

UTILIZATION OF FISHBONE FOR THE STABILIZATION
OF HEAVY METALS IN MUNICIPAL SOLID WASTE
INCINERATION (MSWI) FLY ASH

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**UTILIZATION OF FISHBONE FOR THE
STABILIZATION OF HEAVY METALS IN
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INCINERATION (MSWI) FLY ASH**

A Thesis Submitted

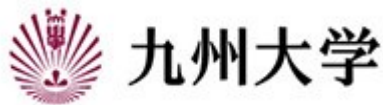
In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Engineering

By

Yue MU



To the

DEPARTMENT OF URBAN AND ENVIRONMENTAL ENGINEERING

GRADUATE SCHOOL OF ENGINEERING

KYUSHU UNIVERSITY

Fukuoka, Japan

January 2017

DEPARTMENT OF URBAN AND ENVIRONMENTAL ENGINEERING
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CERTIFICATE

The undersigned hereby certify that they have read and recommended to the Graduate School of Engineering for the acceptance of this thesis entitled, “*UTILIZATION OF FISHBONE FOR THE STABILIZATION OF HEAVY METALS IN MUNICIPAL SOLID WASTE INCINERATION (MSWI) FLY ASH*” by **Yue MU** in partial fulfillment of the requirements for the degree of **Doctor of Engineering**.

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Abstract

As one of the most effective means for the disposal of municipal solid waste that daily generated in a huge amount, incineration is adopted increasingly as it can reduce the mass and volume of the waste dramatically and recovery energy. Municipal solid waste incineration (MSWI) fly ash is one of the main solid residues derived from the incineration process, which is classified as hazardous waste worldwide owing to the relatively high concentration of heavy metals. Thus, MSWI fly ash requires further treatment before the reuse or recycle, and the final disposal in landfill sites. There have been many technologies for the stabilization of heavy metals in MSWI fly ash, whereas most of them are too complicated or expensive to be practically accepted. Therefore, simple and low-cost new technologies are in demand.

Fishbone is a common type of waste generated from the food and especially fish processing industries. As a bio-waste, fishbone or fish waste are usually treated as the source of organic matters for the by-production. In addition, fishbone is an enriched natural source of hydroxyapatite (HAP) which is reported to possess the ability on the stabilization of heavy metals by producing metal-HAP bonding. Ample efforts have been conducted for the utilization of HAP or fishbone on the heavy metal stabilization in the contaminated environments, while there is no practical investigation on the stabilization of heavy metals in MSWI fly ash. Therefore, this research was conducted with the aim of stabilizing the heavy metals by waste fishbone as an environmental-friendly technique for the utilization or final disposal of MSWI fly ash.

In the present research, the MSWI fly ashes from three plants in Japan and various types of fishbone from the market were used. The collected fly ash materials were firstly subjected to different tests for characterization. The feasibility of HAP on heavy metal stabilization was verified by adding fishbone during the leaching process of MSWI fly ash. Then two approaches were taken into account for improving the effectivity of fishbone HAP on the stabilization of heavy metals in MSWI fly ash.

The contents of the thesis are organized as follows:

Chapter 1 introduces the background and objectives of this thesis. The current states of municipal solid waste generation and treatments were reviewed, with the emphasis on the

strategies of MSWI fly ash disposal and the utilization of waste fishbone. Then the motivation and purpose of this research was presented.

Chapter 2 presents the characterization of MSWI fly ash. Various properties of MSWI fly ash were tested, including pH, particle size distribution, thermogravimetric and loss-on-ignition features, elemental composition and leaching property, as well as the mineral composition and transformation. Accordingly, Pb was identified as the main target of the heavy metal stabilization in MSWI fly ash.

Chapter 3 verifies the feasibility of fishbone on the stabilization of heavy metals in MSWI fly ash. Natural fishbone was added during the leaching process of MSWI fly ash. The effectivity of fishbone on Pb stabilization in MSWI fly ash was represented as Pb removal efficiency in the leachate at the presence of fishbone. The results indicated that either longer contact time or higher fishbone dosage benefited Pb stabilization. However, Zn and particularly Cu were encouraged to leach out rather than to stabilize. Besides, higher capacity of fishbone on Pb stabilization was obtained at lower dosage of fishbone, which implied that the relatively abundant supply of heavy metal ions might facilitate the stabilization reactions.

Chapter 4 focuses on the approaches to improve the effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash. According to the observation to the experiments of Chapter 3, providing various L/S conditions and taking ignition as the further pre-treatment on natural fishbone were taken into account. The results from the experiments under various L/S indicated that the preferred effectivity of fishbone on Pb stabilization could be obtained at lower L/S conditions, and Zn turned to be stabilized concurrently. However, the leaching of Cu still existed at all L/S conditions. In the second approach, candidate ignition temperatures were selected based on the potential mineral phase transformation of fishbone. These ignited fishbone from different ignition temperatures was involved into the stabilization processes as natural fishbone subjected previously. Accordingly, 430 °C was chosen as the optimal ignition temperature for the pre-treatment of fishbone, because the product showed better performance on Pb stabilization, and prevented the leaching out of Cu and P into the leachate of MSWI fly ash. The fishbone ignited at 430 °C brought higher Pb removal efficiency than the natural one under various scenarios, while it was not proportionate to the mass loss during the ignition. The ignition process not only removed

the non-HAP fraction of fishbone but also promoted the crystallinity of HAP; however, the latter was not beneficial to the stabilization of heavy metals in MSWI fly ash.

Chapter 5 summarizes the conclusions of the study, and makes recommendations for the future researches.

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List of abbreviations

3R	Reduce, reuse and recycle
APC	Air pollution control
BA	Bottom ash
FA	Fly ash
HAP	Hydroxyapatite
L/S	Liquid/solid
LOI	Loss-on-ignition
MSW	Municipal solid waste
MSWI	Municipal solid waste incineration
OECD	Organization for Economic Co-operation and Development
S/S	Stabilization / solidification
TC	Total carbon
TG	Thermogravimetry
TG-DTA	Thermogravimetry and differential thermal analysis
WTE	Waste-to-energy
XRD	X-ray diffractometry
XRF	X-ray fluorescence

Chapter 1 Introduction

1.1 Municipal solid waste (MSW) generation and management

1.1.1 General introduction of MSW

Municipal solid waste (MSW) is the trash that are generated as a result of the products after or brought by being used in the municipality, and for every city, the final disposal of MSW is the last phase of the urban sanitation system (Karak et al., 2012). According to the sources, MSW include primarily residential, institutional, commercial and municipal service (like street cleaning) wastes (Yousuf and Rahman, 2007; Zhang et al., 2010).

Accompanying with the fast economic development and urbanization, tremendous amount of the MSW is generated around the world (Islam, 2016). Only in 10 years, the generation of MSW has increased from 0.68 billion tons per year by 2.9 billion urban residents to 1.3 billion tons per year by 3 billion urban residents, which means that the growing rate of MSW is even faster than that of urbanization. And in the future, the situation seems to remain dire; the numbers are predicted as 2.2 billion tons per year and 4.3 billion urban residents by 2025 (Hoornweg and Bhada-Tata, 2012).

The quantity of MSW varies dramatically due to its association with the economic status of the local society (Shekdar, 2009). There is some data taken from a literature (Zhang et al., 2010) as an example to show the comparison among some selected countries of Organization for Economic Co-operation and Development (OECD) and China (Table 1-1).

Table 1-1 Waste generation in selected OECD countries and China

Countries	Total amount of MSW generation (1000 tons)	MSW generation rate (kg/capita/day)
USA (2005)	222,863	2.05
France (2005)	33,963	1.48
Germany (2005)	49,563	1.64
Denmark (2005)	3,900	2.03
Switzerland (2005)	4,855	1.78
Mexico (2005)	36,088	0.93
Japan (2005)	51,607	1.10
Korea (2005)	18,252	1.04
China (2006)	212,100	0.98

The physical composition is a vital factor to classify the MSW for the design and operation of the proper management. The characteristics and composition of MSW vary dramatically, because they are affected not only by the economic status of the city, but also by the the topography of the area, seasons, food habits of the citizens and commercial status (Palanivel and Sulaiman, 2014). The data extracted from a literature (Zhang et al., 2010) about the variation of the composition of MSW in various cities of China is shown in Table 1-2, which are located in different areas and quite varied in climate, food style and economic status.

Table 1-2 MSW composition in various cities of China

Composition (%)	Organic garbage	Paper	Plastic	Glass	Metal	Textile fiber	Wood timber
Beijing (2006)	63.39	11.07	12.70	1.76	0.27	2.46	1.78
Shanghai (2009)	66.70	4.46	19.98	2.72	0.27	1.80	1.21
Tianjin (2007)	56.88	8.67	12.12	1.30	0.42	2.47	1.93
Shenyang (2007)	73.70	7.60	5.20	2.40	0.30	0.90	1.70
Hangzhou (2009)	57.00	15.00	3.00	8.00	3.00	2.00	2.00
Tibet (2009)	72.00	6.00	12.00	—	1.00	7.00	—
Chongqing (2006)	59.20	10.10	15.70	3.40	1.10	6.10	4.20
Hong Kong (2009)	44.00	26.00	18.00	3.00	2.00	3.00	1.00

— : data absent

The matters that are contained in MSW could be sorted roughly into four kinds- compostable organic matters (like fruit/vegetable peels, food waste), recyclable matters (like paper, plastic, glass, metals, etc.), toxic substances (paints, used batteries, etc.) and soiled waste (Singh et al., 2011). And the ratio of various matters could be quite different according to the regions.

There is a variety of treatment processes of MSW management for conversing to other useful materials or energy, and the three most widely adopted ones are thermal conversion, biochemical conversion and landfilling. The typical MSW processing technologies and their products are shown in Figure 1-1.

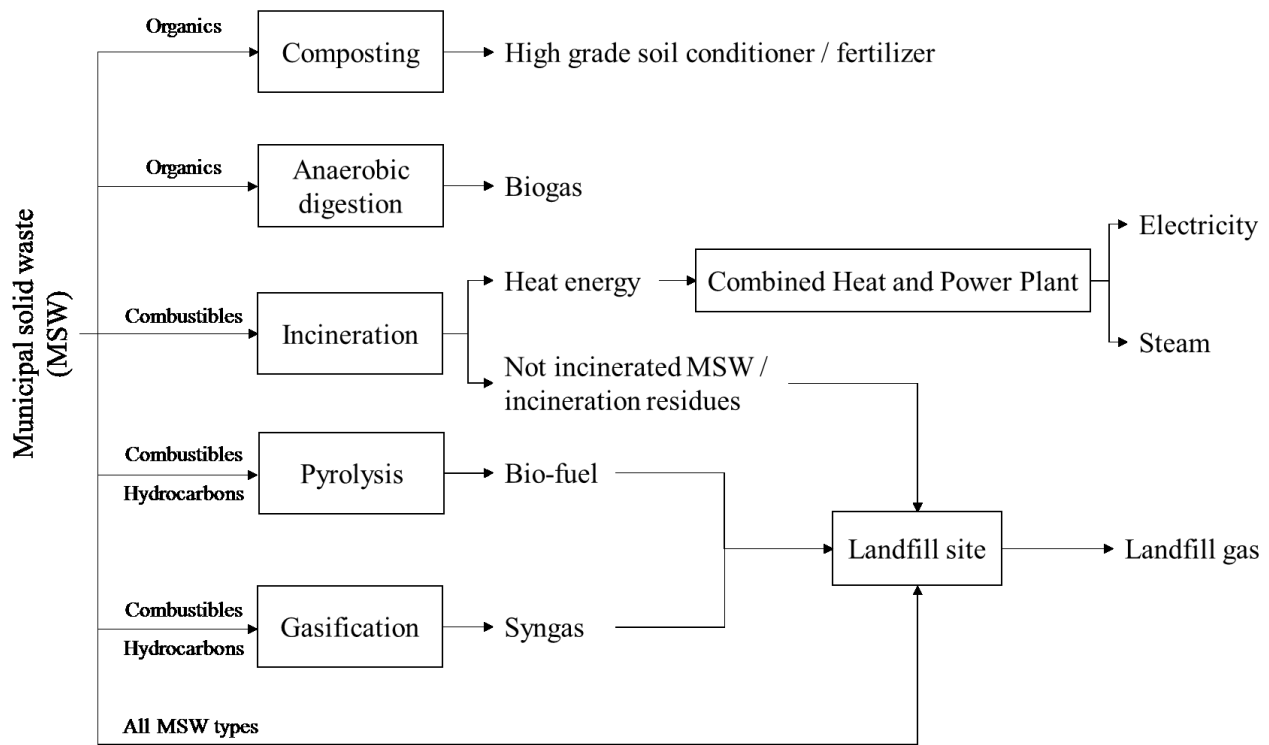


Figure 1-1 Typical MSW processing technologies and their products (Ng et al., 2014)

As shown above, the main strategy of MSW treatment or processing is to convert the waste to various forms of energy, which is called waste-to-energy (WTE) concept. The technologies could be used separately or combined, based on the local economic status and other situations. Sorting collection of MSW may contribute to the higher WTE conversion, but it is not the compulsory requirement, especially for incineration. Landfill is the primary and final disposal site for MSW.

1.1.2 MSW generation and management in Japan

According to the statistical data released by Ministry of Environment of Japan (2016), totally 44.32 million tons of municipal solid waste were generated in the fiscal year of 2014, which decreased by 17% comparing with that of 2004 (53.38 million tons). The MSW generation rate was 0.95 kg/capita/day, which is also continuously reducing in the recent 10 years. The trend of the amount and generation rate of MSW in Japan in 2004-2014 is shown in Figure 1-2.

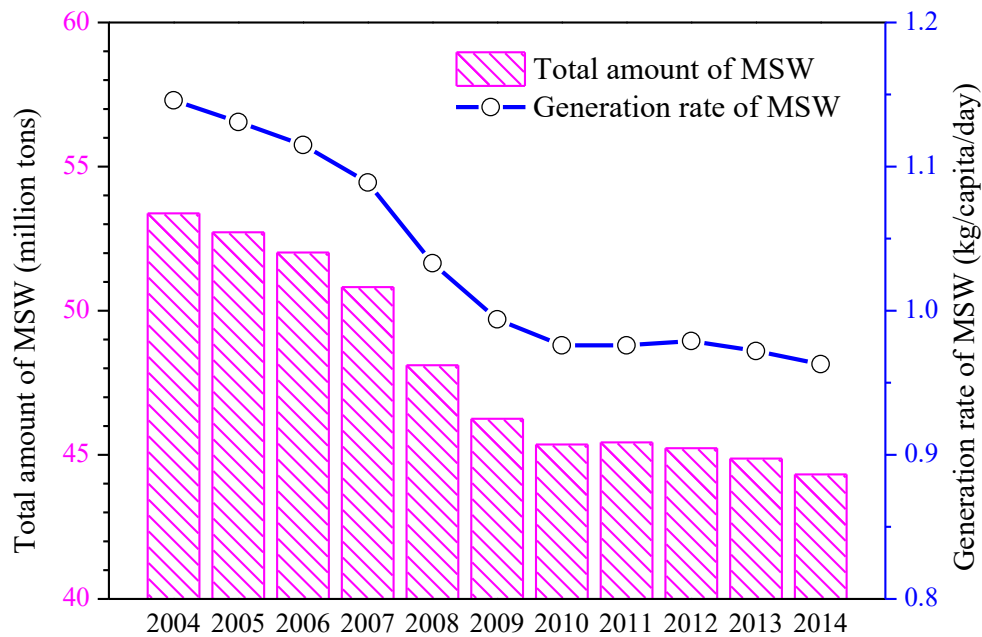


Figure 1-2 Amount and generation rate of MSW in Japan in 2004-2014

The generation of MSW in Japan kept decreasing year by year, while in the recent 5 years, the decreasing speed has become quite slow both in MSW generation and in the generation rate, which implies that the amount of MSW could be relatively constant in a foreseeable long period as observed in 2014. However, the generation of MSW is still quite huge. Therefore, the 3R approach (reduce, reuse and recycle) is playing a significant role in the waste management. 3R approach makes the demand of raw material for new production diminished, and the burden from the treatment of MSW (like energy consumption in the process) eased, as well as helps to alleviate the pressure that finding the final disposal location- the landfilling site- as the quick urbanization. All the advantages taken from the 3R approach implement would finally benefit to the environmental protection.

Japan is well known as a leader country in the waste management, especially in recycling. The flow chart of the MSW management is shown in Figure 1-3 with the data of fiscal year 2014 that released by Ministry of Environment of Japan (2016).

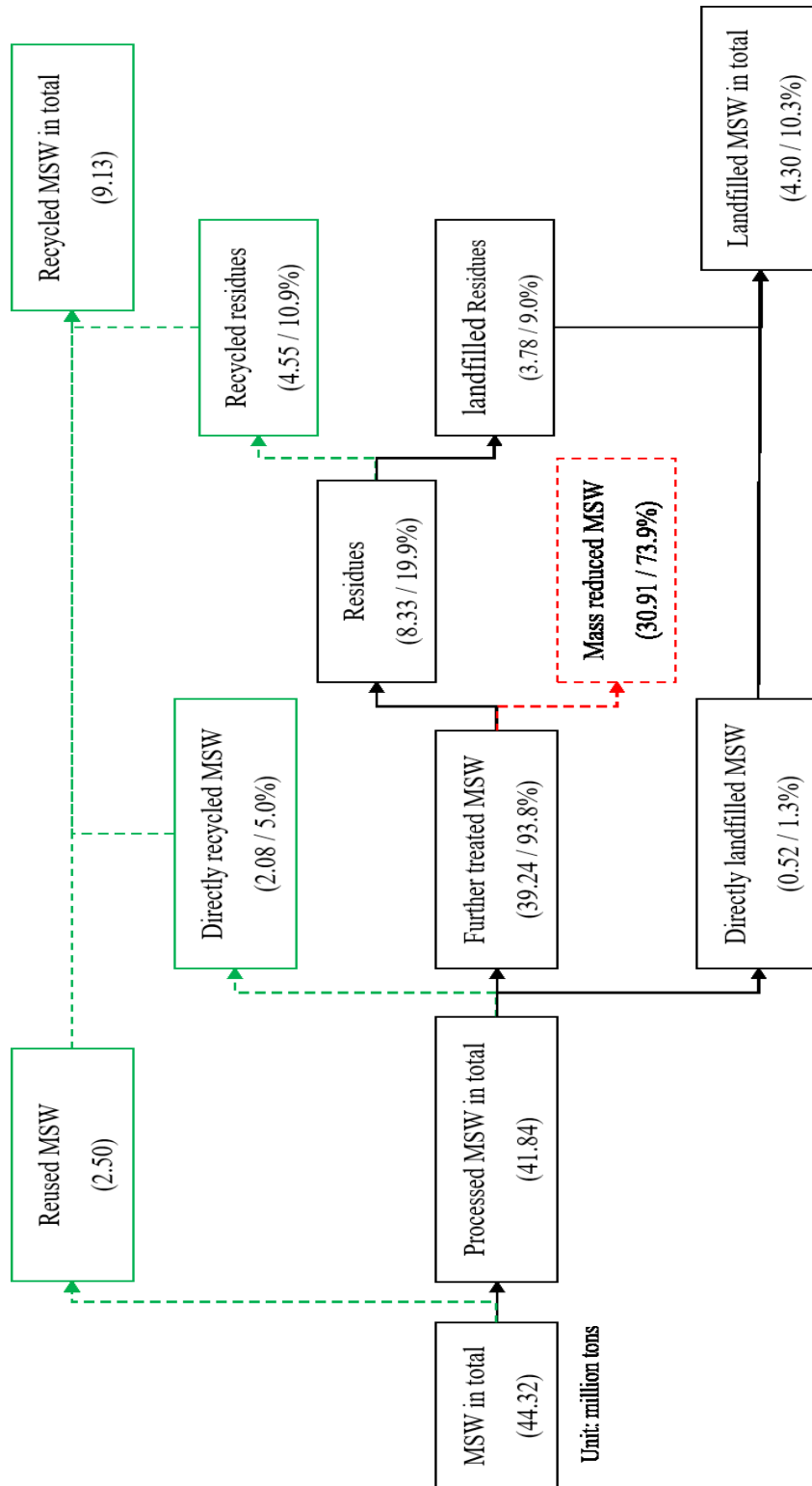


Figure 1-3 Flow of MSW management in Japan in 2014

There are solid and dash lines in three colors in Figure 1-3. Green dash line means the waste could be reused or recycled; black solid line means the waste are going to landfill sites; and red dash line and box mean the waste are totally mass reduced. As shown in Figure 1-3, it could be found that reuse and recycling were considered during the whole process and led to 20% recycling of the original MSW (9.13/44.32). The waste for final disposal (landfilling site) only occupied 10.3% of the total processed MSW thanks to the huge amount reduction (73.9%) occurred in the further treatment step. Therefore, the technologies that adopted for further treatment of MSW are crucial for the implement of reducing MSW in final disposal. The technology, that could dramatically reduce MSW and make the inevitable residues in relatively lower environmental risk, as well as produce useful energy or products, would be definitely of high concerns. In Japan (2014), 33.47 million tons of MSW were directly transferred to incineration plants, which is 80% of total processed MSW (41.84 million tons).

1.2 Municipal solid waste incineration (MSWI) fly ash

1.2.1 Municipal solid waste incineration (MSWI) technology

As mentioned in the previous section, a huge amount of MSW is generated around the world day by day, and the increasing trend could be also foreseen, which has been a pressing issue. A variety of processing technologies has been developed for MSW management and recovery energy during the processing (*see Figure 1-1 on Page 4*), while as the simple and inexpensive method, landfilling was dominant in the fresh MSW disposal for a long period, even currently in some developing or underdeveloped countries. However, landfilling has high environmental risks, for example, it may cause groundwater pollution or soil contamination due to the leaching of toxic components (Saikia et al., 2007). Furthermore, along with the urbanization occurred around the world (*see Section 1.1*) and the resistance of the citizens nearby, the spaces for landfilling site have been shrunk gravely. Additionally, from the viewpoint of 3R approach (especially “reduce”), the technologies that could cut the amount of waste sent to landfill would be certainly preferred. Accordingly, incineration is of increasing concerns in the recent decade.

Municipal solid waste incineration (MSWI) technology is deemed one of the commonest and most effective techniques for treating the generated waste with reduction, detoxification and utilization in many countries, as it can reduce the waste volume by up to 90% and the waste mass by 70% (Lei et al., 2016; Nixon et al., 2013). Although the residue from MSWI is still need to be

disposal into landfill, but it has efficiently reduced the demand of the space. As a renewable source of fuel instead of fossil fuel, MSWI could recovery energy and supply heat and electricity to the consumers (Sun et al., 2016). The solid residues (ashes) from MSWI could be partly used as a low cost and environmentally appreciated aggregate for constructions or additives in cement when pre-treated and verified as met some quality standards before sent to landfill, which is helped to further reduced the landfill usage (del Valle-Zermeño et al., 2013; Li et al., 2012). Same as other alternatives of MSW treatment, incineration also decompose the organic matters into simpler carbon forms such as carbon dioxide (CO₂) and methane (CH₄). Although the gaseous emission is unavoidable, incineration is the best way among all MSW treatments to reduce the elimination of CH₄ by balancing the two gases generation (Rand et al., 2000). Both the contributions to the reduction of fossil fuel usage and CH₄ emissions, MSWI helps to reduce greenhouse gas emissions.

The advantages mentioned as above make MSWI adopted by most developed countries currently (Rocca et al., 2012), while it still criticized due to its own drawbacks, mainly associated with the cost, the unavoidable gaseous emissions (carbon dioxide and dioxins) and hazardous discharge (Orozco et al., 2007; Quina et al., 2010). An incineration plant may involve both heavy investigation at the beginning and high maintaining cost throughout the operation, which makes it difficult to be accepted by developing and underdeveloped countries. Furthermore, the complexity of an incineration plant results to the requirement of highly skilled staff and careful maintenance, which may be a technical barrier for its popularization. In addition, with the dramatic reduction of the mass and volume of MSW, the toxic components or elements would be concentrated, which lead to the evident increase of the environmental risk and difficulties during processing the residues. Therefore, finding the practical, proper and effective methods for the treatment of solid residues is of high concerns.

1.2.2 MSWI residues

After incineration process, the MSW was combusted into solid residues which are generally classified as bottom ash (BA) and fly ash (FA) (Quina et al., 2008a). Bottom ash is mainly the residues from combustion, and fly ash is captured by fabric filters or electrostatic precipitators in the flue gas cleaning unit- air pollution control (APC) system. In this unit, the sorbent, such as slaked lime (Ca(OH)₂) or caustic soda (NaOH), is added for removing the acid gas (mainly HCl) (Chen et al., 2012; Lin et al., 2003; Wang et al., 1998). Thus the APC residue actually a mixture

of scrubber residues and real fly ash. The units and mass streams of a MSWI plant is shown in Figure 1-4.

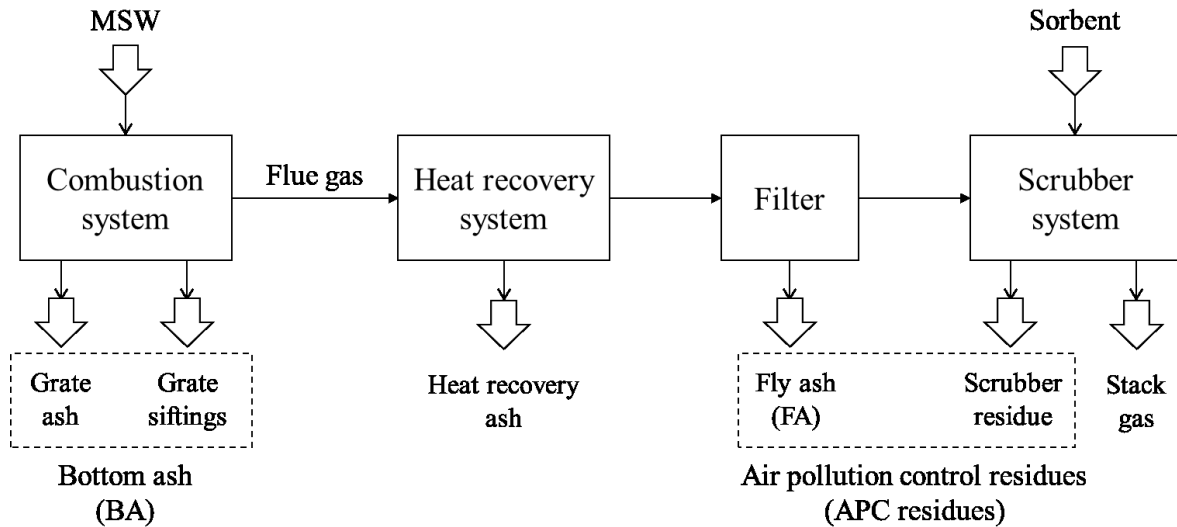


Figure 1-4 Units and mass streams of a MSWI plant (Ecke et al., 2000)

Although taking a quite big portion (about 80% in amount), bottom ash that is rich in calcium oxide and silica but poor in heavy metal is commonly treated as a non-hazardous waste, and is relatively easily recycled as a secondary material or landfilled (Chimenos et al., 1999; del Valle-Zermeño et al., 2015; Forteza et al., 2004; Huang et al., 2006; Song et al., 2015). On the contrary, fly ash is worldwide classified as hazardous waste, as it contains various organic compounds, high contents of toxic heavy metal metals and soluble chlorides (Colangelo et al., 2012; Zhang et al., 2011, 2016). Hence, adequate pretreatments on fly ash are required for stabilizing the heavy metal in order to avert undesirable environmental risks before the utilization or final disposal (Ferreira et al., 2003; Garcia-Lodeiro et al., 2016). As shown in Figure 1-4, fly ash is rarely exhausted separately, and it is the major source of the toxic matters in APC residues, thus many researches with the objective of fly ash may launch the experiments using the sample of APC residue, as we did in this work.

