released with 8% calcium content in the ash. In this experiment, there is 13% of calcium in the acid washed ash. It is very likely that the high calcium concentration influences the release of phosphorus and leads to low phosphorus concentration in the solution. The possible explanation could be that calcium precipitates with phosphate and bonds it in the ash. Therefore, the reason that this method does not work probably may be the high content of calcium in the ash and the inefficiency of the acid washing process.

Table 20 Metal contents in final P-rich solution.

Unit: mg/kg ash	Mg	Al	Cr	Fe	Ni	Cu	Zn	Cd	Pb
pH=11	4.16	29.19	0.82	41.55	0.99	0.91	7.39	0.35	0.75
pH=12	3.62	5.71	1.41	34.88	0.97	0.82	9.29	0.30	5.06
pH=13	3.68	5.58	0.81	37.36	0.82	1.11	18.79	0.29	42.97

Due to the lower solubility of many metals in alkaline environment than in acidic, the metal contents in the final product are really low (see Table 20) compared to method I. If it is possible to find a more effective way to decrease calcium content, a less contaminated phosphorus product can be obtained by leaching with base. For instance, repeating the acid washing step as discussed about twice or three times may release more calcium in this process.

6.2 Technology evaluation

The evaluation is based on the LCA methodology. The assessment is streamlined due to the initial nature of this study and the limited time and data sources. The inputs and outputs through technosphere are collected via literature review. As for the emissions of processes to be compared, they are collected from online LCA databases, for example International Reference Life Cycle Data System (ILCD) and ecoinvent etc. The evaluation is only concentrated on the production process and the developed recovery process.

6.2.1 Resource requirement

This section provides an overview of the material and energy consumption of the developed recovery process and the conventional processes.

6.2.1.1 Developed technology

Quantification of resources' input and output for developed process is summarized in Figure 15. However, the energy consumption is excluded since the stirring equipment at a large scale is likely to be in a different design than in the lab. A large quantity of ash is obtained via simple calculation by multiplying the needed materials. The low content of phosphorus in the ash results in a large demand for ashes. Correspondingly the consumption of HCl is also high for neutralising the high alkalinity of the ashes and for providing a low pH environment in order to release phosphate. Provided the costs of sodium hydroxide and hydrochloric acid are 2500 and 850 SEK/t respectively (Levlin et al., 2005), the cost of chemical use would be 90,000 SEK/t P_2O_5 produced. The raw material and energy cost for dry process is 42,000 SEK/t P_2O_5 (calculated based on data in Bryant et al., 1970, taking monetary depreciation into account). It is noteworthy to state that the remaining leachate could be subsequently treated as a potential alternative resource for heavy metals recovery and the acidic condition of the leachate saves the acid would be used otherwise.

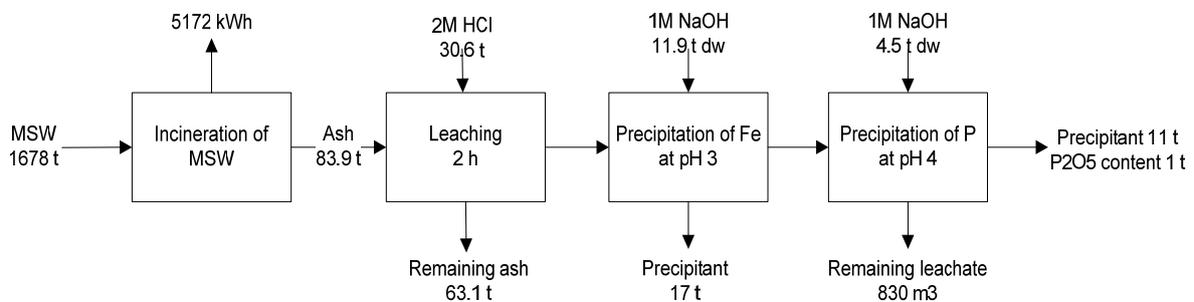


Figure 15 Developed leaching process for recovery of phosphorus.

6.2.1.2 Conventional technology

Two conventional processes are described in this section and the material flows are served as parameters in the SimaPro Software, thereby generating the environmental impact for comparison with the developed technology.

6.2.1.2.1 Wet process

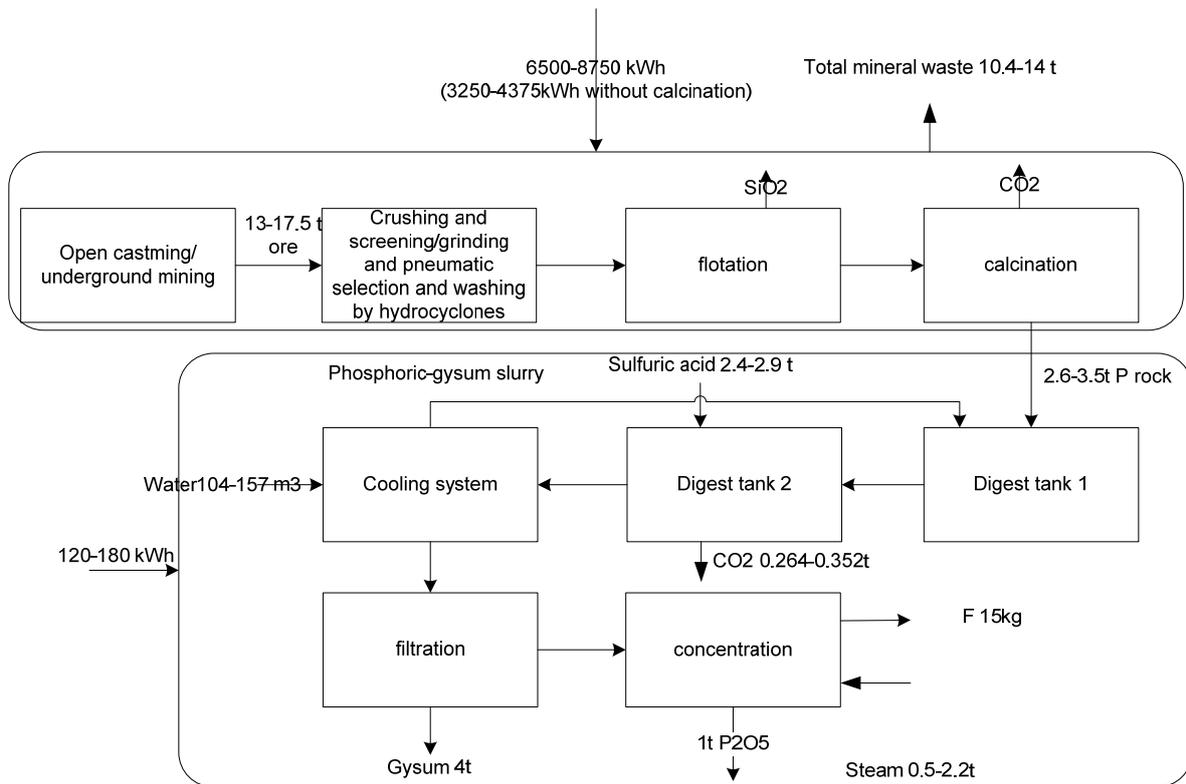


Figure 16 Wet process. (Source: Davis, 1999;Becker, 1989;Hocking, 2005)

The flow sheet in Figure 16 shows the major processes from the stage of mining to the production of phosphate. After excavation, the ores must be beneficiated before going to the production of phosphate. First step is to reduce the volume of rock by crushing and grinding. Next the ground ores will be passed to a flotation facility to remove the silicates. Some of the ground ores will undergo calcinations to turn CaCO_3 into CaO , releasing CO_2 and to break down the organic compounds at the same time. If this stage is included, the energy consumption of the process will be doubled as without calcinations, because heating in this step requires large energy consumption. Subsequently, phosphoric gypsum slurry from the following step will be circulated to digest tank 1 to remove CO_2 . By reducing the CO_2 in the tank 1, the intensive reaction in tank 2 generates fewer bubbles thereby facilitating the operation. Then, diluted sulphuric acid is added to attack phosphate rock to yield phosphoric acid. After cooling down, the acid will be filtered and concentrated. Detailed process description can be found in several documents and books (Berker, 1989;EFMA, 2000;Hocking, 2005).