1.2.3 Utilization of MSWI ashes

Both of bottom ash and fly ash have been detected the potentials in recycling. Otherwise they would be disposed into landfill sites after proper treatments (see Figure 1-1 on Page 4). Therefore,

the studies about MSWI residues have raised concerns in the field of waste management (Sabbas et al., 2003). Many efforts have been made to recycle the MSWI residues as a second raw materials or additives in constructions after some proper treatments, and some examples of the applications summarized by researchers are shown in Table 1-3.

Table 1-3 Applications of MSWI ashes (Lam et al., 2010)

Type	Application	Composition%	Country
BA	Aggregate in concrete	Up to 50%	France
BA	Road base		Spain
BA	Adsorbent for dyes		India
BA	Concrete		Italy
Mixed ash	Cement clinker	Up to 50%	Portugal
Mixed ash	Cement clinker	44%	Japan
Mixed ash	Aggregate in concrete		Spain
FA	Concrete	50%	France
FA	Eco cement	50%	Japan
FA	Ceramic tile (Binder for stabilizing)		China
FA	Sludge	45%	China
FA	Glass ceramic	75% FA, 20% SiO ₂ , 5% MgO, 2% TiO ₂	Korea
FA	Glass ceramic (low melting temperature)		China
FA	Cement clinker	Replace up to 30% of raw material	China
FA	Blended cement	Up to 45%	UK

It could be seen that the main utilization of MSWI ashes is in concrete or cement field. Although the composition of MSWI in the products of different countries varied, the ratio of MSWI ashes in the products is rarely beyond 50%, maybe due to the consideration of engineering and the material safety. Because of the toxic property, fly ash needs more complex pre-treatments that raised the cost of its utilization. Therefore, from the perspectives of recycling and final disposal, the effective, low-cost and environment-friendly techniques for processing MSWI fly ash are in demand.

1.2.4 Technologies of heavy metal stabilization in MSWI fly ash

APC residues, same as the MSWI fly ash included, is classified as hazardous material attributing to containing high content of leachable heavy metals (e.g. Pb, Zn), soluble salts (e.g. NaCl, KCl, Ca-bearing salts) and toxic organic micro-pollutants (e.g. dioxins and furans) (Quina et al., 2008b). The heavy metal and organic micro-pollutants are mainly from the combustion of fresh MSW, i.e. MSWI fly ash; and soluble salts are generally the products of the absorption of acid gas by sorbent (see Section 1.2.2 on Page 8). Accordingly, stabilizing the heavy metal is one of the crucial missions for processing APC residue and MSWI fly ash.

Many endeavors have been made for the heavy metal treatment in APC residues / MSWI fly ash, and the appropriate treatments could be sorted into three groups; (i) physical/chemical separation, (ii) stabilization / solidification (S/S) and (iii) thermal methods (Hu et al., 2015). Figure 1-5 shows a scheme of the methods, where further subdivisions for each kind of treatment are also indicated (Quina et al., 2008a; Zacco et al., 2014).

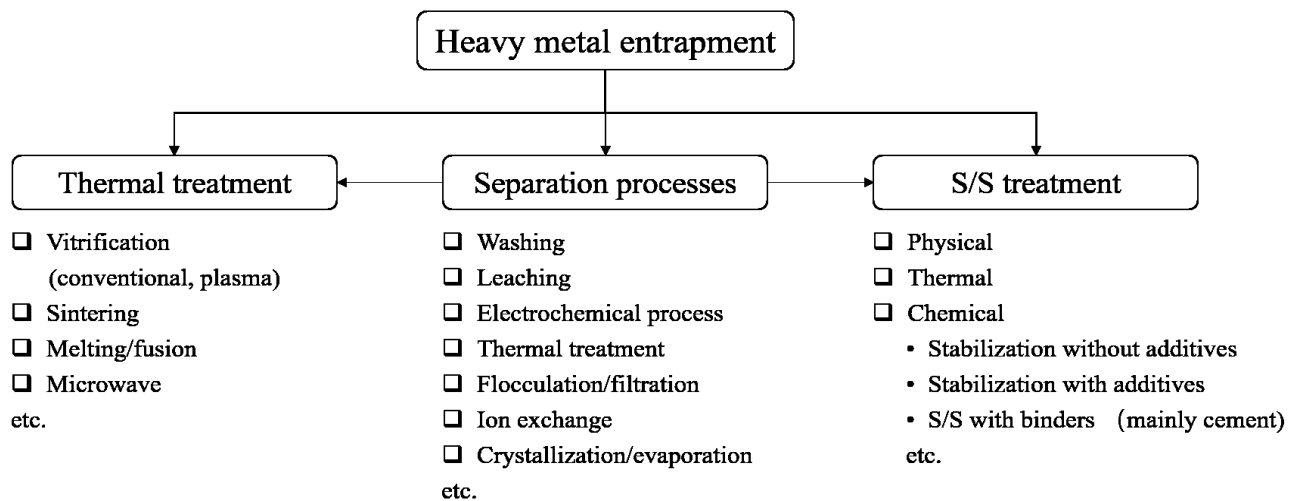


Figure 1-5 Groups of methods and subdivisions of heavy metal entrapment in APC residues

Separation processes are in practice used as a pre-treatment step aiming to improving the quality of the residues, and the major techniques are washing and leaching. Plenty of water or other fluid solutions is involved to dissolve salt and heavy metal into liquid phase and the target species could be easily recovered after the separation. Then thermal or S/S treatments are usually needed for the further disposal.

Thermal treatment technologies are certificated the validity on preventing the leaching out of heavy metal after treatment by creating a more homogeneous and denser product. However, the disadvantage of this thermal treatment is quite obvious, that is the economic issues due to energy consumption during the process. In some cases, the cost of thermal treatment may be up to 10 times than that of S/S treatment (Lindberg et al., 2015). Although the high temperature in thermal treatment could destroy the dioxin, furans and other organic pollutions effectively (Sakai and Hiraoka, 2000), the high economic burden on operation makes it hard to be adopted enduringly and widely.

Stabilization/solidification (S/S) treatment is now the most common option for heavy metal immobilization in MSWI fly ash. Stabilization is to convert the contaminants (such as heavy metal) into less soluble or less toxic forms; and solidification involves the transformation of target components from a liquid or sludge phase to solid phase. Stabilization is not obligatorily followed by solidification. The stabilization by additives is dominant among the techniques in S/S treatment field, and the additives could be hydraulic binder or chemical or chemical products from natural or synthetic resources (Zacco et al., 2014). Additives and water are well mixed with APC residue, and the reactive products are supposed to be of low dissolubility, by which the heavy metals are immobilized by various mechanisms. Many techniques have been actually developed, while some of them are step-tedious or costly (Lundtorp et al., 2002; Piantone et al., 2003). The most frequently and widely used S/S treatment is cement-based process, which is considered as being easily and simply operated and providing stable products under a relatively low cost (Cinquelpalmi et al., 2008). However, the drawback of this technique could not be neglected; the volume of the final product would be almost doubled as that of initial residues, which excessively occupied the landfill space (Sun et al., 2016). Another thing needs to point out that S/S processes are not effective for treating soluble salts.

As mentioned above, the new techniques in S/S field, which are low-cost, easy-operated, and with low volume increasing, are worth to be of concern. And the selection of the additives that should be cheap, effective and of easy availability would be the crucial point.

1.3 Fishbone and hydroxyapatite (HAP) on stabilization of heavy metal

1.3.1 Fish waste and fishbone

Fish is supplied to retail customers or small-sized shops for daily life or underwent further treatment for products, and from both of them fish waste is inevitably generated. On the one hand, there is a large amount of fishbone waste daily exhausted (Ozawa and Suzuki, 2002). The fish tissue residues that involved into waste is probably over 50% of the total fish capture (Kristinsson and Rasco, 2000). Hence the daily exhausted fish waste is in a huge amount; on the other hand, comparing with other wastes, this type of waste needs to be managed properly in a quite short period of time, in order to avoid the attendant environmental risks incidentally caused by their rapid corruptibility of the organic fractions (Bin et al., 2013). As a result, fish waste, which is common in coastal areas (especially from the fish processing industry), is becoming one of the pressing issues for such communities, regions, even some countries.

As a kind of highly perishable commodity, a big portion of fish is required for various kinds of processing, the percentage in 2000 was over 60% of total world fisheries production (Arvanitoyannis and Kassaveti, 2008). Thanks to this situation, fish waste is naturally agminated-exhausted as other wastes from industries. It is suggested that finding out the appropriate approaches for treatment or recycling of fish wastes is of practical significance and of certain feasibility for both environmental management and economic benefits. That treating fish waste as a by-product is an important chance updating for cleaner production, as it may not only generate additional revenue but reduce the cost for waste disposal.

Fish waste is traditionally treated as a kind of bio-waste. Fish waste has been used as the ingredient of the animal feed for decades owing to its high-quality protein and energy containing, especially the offal (Gabrielsen and Austreng, 1998). It could serve as the common source of proteins or nitrogen and meet partial requirements of the animals (Esteban et al., 2007; Hammoumi et al., 1998; Kotzamanis et al., 2001). In the recent decades, due to containing required oils and fats, fish waste is used as a supplier of the raw materials for biodiesel, which is an additive or substitute of diesel fuel derived from petroleum (Alcantara et al., 2000; Kato et al., 2004). A third

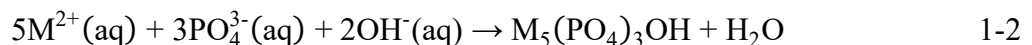
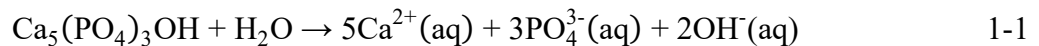
important utilization of fish waste is extracted useful segments for food industry and cosmetics. And a number of compounds has been successfully isolated as reported including fish protein hydrolysate (FPH) for cryoprotectant (Khan et al., 2003), enzymes (Tavares et al., 1997), collagen (Morimura et al., 2002; Nagai and Suzuki, 2000) that have antimicrobial capability. There are still some miscellaneous uses of fish waste not listed here.

It is found that the major methods for recycling fish waste are focused on the recovery the useful components (mainly proteins) in the organic fractions, which are rich in meat, offal and skin; while waste fishbone, which is holding the significant portions of inorganic material, has not been fully taken advantage. And the inorganic part of fishbone has its distinct value from other fish wastes as it is the natural supply of hydroxyapatite (HAP), whose calcium possesses the exchange capacity with heavy metal ions (Narasaraju and Phebe, 1996; Tan et al., 2014; Vila et al., 2012).

1.3.2 HAP and its effectivity on heavy metal stabilization in contaminated environments

Apatite is a group name for a series of related phosphate minerals, which is naturally the main mineral component of phosphate rocks. Apatite has gained certain attention owing to its effectivity on heavy metal reduction from the polluted environments by forming insoluble metal phosphate (Chen et al., 1997; Nzihou and Sharrock, 2010), thus many researches were conducted by apatite mineral (Aklil et al., 2004; Saxena and D'Souza, 2006).

Hydroxyapatite (HAP) is a naturally occurring mineral phase of calcium apatite. The formula of HAP is $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, while it is also written as $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ in some cases or researches to denote that the crystal unit is comprised of two entities. As a member of apatite family, HAP is also found in a significant capacity on heavy metal stabilization, and the mechanism was reported as a dissolution-precipitation process shown in Equations 1-1 and 1-2 (Admassu and Breese, 1999):



where M^{2+} is a divalent metal.

There are two points indicated from these formulas- (i) there should be water (liquid) as media involved in the reaction process; (ii) the stabilization of heavy metal is that new-formed metal-

HAP is in solid phase or of low dissolubility, by which the heavy metal could be isolated from the contaminated environments or immobilized in the solid phase.

Although two formulas were used to describe the reaction between metal ions and HAP, there are actually two hypotheses about the mechanism of the formation of metal-HAP. The one is the dissolution-precipitation mechanism as mentioned above, that Ca cations of HAP were firstly dissolved into liquid phase and then the divalent metals containing in the aqueous solution linked to the vacancy of HAP. The other one is concerned that the divalent metal cations were adsorbed to the surface of HAP by their diffusion and then the replaced cations were released, which could be described as ion-ion exchange mechanism (Kizilkaya and Tekmay, 2014; Oliva et al., 2011; Sugiyama et al., 2003). Many researches have conducted some discussions while the conclusion is still open to debate. However, there is no dispute about the necessity of the aqueous condition and the formation of metal-HAP as the final product.

The effectivity of HAP on heavy metal stabilization or removal capacity has been successfully observed on a series of elements like Pb, Zn, Cu, Ni, Cd *et al.* from contaminated environments, mostly in or from aqueous solutions (Choi and Jeong, 2008; Feng et al., 2010; Gupta et al., 2012; Yaacoubi et al., 2014). Both synthetic and natural HAP have proved effectivity for heavy metal stabilization, while synthetic HAP has been investigated more extensively (Corami et al., 2008; Dybowska et al., 2009; Suzuki et al., 1981). In the recent decade, considering that most synthetic HAP products may be too expensive for the application, the biogenic HAP has raised more attention as a cheaper and environmental-friendly alternative (Oliva et al., 2012; Ozawa and Kanahara, 2005; Wang et al., 2016; Zayed et al., 2013). Fishbone, a natural source of HAP from waste material, is deserved to be concerned, not only for its effectiveness on decreasing the concentration of heavy metals, but also for recycling the waste itself. Some researches of heavy metal removal using HAP derived from natural or treated fishbone have been conducted (Admassu and Breese, 1999; Kizilkaya et al., 2010; Lim et al., 2012; Oliva et al., 2010; Ozawa et al., 2003). In addition, these researches were mainly conducted using standard metal solutions or in low metal concentrations under a relatively controlled condition.

1.4 Research motivation, purpose and objectives

As mentioned above, owing to the urbanization and economic development, the space for new landfilling sites has become insufficient, thus the enormous amount of MSW that daily generated

could not be processed directly into the landfill sites as the way used in the past long period. From the viewpoint of material and energy recycling, incineration an available and acceptable option for MSW treatment, which is adopted increasingly. Though the mass and volume of MSW could be decreased dramatically during incineration, the solid residues exhausted needs to treat in a proper way, especially the part of fly ash that is worldwide classified as hazardous waste.

As the major toxic components in MSWI fly ash, heavy metal has got great attention in the research field of waste management. Many methods have been developed for stabilizing the leachable heavy metal (major in divalent, e.g. Pb, Zn) in MSWI fly ash. However, most of the technologies were step-tedious or costly, thus the relatively cheap, easy-operated cementitious S/S treatment is taking the major share of the stabilization of heavy metal in MSWI fly ash, even with the obvious drawback that increasing the mass and doubled the volume of the waste after the treatment. Therefore, the attempt for developing the new techniques, which would be environmental-friendly, low-cost, easily operated, and better with low volume increasing, should be of certain concerns.

Fishbone was taken into account as a candidate of additive for the heavy metal stabilization in MSWI fly ash in this research, because it is a natural source of HAP and a waste needed to be treated. Calcium in HAP possesses the exchange capacity with heavy metal ions and newly-formed metal-HAP is supposed to be in low solubility, thus the heavy metal could be stabilized. HAP-based treatment on heavy metal stabilization has been used in some contaminated environments, while no researches have specifically focused on MSWI fly ash to date. Additionally, the experiments in the previous researches was usually conducted using standard metal solutions of heavy metal and in relatively high concentration under a relatively controlled condition, which may be hard to simulate the real situation provided by MSWI fly ash samples. Furthermore, the mechanism of the stabilization of heavy metal by HAP is still controversial.

Therefore, the present research was conducted with the aim to (a) confirming the feasibility that using waste fishbone stabilized the heavy metal in MSWI fly ash; (b) improving the effectivity of fishbone on heavy metal stabilization in MSWI fly ash; (c) providing more evidences for the discussion of the mechanism of the reaction between HAP (waste fishbone) and heavy metals.

Based on the consideration of the practicability of the technique, the experiments and the conditions for the reactions were designed with the respect of the original state of MSWI fly ash

and fishbone, and the simpler techniques would be given the priority when the pre-treatment is considered. It means that excessive tough work on modifying the samples properties or controlling the reactive conditions was out of concerns in this research. If could be treated as a by-product instead of a waste, fishbone may get a further opportunity for cleaner production of both fish processing and MSWI fly ash processing, as it can potentially generate additional revenue as well as reduce disposal costs for these materials.

1.5 Structure of this thesis

Totally five chapters are included in this thesis (Figure 1-6).

There is an introduction in Chapter 1 to provide the background and basic information about the two key research objectives- MSWI fly ash and waste fishbone. Their generation, current disposal approaches and potential utilizations as well as relative technologies were reviewed in this chapter, by which the motivation of this research were presented.

The experiments with the results and discussions are stepwise described in Chapter 2-4. The investigation is started from characterizing MSWI fly ash, and the target elements that should be focused on would be distinguished (Chapter 2). Then waste fishbone working as an additive for the stabilization of heavy metal in MSWI fly ash was of concern. The feasibility of fishbone on the stabilization of heavy metal in MSWI fly ash would be verified firstly, and the real condition for the reaction of the stabilization and the major co-existing elements could be confirmed (Chapter 3). The following attention would be taken by the approaches for improving the effectivity of fishbone on the stabilization. Considering that the complexity and cost may be the barriers for the adoption of the techniques for waste disposal, the proposals are designed with the respect of the primary conditions provide by MSWI fly ash and limiting the input of energy and extra materials. When the pre-treatment is launched, the simpler techniques would take the priority (Chapter 4).

Finally, there is a conclusion of this study, and some recommendations would be also released in the last chapter.

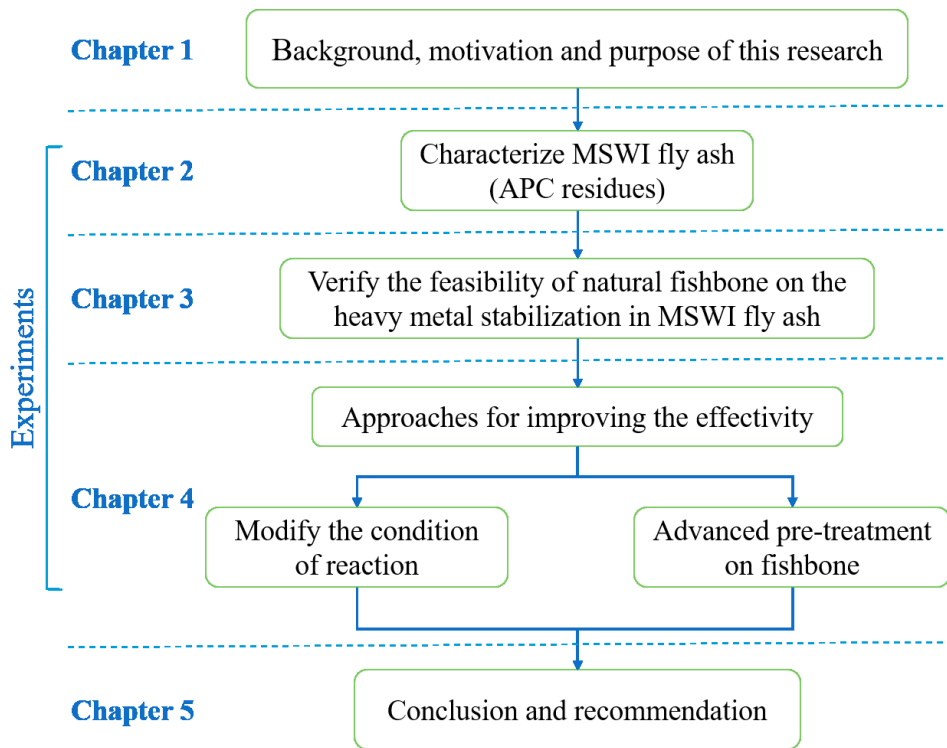


Figure 1-6 Structure of this thesis

Chapter 2 Characterization of municipal solid waste incineration (MSWI) fly ash

2.1 Introduction

The characters of diverse kinds of solid wastes quite differ from one to another according to their original properties and generated processes. And these characters are deemed as the determinant factors for evaluating the potential and possibilities of reuse or recycling, or making the decisions of the proposal strategies of the wastes.

As a non-negligible kind of solid wastes, various parameters have been employed to describe the physical, chemical and mechanical properties of the incineration residues (Ibáñez et al., 2000; Kim et al., 2010; Yang et al., 2014). There are some factors like pH, particle size distribution and bulk composition widely used in many research fields of wastes; while there are also some factors employed in other research fields or industries of solid waste or material not having caused enough concerns in the field of municipal solid waste incineration (MSWI) fly ash yet, for instance loss-on-ignition (LOI) and related mineral phase transformation.

LOI is one of those parameters that refers to the mass loss of solid samples, which can be due to the loss of moisture, carbon, and so forth, when it is heated in an oxidizing atmosphere at specific temperatures. LOI is widely used to estimate the organic and/or carbonate content of different kinds of samples (Heiri et al., 2001). As a proxy for the characteristics of solid samples, LOI has been employed for decades in several research fields and industries tested under varied ignition temperature and time for particular purposes. In the soil science, LOI is measured stepwise at 360-800 °C for 2-12 h for estimating the soil organic carbon, organic matter or inorganic carbon contents (Ghabbour et al., 2014; Massaccesi et al., 2015; Wang et al., 2013). In the geological science field, the ignition conditions are controlled between 550-950 °C for over 2 h of exposure in order to estimate the organic and inorganic carbon contents (Santisteban et al., 2004; Wang et al., 2011). In the environmental science field, LOI is used to provide a rough approximation of the amounts of total organic matter, volatile species (at 500/550 °C) and carbonates (at 900 °C) in the solid fraction of sludge when samples are heated for specific periods (Shathika Sulthana Begum et al., 2013; Vemic et al., 2015). LOI is also used in the field of combustion materials. In the coal-

fired power generation industry, there has been a standard method of using LOI for measuring the carbon content of fly ash at the relatively high temperatures to describe the efficiency of the combustion process and to estimate further utilities (Burriss et al., 2005; Styszko-Grochowiak et al., 2004; Zhang and Honaker, 2015). In addition, LOI is a prerequisite parameter commonly used for measuring the bulk chemical composition of the solid materials using X-ray fluorescence (XRF) technique (Husillos Rodríguez et al., 2013; Kiattikomol et al., 2001), thus a relatively precise and reasonable LOI result is required. Though sharing a certain resemblance with other combustion materials as generated from the high-temperature combustion process and being captured by an air pollution control (APC) system, MSWI fly ash has distinctive features in mineral and chemical compositions resulting from the complexity of raw materials, which may lead to different LOI results under different ignition conditions. However, there has been no universal standard protocol for estimating LOI in MSWI fly ash until now.

Ignition time and temperature were mentioned as the critical factors that can compromise the reproducibility and the comparability of the results (Hoogsteen et al., 2015; Konen et al., 2002). Various volatile salts, structural water and inorganic carbon may also contribute to LOI as a function of ignition temperatures (Sutherland, 1998; Walter E. Dean, 1974). The ignition time may affect the existence of unstable components in the residues. Hence ignition condition also may effect on the transformation of minerals in MSWI fly ash, which is a considerable aspect for understanding the LOI variations (Brown and Dykstra, 1995; Vandenberghe et al., 2010). To date, no researches have specifically focused on this matter.

In this chapter, the common parameters (like pH, particle size distribution and elemental composition) of MSWI fly ash were included. Besides, the less-discussed parameters (like thermogravimetric and LOI features, mineral phase composition and transformation) were also focused on. In addition, the critical factors about the hazardous property and treatment as the leaching behaviors of major elements were also of concern.

2.2 Experiments

2.2.1 Sample collection and preparation

As mentioned in Section 1.2.2, fly ash is usually exhausted as a part of APC residue, thus many researches investigating on the heavy metal entrapment in MSWI fly ash used the sample of APC residues instead, as what we did in this research. Considering that fly ash is the major source

of heavy metals in the residues, the samples were directly called as MSWI fly ash in the experiments.

The MSWI fly ash were obtained from three incineration plants- S and R located in City F, and K in City K, Japan. These incineration facilities are used to treat the municipal solid waste generated by the corresponding regions of the two cities. The facilities S, R, and K employ the stocker-type technology with the waste treatment capacity of 750, 900 and 300 tons per day, respectively. For the APC system, electrostatic precipitator is used in plant S, while fabric filters are used in plants R and K (Table 2-1). The original samples were at dry state, the moisture of which were 0.69%, 2.72% and 0.73% for S, R and K tested by freeze-drying, respectively. The original samples were well homogenized and then stored in airtight containers before proceeding to the following experiments.

Table 2-1 Information of the incineration plants of sample sources

Incineration plants	S	R	K
Location (city)	F		K
Incinerator	Stocker-type		
Capacity (t/d)	750	900	300
APC unit	Electrostatic precipitator (EP)	Bag filter (BF)	

2.2.2 pH measurement

For measuring the pH of solid sample, the additional liquid phase is requisite. In this research, super-pure water was added to get a mixture with a liquid/solid (L/S) ratio of 10. Then the pH of mixtures of different fly ash sample was tested by pH meter (F-53, Horiba).

2.2.3 Particle size analysis

The particle size distribution was measured by laser diffraction analyzer (Macrotrac MT3000) using the freeze-dried original sample. An adequate amount of sample was suspended in water, and the analysis was launched after 1 min of ultrasonic treatment. The tests for each sample were run in duplicate. The measurements were carried by an external service.

2.2.4 Thermogravimetry (TG)

Thermogravimetry (TG) was conducted to detect the relationship between the mass loss of the sample and the temperature in a TG-DTA 2000SA (Bruker AXS) apparatus. Approximately 20 mg of the freeze-dried fly ash sample was taken for each test and aluminum oxide (Al_2O_3) was used as the inert control material. Both the fly ash sample and aluminum oxide were simultaneously settled and heated in the air atmosphere and the tests were run in triplicate. The temperature program was set to elevate from the ambient temperature to 1100 °C in the step of 10 °C/min. The temperature was held constant at maximum for 15 min at the end of each test.

2.2.5 Loss-on-ignition (LOI)

Fly ash consists of fine particles (*see Section 2.3.2 on Page 24*), which provide a property to easily absorb moisture from the atmosphere. To avoid the deviation caused by the moisture absorption, the stored fly ash samples were ground by mechanical milling machine for 1 min and then dried in an oven at 105 °C for over 6 h to attain a relatively constant mass before the ignition process. According to the curves obtained from TG tests (*see Section 2.3.5 on Page 29*), three conditions (440, 700 and 900 °C) were selected as the ignition temperatures. About 2 g of pulverized samples were placed in the capped crucibles, heated in a muffle furnace from the ambient temperature to the target temperatures, and then ignited for 1 or 2 h. The weights of the samples before and after ignition were recorded and the difference was noted as LOI through Equation 2-1:

$$LOI (\%) = \frac{\text{mass loss of sample}}{\text{mass of original sample}} \times 100 = \frac{W_1 - W_2}{W_1 - W_0} \times 100 \quad 2-1$$

Where W_0 , W_1 and W_2 are the masses of blank crucible, crucible with sample before and after ignition, respectively.

The LOI measurements were launched in duplicates in each scenario, and the average LOI was deemed as the representative value.

2.2.6 Mineral phase composition detection

The mineral phases of the freeze-dried original samples and the samples after ignition in each condition mentioned in *Section 2.2.5* were analyzed by X-ray diffractometry (XRD, Rigaku Multiflex) using $CuK\alpha$ radiation generated at the voltage of 44 kV and the beam current of 30 mA.

Specimens were scanned from 2-75 deg. (2θ) by 0.02 deg. (2θ)/step, and the X-ray irradiation time of 2 sec./step. The mineral phases were identified by the software *Jade 6.0*.

2.2.7 Bulk compositional analysis

Major, minor, and, trace elements were determined by XRF (ZSX Primus II, Rigaku) using the pulverized samples described in *Section 2.2.5*. Considering that higher ignition temperature could induce structural change of the mineral phases by which extra components might contribute to the LOI results, the minimum LOI value obtained from 440 °C/2 h scenario was used as an essential parameter for conducting XRF analysis. Total carbon (TC) content was measured using the fly ash samples by TOC-Z (Shimadzu) combined with solid sample combustion unit (SSM-5000A, Shimadzu) at 900 °C.

2.2.8 Leaching test

The leaching tests of MSWI fly ash were conducted in 250 ml polypropylene bottles at room temperature. Each bottle contained 10.00 g of fly ash and 100.0 ml of super-pure water as leachant. All bottles were shaken at a speed of 200 rpm with leak-proof lid for 6 h. Then to obtain leachate, bottles were centrifuged at 3000 rpm for 20 min, and then solid and liquid parts were separated by vacuum filtration through 0.45 μm pore-size membrane. The leachate was stored in a polypropylene bottle for further analyses. The concentration of heavy metals in the leachate was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, 720 ICP-OES, Agilent Technologies).

2.3 Results and discussion

2.3.1 pH of MSWI fly ash

The fly ash samples were well mixed with super-pure water to L/S 10, then the pH meter was used to test the pH of the mixture, which is represented the pH of MSWI fly ash. The samples from different sources were called as fly ash S/R/K corresponding with the plants. The pH of fly ash S, R and K was 12.28, 12.11 and 12.26, respectively. Though different APC units were employed in the three incineration plants, the pH of fly ash samples was quite high and almost the same due to the big amount of alkaline salt addition (*see Section 2.2.1*).

It is indicated that MSWI fly ashes were sharing the same property in pH regardless of the sources. The influence of the extremely alkaline condition should be of high concern when considering the disposal of fly ash. The methods or technologies that need to adjust the reaction

condition to relatively low pH for the treatment or utilization of MSWI fly ash should be adopted very cautiously, because it would cost a large amount of acid, which may bring big cost and extra risk on the operation.

2.3.2 Particle size distribution

The MSWI fly ash samples was suspended in water and then the particle size distribution was measured by laser diffraction analyzer. The results for the calculated mean diameter and surface area, as well as the particle size distribution of MSWI fly ash are presented in Table 2-2, Table 2-3 and Figure 2-1.

According to Table 2-2, the mean volume diameter (MV), mean number diameter (MN), mean area diameter (MA) of each sample were quite different due to defined calculated methods. Therefore, the indicator chosen from them should be decided based on the specific targets. However, when comparing the three samples, the data from the same index were analogical, which is indicated that the fly ash from varied resources are sharing resemblance, regardless of the type of APC system.

As shown in Figure 2-1 and Table 2-3, the particle diameters of the three kinds of fly ash were 3-350 μm , and 90%-95% were below about 250 μm , which is accordant with the common description that fly ash consists of fine particles (Hartmann et al., 2015). Clear bimodal distribution was observed on the curves of frequency (solid line) in Figure 2-1 (a) and (c), and more than one peaks could be designated on Figure 2-1 (b) as well, which is indicated that the particle size distribution of MSWI fly ash is lead to be bimodal form regardless of the type of APC system. This phenomenon was also mentioned by some researchers (Thipse et al., 2002). The peaks were almost appeared at the same positions; the left peak were at 65 μm for the three samples, and the right peaks were shown at between 160-190 μm . However, the relative strength of the two peaks were case by case. The most particles were in the diameter of 160-190 μm for the samples of fly ash S and K (Figure 2-1 (a) and (c)), which occupied 4%-4.5% of the total particles; while the most frequent particle size for fly ash R is about 65 μm . In addition, the particles of fly ash R were generally fine and uniform comparing with other two samples.

Table 2-2 Calculated mean diameter and surface area of MSWI fly ash

Parameter	Fly ash S	Fly ash R	Fly ash K
Mean Volume Diameter (MV, μm)	92.29	76.73	86.58
Mean Number Diameter (MN, μm)	5.00	4.85	6.27
Mean Area Diameter (MA, μm)	30.59	20.91	34.22
Calculated Surface Area (CS, m^2/cm^3)	0.20	0.29	0.18

* The data are the average of duplicate measurements for each sample.

Table 2-3 Cumulative frequency for different particle size of MSWI fly ash

Cumulative frequency (%)	Particle size (μm)		
	S	R	K
10	12.28	7.75	14.20
20	24.84	13.31	26.95
30	39.03	20.95	40.91
40	52.89	31.96	54.03
50	69.02	46.57	69.32
60	93.54	65.06	91.77
70	128.55	91.13	120.20
80	162.85	132.85	147.35
90	200.80	196.50	178.35
95	230.80	246.50	203.15

* The data are the average of duplicate measurements for each sample.

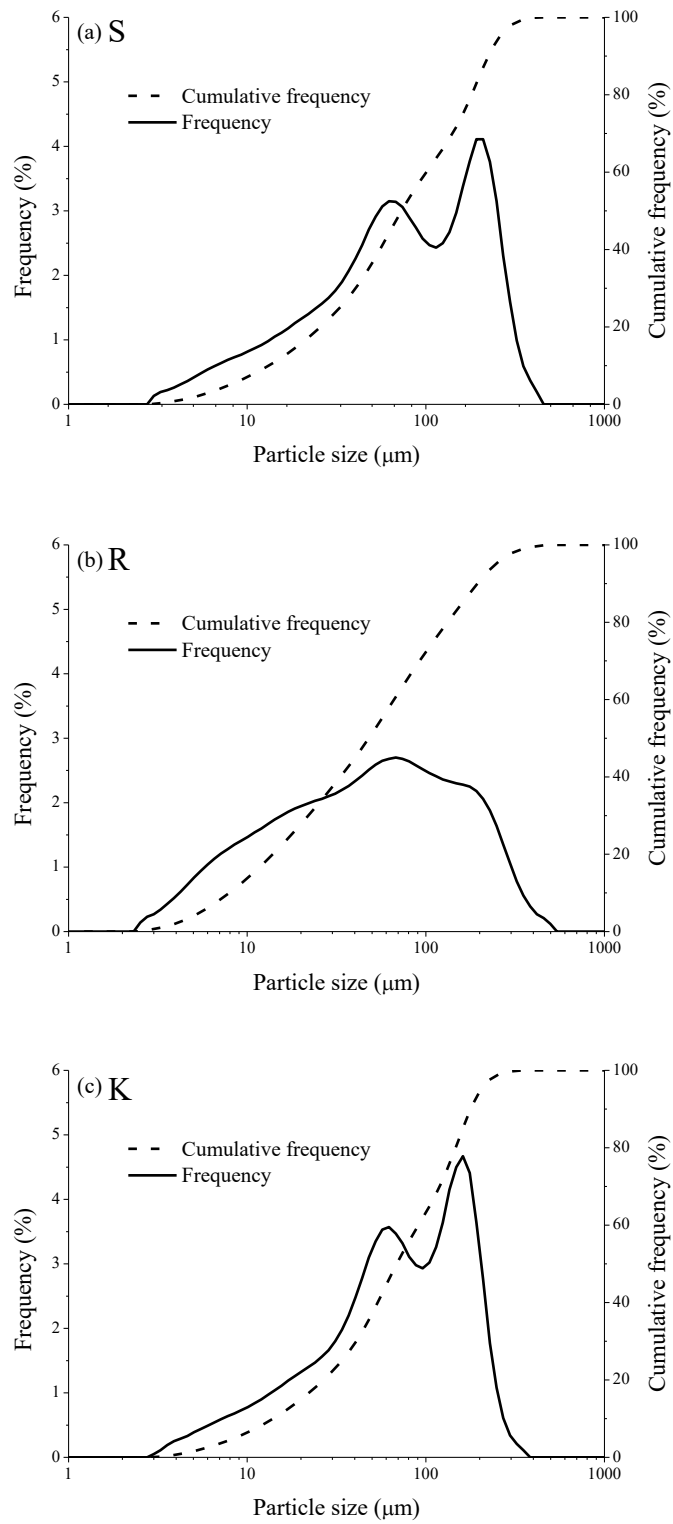


Figure 2-1 Particle size distribution of MSWI fly ash

2.3.3 Elemental composition and total carbon (TC) content

Elemental composition of the fly ash samples was analyzed by XRF. Major, minor and trace elements of the samples from three sources of fly ash are presented in Table 2-4. The proportion of each element varied for the different sources of samples. Ca, Cl, Si, Na, K, Al, Mg and S were the major elements in MSWI fly ash, the contents of which were over 1%. As a result of the addition of sorbent (usually $\text{Ca}(\text{OH})_2$) in APC unit, Ca was found in an overwhelming amount in all samples, and the proportions fluctuated in a wide range (30-54%); while the second major element (Cl) was relatively constant at about $22\pm 2\%$ in all samples from different sources. Among heavy metals, Zn and Pb took the first two places in terms of concentration, the contents of which were considerably higher than that of others. Besides the elements mentioned above, the others were counted as minor and trace constituents.

Table 2-4 Elemental composition of MSWI fly ash

Composition (mass %)	CaO	SiO ₂	Na ₂ O	K ₂ O	Al ₂ O ₃	MgO	P ₂ O ₅
S	30.53	9.26	10.69	6.00	4.91	2.86	1.40
R	41.39	9.27	7.08	3.29	2.34	2.47	0.61
K	54.31	4.02	4.36	2.82	2.10	2.44	0.72
Composition (mass %)	Fe ₂ O ₃	TiO ₂	MnO	Cl	S	F	LOI*
S	1.15	1.12	0.05	22.32	2.31	0.10	3.35
R	0.45	0.44	0.02	23.87	1.99	0.05	4.91
K	0.80	0.56	0.03	19.78	1.55	0.07	5.12
*LOI displays the representative values obtained from 440 °C/2 h scenario.							
Composition (ppm)	Zn	Pb	Cu	Sb	Ba	Cr	Sr
S	29830	6166	1221	944	616	325	262
R	13823	2114	665	627	271	144	196
K	9322	1850	500	557	239	142	312
Composition (ppm)	Cd	Sn	Ni	As	Co	V	
S	252	114	69	41	6	3	
R	176	69	34	14	5	1	
K	181	46	38	12	9	1	

The Total carbon (TC) contents of the three fly ashes were measured at 900 °C, and the results for fly ash S, R and K were 1.23, 0.92 and 1.12%, respectively.

2.3.4 Leaching property

Leaching tests could provide a good insight into the mobility of heavy metals. A 6 h-leaching process was launched with super-pure water as leachant for every fly ash at a L/S ratio of 10. Then the concentration of heavy metals in the leachate was measured by ICP-AES, and the results were shown in Table 2-5.

Many kinds of heavy metal were detected in the leachate of fly ash, while most of them were in low concentration. Although the concentration in different samples was fluctuated, the most leachable heavy metals were easily identified by their high contents, which were Pb and Zn; in all samples, their concentrations were obviously high than other metals, especially Pb. Considering the toxicity, Pb was absolutely the main target in the heavy metal stabilization.

As mentioned in *Section 2.2.1*, different types of APC units were employed by the three incineration plants that provided the fly ash samples; electrostatic precipitator is used in Plant S, while fabric filters are used in Plants R and K. Though the different status of fresh waste was considered, the results shown in Table 2-5 seems to imply that the heavy metal was more captured by fabric filter. Pb and Zn in the leachate of fly ashes R and K was 2-3 times higher than that in the leachate of fly ash S; while between fly ashes R and K, the amount of Pb and Zn were not in that much difference, especially Pb, both of which were about 30 mg/l in the leachates.

Table 2-5 Heavy metal in the leachate of MSWI fly ash

Fly ash	Concentration in the leachate (mg/l)											
	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Ti	V	Zn
S	0.01	0.00	0.69	0.11	0.04	0.00	0.23	0.00	16.05	0.00	0.01	2.68
R	0.00	0.00	0.24	0.17	0.10	0.00	0.09	0.01	32.63	0.00	0.04	5.62
K	0.00	0.00	0.14	0.15	0.02	0.00	0.09	0.00	30.50	0.00	0.03	8.23

2.3.5 Mass loss feature as a function of temperature

Considering that the incineration temperature for municipal solid waste is commonly around 850-1000 °C (Bayuseno et al., 2009; Rocca et al., 2012), the maximum temperature in this test of mass loss feature is set at 1100 °C. The TG results of all MSWI fly ash samples are shown in Figure 2-2. Continuous mass losses were observed in all the samples with the temperature increase. According to the mass loss feature, the curves were divided into five sections- the weight of the samples rarely changed from ambient temperature to 440 °C; then an obvious mass loss appeared from 440 to 700 °C. The mass loss became even faster between 700- 900 °C; and under higher temperature condition, the weight of the sample rapidly decreased until the temperature rose to 1100 °C. The mass loss almost reached the maximum and became relatively constant when the temperature was maintained for 15 min.

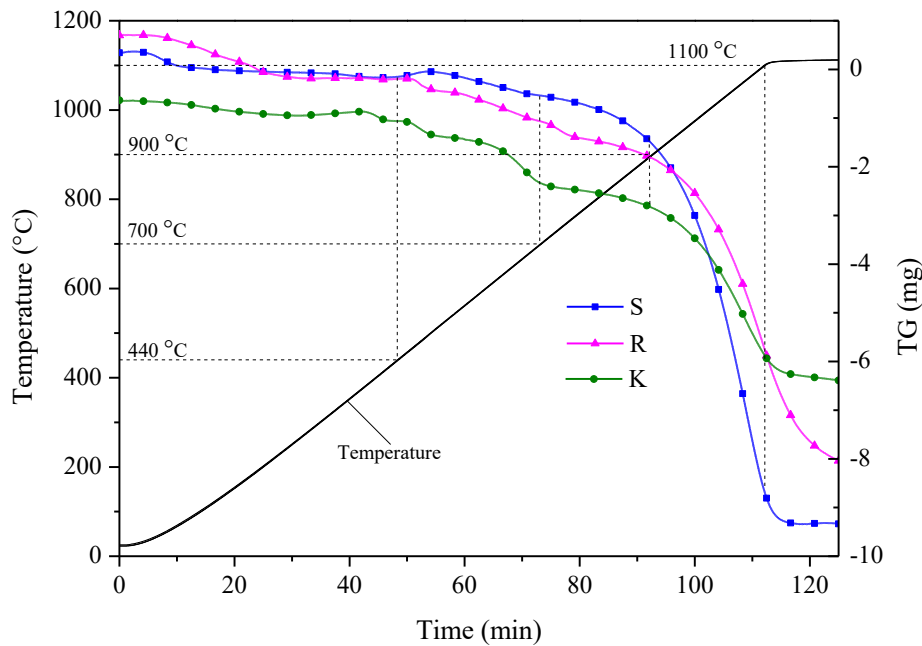


Figure 2-2 TG analysis results of MSWI fly ash

2.3.6 LOI under various ignition conditions

The ignition temperature candidates for LOI were selected at 440, 700 and 900 °C based on TG results (Figure 2-2 on Page 29). and the ignition time was set at 1 or 2 h for adequate potential

reactions in order to monitor the effect of ignition temperature and time on LOI. The representative LOI value under different ignition conditions are presented in Figure 2-3.

The samples from the different sources (Plants S, R and K) presented various LOI values. This might be due to the composition variation of waste throughput, relevant amount of sorbent added to APC units for acid gas abatement, as well as the APC technology employed in each facility (*see Section 2.2.1 on Page 20*). For each set of sample, there was a relatively slight increase of LOI between the ignition time of 1 or 2 h under the same temperature; while the LOI values dramatically rose as a function of ignition temperature increase. In addition, LOI elevated more obviously during 440- 700 °C than that of 700- 900 °C.

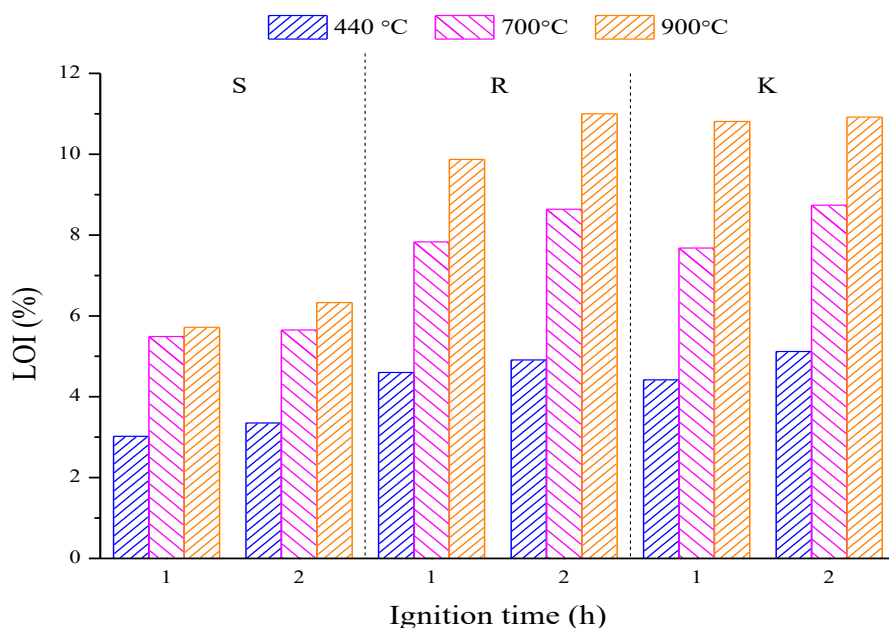


Figure 2-3 Representative LOI values under different ignition conditions

By comparing the LOI and TC values shown in *Section 2.3.3*, it is observed that LOI value under any ignition condition was always larger than the TC value for each sample. Therefore, it could be inferred that besides carbon, there were also additional components that were lost via volatilizing of less stable or unstable phases, formation and liberation of gaseous species such as H₂O, H₂S, and SO₂ or the interaction between two or more compounds during the ignition process. In addition, this transformation was supposed to be expressed partially by the mineral phase transformation after ignition; the detailed information is discussed in *Section 2.3.7*.

2.3.7 Mineral phase and the transformation under various ignition conditions

The original and ignited fly ash samples obtained from the LOI tests (*see Section 2.3.6 on Page 29*) were precisely analyzed by XRD, and all tests were run in duplicate. The mineral phase arrays of the original and identified samples were identified by software package Jade 6.0 consulting with the elemental composition got from XRF (*see Section 2.3.3 on Page 27*). The mineral phase composition of three original fly ash samples were shown in Table 2-6.

Table 2-6 Mineral phase composition in the original samples of fly ash

Mineral phase	Formula	Fly ashes		
		S	R	K
Anhydrite	CaSO ₄	√	√	√
Carbon	C	√		
Calcite	CaCO ₃	√	√	√
Calcium Chloride Hydroxide	CaClOH		√	√
Chlorocalcite	KCaCl ₃		√	
Friedel's salt	Ca ₂ Al(OH) ₆ Cl·2H ₂ O	√		
Halite	NaCl	√	√	√
Lime	CaO	√		√
Mayenite	Ca ₁₂ Al ₁₄ O ₃₃	√		
Portlandite	Ca(OH) ₂			√
Sylvite	KCl	√	√	√

Due to the over-whelming high contents of Ca and Cl in fly ash (*see Table 2-4 on Page 27*), the mineral arrays hereby consist of Ca- and Cl-bearing phases. Considering the strong intensities and the plentiful positions of the peaks of these mineral phases, the phases containing minor or trace elements were easily overlapped and hard to identify. When the fly ash samples were ignited, the mineral transformation thus mainly occurred between the Ca- and Cl-containing phases.

To evaluate the effect of ignition temperature on LOI results, the ignition tests were launched for different periods. However, the results revealed that the mineral phases were almost identical in the samples ignited for 1 or 2 h at the same temperature. The following discussion about the transformation of mineral phases affected by the ignition process is based on the 2 h scenario. The samples from the same source but in different states (original and ignited under various conditions) were sorted as a group, thus three groups are being discussed corresponding to three incineration plants (S, R and K). The XRD patterns of the three groups are presented in Figure 2-4, Figure 2-5 and Figure 2-6 within the 2θ range of 10 (S) /20 (R and K) to 50 deg. where the major peaks of the existing mineral phases can be clearly observed.

Group S

In Group S (*Figure 2-4 on Page 35*), the main mineral phases of the original sample were sylvite (KCl) and halite (NaCl). Their peaks grew weaker when the sample was heated at 440 °C, while not changed obviously even at higher temperatures. Friedel's salt ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$) was only observed in the original state and almost completely disappeared at 440 °C, which implied its thermal sensitivity; while zincite (ZnO) was the only phase that was detected in the ignited samples. According to the bulk analytical results (*Table 2-4 on Page 27*), there should be some Zn-containing phases in the original fly ash, which were not clearly identified on the XRD pattern due to peak position overlap by other major phases or low abundance. With the temperature elevating, the original Zn-containing phases could have been converted to zincite that was stable at higher temperature. Anhydrite (CaSO_4) was detected in each sample, and its intensity did not change dramatically even at high temperature (900 °C). Anhydrite is a mineral phase that can remain unchanged at high temperatures up to 990 °C ([Brown and Dykstra, 1995](#)). Carbon (C) was obviously found in the original state, and gradually decreased as a function of temperature increase. It almost totally disappeared at 900 °C, and it is supposed to be one of the most critical constituents that directly contributes to the elevation of both LOI and TC values by oxidizing and converting to gaseous species such as CO_2 or CO. Both calcite (CaCO_3) and lime (CaO) were identified in the original and 440 °C cases. However, the calcite peak became stronger at 440 °C, while the lime peak became weaker. This might indicate the partial transformation of lime to calcite as a result of carbonation process ($\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$). The decomposition of calcite ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) initiated when the temperature rose from 440 °C toward 700 °C ([Collettini et al., 2013](#)), hence calcite peak disappeared at 700 and 900 °C. According to the TG results (*Figure 2-2 on Page 29*),

an obvious weight loss occurred during 440-700 °C, so besides carbon, calcite decomposition might also contribute to this mass loss. The peak of lime and calcite disappeared and mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) became more outstanding concurrently when ignited at 700 °C, which implied that lime might have involved in the formation of the other mineral phases. The peak of mayenite was more obvious at higher temperature. Few changes of mineral phases were observed when the temperature rose to 900 °C.

Group R

In Group R (*Figure 2-5 on page 36*), sylvite, halite and calcium chloride hydroxide (CaClOH) were the major mineral phases in the original sample. In addition, anhydrite, calcite and chlorocalcite (KCaCl_3) were among the main phases. In this facility, calcium hydroxide ($\text{Ca}(\text{OH})_2$) is being added at the APC unit to absorb acid gases particularly hydrogen chloride (HCl) from the flue gas. Both calcium chloride (CaCl_2) and calcium chloride hydroxide could be generated from the reaction between calcium hydroxide and hydrogen chloride, however calcium chloride hydroxide took the lead among the mineral assemblages ([Chen et al., 2012](#); [Wang et al., 2010](#)). After ignition at 440 °C, the mineral phase components did not change remarkably. The variation of peak intensities showed different trends- halite remained almost unchanged, while sylvite was detractive. The peak of calcium chloride hydroxide strongly enhanced, and chlorocalcite increased slightly, which indicated the formation of Cl-binding phases at higher temperatures. Anhydrite and calcite also increased in the same manner as in Group S under the same condition.

After ignition at 700 °C, two significant transformations of Cl- and Ca-containing mineral phases occurred. On one hand, the peak of chlorocalcite sharply increased and became the second major phase, whereas calcium chloride hydroxide and sylvite were obviously weakened. This may imply a transformation from calcium chloride hydroxide to chlorocalcite. [Wang et al., \(2010\)](#) attributed the formation of chlorocalcite to a complex carbonation reaction of the CaClOH phase in the presence of KCl . On the other hand, anhydrite disappeared, while chlorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$) began to grow and to play the role of a main mineral phase, which may imply chlorellestadite formation at the expense of anhydrite and Si- and Cl-bearing phases. It was difficult to clearly specify the existence of any Si-containing phase in the ignited samples possibly due to the peak position overlap or the lack of crystalline structure; however, the existence of Si in the system was proved by the bulk analytical results in the original sample (*Table 2-4 on Page*

27). Hence, the recent phase transformation could have happened in the course of ignition. At 700 °C calcite disappeared with the new phase of mayenite emerging, which was similar to a trend in Group S. When ignition temperature rose to 900 °C, the mineral phases did not significantly change comparing with that of 700 °C.

Group K

The mineral phase composition and transformation of Group K (*Figure 2-6 on Page 37*) were generally similar to that of Group R (*Figure 2-5 on Page 36*), which could have been resulted from employing identical APC system in the two plants. The Ca content of the original sample from Plant K was significantly higher than that of Plant R according to the bulk analytical results (*Table 2-4 on Page 27*). Therefore, additional forms of Ca-containing mineral phases, like portlandite ($\text{Ca}(\text{OH})_2$) and calcium silicate (Ca_2SiO_4), were observed in this group. Besides the Ca-containing mineral phases discussed in Group S and R, additional phase transformations were discovered in Group K because of ignition. Portlandite ($\text{Ca}(\text{OH})_2$) was detected in the original state and disappeared after ignition at 440 °C. Lime showed a different performance comparing with Group S under the same condition, and sharply increased after 440 °C ignition, possibly due to the decomposition of portlandite into lime ($\text{Ca}(\text{OH})_2 \rightarrow \text{CaO} + \text{H}_2\text{O}$).

The main mineral phase transformation also seems to have occurred during 440-700 °C. Calcium chloride hydroxide and sylvite strongly decreased while chlorocalcite appeared and became one of the main phases. In addition, chlorellestadite and mayenite began to emerge from 700 °C while anhydrite and calcite disappeared. Moreover, there were two notable differences comparing with the previous groups. Calcium silicate (Ca_2SiO_4) was also generated after 700 °C ignition and remained stable until 900 °C. Besides, lime existed in all samples of Group K; even the peak was more obvious after 900 °C ignition. This might indicate that a fraction of Ca initially formed mineral phases combined with C and S in the system. Then these minerals inclined to combine with Al or Si to form additional phases during the thermal treatment, leading to the formation of more complex products (e.g. chlorellestadite and calcium silicate in Group K). Finally, lime was the terminal (more stable) form of the Ca-containing minerals at higher temperatures when some mineral phases became partially destabilized under the experimental condition. When ignition temperature rose to over 900 °C, mineral phase composition did not significantly change comparing with that of 700 °C, similar to a trend that was observed in the Groups S and R.