6.2.1.2.2 Dry process

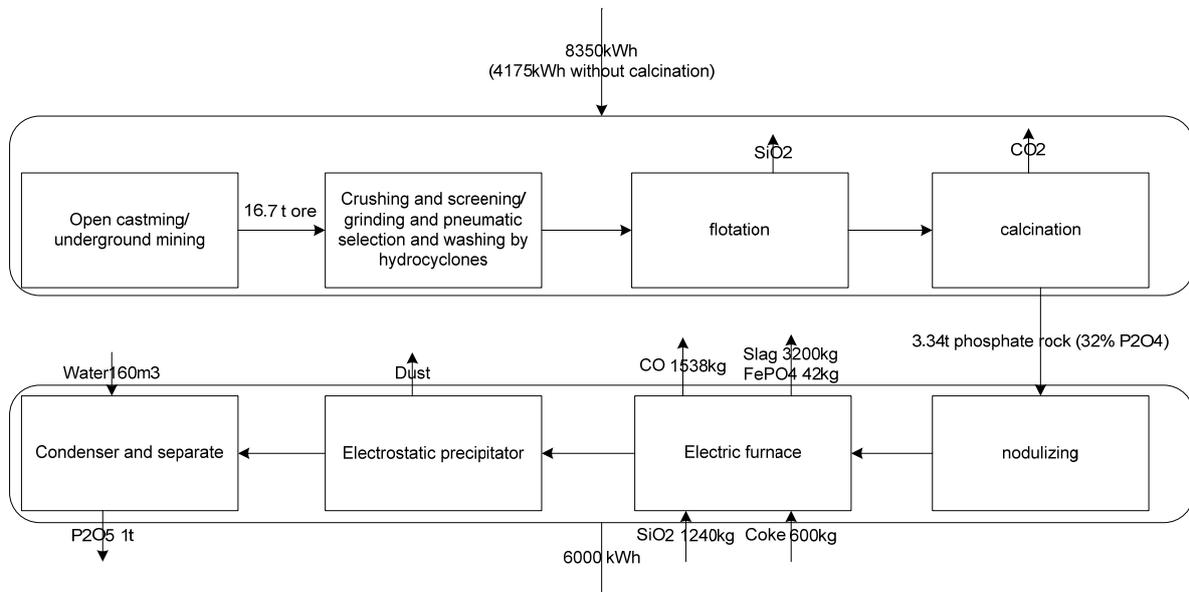


Figure 17 Dry process (Source: European Commission, 2007; Hocking, 2005; Davis, 1999)

The beneficiation of ores is identical as in the wet process but the requirements of raw material in the dry process are less strict in terms of size and mineral form. Because the product phosphorus is in gas phase, the ground rock will be nodulised to create enough space in between for the gases to pass through. In the electric furnace, silicates and coke are added and heated to 1500 °C. As a result, elemental phosphorus is produced in the gas stream. Dust entrained will be separated by electrostatic precipitator and the phosphorus is collected by a water scrubber and kept in the water. Further procedures are required if the final product should be phosphoric acid. Then the elemental phosphorus is separated from water and combusted with oxygen to generate diphosphorus pentoxide which is finally hydrated to form high grade phosphoric acid. Phosphoric acid mist is the major emission in the thermal phosphoric acid production. Emitting rate varies from 3.5 to 597mg/m³ stack gas (MCA and PHS, 1970). CO is also formed during the production, which can be utilised as internal fuel for either the preparation of material or for furnace heating if using the fossil fuel furnace (Leder et al. 1985).

6.2.1.3 Thermo-chemical treatment

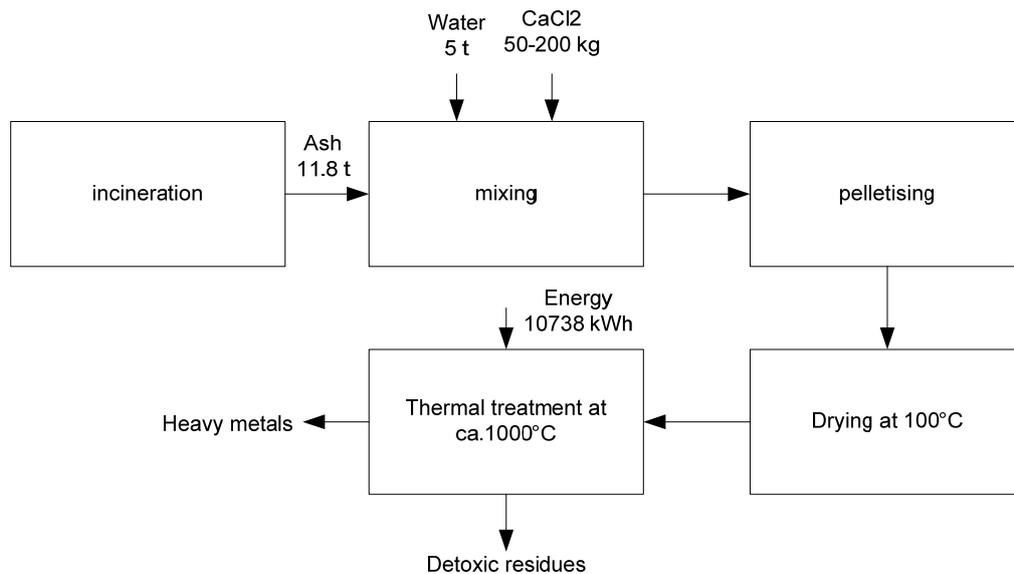


Figure 18 Thermo-chemical treatment (Adam et al., 2009;Mattenberger et al. 2008)

This process is used to remove the heavy metals from the SSA. After mixing the ash with Cl and water, the ashes are pelletized to reduce losses of phosphorus via entrainment. The pellets are heated and Cd, Pb, Cu and Zn become volatile as metal chlorides in the high temperature and are separated from ashes. P is stable under the same condition thus remaining in the ash. Cd and Pb can be removed by 99% and Cu and Zn less from 80% to 90%. Cr and Ni are hardly removed in this process. The limits for Cr and Ni in fertilizers are 40 and $25\text{g}(\text{ha},\text{year})^{-1}$ in Sweden and $15,000$ and $300\text{g}(\text{ha},\text{year})^{-1}$ in EU (Pettersson et al., 2008). The calculated values of Cr and Ni for MSWI ash are 293 and $3373\text{g}(\text{ha},\text{year})^{-1}$. Both values exceed the Swedish limit, while remain under the European limits. Further treatment of MSWI ash is therefore needed if this method were used in Sweden. The treated ash contains fewer heavy metals and could be used as fertilizer.

6.2.1.4 Resources requirement summary

Table 21 shows the resources needed for the production of phosphorus and the main waste streams after the processes. To produce 1 ton of phosphorus from MSWI ash, 83.9 tons of ash are required. This large amount is a result of the low concentration of phosphorus appears in the ash compared to other P sources. The amount of leachate remaining is also substantial and a majority of the heavy metals in the ash are present in the leachate after low pH leaching. They might be an abundant source of metal with appropriate extraction method. On the other hand, the ash residues after leaching process contain much less heavy metals indicating potential usage of this material. However, care has to be given to the final disposal or the use of industrial material. There would be moderate energy consumption in the developed recovery process for stirring and other mechanical movements. However, the consumption is not available at this stage.