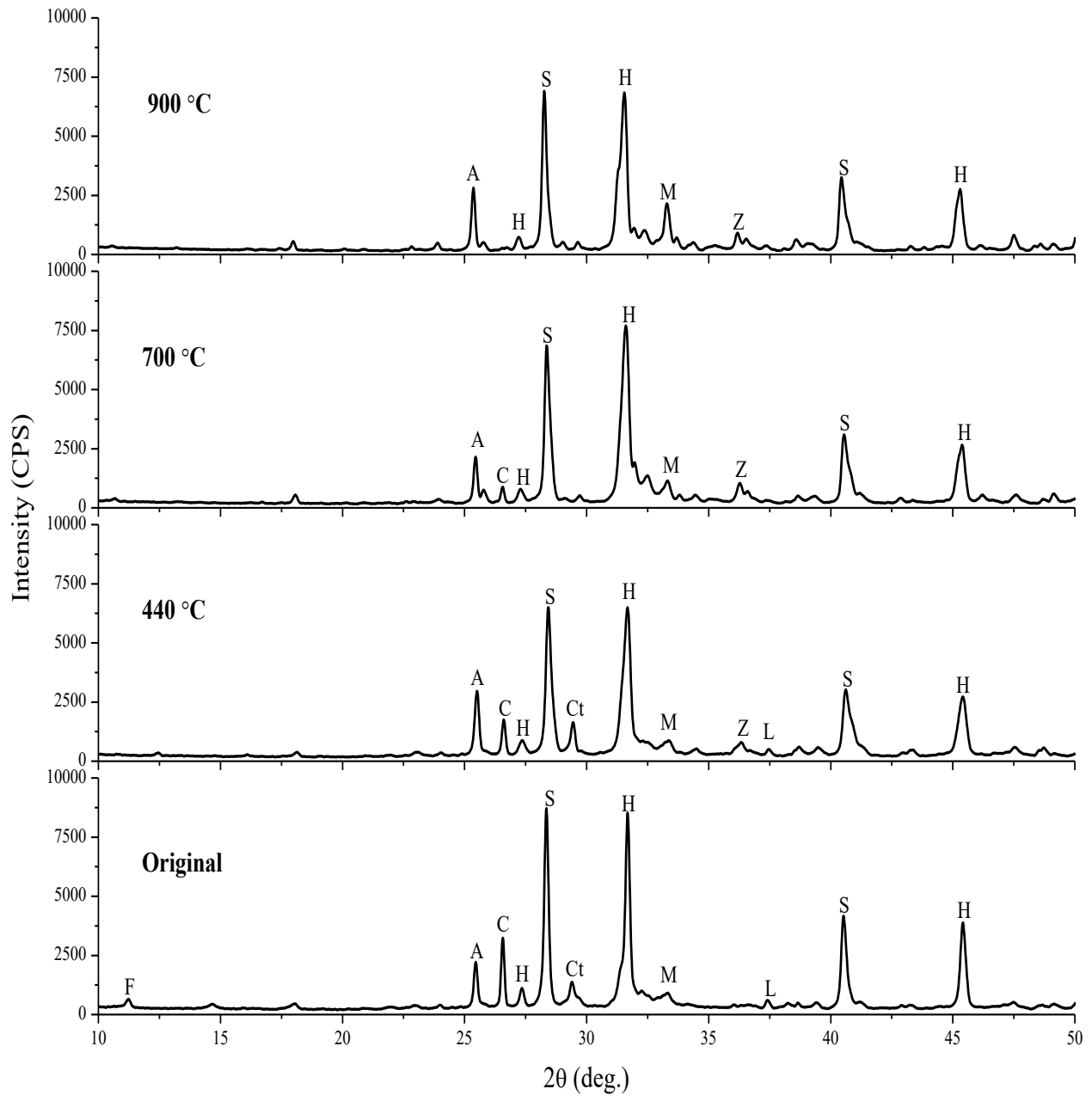


Figure 2-4 XRD patterns of Group S

A: anhydrite (CaSO_4), C: carbon (C), Ct: calcite (CaCO_3), F: Friedel's salt ($\text{Ca}_2\text{Al}(\text{OH})_6\text{Cl}\cdot 2\text{H}_2\text{O}$), H: halite (NaCl), L: lime (CaO), M: mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$), S: sylvite (KCl), Z: zincite (ZnO).

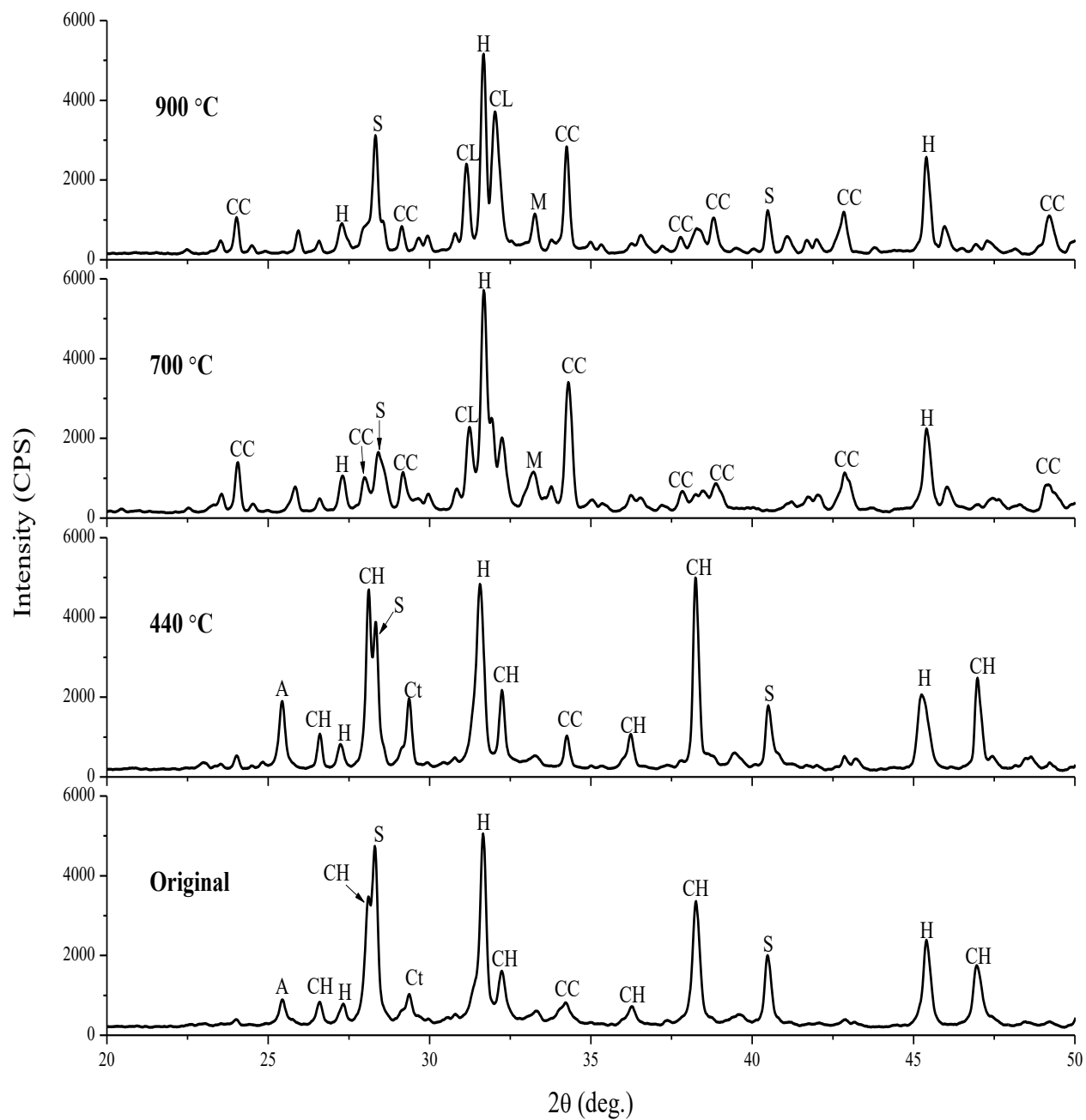


Figure 2-5 XRD patterns of Group R

A: anhydrite (CaSO_4), CC: chlorocalcite (KCaCl_3), CH: calcium chloride hydroxide (CaClOH), CL: chlorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$), Ct: calcite (CaCO_3), H: halite (NaCl), M: mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$), S: sylvite (KCl).

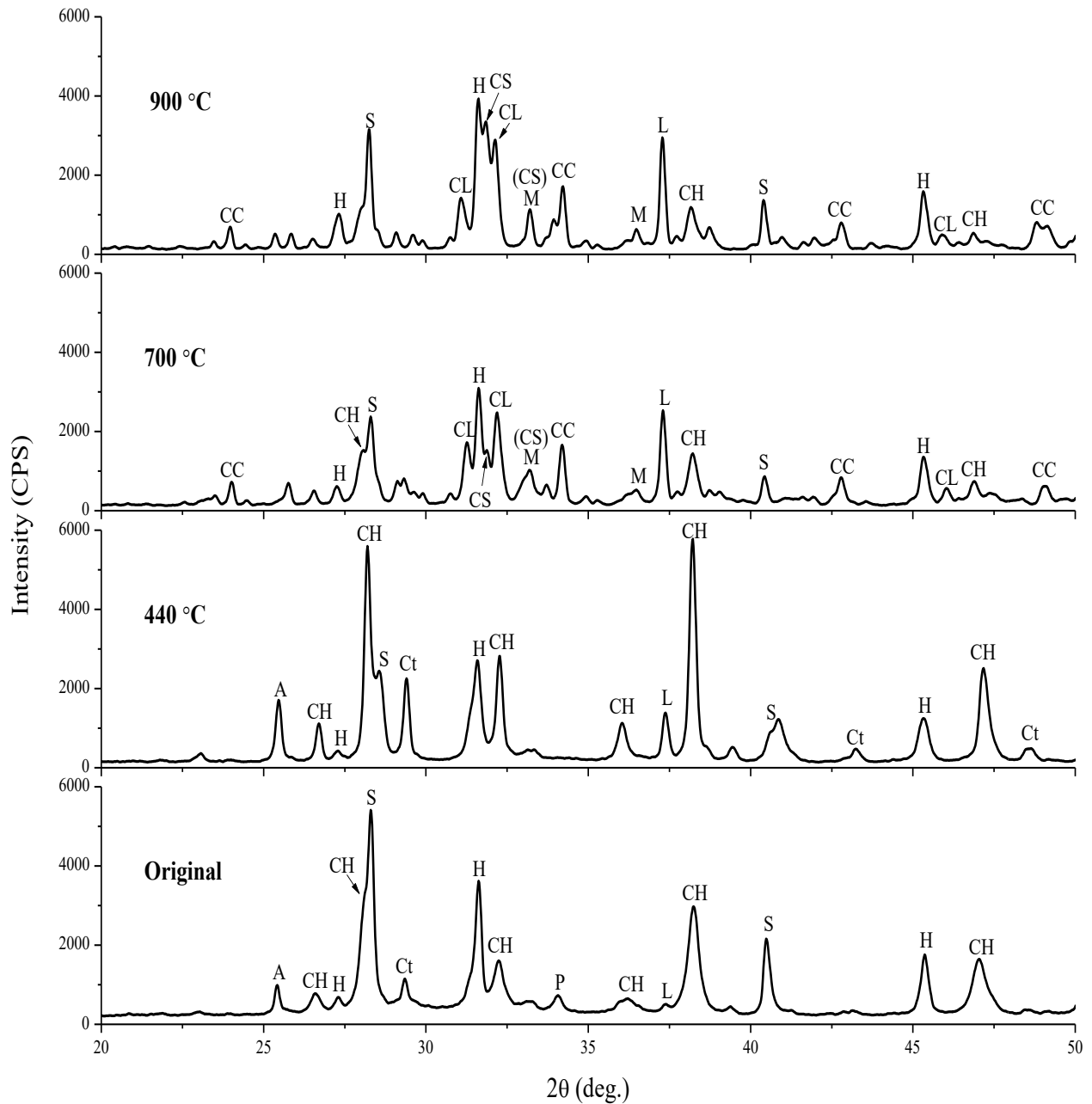


Figure 2-6 XRD patterns of Group K

A: anhydrite (CaSO_4), CC: chlorocalcite (KCaCl_3), CH: calcium chloride hydroxide (CaClOH), CL: chlorellestadite ($\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{Cl}_2$), CS: calcium silicate (Ca_2SiO_4), Ct: calcite (CaCO_3), H: halite (NaCl), L: Lime (CaO), M: mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$), P: portlandite ($\text{Ca}(\text{OH})_2$), S: sylvite (KCl).

To sum up, generally the mineral phases did not change dramatically until ignition at 440 °C. LOI partially resulted from the loss of structural water and the decomposition of some unstable minerals (e.g. Friedel's salt in Group S and $\text{Ca}(\text{OH})_2$ in Group K). Significant mineral phase transformations occurred between 440-700 °C, during which LOI increased more remarkably. MSWI fly ash is a Ca- and Cl-rich material; therefore, the mineral phase transformation was essentially related with Ca- and Cl-containing phases. The behavior of some mineral phases such as anhydrite or lime varied in different samples under the same ignition condition. This implied that the mineral phase transformation and the occurrence of newly formed phases were determined not only by the ignition condition but also by the content of the co-existing components. Mineral phase components rarely changed when ignition temperature rose from 700 to 900 °C.

Accordingly, the transformation of mineral phases was construed as a critical factor that could be affected by the ignition process for estimating the mass loss (viz. LOI). The reactions occurred under different ignition conditions may involve varied elements in the process of mass loss, which may cause certain deviation of the results. In turn, the mineral phase transformation is also helpful to understand the source of LOI and to select the proper condition for specific objectives. On the viewpoint of using LOI as a parameter for elemental composition analysis, the priority should be given to preventing/minimizing the breakdown of the original array of minerals of fly ash when determining the test condition, that is with special emphasis on the liberation of unbound moisture, the volatile species such as organic carbon, and the decomposition of unburned materials in the course of ignition process. As a consequence of this part of research, the lowest ignition temperature (440 °C) for 2 h was suggested as a principal measurement condition of LOI in MSWI fly ash.

2.4 Section summary

MSWI fly ash was one of the main solid residues from the incineration process, which was worldwide classified as hazardous waste and needs further treatment before the final disposal in landfill sites.

Because of the alkaline sorbent addition in the APC unit for the absorption of the acid gas, MSWI fly ash was in quite high pH (> 12). The particle size distribution proved that fly ash was in fine particles. According to the chemical composition analysis, Ca and Cl was at an overwhelming high concentration, and Zn and Pb took the two major elements among the metals. From

the leaching test, main leachable elements could be observed; the main leachable heavy metals were Pb and Zn, while Pb concentration was much higher than that of Zn, which was opposite to the chemical composition. Therefore, the research on the stabilization of heavy metal in MSWI fly ash would primarily focus on Pb. The XRD patterns were shown that there was abundant content of soluble salts. The feature of the mineral phase transformation was also observed after the ignition. Generally, the mineral phases did not change dramatically until ignition at 440 °C. LOI partially resulted from the loss of structural water and the decomposition of some unstable minerals (e.g. Friedel's salt in Group S and Ca(OH)_2 in Group K). Mineral phase components rarely changed when ignition temperature rose from 700 to 900 °C. Significant mineral phase transformations occurred between 440-700 °C, during which LOI increased more remarkably. MSWI fly ash is a Ca- and Cl-rich material; therefore, the mineral phase transformation was essentially related with Ca- and Cl-containing phases. The behavior of some mineral phases (such as anhydrite or lime) varied in different samples under the same ignition condition. This implied that the mineral phase transformation and the occurrence of newly formed phases were determined not only by the ignition condition but also by the content of the co-existing components. It was supposed to present some information about the heavy metal phases in the fly ash, but the peaks could not be identified due to the position overlap with the strong peaks of the major phases.

Chapter 3 Feasibility of natural fishbone on the stabilization of heavy metals in MSWI fly ash

3.1 Introduction

Fishbone has been reported as one of the natural sources of hydroxyapatite (HAP) which is deemed possessing an ability of stabilizing divalent metals via generating the insoluble metal-HAP phases. Therefore, some investigations that using HAP from various sources (including fishbone) to stabilize or remove heavy metals from contaminated environments have been released (*see Section 1.3.2*). Heavy metals were also of high concerns in the treating process of municipal solid waste incineration (MSWI) fly ash because of their leachabilities and toxicities. Many techniques have been developed for the implements of heavy metals in MSWI fly ash, most of which, however, are with their own drawbacks (*see Section 1.2.4*). In addition, there has rare studies about using waste fishbone on the stabilization of heavy metals in MSWI fly ash. In Chapters 3-4, the utilization of fishbone on the stabilization of heavy metals in MSWI fly ash would be investigated. In this chapter, the feasibility of natural fishbone on the stabilization of heavy metals in MSWI would be verified firstly.

There is a specification in advance. As mentioned in *Section 1.2.2*, fly ash is usually exhausted as a part of APC residue, thus many researches on the entrapment of heavy metals in MSWI fly ash actually used the sample of APC residues instead. And in the present research, APC residues were also employed. Considering that the heavy metals are essentially derived from fly ash, the term APC residue is considered equal with the term fly ash in most cases of the context.

In this research, Pb was primarily focused on as the main target heavy metal that needed to stabilize in MSWI fly ash based on its leachability (*see Section 2.3.4*) and environmental significance. Besides, Zn and Cu were also under the supervision; the former was secondly abundant element in the leachate of MSWI fly ash, and the latter was in varied performances under the different experimental conditions. Although there have been some references in other contaminated environments, the feasibility of using natural fishbone on the stabilization of heavy metals in MSWI fly ash still needs to verify. Because MSWI fly ash with alkaline sorbent included

was providing an extremely high-pH ambient for the reactions of the stabilization, which is quite different from the controlled conditions given in the most experiments in other previous researches.

Considering the resemblance among MSWI fly ashes from different sources (*see Chapter 2*), the representative sample would be adopted for the experiments of the stabilization reaction with fishbone. Then the fly ash from MSWI plant K in Japan (mentioned as *fly ash K*) was selected, because Pb and Zn in the leachate were in a relatively high concentration comparing the other two MSWI fly ash samples. There were three kinds of fishbone collected from the markets, and the mineral components of them were tested, in order to confirm the existence of HAP and whether any differences resulting from the fish species. Then two kinds of fishbone were selected to involve in the experiments of the stabilization of heavy metals in MSWI fly ash.

From the viewpoint of the implement of 3R approach (*see Section 1.1.2*), the primary strategy for waste disposal should be reuse-oriented after the treatment. Therefore, the separation process for the entrapment of heavy metals was taken into account as the primary experimental scenario. Batch leaching test was selected, because it is a generally accepted method for estimating the environmental impact of heavy metals via measuring the amount that leached out during the tests. There would be more setups that are tested in the following study, so this experiment was called as *Plan A* for distinguishing with other schemes.

In *Plan A*, the natural fishbones were simply pre-treated into powder and directly added during the leaching process of MSWI fly ash. The results got from different fishbones would be compared for the estimate whether fish species would affect the effectivity on the stabilization of heavy metals or not. The effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash was calculated by the sequestration amount of heavy metal detected in the leachate. In addition, the capacity of fishbone on heavy metal stabilization was assessed via the amount of heavy metal stabilized by the unit weight of fishbone. Moreover, the relevant or irrelevant factors on the reaction of stabilization were also recorded. The outline and structure of Chapter 3 are shown in Figure 3-1.

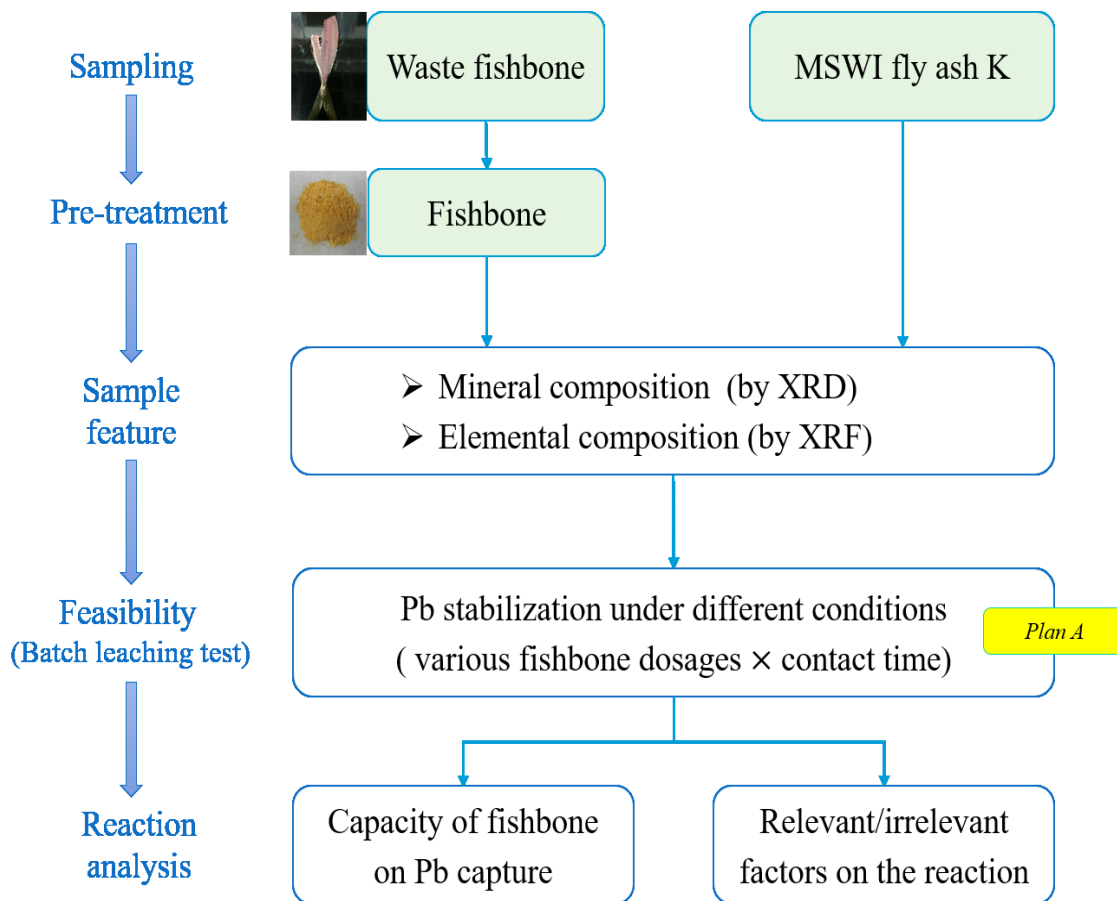


Figure 3-1 Outline and structure of Chapter 3

3.2 Experiments

3.2.1 Collection and preparation of lime-treated MSWI fly ash

MSWI Fly ash K was obtained from an incineration plant located in City K, Japan (one of the fly ashes used in Chapter 2). It was selected as the representative, for Pb and Zn were relatively abundant in its leachate (see Table 2-5 on Page 28). The original fly ash sample was in dry state, the moisture content of which was below 2% tested by freeze-drying, thus it was directly used for the reaction of heavy metal stabilization with fishbone, except the X-ray fluorescence (XRF) analysis. For accurate elemental composition, fly ash K was ground by mill and dried in oven at 105 °C before XRF test in order to avoid the deviation caused by moisture.

3.2.2 Collection and pre-treatment of fishbone

Three kinds of fishbone, including *Japanese horse mackerel* (*Aji* in Japanese), *White croaker* (*Guchi* in Japanese) and *Lizardfish* (*Eso* in Japanese), were collected from the market in City F, Japan, which are all common commercial fishes daily supplied to the Japanese customers. For easy recognition in this thesis, their Japanese names (*Aji*, *Guchi*, *Eso*) would be used in all cases that fishbone name were needed. The collected fishbone was wet but almost free from soft tissues. To obtain the clean fishbone (rare in meat or other organic components) and improve the availability that fit for experiments, pre-treatments were carried as followed. The original fishbone was boiled for 5 min, and then cleaned by brush to exclude all soft tissues on the surface. The clean fishbone was dried until becoming hard and friable in an oven at 40 °C. The dried fishbone was ground into powder state (*Figure 3-2*). The fishbone powder is used in the experiments with the target to test the feasibility and effectivity of natural fishbone on the stabilization of heavy metal in MSWI fly ash.

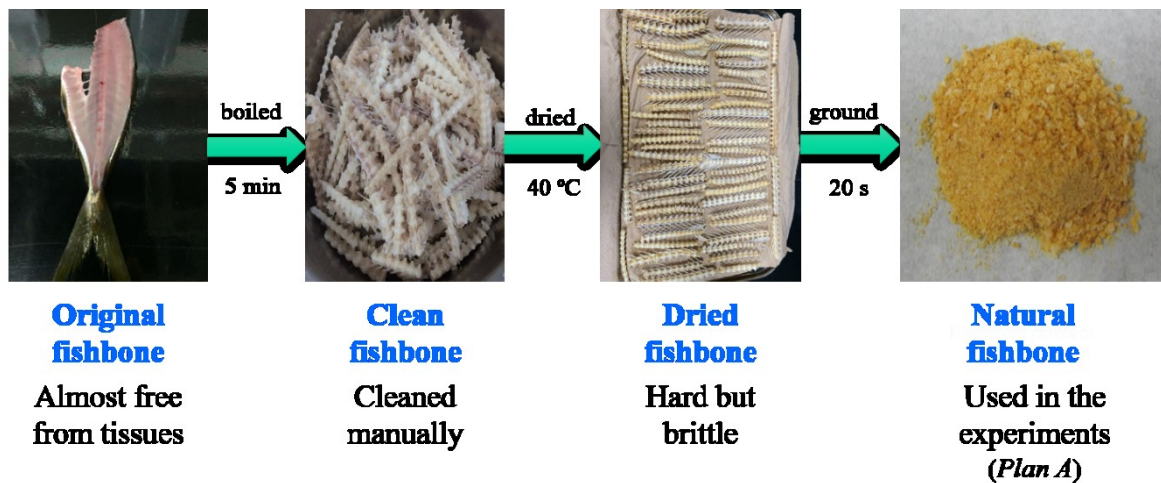


Figure 3-2 Pre-treatment process on fishbone (Eso as example)

3.2.3 Bulk compositional analysis

The solid samples of both fly ash and fishbone were conducted by XRF measurements for the compositional information, but the preparation processes and devices were different based on their statuses. For fly ash, the sample was ground by mechanical milling machine for 1 min and then dried in an oven at 105 °C until a relatively constant mass in order to avoid the deviation caused

by moisture. Then the elemental composition were determined by XRF (ZSX Primus II, Rigaku), the essential parameter LOI of which was measured under 440 °C/2 h scenario (*more details in Chapter 2*). For fishbone, the elemental composition of natural fishbone powder was directly determined by a compact XRF apparatus (EDX-7000, Shimadzu) using standardless measurement technique.

The concentration of target elements in the leachate of MSWI fly ash from batch leaching tests under various conditions was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES, 720 ICP-OES, Agilent Technologies) and Ion Chromatography (IC, DX-120, Dionex).