Table 21 Resources requirements normalised to 1 ton production of P_2O_5

Method	Material	Flow	Quantity	Unit
Developed recovery process	MSWI ash	Input	83.9	Ton
	HCl	Input	30.6	Ton
	NaOH	Input	26.4	Ton
Wet process	Waste ash	Output	63.1	Ton
	Waste leachate	Output	830	m ³
	Phosphate rock	Input	13-17.5	Ton
	Sulphuric acid	Input	2.4-2.9	Ton
	Water	Input	104-157	m ³
	Energy	Input	7600-10200	kWh
	Steam	Input	0.5-2.2	ton
	Gypsum	Output	4	Ton
	Mining waste	Output	10.4-14	Ton
	Fluorine	Output	15	kg
Dry process	Phosphate ore	Input	16.7	Ton
	SiO ₂	Input	1240	kg
	Coke	Input	600	kg
	Water	Input	160	m ³
	Energy	Input	11900	kWh
	Mining waste	Output	13.3	Ton
	CO	Output	1538	kg
	Slag	Output	3200	kg
	FePO ₄	Output	42	kg
Thermochemical	SSA	Input	11.8	Ton
	Water	Input	5	Ton
	CaCl ₂	Input	50-200	kg
	Energy	Input	10738	kWh

6.2.2 Environmental impact assessment

6.2.2.1 Flowchart and Scenario

In order to compare environmental impacts of different processes, a common base must be built to make more comparable results. For this purpose, a flowchart of the phosphorus is drawn in a life cycle perspective to investigate the unit processes within the determined boundary, as depicted in Figure 19. The comparison in this study is between conventional P production and recovery of phosphorus from MSWI ash. However, the two processes are in the same life cycle and should at least share some of the emission load. The simplest way to address this problem is to cut off the process and to isolate the production burden. In other words, the comparison will on a cradle-to-gate or gate-to-gate basis, disregarding waste stream and ends at the production of phosphorus, as shown in Figure 20 (a) and (b). Or the comparison can address the question if the ashes should be recovered or landfilled. In this scenario, processes before incineration are identical for both the landfill and recovery. Therefore they can be neglected as the objective of this scenario is to compare the differences of different options. The recovery of phosphorus can save the virgin resources that otherwise

would be used. Because of this, the production, however, should be considered as a credit for recovery. The pictorial description can be seen in Figure 20 (c).

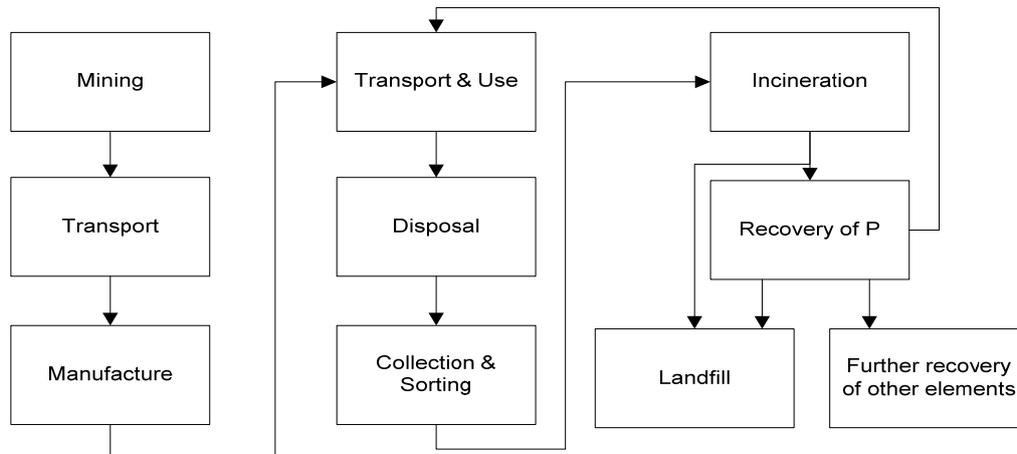


Figure 19 Initial flowchart of the phosphorus life cycle

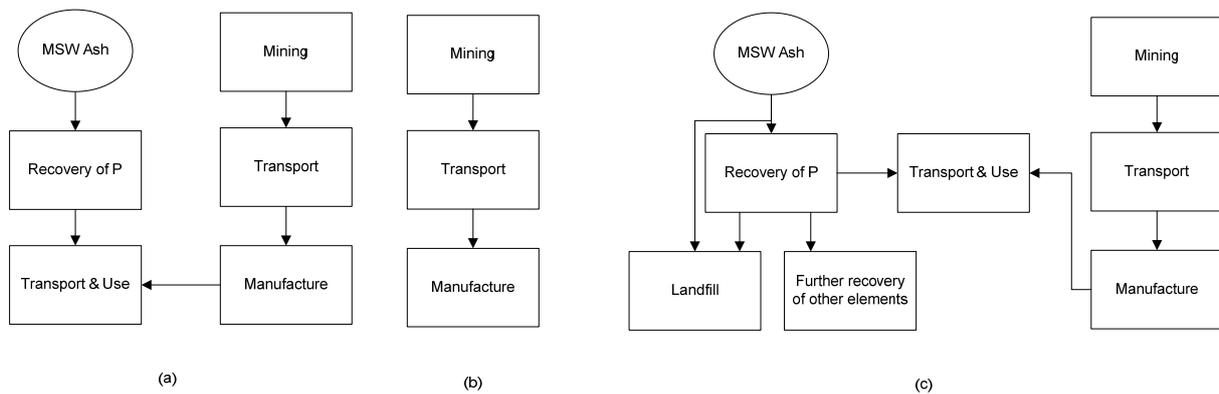


Figure 20 Different scenarios. (a) represents the developed recovery process with credits from virgin production. (b) represents conventional production. (c) represents landfill and recovery process. For the comparison, the boundary should end at recovery of P, but considering the avoided virgin production., The system boundary needs to be expanded to include the conventional production. (a) and (b) compose the first scenario and (c) is the second scenario.

6.2.2.2 Goal and scope

The *functional unit* of these two scenarios is production or recovery of 1 ton of phosphorus (in form of P_2O_5). There are several impact assessment methods available, such as CML2001, EDIP97 and Eco-indicator99. The CML2001 was used in this study. It is a midpoint method that reveals impacts in some common impact categories, for example eutrophication, global warming, acidification and probably the most important one in this method, toxicity. Furthermore, ionising radiation is considered as well due to that significant amount of radiation can be found in some phosphoric rock.

A *time horizon* of 20 years is chosen, while 100, 500 years and infinite are only shown in appendix. *Geographical boundary* is set to be global since the phosphorus depletion is a global issue and subsequently the data collection will be focusing on average data. For the

type of LCA, change-oriented LCA is chosen as the main objective is to examine the feasibility and the necessity of phosphorus recovery from MSWI ash.

6.2.2.3 Characterisation result

Figure 21 shows the normalised result of the yielding of phosphorus as two isolated processes. As can be seen, the developed process has more impact on toxicity in both human and ecosystem toxicity categories as well as abiotic depletion, global warming and ionising, whereas in the categories acidification and eutrophication conventional production has higher impacts. The highest impacts come mainly from health related categories, consistent with the emphasis of the human and ecosystem toxicity from the CML method (Dreyer et al. 2003). However, if assigning an allocation factor (detail will be discussed later) of sodium hydroxide production on recovery process, the result alters. The environmental impacts caused by the developed recovery process drop significantly and become lower than the ones caused by conventional P productions. For the ecotoxicity, different patterns can be found. In fresh aquatic and fresh water sediments, impact of production is always lower than the developed recovery process with or without the allocation, whereas the opposite is true to the marine aquatic and marine sediment categories. The various impacts on freshwater and marine system are probably due to the different path in which the pollutants enter the ecosystem. Without allocation, the environmental impact of recovery process is higher than the production while with allocation impact of recovery process is lower than production.