3.2.4 Mineral phase detection

The mineral phases of fishbone and fly ash were analyzed by X-ray diffractometry (XRD, Rigaku Multiflex) using $CuK\alpha$ radiation generated at the voltage of 44 kV and the beam current of 30 mA. Specimens were scanned from 2-75 deg. (2θ) by 0.02 deg. (2θ)/step, and the X-ray irradiation time of 2 sec./step. The mineral phases were identified by the software *Jade 6.0*.

3.2.5 Stabilization of heavy metals in MSWI fly ash via adding natural fishbone during leaching process (*Plan A*)

The effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash was primarily verified by directly adding natural fishbone into the leaching process of fly ash (*Plan A*). In this scheme, fishbone was supposed to be the additive involved in the separation process of heavy metal from MSWI fly ash (*see Figure 1-5 on Page 11*). There are two kinds of fishbone selected for the batch leaching test, which were Aji and Eso. Actually, the experiments for verifying the feasibility of fishbone on the stabilization of heavy metal in MSWI fly ash were conducted stepwise; Aji was involved as preliminary test, thanks to which the experiments in Eso case could be designed more reasonably. Therefore, the experiments of Aji and Eso were sharing some resemblance instead of in parallel.

Batch leaching tests were conducted in 250 ml polypropylene bottles at room temperature. All bottles were shaken at a speed of 200 rpm with leak-proof lid. To obtain leachate, bottles were centrifuged at 3000 rpm for 20 min, then solid and liquid parts were separated by vacuum filtration through 0.45 μ m pore-size membrane. The leachate was stored in a polypropylene bottle for further analyses.

In the batches of Aji group, every experimental set consisted of 5 bottles, each containing 10.00 g of fly ash, 100.0 ml of super-pure water as leachant and different doses of Aji fishbone. The following doses of fishbone were supplied to each bottle: 0, 0.50, 1.00, 1.50, 2.00 g in order to obtain various fishbone/fly ash ratios at 0 (control group), 5%, 10%, 15%, 20% (test groups) by weight. Contact times of 3, 6, 24 and 72 h were investigated.

In the batches of Eso group, every experimental set consisted of 9 bottles, each containing 10.00 g of fly ash, 100.0 ml of super-pure water as leachant and different doses of Eso fishbone. The following doses of fishbone were supplied to each bottle: 0, 0.50, 1.00, 1.50, 2.00, 3.00, 5.00, 7.00, 10.00 g in order to obtain various fishbone/fly ash ratios at 0 (control group), 5%, 10%, 15%, 20%, 30%, 50%, 70% and 100% (test groups) by weight. Contact times of 3, 6 and 72 h were investigated. The experimental setup of *Plan A* was shown in Figure 3-3.

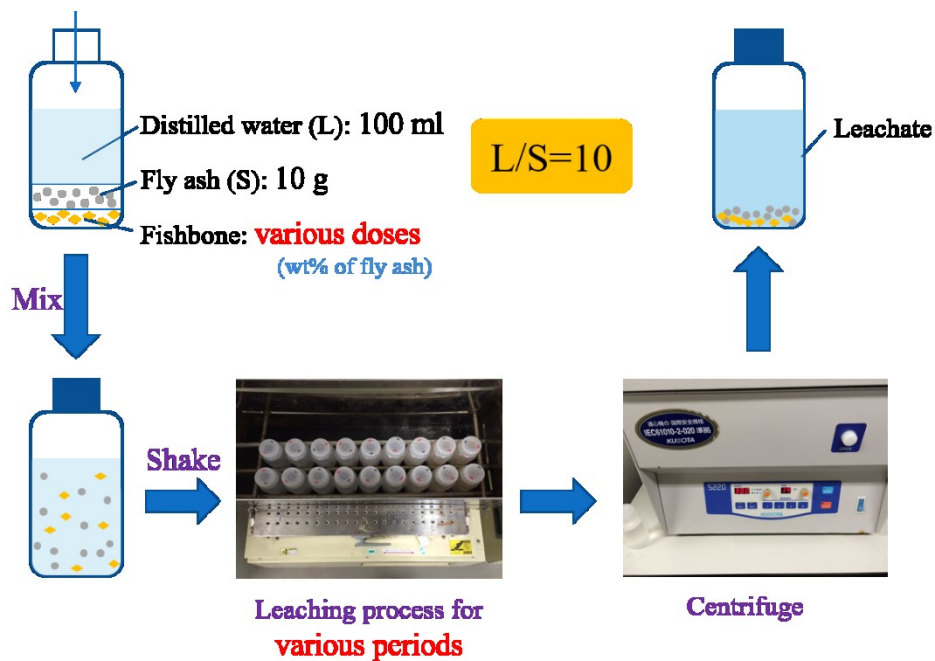


Figure 3-3 Experimental setup of *Plan A*

3.2.6 pH measurement

The pH of all the leachates from each leaching batch was tested by pH meter (F-53, Horiba).

3.3 Results and discussion

3.3.1 Elemental and mineral composition of MSWI fly ash

Elemental and mineral composition of the fly ash K were analysed by XRF and XRD, and the results were presented in Table 3-1 and Figure 3-4.

Table 3-1 Elemental composition of MSWI fly ash K

Composition (mass %)	CaO	SiO ₂	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	P ₂ O ₅
Fly ash K	54.31	4.02	4.36	2.82	2.44	2.10	0.72
Composition (mass %)	Fe ₂ O ₃	TiO ₂	MnO	Cl	S	F	LOI*
Fly ash K	0.80	0.56	0.03	19.78	1.55	0.07	5.12
*LOI displays the representative values obtained from 440 °C/2 h scenario.							
Composition (ppm)	Zn	Pb	Cu	Sb	Ba	Cr	Sr
K	9322	1850	500	557	239	142	312
Composition (ppm)	Cd	Sn	Ni	As	Co	V	
K	181	46	38	12	9	1	

According to the XRF results, Ca, Cl, Na, Si, K, Mg, Al and S were the major elements, the contents of which were over 1%. As explained above (*see Section 3.2.1*), the fly ash sample was mixed with slaked lime (Ca(OH)₂) that was added for acid gas abatement (mainly HCl), thus Ca and Cl were found in an overwhelming high concentration (55% and 20%). Among heavy metals, Zn and Pb were much more abundant than other elements. Besides the elements mentioned above, the other elements in lower concentration were counted as minor and trace constituents.

The minerals detected in fly ash K was well in line with the results of elemental composition. Owing to the over-whelming high contents of Ca and Cl, the mineral arrays hereby consist of Ca- and Cl-bearing phases. And the phases were almost in high solubility, hence the leachate would be quite rich in soluble salt. Out of the expectation, the phases containing minor or trace elements (including Pb and Zn) were easily overlapped and hard to identify due to the strong intensities and the plentiful peaks of Ca- and Cl-containing mineral phases. In addition, the portlandite (Ca(OH)₂) was detected out, which means that the sample would be in a quite high pH condition.

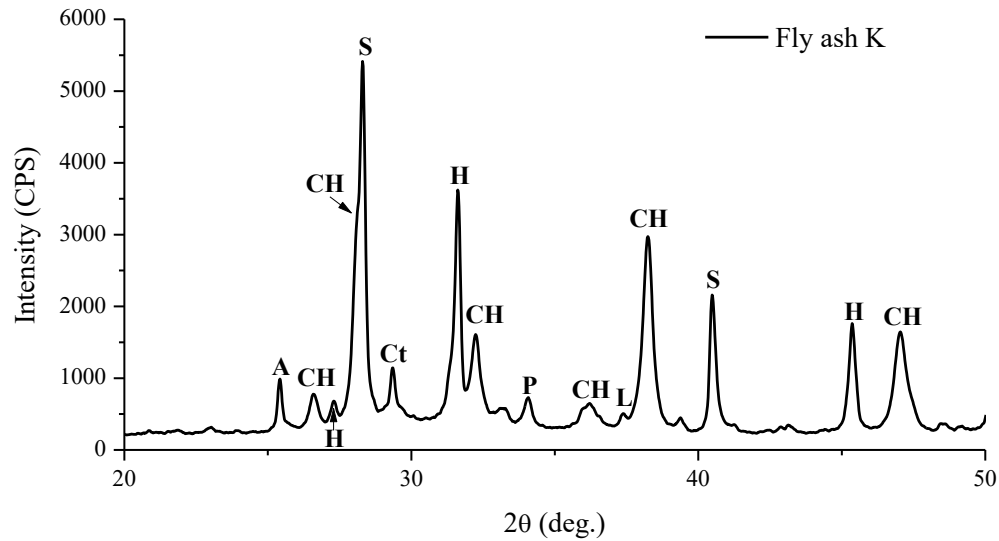


Figure 3-4 XRD pattern of MSWI fly ash K

A: anhydrite (CaSO_4), **CH:** calcium chloride hydroxide (CaClOH), **Ct:** calcite (CaCO_3), **H:** halite (NaCl), **L:** Lime (CaO), **P:** portlandite (Ca(OH)_2), **S:** sylvite (KCl).

3.3.2 Leachable elements from MSWI fly ash

MSWI fly ash was exposed to a 6 h-leaching process, and then the detectable elements in the leachate were analyzed by ICP-AES and IC, the results of which were shown in Table 3-2.

In accordance with the results of elemental and mineral composition (*Table 3-1 and Figure 3-4*), Ca, K, Na and Cl were leached out which were the main co-existing elements in the leachate. And in the part of heavy metal, Zn and Pb were also most abundant among other metals in the leachate, which is similar to original fly ash sample; however, the concentration of Pb was considerably higher than that of Zn. It is indicated that Pb was more leachable than Zn from MSWI fly ash. Considering the toxicity and environmental significance, Pb was primarily focused on in the stabilization of heavy metals in MSWI fly ash. Additionally, there is rare P leached out from MSWI fly ash.

Table 3-2 Leachable elements from MSWI fly ash

Elements (mg/l)	Pb	Zn	Cu	Cr	Mo	V	Fe
Fly ash K	30.50	8.23	0.15	0.14	0.09	0.03	0.02
Elements (mg/l)	Ca	K	Na	Mg	Cl	SO ₄ ²⁻	P
Fly ash K	8841.90	4643.85	3507.23	0.06	25351.61	867.29	0.01

3.3.3 Mineral and elemental composition of various fishbones

Various fishbones were collected for verifying whether any obvious differences about HAP supplying might be brought by fish type. Mineral composition of the fishbones were analyzed by XRD, and the results was presented in Figure 3-5.

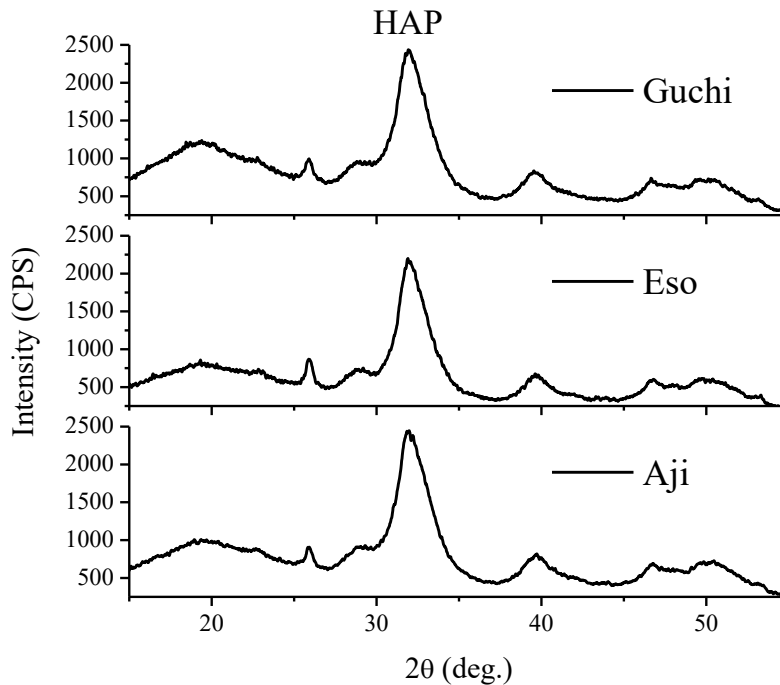


Figure 3-5 XRD patterns of various fishbones

The XRD analysis proved that HAP was the only main phase in fishbone regardless of the fish type, and even the intensities of different XRD patterns were almost at the equal level, which means that the content of HAP in the samples were the same.

Then two fishbones were picked up to conduct the elemental analysis by XRF, and the results were shown in Table 3-3.

Table 3-3 Elemental composition of fishbones

Contents (wt%)	Ca	P	K	S	Sr	Fe	Si	Zn	Cu
Fishbone Aji	79.19	16.75	1.51	1.46	0.65	0.16	0.15	0.07	0.04
Fishbone Eso	76.49	20.05	0.88	1.58	0.43	0.05	0.19	0.10	0.03

The results shown in Table 3-3 indicated that the chemical composition and the contents of various elements were almost the same in different fishbones. Ca and P were the only two major elements in fishbone, which jointly took over 96% by weight. Besides these two elements, the other elements presented lower concentrations, especially the heavy metals in fishbone is considerably low.

Therefore, it was proved that fishbone was a natural source for pure HAP with rare heavy metal content which could be an appropriate alternative for heavy metal stabilization. And fishbone type does not bring any significant differences in the HAP supplying, so waste fishbone could be mixed for this kind of utilization, and it is very possible that this application could be generalized over regions and fish types.

3.3.4 Effectivity of natural fishbone on heavy metal stabilization in MSWI fly ash during leaching process

Both fishbones Aji and Eso were conducted the experiments that verifying the effectivity of natural fishbone on the stabilization of heavy metals in MSWI fly ash. Actually the experiments with fishbone Aji was launched prior to that of fishbone Eso in order to detect the proper experimental condition, which worked as a preliminary experiment. Thus the experiments with fishbones Aji and Eso would be introduced in sequence in order to explain the design of the whole experiments.

The effectivity of Aji fishbone on the stabilization of Pb in MSWI fly ash during leaching process were primarily explored under different fishbone dosages and contact times. Batch leaching tests were conducted under different Aji fishbone/fly ash ratios as 0 (control group), 5%, 10%, 15% and 20% (test groups) by weight and various contact times as 3, 6, 24, and 72 h. Then the concentration of heavy metal (especially Pb) and potential relevant element (P) in the leachates were identified by ICP-AES. The effectivity of fishbone on Pb stabilization was represented by Pb

removal efficiency in the leachate, which was calculated as the percentage of the sequestered fraction of Pb in the leachate of each test group relative to the Pb concentration in the leachate of its control group (*Equation 3-1*). The results of Pb and P concentration and the correlation between Pb removal efficiency and P concentration in the leachates at the absence/presence of Aji fishbone were are shown in Table 3-4 and Figure 3-6.

$$\text{Pb removal efficiency (\%)} = \left(1 - \frac{C(\text{Pb in test group})}{C(\text{Pb in control group})} \right) \times 100 \quad 3-1$$

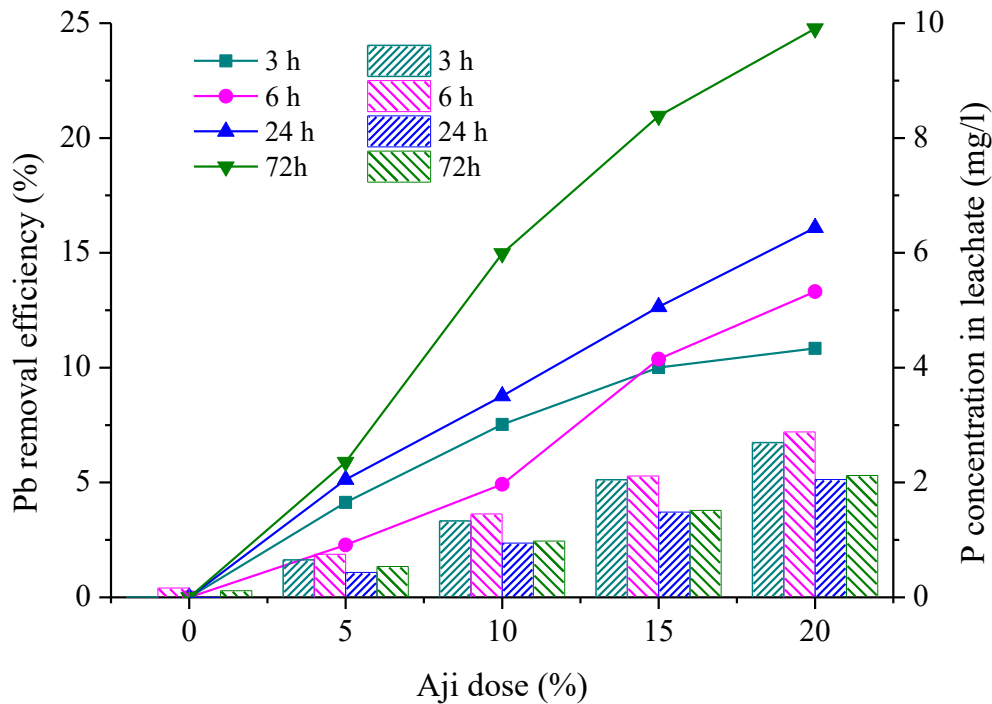


Figure 3-6 Correlation between Pb removal efficiency (solid lines) and P concentration in the leachate (vertical bars) under various Aji doses and different contact times (*Plan A*)

Table 3-4 Concentration of Pb and P in the leachates of fly ash with Aji fishbone (*Plan A*)

Aji dose (%)	Pb (mg/l)				P (mg/l)			
	3 h	6 h	24 h	72 h	3 h	6 h	24 h	72 h
0	31.65	27.67	29.78	29.75	0.01	0.16	0.00	0.12
5	30.34	27.04	28.25	28.00	0.65	0.75	0.43	0.54
10	29.26	26.31	27.17	25.30	1.33	1.45	0.95	0.98
15	28.48	24.80	26.01	23.52	2.05	2.11	1.49	1.52
20	28.21	23.99	24.99	22.38	2.69	2.88	2.05	2.12

The results shown in Table 3-4 and Figure 3-6 proved that the Pb could be leached out from fly ash within the first few hours. Aji fishbone could stabilize Pb by directly added into the leaching process of MSWI fly ash, and the stabilization was proceeding with the time, thus higher dosage of fishbone and longer contact time both benefited the stabilization. In the given range, Pb removal efficiency were in a linear growth with the fishbone adding, and the highest Pb removal efficiency reached 24.76% after a 72 h-leaching process when Aji fishbone dosage was 20%. However, Pb removal efficiency has reached 16% when the contact time was 24 h, hence whether extending contact time for higher Pb removal efficiency is necessary and acceptable should be further confirmed in bigger dosage fishbone addition condition.

There is rare P initially in the leachate of MSWI fly ash, while P concentration were increased after the fishbone addition, which suggested that P in the leachate almost totally derived from Aji fishbone. P was released by fishbone in the first few hours (at least 6 h) and then there was an obvious decline of P content in the leachate between 6-24 h, while the Pb removal efficiency continuously increased during across the whole period, presumably the reduction of P in the leachate after longer contact time has been involved in Pb stabilization. This evidence supports the idea that Pb immobilization by fishbone (HAP) is a dissolution-precipitation mechanism (*see Section 1.3.2 on Page 14*). The highest P concentration of 2.88 mg/L appeared in the leachate of the 6 h-leaching test when the dosage of Aji fishbone was 20%, which receded to 2.12 after the 72 h leaching process.

Besides Pb, divalent metals of Zn and Cu were also observed, through both of which were not included in the list of the chemicals or elements controlled in landfill sites in the environmental standards due to their low toxicities. Out of the expectation that basing on the mechanism of the reaction between HAP and divalent metals (*see Equation 1-1 and 1-2 on Page 14*) which assumed that HAP should stabilized Cu and Zn concurrently with Pb, the concentration of Cu and Zn were increased, especially there is a distinct increasing trend for Cu in the leachates. The concentration of Cu and Zn in the leachates at the absence/presence of Aji fishbone is shown in Table 3-5.

Table 3-5 Concentration of Cu and Zn in the leachates of fly ash with Aji fishbone (*Plan A*)

Aji dose (%)	Cu (mg/l)				Zn (mg/l)			
	3 h	6 h	24 h	72 h	3 h	6 h	24 h	72 h
0	0.22	0.13	0.10	0.07	8.69	6.87	10.33	7.29
5	0.31	0.31	0.58	2.40	8.77	6.99	10.64	7.76
15	0.39	0.49	1.09	3.91	8.98	7.08	11.00	7.30
15	0.44	0.67	1.65	5.36	9.08	6.94	11.20	7.43
20	0.50	0.86	2.22	6.45	9.52	7.06	11.11	7.81

It was shown that both Cu and Zn would be increased in the leachates after adding Aji fishbone into the leaching process of fly ash. The increment of Zn concentration in the leachates with the fishbone addition was slight, and the amount of increasing was uncorrelated with the contact time; while Cu concentration in the leachates with the fishbone addition was increased dramatically, and the increment were obviously impacted by the contact time. However, because of the much lower content in the initial solid fly ash, the amount of Cu in the leachates was consistently lower than that of Zn and Pb even after 72 h leaching process. Little amount of Cu and Zn were detected in fishbone powders (*see Table 3-3 on Page 49*), thus the additional Cu and Zn were more likely from fly ash. It implied that fishbone might provide some matters that prompting Cu and Zn released from fly ash, which might be the non-HAP components (like organic matters) in the fishbone powder.

As the attempt of using fishbone on the stabilization of heavy metal in MSWI fly ash, the experiments using Aji fishbone proved the feasibility. Additionally, some notable findings that differ from other previous researches, as well as some evidences for the discussion of the mechanism of the stabilization of heavy metal by fishbone, were observed, which would be confirmed and further discussed in the analogical experiments using Eso fishbone.

As reviewed in Chapter 1, an inevitable defect of the current main technology for heavy metal stabilization in MSWI fly ash is that the final products would be in a much bigger volume (*see Section 1.2.4 on Page 11*). According to the observation in the present experiments, the volume of the final product (the mixture of fishbone and fly ash) was not increased dramatically because of the differences on the particle size and the density between fly ash and fishbone powder. Moreover, the solid mixture was roughly layered after the centrifugation, which make the separation of them a possibility. Therefore, adopting a bigger dosage of fishbone for a better Pb removal efficiency was taken into account in the experiments of Eso cases.

Batch leaching tests were conducted under different Eso fishbone/fly ash ratios as 0 (control group), 5%, 10%, 15%, 20%, 30%, 50%, 70% and 100% (test groups) by weight and various contact times as 3, 6 and 72 h. Then the concentration of target elements (Pb, Cu, Zn and P) in the leachates were identified by ICP-AES. The Pb removal efficiency in the leachate was also calculated by Equation 3-1 (*Page 50*). The results of Pb and P concentration and the correlation between Pb removal efficiency and P concentration in the leachates at the absence/presence of Eso fishbone are shown in Table 3-6 and Figure 3-7.

Allowing the nuance among the fly ash samples, the results shown in Table 3-6 and Figure 3-7 indicated that the Pb could be leached out from fly ash within the first few hours. Eso fishbone could also stabilize Pb by directly added into the leaching process of MSWI fly ash, and the stabilization was proceeding with the time, thus both higher dosage of fishbone and longer contact time benefited to the effectivity of fishbone for Pb sequestration from the leachate. However, excessive long contact time was not that effective on the improvement of Pb stabilization by fishbone- The highest Pb removal efficiency reached 59.31% after a 72 h leaching process when the fishbone was added at an equal weight with fly ash. However, it has reached 55.20% when the contact time was only 6 h. This means that only 3.12 mg/l of Pb on average was sequestered from the leachates when contact time was extended from 6 h to 72 h. Considering the energy

consumption, therefore, higher dosage of fishbone was more effective and recommended for enhancing the Pb stabilization in this scenario. Comparing the growth of Pb removal efficiency in low fishbone dosage (< 30%) and higher fishbone dosage (> 50%), the excess fishbone could not result in higher Pb removal efficiency as expected. Possibly the lower Pb concentration in the leachate reduced the metal ion supply for metal-apatite formation (*see Equation 1-1 and 1-2 on Page 14*).

Table 3-6 Concentration of Pb and P in the leachates of fly ash with Eso fishbone (*Plan A*)

Eso dose (%)	Pb (mg/l)			P (mg/l)		
	3 h	6 h	72 h	3 h	6 h	72 h
0	28.46	30.50	27.78	0.06	0.01	0.08
5	27.10	29.26	26.29	0.27	0.21	0.26
10	26.63	27.75	24.58	0.47	0.42	0.43
15	25.33	26.58	22.87	0.72	0.70	0.65
20	24.88	25.40	21.53	0.96	0.88	0.79
30	23.15	21.90	18.84	1.39	1.48	1.17
50	20.53	18.59	15.56	2.47	2.65	2.06
70	17.86	16.05	12.86	3.66	4.07	3.50
100	15.29	13.66	11.30	5.27	6.09	5.02

Same as what observed in Aji cases, the amount of P that released from fishbone was increasing in the first few hours (at least 6 h) and then sequestered from the leachate, and Pb removal efficiency increased continuously. Thanks to the bigger dosage of fishbone in Eso cases, the difference of P concentration between 6 and 72 h could be clearly displayed in Figure 3-7. It is shown that the decrement of P was correlated with the sequestration of Pb from the leachate, which is demonstrated that there was P involved in Pb stabilization in the leachate via the dissolution-precipitation mechanism. This fluctuation of P contents (increasing followed by decreasing) in the leachates implied that P was released by fishbone and involved in Pb stabilization were synchronized. The two reactions were taken the advantage successively- in the

first few hours (at least 6 h), the fishbone released P more than that used in Pb stabilization; while the formation of Pb-HAP expended P faster than that released or the release of P was decelerated with the Pb-HAP generation in course of time. It should be pointed that though the existence of dissolution-precipitation pattern on Pb stabilization by HAP from fishbone could be testified, whether ion-exchange pattern also worked simultaneously still need to be further investigated.

It should be noticed that the P concentration in the leachates of Eso cases was apparently lower than that of Aji cases, while their effectivities on Pb stabilization were at the same level, which might result from the different contents of the organic fraction remaining in the fishbone powder. Although the uniform pretreatments were given to both fishbones, the residual organic fraction were hard to control in the current preparation of fishbone products (*see Figure 3-2 on Page 43*).

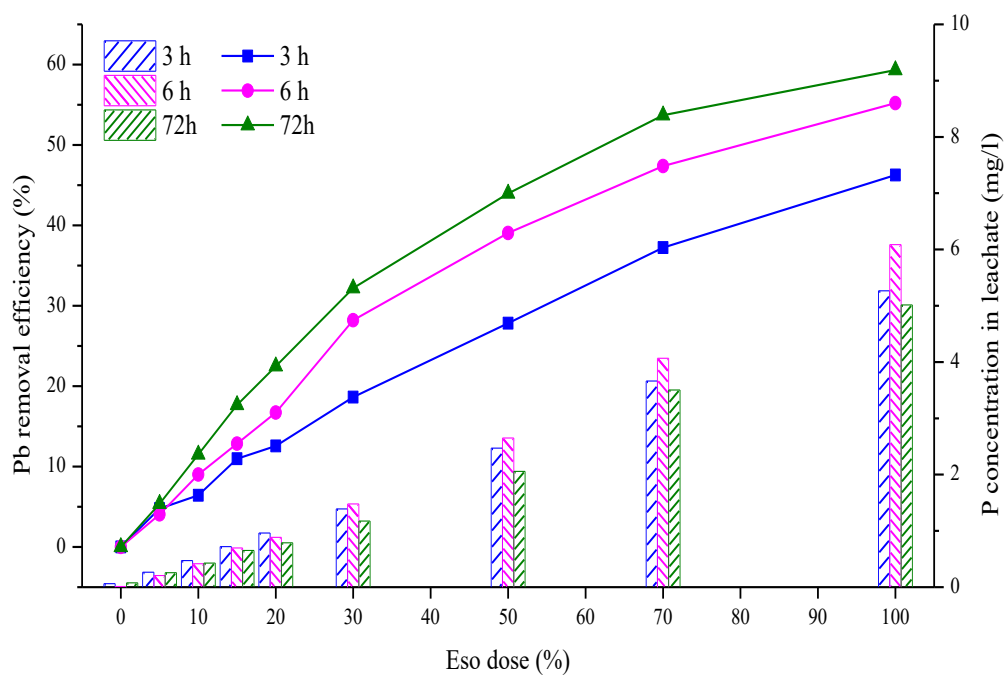


Figure 3-7 Correlation between Pb removal efficiency (solid lines) and P concentration in the leachate (vertical bars) under various Eso doses and different contact times (*Plan A*)

Zn and Cu were also supervised in Eso cases, the concentration of which in the leachates at the absence/presence of Eso fishbone is shown in Table 3-7. Same as what observed in Aji cases,

both Cu and Zn would be increased in the leachates after adding fishbone into the leaching process of fly ash. Same as the previous cases, comparing with Zn that increased mildly, the increment of Cu was noticeable as a function of either fishbone dosage or contact time. The non-HAP components (like organic matters) were supposed to supply some matters that led to the release of Cu and Zn from fly ash, which would be discussed in the following experiments.

Table 3-7 Concentration of Cu and Zn in the leachates of fly ash with Eso fishbone (*Plan A*)

Eso dose (%)	Cu (mg/l)			Zn (mg/l)		
	3 h	6 h	72 h	3 h	6 h	72 h
0	0.11	0.15	0.07	6.45	8.23	4.18
5	0.29	0.36	1.45	6.77	8.45	4.38
10	0.49	0.66	2.77	7.06	8.75	4.54
15	0.65	0.95	3.75	6.77	8.36	4.59
20	0.83	1.24	4.55	6.91	8.25	4.66
30	1.20	1.93	5.89	6.87	7.65	4.80
50	2.08	3.17	7.67	6.94	7.50	5.44
70	3.08	4.23	8.59	7.32	7.66	8.70
100	4.44	5.40	9.51	7.61	8.20	9.18

Whereas the different trend of Pb as well as Cu and Zn, the fluctuation of the amount of total heavy metal was taken into account. Except Pb, Zn and Cu, other heavy metal mentioned in Table 3-2 were not changed significantly and were stable in quite low concentration. Therefore, the concentration of total heavy metal was calculated as the summation of concentration of Pb, Cu and Zn, and the removal efficiency of total heavy metal was also calculated by Equation 3-1 (*Page 50*), the results of which both in Aji cases and Eso cases were shown in Table 3-8 and Table 3-9, respectively.

Table 3-8 Concentration and removal efficiency of total heavy metal in the leachates of fly ash with Aji fishbone (*Plan A*)

Aji dose (%)	Total heavy metal* (mg/l)				Removal efficiency of total heavy metal (%)			
	3 h	6 h	24 h	72 h	3 h	6 h	24 h	72 h
0	40.56	34.68	40.20	37.11	0.00	0.00	0.00	0.00
5	39.42	34.34	39.47	38.16	2.81	0.98	1.82	-2.82
10	38.63	33.89	39.26	36.51	4.76	2.28	2.34	1.63
15	38.00	32.40	38.87	36.30	6.32	6.56	3.32	2.18
20	38.24	31.90	38.32	36.64	5.74	8.00	4.70	1.27

*Total heavy metal = Pb + Zn + Cu

Table 3-9 Concentration and removal efficiency of total heavy metal in the leachates of fly ash with Eso fishbone (*Plan A*)

Eso dose (%)	Total heavy metal* (mg/l)			Removal efficiency of total heavy metal (%)		
	3 h	6 h	72 h	3 h	6 h	72 h
0	35.01	38.88	32.02	0.00	0.00	0.00
5	34.16	38.07	32.11	2.43	2.07	-0.27
10	34.17	37.16	31.89	2.40	4.43	0.41
15	32.75	35.88	31.21	6.46	7.70	2.55
20	32.62	34.89	30.74	6.84	10.25	4.01
30	31.22	31.47	29.52	10.83	19.05	7.80
50	29.55	29.26	28.67	15.61	24.75	10.47
70	28.26	27.94	30.15	19.28	28.15	5.84
100	27.34	27.27	29.99	21.91	29.86	6.34

*Total heavy metal = Pb + Zn + Cu

The results shown in Table 3-8 and Table 3-9 indicated that the amount of total heavy metal in the leachates was decreased after the fishbone addition, though the concentration of Cu and Zn was increased. For the total heavy metal, the biggest removal efficiency was obtained after a 6 h leaching process, both in Aji and Eso cases. Then the significant increase of Cu content in a function of contact time would affect the results dramatically. Based on the possibility of the separation of fishbone and fly ash after mixed leaching process, a two-round 6 h-leaching process may be worth considering for both Pb and total heavy metal abatement in MSWI fly ash, especially as a pretreatment of fly ash for further utilization.

3.3.5 Interaction with co-existing elements during heavy metal stabilization

All leachable elements mentioned in Table 3-2 were monitored together with the target elements (Pb, P, Cu and Zn), and they were rarely showing any clear trend in the concentration. For the heavy metals (Cr, Mo, V, Fe), they were stable in a low concentration. For the common metal (Ca, K, Na), they were existing in most solutions and in a quite high concentration, thus they would be treated as background. For Cl and SO_4^{2-} , they may worked with HAP for divalent heavy metal stabilization according to some references (Admassu and Breese, 1999). However, their concentration was so high that the slight change caused by their participation to the stabilization of heavy metal might be hard to observe. Therefore, only Pb, P, Cu and Zn would be under the supervision in the following experiments.

3.3.6 Capacity of fishbone on heavy metal stabilization in MSWI fly ash

The removal efficiency of Pb or total heavy metal discussed in the previous section was helpful to present the effectivity of the designated fishbone on the heavy metal stabilization in the current fly ash samples, thus it could be used as indicator for estimating the proper dosage of fishbone in each specific condition. However, the contents of heavy metal in MSWI fly ash from various sources could be fluctuated in a wide range, thus removal efficiency of heavy metal might be not a proper reference directly used in other fly ash cases. Furthermore, the nuances of the HAP contents might exist among different fishbone, which affect the selection of fishbone that suitable for this technique. Therefore, the capacity of fishbone on heavy metal stabilization was employed in order to estimate the difference of effectivity brought by the fishbone species, which was defined and calculated as the amount of heavy metal stabilized by unit mass of fishbone (*Equation 3-2*):

$$\text{Capacity on Metalstabilization (mg/g)} = \left(1 - \frac{C(\text{Metalin test group})}{C(\text{Metalin control group})} \right) \times 0.1 \div m(\text{fishbone}) \quad 3-2$$

Where Metal could be the target heavy metal (Pb, Zn, Cu) or total heavy metal (Pb+Zn+Cu), and 0.1 is the volume of leachant (100 ml).

When fishbone was added directly in the leaching process of MSWI fly ash, only Pb concentration in the leachates was shown in a decreasing trend. Hence, the capacities of both Aji and Eso fishbones on Pb stabilization were calculated and the results were shown in Table 3-10.

Table 3-10 Capacity of fishbone (Aji and Eso) on Pb stabilization (*Plan A*)

Fishbone dose (%)	Capacity of Aji (mg/g)				Capacity of Eso (mg/g)		
	3 h	6 h	24 h	72 h	3 h	6 h	72 h
5	0.26	0.13	0.31	0.35	0.27	0.25	0.30
10	0.24	0.14	0.26	0.45	0.18	0.27	0.32
15	0.21	0.19	0.25	0.42	0.21	0.26	0.33
20	0.17	0.18	0.24	0.37	0.18	0.25	0.31
30	--	--	--	--	0.18	0.29	0.30
50	--	--	--	--	0.16	0.24	0.24
70	--	--	--	--	0.15	0.21	0.21
100	--	--	--	--	0.13	0.17	0.16

-- : lack of data.

It is indicated that the capacities of Aji and Eso on Pb stabilization was at the same level, so it was supposed that fishbone could be used for the heavy metal stabilization in MSWI fly ash regardless of fish species. Generally, longer contact time could bring higher amount of stabilization on unit mass of fishbone, but the improving was not that effective, hence excessive long contact time should be adopted cautiously. In line with the curves of Pb removal efficiency (*Figure 3-6 and Figure 3-7*), higher capacity could be obtained at the relative low fishbone dosage (<30%), and the capture of heavy metal by unit mass of fishbone was decreased gradually when given

higher dosages. It is demonstrated that the Pb-HAP was more easily formed under a rich supplying condition of Pb ions, which may be an evidence supporting for the dissolution-precipitation mechanism. In addition, there was another consideration brought by this results that the formation of Pb-HAP might be promoted by supplying a more stable reaction condition (like low liquid/solid condition) which could provide longer time for each combination.

3.3.7 pH of leachate

The pH of the leachates from the leaching process of MSWI fly ash at the absence/presence of fishbone were listed in Table 3-11. It was indicated that all the leachates, either at the absence/presence of fishbone or in Aji/Eso cases, were in a quite high pH of 12-12.5. Adding fishbone brought a pH decrease, which was displayed more clearly by the leachates at higher fishbone dosage in Eso cases. Considering that the reaction between Pb and HAP could be seen as a kind of reciprocal reaction (*see Equations 1-1 and 1-2 on Page 14*), thus the decreasing of pH might not be inferred resulting from the stabilization.

Table 3-11 pH of the leachates of MSWI fly ash in Aji and Eso cases (*Plan A*)

Fishbone dose (%)	pH of the leachates in Aji cases				pH of the leachates in Eso cases		
	3 h	6 h	24 h	72 h	3 h	6 h	72 h
0	12.42	12.42	12.40	12.40	12.24	12.29	12.41
5	12.36	12.42	12.37	12.38	--	--	12.39
10	12.36	12.39	12.40	12.37	12.25	12.30	12.35
15	12.40	12.40	12.39	12.36	--	--	12.37
20	12.43	12.37	12.38	12.36	12.23	12.33	12.39
30	--	--	--	--	12.27	12.32	12.30
50	--	--	--	--	12.23	12.27	12.23
70	--	--	--	--	12.18	12.22	12.16
100	--	--	--	--	12.14	12.10	11.99

-- : lack of data.

3.4 Section summary

Based on the leaching property of MSWI fly ash and the toxicity of metals, Pb was become the first and primary target element in the plan of the stabilization of heavy metals in MSWI fly ash. Besides, the other two divalent heavy metal of Zn and Cu were also taken into account, which were released increased in contrast to the expectation. The original fishbone was simply pre-treated to fishbone powder that was employed in the experiments.

Few differences in the mineral and chemical compositions, as well as the effectivities on the stabilization of heavy metals brought by different fishbone species. When fishbone was directly added during the leaching process of fly ash for heavy metal stabilization, higher dosage of fishbone and longer contact time benefited the Pb sequestration from the leachate, but the latter was also not so effective on improving the Pb removal efficiency comparing with the former. The highest Pb removal efficiency 59.31% at the Eso fishbone dosage of 100% after a 72 h leaching process, and the Pb concentration has been decreased from 27.78 to 11.30 mg/l in the leachate. However, Zn and Cu, on the contrary, were both increased in the leachate, while the behaviours of Zn and Cu were in different patterns. Zn was increased mildly, while the increment of Cu was noticeable as a function of either fishbone dosage or contact time, and the influence of contact time was bigger. The additional release of Zn and Cu might be from MSWI fly ash on the effect of the non-HAP fraction (mainly organic residues) in the fishbone. The capacities of the fishbone on the stabilization of Pb and total heavy metal (Pb+Zn+Cu) were also assessed. Higher concentration of Pb ions in the leachate led to the higher capacity of fishbone on the stabilization. Even with the situation of releasing Cu and Zn, total heavy metal was reduced in the leachate with the fishbone addition. However, the optimal removal efficiency of total heavy metal was obtained at proper short contact time, and then it would be implicated by the dramatic increment of Cu.

Besides Pb, Zn and Cu, other elements that leached out were not obviously influenced at the presence of fishbone. The pH of the leachate was slightly decreased with adding fishbone into the leaching process (from 12.5 to 12.0), which not significantly affect the environment of the stabilization of heavy metals by fishbone in MSWI fly ash.

Chapter 4 Approaches of improving the effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash

4.1 Introduction

In Chapter 3, as a natural source of hydroxyapatite (HAP) whose Ca possesses the exchange capacity with heavy metal ions for metal stabilization, fishbone has been proved its feasibility and effectivity that could be used for the stabilization of heavy metal in municipal solid waste incineration (MSWI) fly ash via added during the leaching process (*Plan A*). This scenario was primarily settled for the stabilization of heavy metals by fishbone based on the consideration that fly ash could possibly be used after this treatment. In the further investigation described in this chapter, more experimental scenarios would be designed to improve the effectivity, which were induced from the basic *Plan A*.

Based on the leaching property of MSWI fly ash (*see Table 2-5 on Page 28 and Table 3-2 on Page 48*), Pb was still the first and primary target element in the stabilization of heavy metals in MSWI fly ash in this chapter, for it is the most leachable and most toxic heavy metal. Besides, the other two divalent heavy metals of Zn and Cu were also taken into account. Zn took the second-high concentration among heavy metals in the leachate of MSWI fly ash. In addition, both Zn and especially Cu were increased in the leachates at the presence of fishbone in *Plan A*, which was in contrast to the expectation. Three kinds of original fishbones collected from the market could be pre-treated into powder after a simple process (*see Figure 3-2 on Page 43*). The fishbones that were tested and used in *Plan A* have proved that there were few differences brought by fishbone species, neither in the mineral/chemical compositions, nor in the effectivities on the stabilization of heavy metals in MSWI fly ash. This is indicated that this technique might be used in a wide region because of no limitation on the fish species. Hence, Eso fishbone was selected as the representative involved in the experiments of this chapter for the further investigation.

In *Plan A* of Chapter 3, fishbone was directly added during the leaching process for the stabilization of heavy metals in MSWI fly ash. Then the results demonstrated that higher dosage of fishbone and longer contact time benefited the Pb sequestration from the leachate. The highest Pb removal efficiency could reach 59.31% at the Eso fishbone dosage of 100% after a 72 h leaching

process (see Figure 3-7 on Page 55), which meant that Pb concentration has been decreased from 27.78 to 11.30 mg/l in the leachate (see Table 3-6 on Page 54). However, Zn and Cu, which were supposed to be removed concurrently, were both actually increased in the leachate. The behaviours of Zn and Cu were in different patterns- Zn was increased mildly, while the increment of Cu was noticeable as a function of either fishbone dosage or contact time, and the influence of contact time was bigger (see Table 3-5 on Page 52 and Table 3-7 on Page 56). The additional release of Zn and Cu might be from MSWI fly ash on the effect of the non-HAP fraction (mainly organic residues) in the fishbone. Although not restricted because of their low toxicities, the methods that reduce or prevent the releases of Zn and Cu with the stabilization of Pb were certainly preferred. The capacities of the fishbone on the stabilization of Pb and total heavy metal (Pb+Zn+Cu) were assessed. It has been observed that fishbone species did not bring obvious differences in the capacity; higher concentration of Pb in the leachate led to higher capacity of fishbone on the stabilization (see Table 3-10 on Page 59). Thus, promoting Pb supply to fishbone in the leachate for a better effectivity of the stabilization would be considered. Even with the situation of releasing Cu and Zn, total heavy metal was reduced in the leachate with the fishbone addition. However, the optimal removal efficiency of total heavy metal was obtained at proper short contact time (6 h in Plan A), and then it would be implicated by the dramatic increment of Cu (see Table 3-8 on Page 57 and Table 3-9 on Page 57). Moreover, extending contact time was not so effective on improving Pb removal efficiency comparing with increasing fishbone dosage (see Figure 3-7 on Page 55). Therefore, excessive long contact time would be adopted cautiously in the utilization and in the further investigation.

In this chapter, the approaches for improving the effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash were detected based on the discussions in the previous chapters. Eso fishbone were selected as the representative and performed in the all experiments. As the most leachable and most toxic heavy metal, Pb was certainly taken the priority in the stabilization process. Besides, both Zn and Cu were also focused on. Moreover, the techniques that could enhance the effectivity of Pb stabilization with inhibiting the release of Zn and Cu would be preferred in order to prevent potential extra environmental impact. Two approaches would be conducted for the better effectivity of the stabilization. The one is to build different liquid/solid (L/S) conditions, in order to provide a richer supply of metal ions (Pb) to fishbone (HAP) for the stabilization (defined as Plan B). Furthermore, this approach would be also a relatively stable

condition for the reaction between metal ions and fishbone (HAP). The other one is to obtain purified HAP via igniting natural fishbone powder as a pretreatment in order to cut down the non-HAP fraction (especially the organic matters) in fishbone, by which the influence of non-HAP matters could be substantially limited. The ignited fishbone would be conducted the experiments for the stabilization of heavy metals in the ways that directly being added in the leaching process (defined as *Plan CA*) and reacting with fly ash under various L/S conditions (defined as *Plan CB*). Generally, the 6 h-leaching process would be adopted to estimate the leaching amount of heavy metals. In each scenario, the effectivity of the stabilization and the capacity of fishbone as well as the pH of the leachates would be reported.

The outline and structure of Chapter 4 is shown in Figure 4-1.

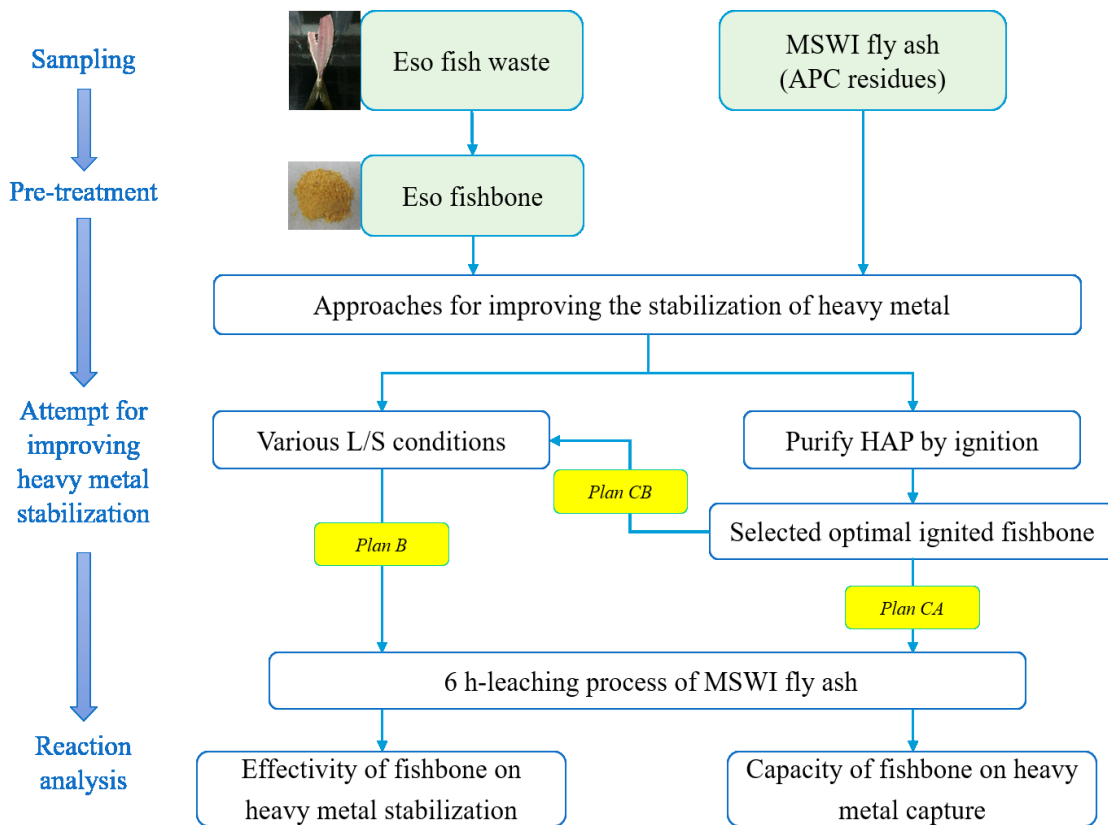


Figure 4-1 Outline and structure of Chapter 4

4.2 Experiments

4.2.1 Collection and preparation of MSWI fly ash

MSWI fly ash K was the same sample used in Chapter 3, which was selected as the representative for there was relatively high concentration of Pb and Zn detected in its leachate (*see Table 2-5 on Page 28*). Fly ash K was obtained from an incineration plant located in City K, Japan. The original fly ash sample was in dry state, the moisture content of which was below 2% tested by freeze-drying, thus it was directly used in the experiments of the stabilization between heavy metals and fishbone or ignited fishbone.

4.2.2 Collection and basic pre-treatment on fishbone

Lizardfish (Eso in Japanese) fishbone was collected from the market in City F, Japan, which one of the common commercial fishes daily supplied to the Japanese customers. For the easy recognition in this thesis, the Japanese names (*Eso*) would be used in all cases that fishbone name needed. The collected fishbone was wet but almost free from soft tissues. To obtain the clean fishbone (rare in meat or other organic components) and improve the availability that fits for experiments, pre-treatments were carried as followed. The original fishbone was boiled for 5 min, and then cleaned by brush to exclude all soft tissues on the surface. The clean fishbone was dried until becoming hard and friable in an oven at 40 °C. The dried fishbone was ground into powder state (*Figure 4-2*).

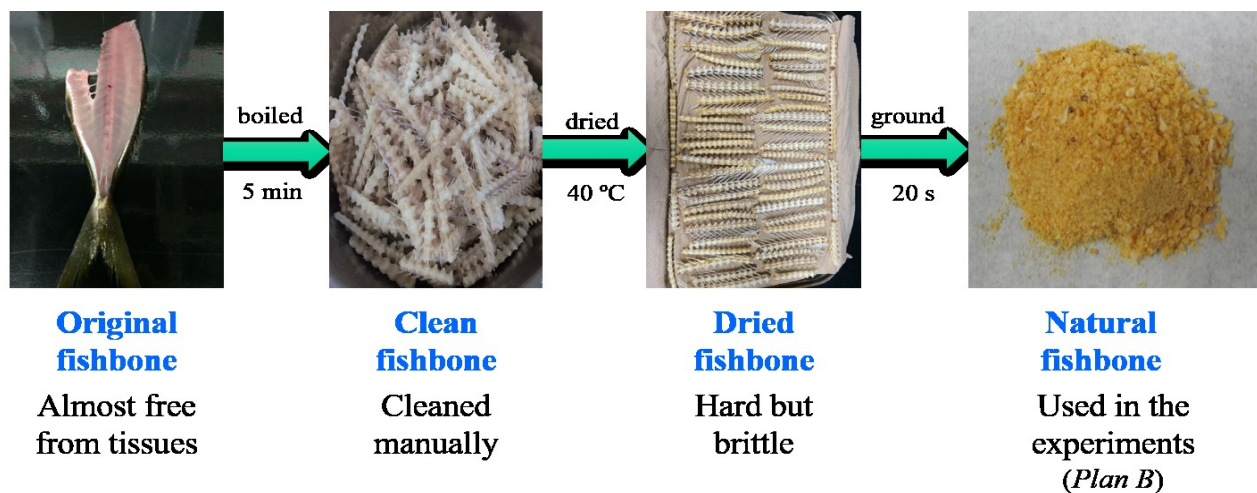


Figure 4-2 Basic pre-treatment process on Eso fishbone

The natural Eso fishbone powder was used in the experiments conducted at various initial L/S conditions (*Plan B*) with the aim to improve the effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash via providing a richer supply of metal ions (Pb) to fishbone (HAP) for the stabilization under a relatively stable condition.

4.2.3 Thermogravimetry and differential thermal analysis (TG-DTA) on fishbone

Thermogravimetry and differential thermal analysis (TG-DTA) was conducted to detect the feature of mass loss of fishbone during the ignition, as well as the temperature for the potential phase transformation in fishbone, by the instrument of TG-DTA 2000SA (Bruker AXS) apparatus. Approximately 20 mg of natural Eso fishbone sample (*see Figure 4-2 on Page 65*) was taken for each test and aluminum oxide (Al₂O₃) was used as the inert control material. Both natural Eso fishbone powder and aluminum oxide were simultaneously settled and heated in the air atmosphere and the tests were run in triplicate. The temperature program was set to elevate from the ambient temperature to 1100 °C in the step of 10 °C/min. The temperature was held constant at maximum for 15 min at the end of each test.

4.2.4 Ignition pre-treatment and mass loss of fishbone

To obtain the purified HAP and remove the non-HAP fraction (mainly organic matters), fishbone was ignited under designated high temperatures. According to the curves obtained from TG-DTA tests (*see Section 4.3.4 on Page 81*), five conditions (250, 330, 430, 550 and 700 °C) were selected as the ignition temperatures. The natural Eso fishbone powder was placed in the crucibles, and then heated in a muffle furnace from the ambient temperature to the target temperatures. The ignition lasted for 2 h. The weights of the fishbone before and after ignition were recorded and the mass loss was calculated through Equation 4-1:

$$\text{Mass loss (\%)} = \frac{\text{mass loss of sample}}{\text{mass of original sample}} \times 100 = \frac{W_1 - W_2}{W_1 - W_0} \times 100 \quad 4-1$$

Where W_0 , W_1 and W_2 are the masses of blank crucible, crucible with sample before and after ignition, respectively.

4.2.5 Mineral phase detection of natural and ignited fishbone

The mineral phases of natural and ignited Eso fishbone obtained from *Section 4.2.4* were analyzed by X-ray diffractometry (XRD, Rigaku Multiflex) using CuK α radiation generated at the voltage of 44 kV and the beam current of 30 mA. Specimens were scanned from 2-75 deg. (2θ) by

0.02 deg. (2 θ)/step, and the X-ray irradiation time of 2 sec./step. The mineral phases were identified by the software *Jade 6.0*. A sample of Eso fishbone ignited at 800 °C for 2 h was also analyzed as a reference.

4.2.6 Stabilization of heavy metals in MSWI fly ash by natural fishbone under various L/S conditions (*Plan B*)

At the lower L/S conditions, fishbone HAP would be surrounded by the plenty ions of heavy metal for more potential formation of metal-HAP. Thus, in order to improve the effectivity of fishbone on the stabilization of heavy metal in MSWI fly ash via providing a richer supply of metal ions (Pb) to fishbone (HAP), the influence of L/S condition for the stabilization was taken into account. Various L/S conditions were provided for the stabilization of heavy metals with fishbone HAP (defined as *Plan B*). In this scenario, fishbone was supposed to be an additive working in solidification/stabilization (S/S) approach (see *Figure 1-5 on Page 11*).

The experiments were conducted in 250 ml polypropylene bottles at room temperature. Only the weight of fly ash was counted as solid (S) for comparing the results among different scenarios. In each bottle, 10.00 g fly ash, 5.00 g natural Eso fishbone (fishbone dosage of 50%) and different volume of super-pure water were added. The initial L/S were set at 10, 5, 3, 1.5, 1 and 0.5 ml/g, and accordingly the admixtures presented a high L/S (10, 5, 3 ml/g) or low L/S (1.5, 1, 0.5 ml/g) state. The bottles were settled for 2, 4, 12 and 24 h.