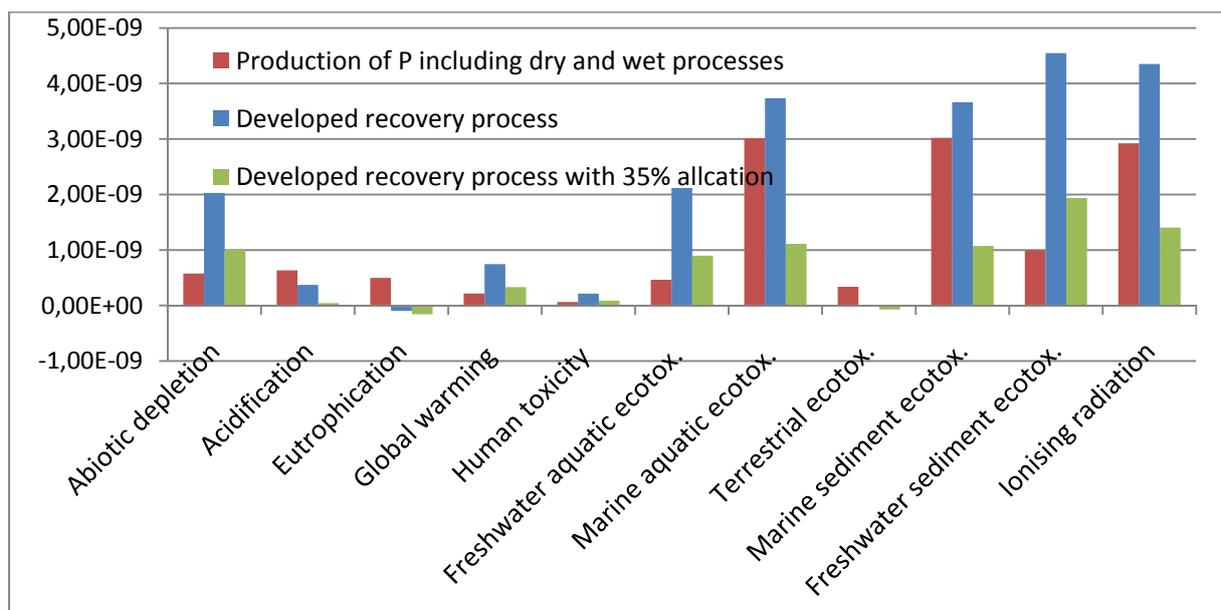


Figure 21 Comparison in selected categories between conventional production and recovery of phosphorus. Complete categories results can be found in the appendix. The production of P integrates both dry and wet processes in a 1/9 ratio of phosphorus which is according to (Hocking,2005). The percentage allocated to phosphorus is 35% which is calculated based on the mass ratio.

Concerning the radioactivity of the manufacture of phosphorus, most phosphate rocks contain uranium and its decay products with a level 10 to 100 times higher than other natural material (USEPA, 2011a). The typical concentration reported in the US ranges from 5 to 267 pCi/g. Another key issue is the disposal of the waste material the radionuclides reside in. Every 1 ton of phosphoric acid produced via wet process comes along with 5 tons of phosphogypsum. It is estimated that 100 to 280Mt of phosphogypsum are generated per year worldwide (Tayibi et al. 2009). It takes 1200 ha surface area to store 100Mt phosphogypsum with a 5m depth in a

dump in Spain (Perez-Lopez et al. 2007). Remediation of such a large area will certainly be technology and resource demanding. A similar situation with respect to phosphorus furnace slag (from the dry process) can be found, containing radionuclides but at a lower level and in a less water soluble form thus has less mobility (USEPA 2011a). More than 7 tons of phosphorus furnace slag is generated as by-product along the elemental phosphorus production (Hocking, 2005). However, several recycling route can be utilised thereby substantially alleviating the disposal burden. In contrary, the MSWI ash would unlikely contain radionuclides, showing an advantage over phosphate ores.

Impacts of acidification and eutrophication are surprisingly low compared to toxicity and radiation, probably due to the good circulation within the production, even though the phosphogypsum is an acidic waste. The low impacts in acidification and eutrophication could also be a result of the preventing measures applied at the dumping site, for example the lining under the landfill preventing the ions from percolating underground.

The global warming potential is also low. This is probably because a large part of the phosphoric acid is produced via the wet process which consumes much less energy than dry process. Moreover, the consumption of electricity in this study is on an average basis, that is, mixed source from coal burning, hydropower and nuclear power. Therefore, CO₂ result from the energy consumption is relatively low.

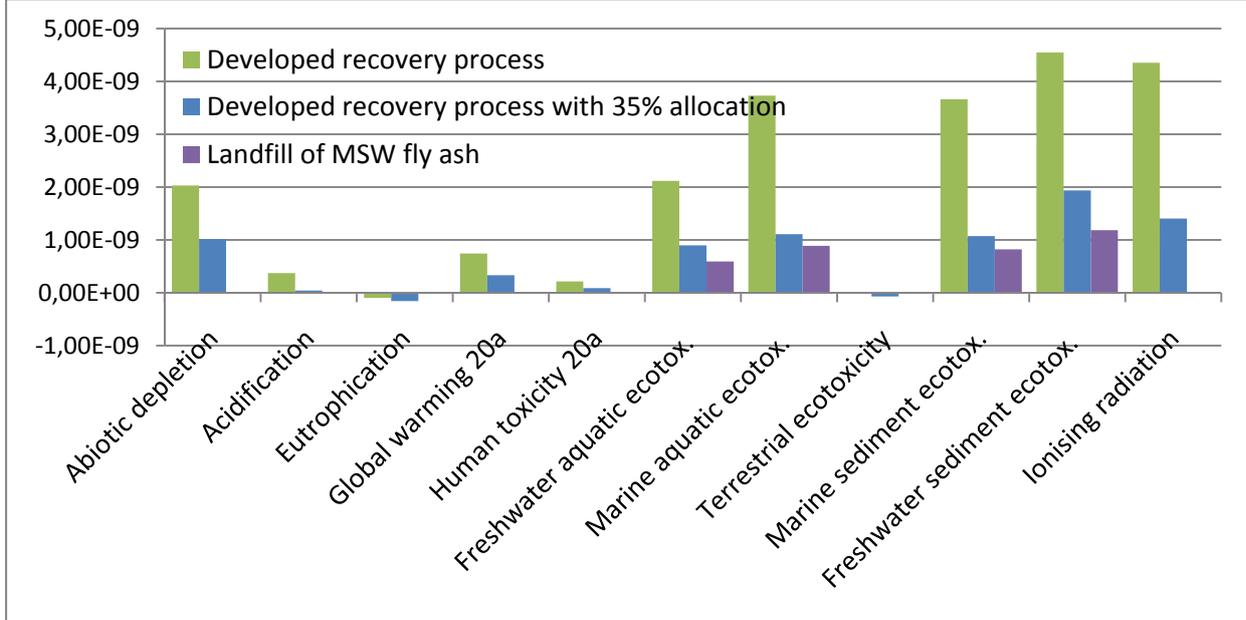


Figure 22 Comparison between landfill of ash and developed recovery method

In the second scenario, landfill or recovery, result has a larger difference, as shown in Figure 22. Recovery process has higher impact in all categories by a large margin. Impact from landfill contributes to ecosystem toxicity only. The result is in line as expected since landfill is a passive treatment and has less impact than the activities in the recovery process, although there is a considerable margin. Another factor that might enlarge the difference is the data source. The landfill data is based on a laboratory leaching experiment. Therefore, the data can oversimplify and neglect some important aspects for example atmospheric emission, possibly from weathering of the landfill, subsequently resulting in less impact shown in the result. After allocation, the impact for developed recovery process is still higher than the landfill, but by a smaller difference.

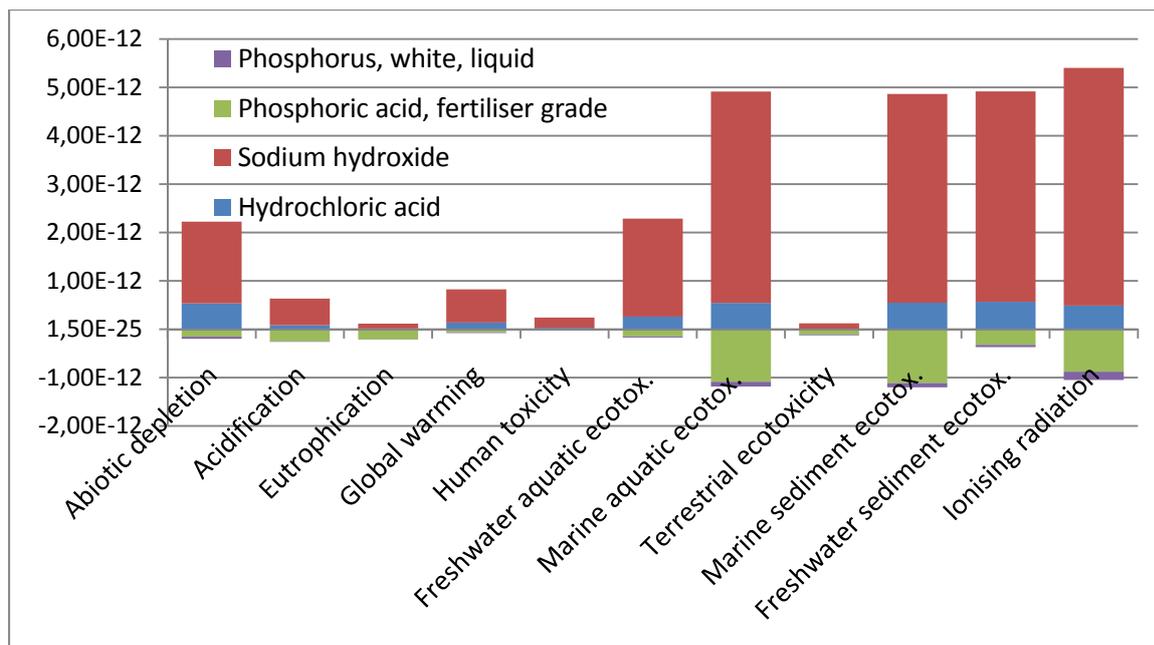


Figure 23 Process contribution of recovery process

In the unallocated scenario the developed recovery process has higher environmental impact than conventional production. In order to improve the developed process, it is necessary to investigate the contribution of each sub process. Figure 23 shows the normalised impact from recovery of phosphorus. As can be seen, majority of the impact derives from the use of sodium hydroxide. In extreme case, it accounts for more than 80% of the total category impact. Therefore, the entire impact assessment is sensitive to the change of sodium hydroxide. If the sodium hydroxide is reduced in amount or substituted to other compounds, the overall result could be changed entirely. There are some P extraction methods using phosphoric rich liquid, such as crystallisation, ion exchange (Morse et al. 1998) and several methods under development for example using orange gel to absorb phosphorus (Biswas et al., 2009).

The negative value in the chart denotes a credit for substituting virgin phosphate rock which compensates proximately 1/10 to 1/5 of the adverse impact. The production process of sodium hydroxide has multi products. Apart from sodium hydroxide, the other two by products are hydrogen gas and chlorine gas and they need to be partitioned for the environmental impact. Furthermore, breaking down the process contribution to substance level (not shown in the figures), nickel and vanadium are found dominating the impact, especially leaching to the ground water leading to a severe effect to the marine ecosystem.

On the other hand, another major chemical use has, hydrochloric acid, much lower environmental impacts compared to sodium hydroxide. However, it is still beneficial to reduce the usage of HCl. It is possible to reduce the usage in the developed recovery process as discussed in previous section (6.1.2).

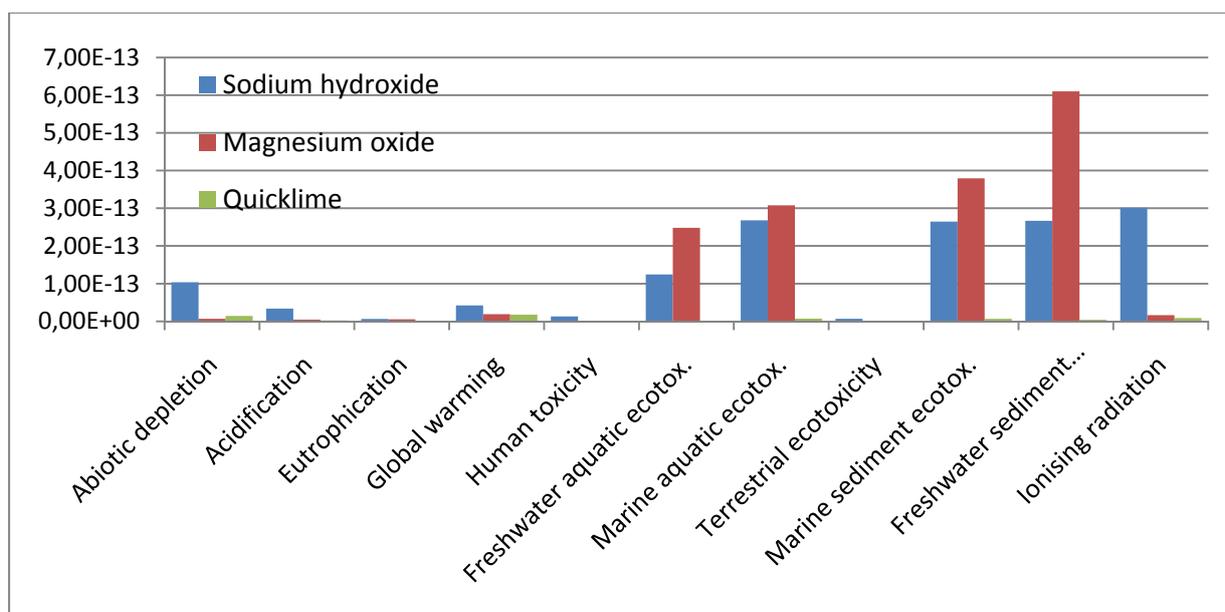


Figure 24 Environmental impact of different alkalis.

Because of the notable impact of sodium hydroxide, replacements by other industrial alkali are recommended. Two alternatives are possible for the substitution. To begin with, lime, namely CaO and $\text{Ca}(\text{OH})_2$, is a common pH control material in industries. Lime is less caustic and less expensive than sodium hydroxide (Shand, 2007). Secondly, Shand (2007) suggested the use of magnesium hydroxide for its moderate pH. Excessive addition of magnesium hydroxide will give a pH of 9 in contrast to sodium hydroxide and lime, with pH 14 and 12.5 respectively. The environmental impact comparison is shown in Figure 24. Magnesium oxide has the largest impact, followed by sodium hydroxide. The impact of quicklime can be hardly seen compared to the other two. Therefore, lime is an ideal replacement of sodium hydroxide in terms of environmental performance.

From an economic perspective, quicklime is the most economical choice of the three alternatives. The prices of NaOH , MgO and quicklime are 2500SEK, 4095SEK and 750SEK respectively, which are calculated from the prices in 2009 according to the US Geographical Survey (USGS, 2011b). Although MgO might be the alternative with better safety, the highest price and environmental impact hinder the application in a large scale.

6.2.2.4 Environmental impact after replacement of NaOH

The environmental impact of the recovery of phosphorus using quicklime has been estimated. The amount of quicklime is calculated according to the usage of sodium hydroxide. Because calcium hydroxide has two OH^- ions in one molecule, the molar amount of calcium hydroxide needed is half of sodium hydroxide. The calculation gives a result of 11 tons of quicklime compared to 16 tons of NaOH . Applying this number in the recovery process, the comparison has been recalculated, result shown in Figure 25.