After settlement periods, super-pure water was added into each bottle in order to increase the total leachant to 100 ml. Then the admixtures were subjected to a 6 h-leaching process, during which all bottles were shaken at a speed of 200 rpm with leak-proof lid. To obtain leachate, bottles were centrifuged at 3000 rpm for 20 min, then solid and liquid parts were separated by vacuum filtration through 0.45 μ m pore-size membrane. The leachate was stored in a polypropylene bottle for further analyses. The experimental setup of Plan B was shown in *Figure 4-3*.

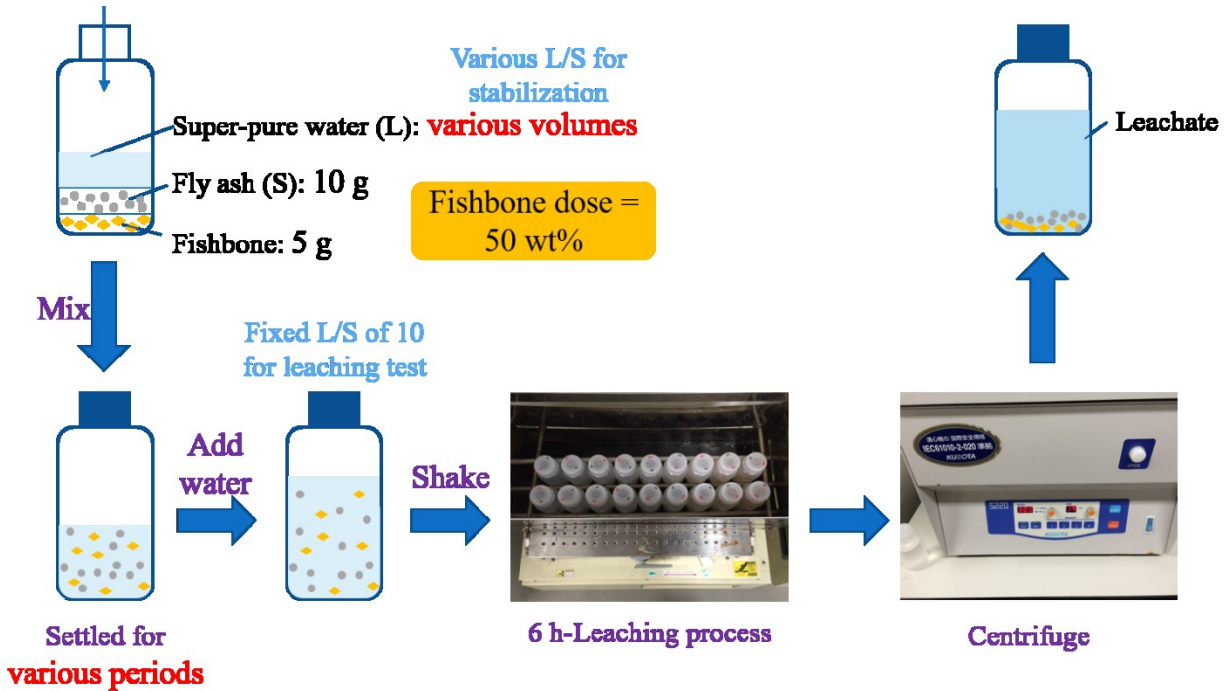


Figure 4-3 Experimental setup of *Plan B*

4.2.7 Selection of optimal temperature for ignition pre-treatment on fishbone

To determine the optimal temperature for the ignition pretreatment, ignited Eso fishbone from different temperatures (*mentioned in Section 4.2.4*) was involved in the experiments of the stabilization of heavy metals in MSWI fly ash. The scenarios that both directly being added in the leaching process (*Plan CA*) and reacting with fly ash under various L/S conditions (*Plan CB*) were considered.

The experiments were conducted in 250 ml polypropylene bottles at room temperature. Only the weight of fly ash was counted as solid (S) for comparing the results among different scenarios. In *Plan CA*, the experimental set consisted of 6 bottles, each containing 10.00 g of fly ash, 100.0 ml of super-pure water as leachant, and 2.00 g of ignited Eso fishbone (fishbone dosage of 20%). The admixtures were subjected to a 6 h-leaching process, during which all bottles were shaken at a speed of 200 rpm with leak-proof lid. In *Plan CB*, the experimental set consisted of 6 bottles, each containing 10.00 g of fly ash, 5.00 g of ignited Eso fishbone (fishbone dosage of 50%), and 10.0 ml of super-pure water (initial L/S of 1, low L/S state). The bottles were settled for 24 h. After

the settlement periods, super-pure water was added into each bottle in order to increase the total leachant to 100 ml. Then the admixtures were subjected to a 6 h-leaching process, during which all bottles were shaken at a speed of 200 rpm with leak-proof lid.

To obtain leachate, bottles were centrifuged at 3000 rpm for 20 min, then solid and liquid parts were separated by vacuum filtration through 0.45 μm pore-size membrane. The leachate was stored in a polypropylene bottle for further analyses.

4.2.8 Stabilization of heavy metals in MSWI fly ash by ignited fishbone (IGN-430) via added in leaching process (*Plan CA*) and under various L/S conditions (*Plan CB*)

According to the results from *Section 4.2.7*, 430 °C was determined as the ignition temperature for the advanced pre-treatment of fishbone. Ignited Eso fishbone at 430 °C (called as IGN-430 Eso fishbone) was consequently subjected in the stabilization of heavy metals in MSWI fly ash in the ways that directly being added in the leaching process (*Plan CA*) and reacting with fly ash under various L/S conditions (*Plan CB*).

The experiments were conducted in 250 ml polypropylene bottles at room temperature. Only the weight of fly ash was counted as solid (S) for comparing the results among different experimental schemes. In *Plan CA*, the experimental set consisted of 6 bottles, each containing 10.00 g of fly ash, 100.0 ml of super-pure water as leachant, and different doses of IGN-430 Eso fishbone. The following doses of fishbone were supplied to each bottle: 1.00, 2.00, 3.00, 5.00, 7.00, 10.00 g in order to obtain various fishbone/fly ash ratios at 10%, 20%, 30%, 50%, 70% and 100% by weight. The admixtures were subjected to a 6 h-leaching process, during which all bottles were shaken at a speed of 200 rpm with leak-proof lid. In *Plan CB*, the experimental set consisted of 6 bottles, each containing 10.00 g fly ash, 5.00 g IGN-430 Eso fishbone (fishbone dosage of 50%), and different volume of super-pure water. The initial L/S ratios were set at 10, 5, 3, 1.5, 1 and 0.5 ml/g. The bottles were settled for 24 h. After the settlement periods, super-pure water was added into each bottle in order to increase the total leachant to 100 ml. Then the admixtures were subjected to a 6 h-leaching process, during which all bottles were shaken at a speed of 200 rpm with leak-proof lid.

To obtain leachate, bottles were centrifuged at 3000 rpm for 20 min, then solid and liquid parts were separated by vacuum filtration through 0.45 μm pore-size membrane. The leachate was stored in a polypropylene bottle for further analyses.

4.2.9 pH measurement

The pH of all the leachates from each leaching batch was tested by pH meter (F-53, Horiba).

4.3 Results and discussion

As described previously, two approaches for improving the effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash would be under the consideration- providing various L/S conditions for a richer supply of metal ions (Pb) to fishbone (HAP), and taking ignition pretreatment on fishbone for purified. Ignited fishbone was also involved in some experiments under different L/S conditions for better Pb removal efficiency. Therefore, totally four scenarios would be discussed as described above, which were named as Table 4-1 for easy recognition.

The experiments of *Plan A* by Aji and Eso fishbone have been discussed in Chapter 3 as the basic condition for the stabilization of heavy metals by fishbone in MSWI fly ash. In this chapter, *Plan B* and *Plans CA/CB* would be studied as the approaches for improving the effectivity. Therefore, the results and discussion would be certainly sorted into two main parts- the discussions about *Plan B* were launched in Section 4.3.1-4.3.3, and the rest parts were belonging to *Plan CA* and *Plan CB*.

Table 4-1 Alpha codes of experiment scenarios

Code	Fishbone status	Experiment condition
<i>Plan A</i>	Natural	Directly adding fishbone during the leaching process of MSWI fly ash
<i>Plan B</i>	Natural	Under various L/S condition
<i>Plan CA</i>	Ignited	Directly adding fishbone during the leaching process of MSWI fly ash
<i>Plan CB</i>	Ignited	Under various L/S condition

4.3.1 Effectivity of natural fishbone on heavy metal stabilization in MSWI fly ash under various L/S conditions (*Plan B*)

There were few differences in the mineral and chemical compositions (*see Section 3.3.3 on Page 48*), as well as the effectivities on the stabilization of heavy metal among different fishbone species (*see Section 3.3.4/3.3.6 on Page 49/58*), thus Eso fishbone was selected as the representative to conduct the experiments in the following studies.

The influence of L/S conditions to the effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash was inspected based on the observation from *Plan A*, which is that higher capacity of fishbone on the stabilization of heavy metal (Pb) was appeared at lower fishbone dosage (see Section 3.3.6 on Page 58). In addition, low L/S condition would be considered as a second pattern for the utilization of fishbone working on the stabilization of heavy metals in MSWI fly ash, that fishbone could treated as the additive in the stabilization/solidification (S/S) treatment (see Section 1.2.4 on Page 11). S/S treatment is orientated to final disposal, which means that the mixture of fly ash and additives would enter the landfill together. Therefore, the increment brought by the additives should be considered (especially the increment of volume), and the matters potentially leached out calling for secondary treatment should be of concern as well.

The stabilization of heavy metals under various L/S conditions were conducted, and the settlement period as the contact time was concerned as well. The mixture of fly ash and fishbone (constant dosage of 50%) with various volumes of super-pure water were settled for 2, 4, 12 or 24 h at room temperature. L/S conditions were set as 10, 5, 3, 1.5, 1 and 0.5 ml/g, thus the mixtures could be grouped into the high L/S conditions ($L/S > 3$ ml/g) and the low L/S conditions ($L/S < 1.5$ ml/g). Only the weight of fly ash was counted as solid (S) for easily comparing the results among other experimental setups. After settlement periods, super-pure water was replenished into each bottle in order to obtain the final L/S at 10 ml/g, which was the same as that in *Plan A*. Then the mixtures were subjected to a 6 h-leaching process. The concentration of heavy metals (Pb, Zn, Cu) and P in the leachates was identified by ICP-AES. The effectivity of fishbone on the stabilization was represented by the removal efficiency of heavy metals in the leachate, which was calculated as the percentage of the sequestered fraction of the metal in the leachates of *Plan B* (L/S test group). The control group was designated as the original concentration of the heavy metal in the leachate at the absence of fishbone after a 6 h-leaching process in *Plan A* (Equation 4-2). As the most toxic heavy metal, Pb was still primarily focused on. The results of Pb and P concentration as well as the correlation between Pb removal efficiency and P concentration in the leachates were are shown in Table 4-2 and Figure 4-4.

$$\text{Metal removal efficiency (\%)} = \left(1 - \frac{C(\text{Metal in L/S test group})}{C(\text{Metal in control group})} \right) \times 100 \quad 4-2$$

Where Metal is the target heavy metal (Pb, Zn, Cu) or total heavy metal (Pb+Zn+Cu).

As shown in Table 4-2 and Figure 4-4, it is indicated that, generally, the lower L/S condition was much more beneficial for Pb stabilization by fishbone in MSWI fly ash, and the removal efficiency was continuously increased with the decreasing of L/S at the same settlement period. Comparing with the Pb removal efficiency obtained in *Plan A* at fishbone dosage of 50% in a 6 h-leaching process (39.05%, the reference value in Figure 4-4), the same removal efficiency could be obtained just by shrinking L/S to less than 3 ml/g in a shorter period. In addition, the mixture of fly ash and fishbone was settled down instead of shaken continuously, which could help to cut off energy consumption. It is also suggested that the stabilization mostly happened during the settlement period, not in the following leaching process; otherwise, all Pb removal efficiency would have been higher than the reference value.

The curves of different settlement periods could be sorted into two groups-short periods (2 and 4 h) and long period (12 and 24 h). The Pb removal efficiency of 2 h case was almost the same as that of 4 h case at the same L/S condition, which was also happened between 12 h and 24 h cases. In addition, either in high L/S conditions or low L/S conditions, bigger difference of Pb removal efficiency among various settlement periods could be observed at higher L/S ratios (L/S of 10 or 1.5 ml/g), and then the effectivities were becoming identical (L/S of 3 or 0.5 ml/g). The influence of settlement period was not so big as that of L/S, and the stabilization could be almost accomplished within the first few hours. Therefore, excessive long settlement period (contact time) was not recommended, similar to what was suggested in *Plan A*. Furthermore, considering that fishbone would be disposed in landfill together with fly ash, the extra Pb removal efficiency brought by settlement period could be treated as the buffer capacity.

Table 4-2 Concentration of Pb and P in the leachates of MSWI fly ash at the presence of natural Eso fishbone under various L/S conditions (*Plan B*)

L/S (ml/g)	Pb (mg/l)				P (mg/l)			
	2 h	4 h	12 h	24 h	2 h	4 h	12 h	24 h
10	18.91	19.35	21.61	21.66	2.54	2.36	2.21	2.16
5	19.47	18.82	19.50	20.91	2.44	2.48	2.15	1.97
3	18.56	17.60	18.20	19.20	2.47	2.44	2.09	1.89
1.5	16.18	15.30	12.49	12.87	2.55	2.35	2.62	2.45
1	11.64	11.29	10.66	10.26	3.09	2.72	2.80	2.68
0.5	11.62	11.88	11.17	10.39	3.01	2.93	3.27	2.96
Ref.#	18.59				2.65			
Ctrl.*	30.50				0.01			

Ref. (reference value): concentration in the leachate of fly ash with Eso fishbone (dosage of 50%) after a 6 h-leaching process (*Plan A*)

* Ctrl. (control group): concentration in the leachate of fly ash (without fishbone) after a 6 h-leaching process (*Plan A*)

There is rare P leached out from fly ash after a 6 h-leaching process at the absence of fishbone (see Table 3-6 on Page 54). Thus, P detected in the leachate of *Plan B* was derived from fishbone, and the fluctuation of P concentration was reflecting the reaction of P with other elements to reform the new phases in low solubility. When $L/S > 1.5$, P detected in the leachates was less than that in *Plan A* at the same fishbone dosage of 50%; while the concentration of P became higher than the reference value when $L/S < 1$ ml/g. At high L/S conditions ($L/S > 3$), P concentration in the leachate decreased as a function of settlement period expending, which was indicated that some reformation P involved in called for a relatively long period.

At high L/S conditions (> 3), the higher Pb removal efficiency obtained when the settlement period was relatively short, while the P concentration in the leachate was generally decreased similar to that was observed in *Plan A*. This might imply that, besides the stabilization of Pb, P released from fishbone could also be involved in other reformation.

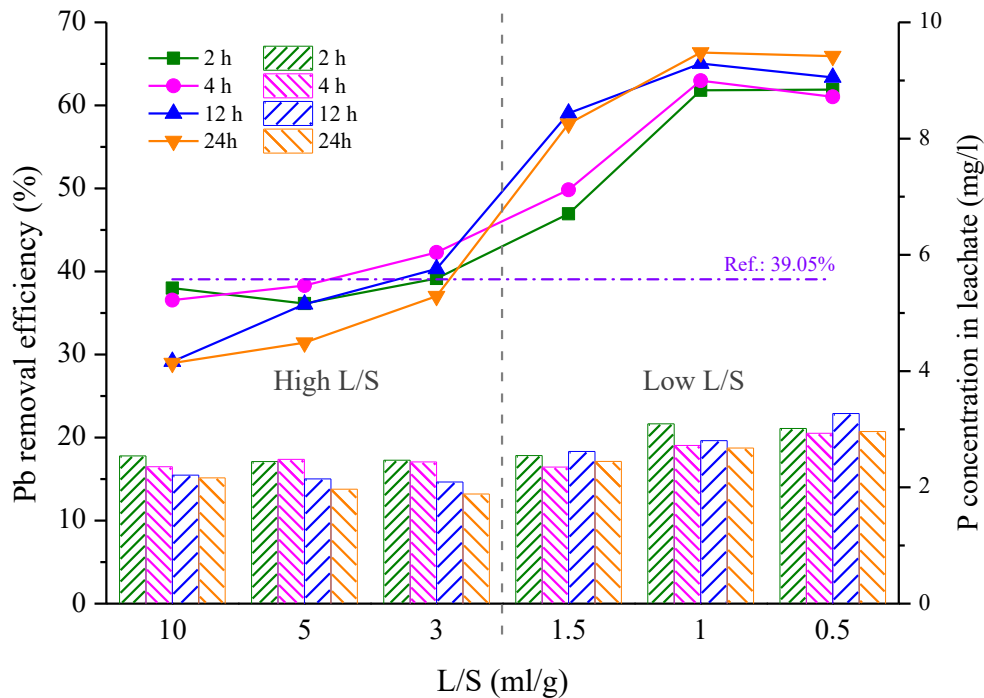


Figure 4-4 Correlation between Pb removal efficiency (solid lines) and P concentration in the leachate (vertical bars) under various L/S conditions and different settlement periods

At L/S conditions (< 1.5), on the contrary, more Pb was stabilized when given longer settlement period. However, when L/S was decreased to lower than 1 ml/g, neither L/S condition nor settlement period was not so effective to improving the Pb stabilization. The highest Pb removal efficiency reached 66.35% in *Plan B* at L/S of 1 ml/g for a 24 h settlement period, with the decreasing of Pb concentration from 30.50 to 10.26 mg/l. Presumably, the low L/S condition provided a relatively stable environment for the potential reaction thanks to the low fluidity, and provided a richer supply of Pb ions to fishbone HAP for the formation of Pb-HAP. P concentration in the leachates at low L/S conditions was increased as a function of L/S decreasing and most was higher than that in *Plan A* at the 6 h-leaching case (2.65 mg/l, see Table 3-6 on Page 54). At L/S of 1.5, the biggest enhancement of the Pb stabilization appeared, while P concentration was not changed so much when given longer settlement period. In addition, at low L/S conditions, P concentration remained at a stable content at each L/S, even given much longer settlement period; whereas it was slightly increased with the L/S decreasing. It was indicated that the leaching of P

was not connected with the Pb stabilization and affected by the settlement periods at low L/S conditions. Thus the reformation of Pb-HAP was preferred to an ion-exchange mechanism. Although low L/S condition benefited the stabilization of Pb in MSWI fly ash by fishbone, the effectivity of fishbone on Pb stabilization could be enhanced until reached some certain L/S, which implied that the liquid phase (super-pure water) affected the reaction of stabilization. Considering the extreme high alkaline condition of fly ash, the OH⁻ might hinder the reaction, especially the dissolution process if existed. However, it should be pointed that even in this case, adding acid to modify the pH condition for a better Pb stabilization was not recommended due to the extreme high pH provided by fly ash (>12), which might lead to high cost and high risk in operation.

Cu and Zn were also monitored in all experimental sets of *Plan B*, the concentration of which were both in an increase trend in all leachates of fly ash at the presence of fishbone in *Plan A*. The concentration of Cu and Zn were listed in Table 4-3, as well as Zn removal efficiency calculated by Equation 4-2 (on Page 71).

Although belonging to the unrestricted elements in the relevant environmental standards because of their low toxicities, the concentration of Cu and Zn in the leachates was still preferred to being under control in case turn to be a secondary pollution. However, both Cu and Zn was observed that increased in the leachates at the presence of fishbone in the leaching process of fly ash (*Plan A*). The increasing of Zn concentration in the leachates was mildly, and the increment was almost independent of contact time; while the leaching of Cu was stimulated dramatically by either fishbone dosage or contact time (see Table 3-5/Table 3-7 on Page 52/56). In *Plan B*, it was observed that this performance of Cu and Zn could be modified by given lower L/S conditions.

The concentration of Cu was still increased in the leachates after the fishbone addition in *Plan B*. When L/S was higher than 1.5 ml/g, Cu was generally encouraged to leach out with the time extending, and L/S gave little effects on it. The Cu concentration would exceed the reference value that got in *Plan A* at the fishbone dosage of 50% when the settlement period reached to 24 h. However, when L/S was lower than 1 ml/g, the leaching out of Cu, on the contrary, would be suppressed effectively by either L/S ratio or by settlement period. The lowest Cu concentration in the leachate of fly ash with fishbone (dosage of 50%) could be controlled to 1.90 mg/l in *Plan B*, which has cut 40% of the increment than that in *Plan A*.

Table 4-3 Concentration of Cu and Zn/Zn removal efficiency in the leachates of fly ash at the presence of natural Eso fishbone under different L/S conditions (*Plan B*)

L/S (ml/g)	Cu (mg/l)				Zn (mg/l)				Zn removal efficiency (%)			
	2 h	4 h	12 h	24 h	2 h	4 h	12 h	24 h	2 h	4 h	12 h	24 h
10	2.87	2.72	2.89	3.40	7.77	8.22	10.39	11.21	5.61	0.14	--	--
5	2.81	3.22	2.94	3.60	7.91	8.44	8.68	9.93	3.87	--	--	--
3	2.91	3.16	3.19	3.58	6.92	6.66	6.94	7.36	15.95	19.07	15.74	10.57
1.5	3.00	3.08	3.61	3.61	5.51	5.02	4.20	3.62	33.12	39.03	49.01	56.04
1	3.39	3.14	2.91	2.70	4.47	4.14	3.92	3.14	45.73	49.68	52.34	61.87
0.5	3.03	2.63	2.52	1.90	3.80	3.83	3.57	3.09	53.82	53.42	56.64	62.43
Ref.#	3.17				7.50				--			
Ctrl.*	0.15				8.23				--			

Ref. (reference value): concentration in the leachate of fly ash with Eso fishbone (dosage of 50%) after a 6 h-leaching process (*Plan A*).

* Ctrl. (control group): concentration in the leachate of fly ash (without fishbone) after a 6 h-leaching process (*Plan A*)

--: lack of data or could not be calculated

The increasing trend of Zn concentration at fishbone presence could be totally convert to decreasing when L/S was lower than 3 ml/g, and the stabilization of Zn were facilitated visibly both by L/S and by settlement period in the low L/S condition ($L/S < 1.5$). At the condition that was L/S of 1 / 0.5 ml/g and settlement period of 24 h, Zn removal efficiency (61.87% / 62.43%) could reach the same level as that of Pb (66.35% / 65.93%), which was indicated that the co-stabilization of Pb and Zn could be realized. Furthermore, comparing the stabilization between Pb and Zn, the removal efficiency of Pb was not changed so much as that of Zn with settlement time expending, which implied that the combination of Pb was much faster than that of Zn in the accomplishment.

As discussed in *Plan A*, the increased Cu and Zn in the leachates of fly ash at the presence of fishbone presumably resulted from the facilitation of the non-HAP fraction (mainly organic matters) in fishbone. Now in *Plan B*, higher Pb removal efficiency were obtained with the

stabilization of Zn and the restraint of the increasing of Cu at the low L/S condition (< 1 ml/g). it was implied that the condition changed resulting from less volume of super-water added in the system hindered the potential effect of non-HAP matters on promoting Zn and Cu leached out. Considering the extreme high content of alkaline salts in MSWI fly ash (APC residue), OH^- was supposed to have some important effects. However, adding acid to modify the pH condition was not recommended which might lead to high cost and high risk in operation.

The concentration of total heavy metal was also taken into account in *Plan B*. Expect Pb, Zn and Cu, other heavy metals were not changed significantly and stable in quite low concentration. Therefore, the same as in *Plan A*, total heavy metal was just including Pb, Cu and Zn, and the removal efficiency of total heavy metal was calculated by Equation 4-2 (*Page 71*), the results of which were shown in Table 4-4.

The same as what happened in *Plan A*, the concentration of total heavy metal was decreased with fishbone addition in all cases of *Plan B*. The concentration and the fluctuation of Pb were much bigger than that of Cu and Zn, thus the concentration of total heavy metal was led by Pb fraction. The increment of Cu was controlled at a relatively even level, so its impact on the total heavy metal was not quite obvious. Instead, Zn was becoming the critical element to the removal efficiency of total heavy metal because of the remarkable decreasing trend at different L/S conditions.

Generally, the concentration of total heavy metal was decreased at lower L/S condition when settled for the same period. However, the fluctuations of total heavy metal with the settlement time extending at the same L/S were in the different patterns at high and low L/S conditions. At high L/S conditions ($L/S > 3$), the total heavy metal in the leachates was increased at longer settlement period. While at high L/S conditions ($L/S < 1.5$), the concentration of total heavy metal was decreased both by longer settlement period and by L/S decreasing, and the influence of L/S was more obvious. When L/S reached 1 ml/g, the removal efficiency of total heavy metal was not enhanced dramatically. Comparing with the reference value from *Plan A*, the total metal could be better removed when L/S was lower than 1.5 ml/g. With the emphasis on the most toxic element Pb, L/S of 1 ml/g would be the optimal condition for the stabilization of heavy metals in MSWI fly ash by natural fishbone.

It should be noticed that although better effectivity of natural fishbone on the stabilization of heavy metals could be obtained in *Plan B*, *Plan A* still should be of concern when fly ash was considered separately recycled after the pre-treatment process.

Table 4-4 Concentration and removal efficiency of total heavy metal in the leachates of fly ash at the presence of natural Eso fishbone under different L/S conditions (*Plan B*)

L/S (ml/g)	Total heavy metal (mg/l)				Removal efficiency of total heavy metal (%)			
	2 h	4 h	12 h	24 h	2 h	4 h	12 h	24 h
10	29.55	30.29	34.88	36.27	24.00	22.08	10.28	6.71
5	30.19	30.47	31.11	34.44	22.34	21.62	19.97	11.41
3	28.38	27.42	28.32	30.14	27.00	29.48	27.15	22.48
1.5	24.69	23.40	20.30	20.10	36.50	39.82	47.80	48.31
1	19.50	18.57	17.49	16.10	49.85	52.23	55.02	58.60
0.5	18.45	18.35	17.27	15.38	52.56	52.80	55.59	60.44
Ref.#	29.26			24.75				
Ctrl.*	38.88			--				

Total heavy metal = Pb + Zn + Cu

--: lack of data or could not be calculated

Ref. (reference value): concentration in the leachate of fly ash with Eso fishbone (dosage of 50%) after a 6 h-leaching process (*Plan A*).

* Ctrl. (control group): concentration in the leachate of fly ash (without fishbone) after a 6 h-leaching process (*Plan A*)

4.3.2 Capacity of natural fishbone on the stabilization of heavy metals in MSWI fly ash under various L/S conditions (*Plan B*)

The capacity of fishbone on the stabilization of heavy metals in MSWI fly ash was defined as the amount of heavy metal stabilized by unit mass of fishbone, which was calculated by Equation 4-3. The control group was designated as the original concentration of metal in the leachate of fly ash after a 6 h-leaching process (*Plan A*). The results were listed in Table 4-5.

$$\text{Capacity on Metal stabilizat ion (mg/g)} = \left(1 - \frac{C(\text{Metal in test group})}{C(\text{Metal in control group})} \right) \times 0.1 \div m(\text{fishbone}) \quad 4-3$$

Where Metal could be the target heavy metal (Pb, Zn, Cu) or total heavy metal (Pb+Zn+Cu), and 0.1 is the volume of leachant (super-pure water, 100 ml).