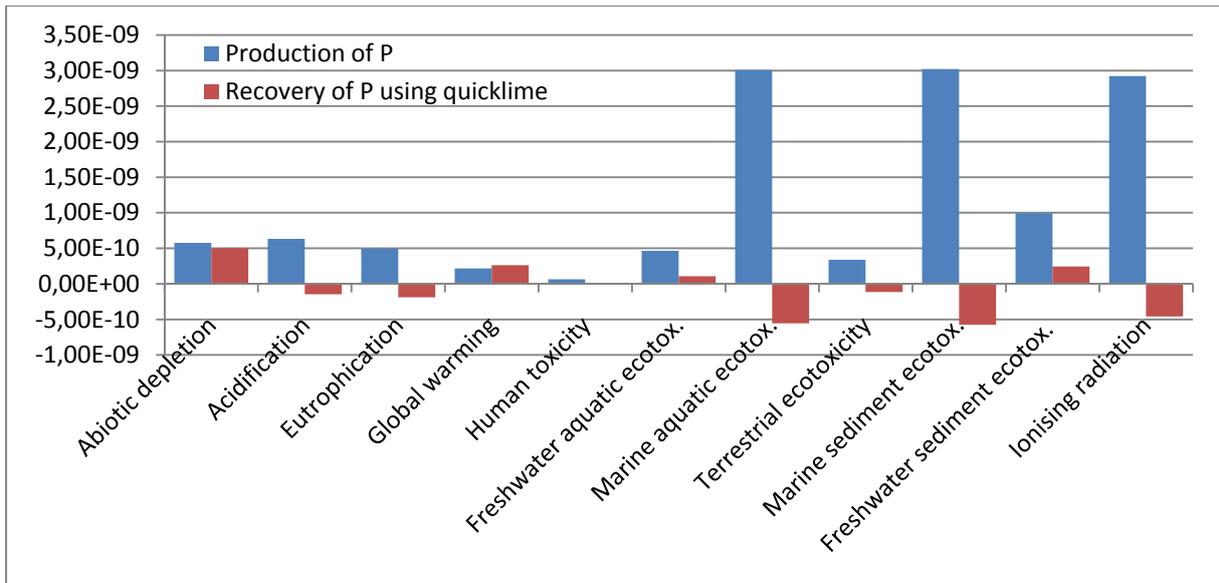


Figure 25 Comparison of conventional production and recovery of phosphorus using quicklime as pH controller.

As can be seen in figure 25, the impacts caused by the developed process dropped substantially. In most the categories, impacts of developed process are close to or below zero except for the abiotic depletion in which the developed process is still more benign than conventional production. Since the impact from quicklime is quite low, some of the impacts are below zero for the credit gaining from avoiding virgin phosphorus production.

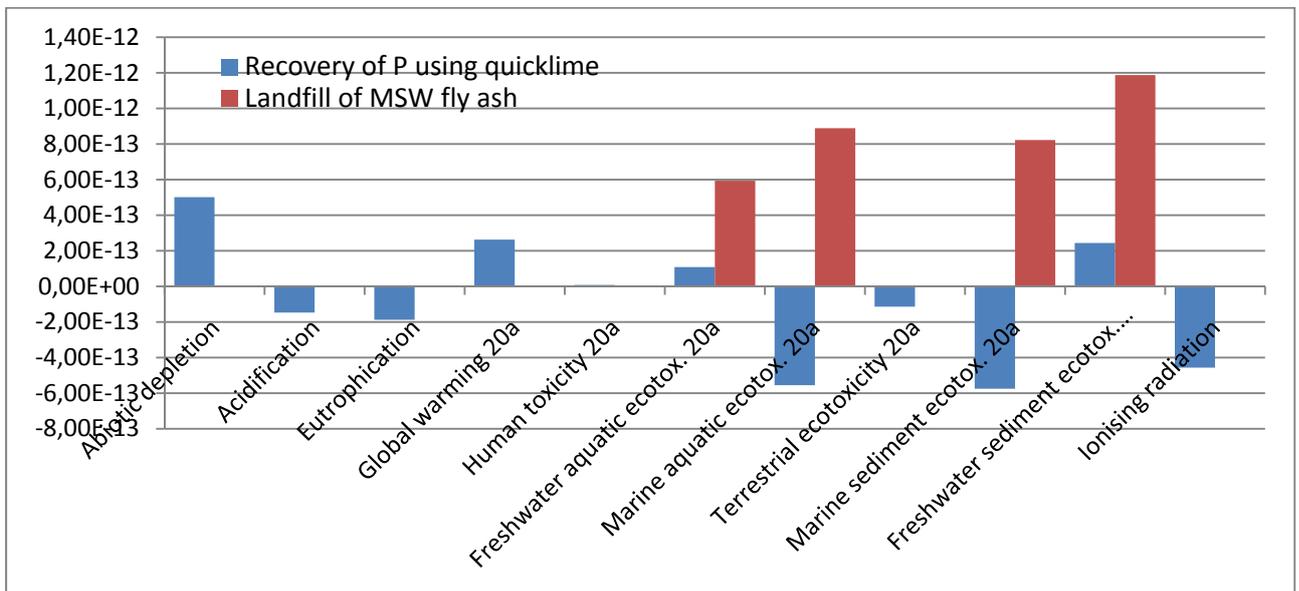


Figure 26 Comparison between developed recovery process and landfill

Figure 26 shows the comparison with landfill and developed process using quicklime. In all the categories that landfill are applicable, the developed process excels with no exception. However, it is prudent to bear in mind that the data regarding air and water emissions of the developed process are not available. If consider these emissions, the result may differ to some extent. Otherwise, the developed process is promising with some adjustment.

6.2.2.5 Uncertainty

One of the biggest uncertainties is the remaining leachate which can undergo further recovery of other elements. If that were the case, the burden must be allocated according to the multi output or introduce the credit for avoiding the virgin resource from being used. Finally the disposal of this leachate will possibly bring some adverse environmental impacts.

Emissions from the leaching process are needed for more thorough assessment. The impact characterised in this study for the developed recovery process is based on the chemical use due to the lack of data concerning emissions and energy consumption during leaching. The most likely emission could be chlorides to the atmosphere and metals and chlorides to the aquatic system. Thus the validity of this assessment could be somewhat impaired by the unbalance of data quality for the two different processes.

Due to the diverse nature of the MSW, the incineration ash is also various from place to place and from time to time. Therefore, the amount of ash needed for one ton phosphorus to be recovered differs, so do the emissions.

The comparability of different products is uncertain. The production of conventional phosphorus is usually phosphoric acid or different form of fertilizers whereas phosphorus recovered from developed process is in a phosphate form and needs further processing. For the conventional production, it is assumed that production ends at phosphoric acid and no further processing is needed. Improvement can be made by adding information for turning recovered phosphorus into phosphoric acid or adding process manufacturing fertilizers and using recovered phosphate as fertilizer.

7 Conclusions and recommendations

- MSWI ash is hazardous waste, containing large amount of metals and nutrients. The phosphorus content is about 0.6%. When leaching with 2M HCl, 2h leaching time, 24h sedimentation and L/S ratio=5, almost 100% release of phosphorus can be achieved.
- The phosphorus recovery efficiency of method I is 71%. The phosphorus content in the recovered product is 3.4% and the possible forms are FeHPO_4 , MgHPO_4 and CaHPO_4 . Besides the phosphorus product, there are three by-products in the process. The potential usage of these products are:
 - Phosphorus product could be used as fertilizers after separation of Cd in some of the European countries; or used as low-grade phosphorus materials in phosphate production industry in the near future.
 - Acid insoluble solid fraction could be used as raw materials for construction.
 - First precipitant and final leachate could be used as raw materials for heavy metals recovery.
- Method II has a low recovery efficiency of phosphorus which is less than 1%. The possible reason may be that the calcium content in the ash is too high though the acid washing removed 9% of calcium. Therefore the remaining calcium still can bind most of the phosphorus instead of releasing it to the solution under alkaline environment.
- For the recovery of phosphorus, there are several process developed to recover phosphorus from SSA. However, no effort has been made to recovery phosphorus from MSWI ash yet. There are some measures now used to upgrade phosphate ores might have the potential to recover P from MSWI ash.
- Conventional and developed processes have high environmental impact in the ecotoxicity categories due to the heavy metal emissions. The overall impact comparison differs depending on the allocation of the impact from sodium hydroxide. The developed process has higher impact without allocation for sodium hydroxide whereas it has lower impact with allocation. The use of $\text{Ca}(\text{OH})_2$ instead of NaOH dramatically decreased the environmental impacts for the developed recovery process.
- Recovery of P from MSWI ash is viable. It saves the virginal resources, avoiding the large quantity of waste would have generated. However, the developed process needs to be improved due to the dramatic impact from production of sodium hydroxide. Either substitution of base or substitution of extraction method could lower the impact to a larger extent.
- There are still some remaining questions worth further exploration.
 - The conditions of the gelation, such as temperature, concentration of important elements, pH and time of the formation process, in order to slow or prevent the gelation process.
 - The metal contents in the final product in method II are lower than method I which means less contamination in the phosphorus product, the possible procedures to increase the efficiency of method II could be worthwhile. For instance, repeating the acid washing step twice or three times can release more calcium.

8 Reference

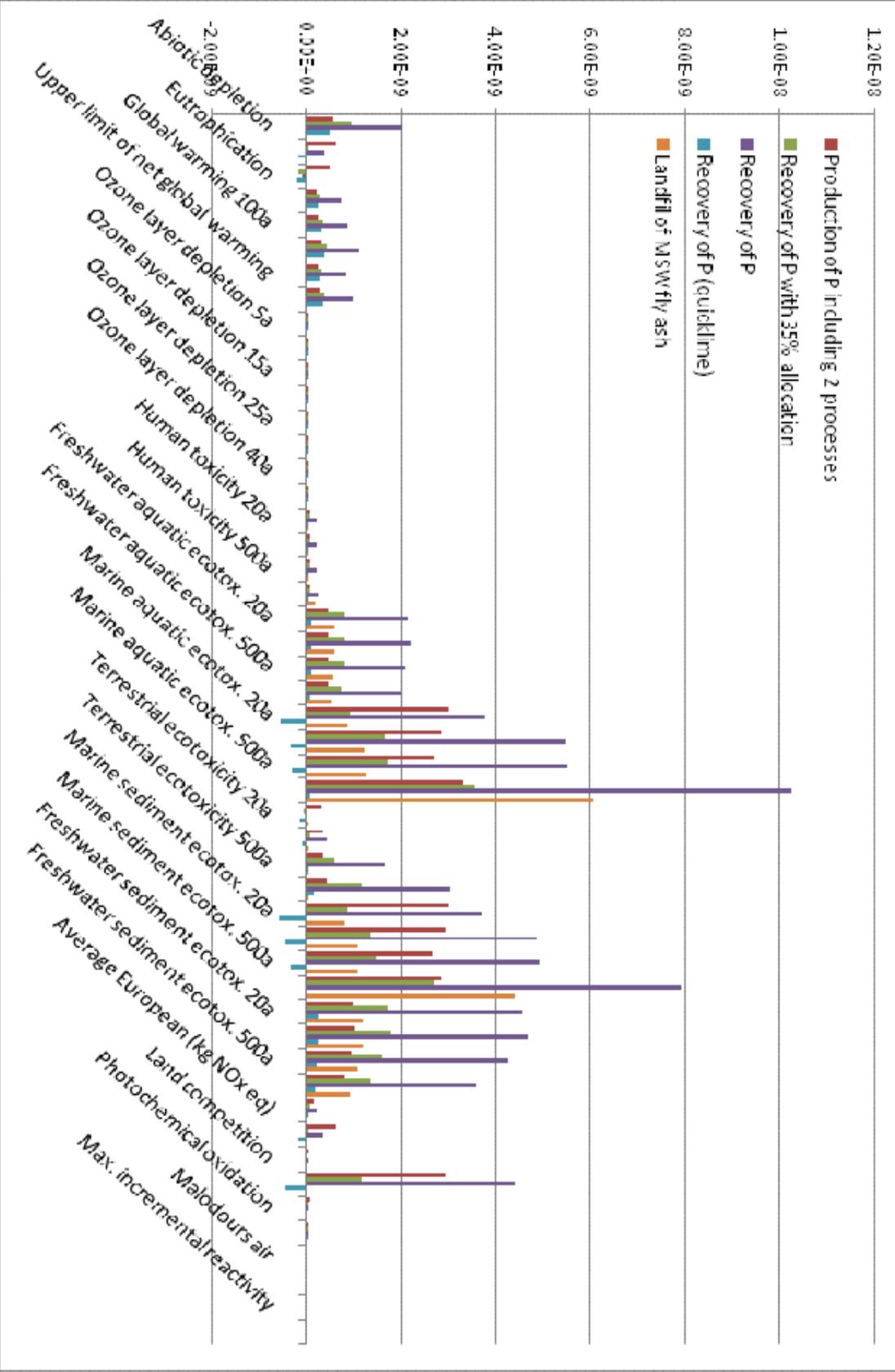
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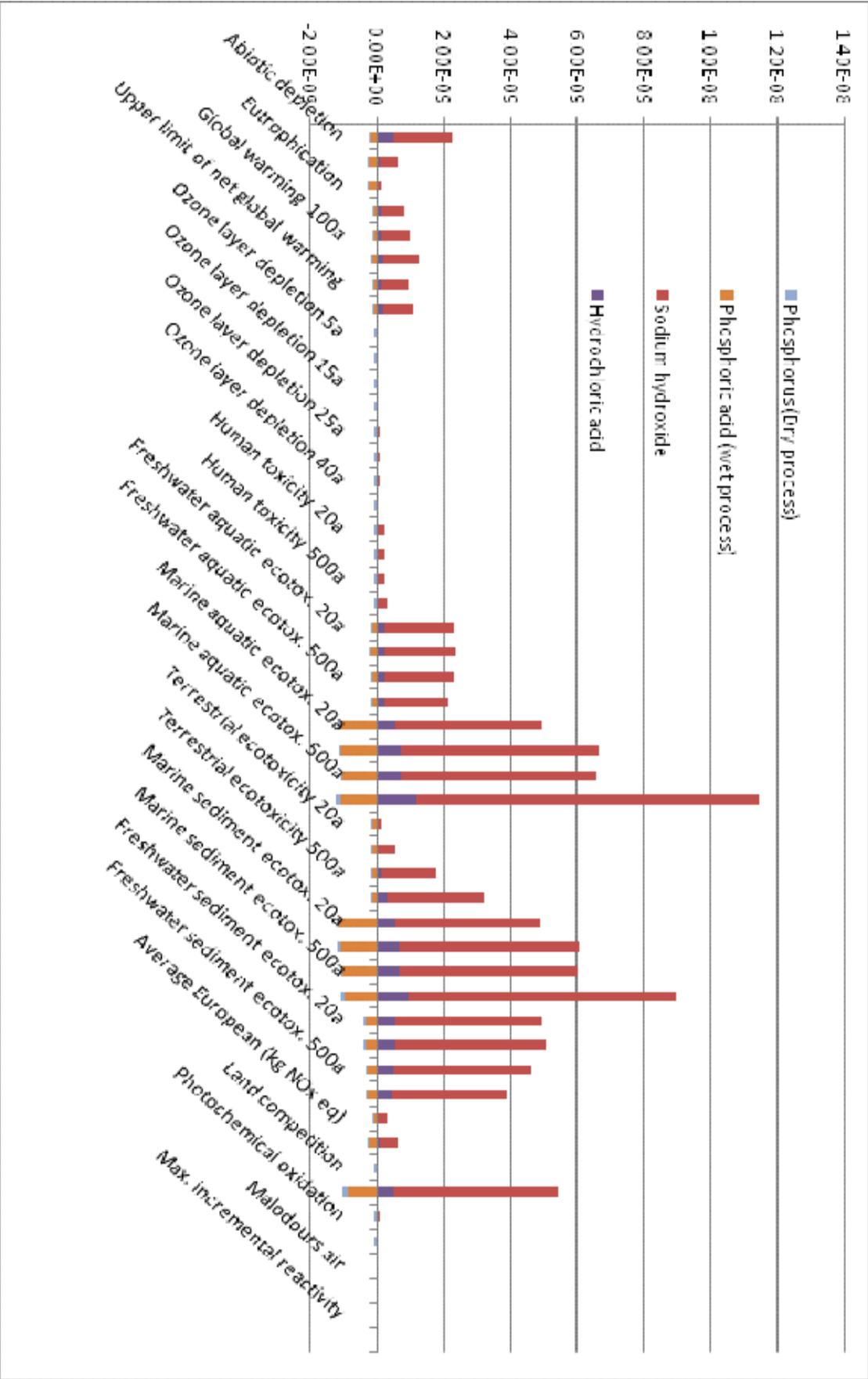
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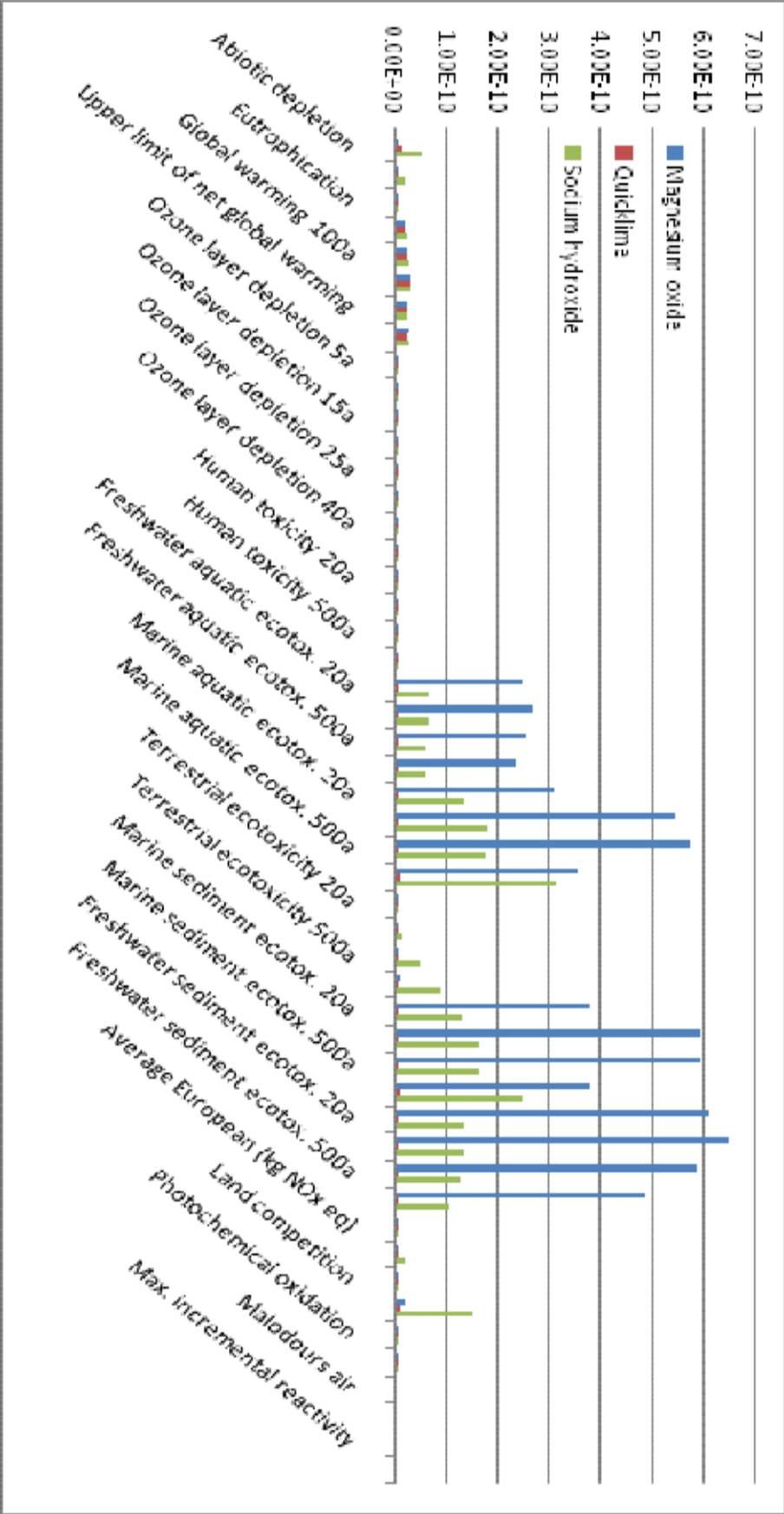
Appendix A –Impact comparison with complete categories



Appendix B –Impact of developed process with complete categories



Appendix C – Alternatives with complete categories



Appendix D – Parameters in SimaPro

	Process name in SimaPro		Known inputs		Remark
Dry process	Phosphorus, white, liquid, at plant/RER S	1kg	Silica sand, at plant/DE S	2.66kg	
			Petroleum coke, at refinery/RER S	1.43kg	This is the only coke available for reduction reaction instead of energy.
			Water, ultrapure, at plant/GLO S	0.013kg	
			Transport, transoceanic freight ship/OCE S	84.3tkm	Calculated from voyages between major mines, production sites and markets.
			Phosphate rock, as P2O5, beneficiated, dry, at plant/MA S	7.16kg	
			Electricity, production mix SE/SE S	11.85kWh	Global average electricity is not available.
Wet process	Phosphoric acid, fertilizer grade, 70% in H2O, at plant/GLO S	1kg	Sulfuric acid, liquid, at plant/RER S	1.47kg	
			Water, ultrapure, at plant/GLS S	0.08kg	
			Phosphate rock, as P2O5, beneficiated, dry, at plant/MA S	1.78kg	
			Transport, transoceanic freight ship/OCE S	20.9tkm	Same as in dry process.
			Electricity, production mix SE/SE S	0.091kWh	Same as in dry process.
			Steam, for chemical processes, at plant/RER S	0.0116kg	
Conventional production	Production of P including 2 processes	1t	Phosphorus, white, liquid, at plant/RER S	0.229t	This is production in Europe. Global data is not available.
			Phosphoric acid, fertilizer grade, 70% in H2O, at plant/GLO S	4.065t	This process is chosen over high grade phosphoric acid because it is the major production of phosphorus.
Developed recovery process	Phosphate, from leaching of MSW ash (P2O5)	1kg	Hydrochloric acid, 36% in H2O, from propylene and chlorine, at plant/RER S	85kg	
			Sodium hydroxide, 50% in H2O, production mix, at plant/RER S	32.8kg	The environmental impacts of the 3 NaOH productions are similar, thus using the average.
Replacement options	Magnesium oxide, at plant/RER S	1kg			
	Quicklime, milled, loose, at plant/CH S	1kg			
Landfill of MSW ash	Landfill of MSW fly ash	1kg			Data collected from Hjelmars 1992 and 1993