Table 4-5 Capacity of natural fishbone on the stabilization of Pb and total heavy metal under different L/S conditions (*Plan B*)

L/S (ml/g)	Capacity on Pb (mg/g)				Capacity on total heavy metal (mg/g)			
	2 h	4 h	12 h	24 h	2 h	4 h	12 h	24 h
10	0.23	0.22	0.18	0.18	0.24	--	--	--
5	0.22	0.23	0.22	0.19	0.23	--	--	--
3	0.24	0.26	0.25	0.23	0.27	0.29	0.27	0.24
1.5	0.29	0.30	0.36	0.35	0.34	0.37	0.44	0.44
1	0.38	0.38	0.40	0.40	0.45	0.47	0.48	0.51
0.5	0.38	0.37	0.39	0.40	0.47	0.46	0.48	0.50
Ref.#	0.24				--			

Total heavy metal = Pb + Zn (Cu was mostly increased in *Plan B*)

Ref. (reference value): capacity of natural Eso fishbone (dosage of 50%) after a 6 h-leaching process (*Plan A*).

-- : value could not be calculated

At the presence of fishbone, Pb as the most toxic heavy metal was primarily focused on, thus the capacity of fishbone on Pb stabilization would be of a constant concern, and treated as an indicator for estimating the availability of this technique. In *Plan B*, higher capacity could generally be obtained with the settlement period expending, but the improvement was not so remarkable, which could be another evidence that Pb stabilization by fishbone would be finished in first few hours. Decreasing L/S could dramatically improve the capacity of fishbone, especially from high L/S conditions to low L/S conditions. The capacity would not be enhanced until L/S reached 1 ml/g. The highest capacity of fishbone on Pb stabilization was 0.40 mg/g, and it appeared several times at the L/S of 1 and 0.5 ml/g. This might be indicated that 0.40 mg/g was the maximum in *Plan B*. Comparing with the reference value obtained in *Plan A*, the capacity has been promoted obviously by providing lower L/S conditions at the same fishbone dosage. This was indicated that

concentrated supply of Pb ions and relatively stable reaction environments benefited the stabilization.

In *Plan B*, Zn could be stabilized when L/S decreased to below 3 ml/g, and in the low L/S conditions ($L/S < 1.5$ ml/g), the improvement of Zn stabilization by longer settlement period was obvious. When calculating the share of Pb in the stabilization in the cases that $L/S < 3$, it could be found that Pb took almost 90% of combination with fishbone at L/S of 3, and then the share decreased to about 80-84% in low L/S conditions ($L/S < 1.5$). In low L/S conditions, the share of Pb in the capacity was decreased with the settlement period expending at the same L/S condition. At the same settlement period, generally, less share of Pb appeared at lower L/S condition, but this trend was more obvious in the cases of shorter settlement periods (2/4 h). When settlement period reached 24 h or L/S reached 0.5 ml/g, the Pb share would be stable at about 80%, which was similar to the ratio of Pb to the total leachable metal (30.50/38.88 mg/l). It was indicated that Pb took the priority in the combination with fishbone (HAP). The speed of the combination between Pb and HAP was faster than that of Zn, but Pb could not take the position of Zn when it has connected to fishbone (HAP). Considering that the system for the combination was in an almost dry state at low L/S conditions ($L/S < 1.5$), ion-exchange mechanism was supposed to be working in the stabilization.

4.3.3 pH of the leachates of MSWI fly ash at the presence of natural fishbone under various L/S conditions (*Plan B*)

The pH of the leachates of fly ash at the presence of fishbone (dosage of 50%) under various L/S conditions was listed in Table 4-6. The same as what was observed in *Plan A*, the leachates that were in a better effectivity of the stabilization of heavy metals were shown in a lower pH. However, all the leachates were in a quite high pH (12.19-12.37). Considering that the reaction between Pb and HAP could be seen as a kind of reciprocal reaction (*see Equations 1-1 and 1-2 on Page 14*), thus the decreasing of pH was inferred not resulting from the stabilization, and probably was related to some reactions about the non-HAP fraction of fishbone (like organic matters).

Table 4-6 pH of the leachates of fly ash at the presence of natural fishbone under various L/S conditions (*Plan B*)

L/S (ml/g)	2 h	4 h	12 h	24 h
10	12.30	12.36	12.26	12.23
5	12.35	12.35	12.25	12.22
3	12.37	12.34	12.25	12.23
1.5	12.32	12.34	12.25	12.22
1	12.31	12.26	12.24	12.19
0.5	12.26	12.27	12.23	12.19
Ref.#	12.27			

Ref. (reference value): pH of the leachate of fly ash with natural Eso fishbone (dosage of 50%) after a 6 h-leaching process (*Plan A*)

Based on the discussions on *Plan A* and *Plan B*, the non-HAP fraction in natural fishbone might cause some unexpected impact to the stabilization of heavy metals in MSWI fly ash. In addition, purified HAP from fishbone might bring a better effectivity on the stabilization of heavy metals with less increment of mass and volume of the final products. Therefore, ignition pretreatment on natural fishbone was taken into account.

4.3.4 Mass loss feature and potential phase transformation of fishbone during ignition

The most critical factor for ignition is the temperature, which determines the change of the chemical and mineral composition of the samples. In order to select the candidate temperatures for the ignition pretreatment on fishbone, thermogravimetry and differential thermal analysis (TG-DTA) was conducted. Considering that the incineration temperature for municipal solid waste is commonly around 850-1000 °C (Bayuseno et al., 2009; Rocca et al., 2012), the maximum temperature in this test was set at 1100 °C, thus the pre-treatment of fishbone could use the common incineration facilities. The TG-DTA result of natural Eso fishbone is shown in Figure 4-5.

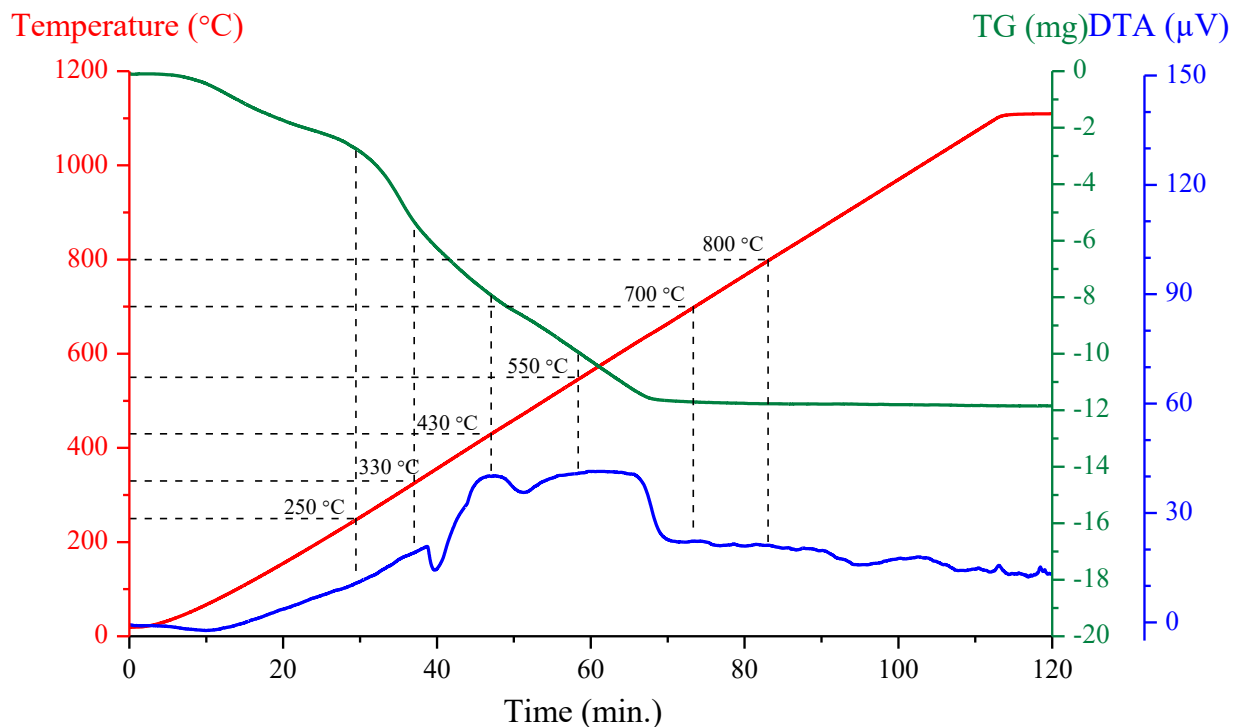


Figure 4-5 TG-DTA results of natural Eso fishbone

On the TG curve (green line), continuous mass loss was observed as a function of temperature. Considering the high water content in organic fraction of the natural fishbone, the ignition temperature was set over 200 °C. The first fast mass loss appeared at 250-330 °C, so two candidate temperatures were set at these two points; then the mass was evenly decreased until about 650 °C, during which there were four negative or positive peaks on the DTA curve (blue line). The positive and negative peaks on DTA presented the phase transformation, which was indicated that fishbone was suffering some significant changes in this range, thus the temperatures before and after every peak- 330, 430, 550 and 700 °C were focused on. After that, both TG and DTA were not changed obviously with the temperature increasing. The decomposition of HAP was started from about 850 °C (Wang et al., 1995), therefore, ignited fishbone at 800 °C was measured as a reference when analyzed the mineral phase transformation by XRD.

4.3.5 Mineral phase transformation and mass loss of natural fishbone during ignition

To obtain the purified HAP and remove the non-HAP fraction (mainly organic matters), natural fishbone was subjected to ignition pre-treatment. According to TG-DTA results (see Figure 4-5 on Page 82), five temperatures (250, 330, 430, 550 and 700 °C) were selected as the candidate ignition temperatures. The mass loss of natural fishbone after the ignition at different temperatures was recorded and presented into percentage that was listed in Table 4-7. Ignited fishbone was quite fragile and performed in different appearances (Figure 4-6), which was named as *IGN-250/330/430/550/700 Eso fishbone* in the thesis. The ignited Eso fishbone was ground manually and then tested by XRD for checking the mineral phase transformation, the patterns of which, as well as the Eso fishbone ignited at 800 °C as the reference, were shown in Figure 4-7.

Table 4-7 Mass loss of natural Eso fishbone under different ignition temperatures

Temperature (°C)	250	330	430	550	700	800
Mass loss (%)	19.82	37.70	45.85	46.54	47.22	48.22

The results shown in Table 4-7 indicated that ignition could effectively reduce the mass of natural fishbone. However, the mass loss process has been almost finished when the temperature reached 430 °C. The maximum of mass loss of natural fishbone under ignition was approximately 50%. The curves shown in Figure 4-7 suggested that HAP was constantly the only mineral phase in natural or ignited fishbone. The state of the mineral phase of HAP in fishbone would not be changed when the temperature was lower than 430 °C. Then the crystallinity of HAP in fishbone was enhanced significantly as a function of ignition temperature when it went higher than 550 °C. The HAP in fishbone was turned to be almost crystalline when the temperature reached 700 °C.

To sum up, the ignition process firstly purified HAP by removing the non-HAP fraction (mainly organic matters), and then increasing the crystallinity of HAP.

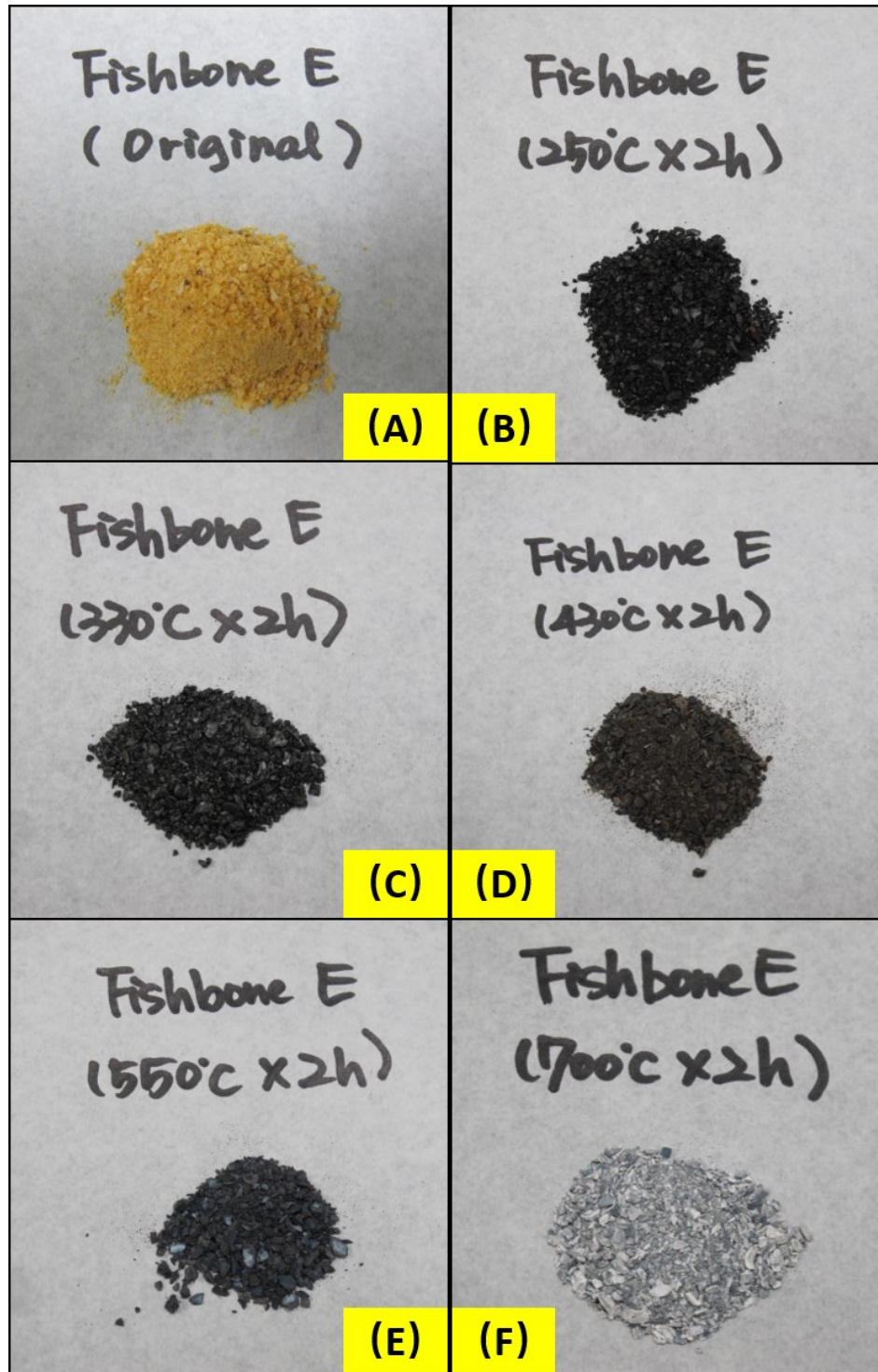


Figure 4-6 Photos of natural and ignited Eso fishbone

(A) natural Eso fishbone; (B) IGN-250 Eso fishbone; (C) IGN-330 Eso fishbone;
(D) IGN-430 Eso fishbone; (E) IGN-550 Eso fishbone; (F) IGN-700 Eso fishbone.

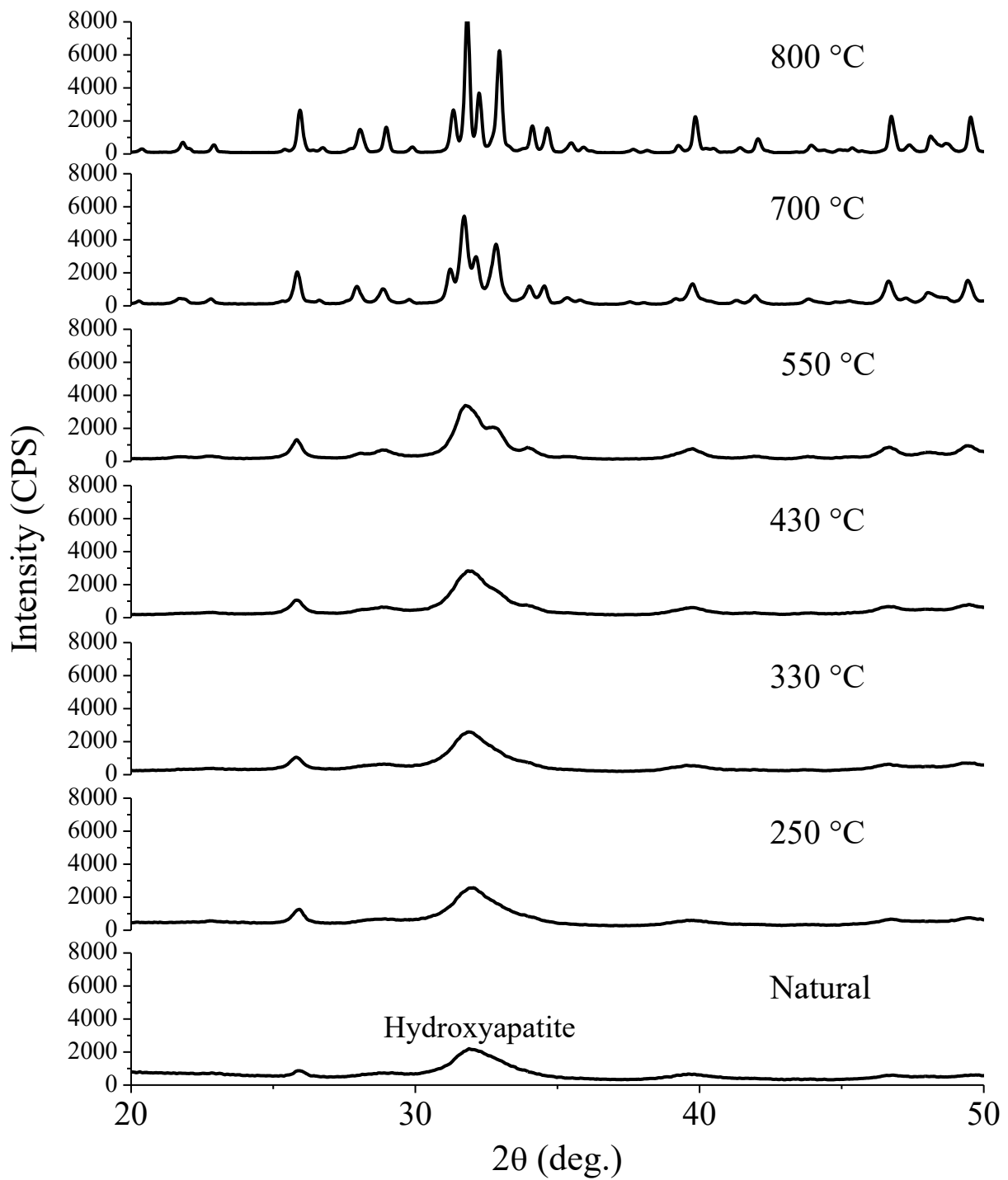


Figure 4-7 XRD patterns of natural and ignited Eso fishbone

4.3.6 Optimal temperature of ignition pretreatment on fishbone

Advanced pretreatment on fishbone was adopted with the aim to improving the effectivity of fishbone on the stabilization of heavy metals (primarily Pb) in MSWI fly ash with a lower increment of volume or mass brought by the additive in the final product. Ignition was taken into account owing to its ability on removing the organic fraction in natural fishbone that was supposed to result in some unexpected effect on the leaching behavior of Cu and Zn (*see Section 3.3.4/4.3.1 on Page 49/70*). Therefore, the selection of the ignition temperature would be according to the performance of ignited fishbone products in the stabilization of heavy metals in MSWI fly ash.

IGN-250/330/430/550/700 Eso fishbone were involved in the stabilization of heavy metals in MSWI fly ash in the ways that directly being added in a 6 h-leaching process (fishbone dosage of 20%, *Plan CA*) and reacting with fly ash under a low L/S condition (L/S of 1, fishbone dosage of 50%, settlement period of 24 h, *Plan CB*). The concentration of heavy metals and P in the leachates from each scenario was analyzed by ICP-AES. The effectivity of ignited fishbone on the stabilization of heavy metals in MSWI fly ash was calculated by Equation 4-4, the control group in which was designated as the original concentration in the leachate of fly ash (fishbone absent) after a 6 h-leaching process (*Plan A*). The concentration of P, Pb, Cu Zn and their removal efficiencies under the two scenarios were shown in Figure 4-8, Table 4-8 and Table 4-9.

$$\text{Metal removal efficiency (\%)} = \left(1 - \frac{C(\text{Metal in test group})}{C(\text{Metal in control group})} \right) \times 100 \quad 4-4$$

Where Metal is the target heavy metal (Pb, Zn, Cu) or total heavy metal (Pb+Zn+Cu).

It was indicated in Figure 4-8 that ignition pretreatment did not always bring higher effectivity on the stabilization of Pb than that of natural fishbone. In *Plan CA*, ignition pretreatment was enhancing the effectivity of fishbone on Pb stabilization. IGN-430 Eso fishbone was in the best performance. The Pb removal efficiency was gradually decreased when adopting the temperatures lower or higher than the optimal one. In *Plan CB*, ignition pretreatment on fishbone was not so effectively improving the effectivity on Pb stabilization as expected. Only the products got from 330-430 °C, ignited fishbone was shown in a better performance than the natural one, and the enhancement was not that obvious. 430 °C was proved to be the optimal ignition temperature in

both two scenarios. When the ignition temperature was in 330-440 °C, ignited fishbone was more effective than the natural one on Pb stabilization.

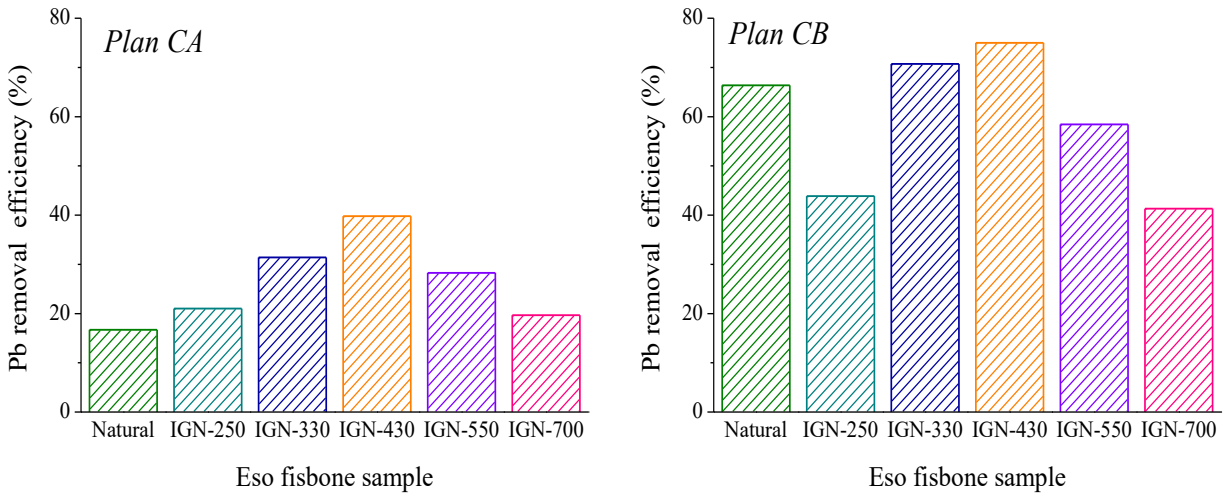


Figure 4-8 Comparison of natural and ignited Eso fishbone on Pb removal efficiency in *Plans CA and CB*

The results of P in the leachates of fly ash at the presence of natural and ignited fishbone (Table 4-8) indicated that P that leached out was relevant to the non-HAP fraction (mainly organic matters) of fishbone. Thus, comparing with the natural fishbone, the leaching of P was obviously decreased to a considerably low concentration when non-HAP fraction was removed or transferred by ignition. When temperature was higher than 330 °C, P concentration in the leachates would be constant.

For Zn stabilization, ignition pretreatment showed positive or negative effects in *Plan CA* and *Plan CB*. In *Plan CA*, there was less Zn appeared in the leachates of ignited fishbone comparing with the natural one; the decrement of Zn was less connected to the ignition temperature. In *Plan CB*, ignition pretreatment generally brought more Zn leached out; the increment of Zn was slight. It was indicated that the ignition pretreatment on fishbone would not give important impact on the Zn stabilization.

For Cu stabilization, the impact of ignition pretreatment for fishbone was significant and similar in *Plan CA* and *Plan CB*. It was shown that ignition temperature was the critical factor for

controlling the leaching behavior of Cu. IGN-250 fishbone brought more Cu detected in the leachate. When the temperature went up to 330 °C, the leaching out of Cu was significantly decreased to almost same content as that by only fly ash itself. Cu would turn to be stabilized when ignition temperature was reached 430 °C, and it was in a considerate low concentration. Then much higher ignition temperature would not bring any improvement.

To sum up, 430 °C was the undisputed optimal temperature for the ignition pretreatment on fishbone among the candidates, which provided the best effectivity of fishbone on Pb stabilization with totally hindering the additional leaching of Cu and P, and did not bring negative impact on Zn stabilization. It should be pointed that, considering that the mass loss of fishbone, ignition process was not only simply purifying the HAP in fishbone (even at the low ignition temperatures), but also increasing the crystallinity of HAP in fishbone. However, the latter was not preferred in the stabilization of heavy metals. Thus the removal efficiency of heavy metal was not doubled when ignition reduced the mass of fishbone by 50%.

According to the discussion about ignition pretreatment on the effectivity of fishbone, IGN-430 Eso fishbone was selected to conduct the experiments about the stabilization of heavy metals in MSWI fly ash by ignited fishbone in the ways that directly being added in a 6 h-leaching process (*Plan CA*) and reacting with fly ash under various L/S conditions (*Plan CB*). The results got from natural Eso fishbone was shown as the reference to present the effect of ignition pre-treatment.

Table 4-8 Concentration of P and heavy metals and their removal efficiencies of natural and ignited Eso fishbone in the leachates (*Plan CA*)

Sample	Concentration (mg/l)				Removal efficiency (%)		
	P	Pb	Zn	Cu	Pb	Zn	Cu
Natural	0.88	25.40	8.25	1.24	16.71	--	--
IGN-250	0.16	24.08	6.23	1.75	21.03	24.26	--
IGN-330	0.06	20.92	6.17	0.20	31.41	25.05	--
IGN-430	0.07	18.36	6.34	0.09	39.78	22.92	39.15
IGN-550	0.07	21.88	6.26	0.10	28.26	23.95	36.39
IGN-700	0.06	24.50	6.16	0.11	19.66	25.21	27.99
Ctrl. *	0.01	30.50	8.23	0.15	--	--	--

* Ctrl. (control group): concentration in the leachate of fly ash (without fishbone) after a 6 h-leaching process (*Plan A*)

-- : value could not be calculated

Table 4-9 Concentration of P and heavy metal and their removal efficiencies of natural and ignited Eso fishbone in the leachates (*Plan CB*)

Sample	Concentration (mg/l)				Removal efficiency (%)		
	P	Pb	Zn	Cu	Pb	Zn	Cu
Natural	2.68	10.26	3.14	2.70	66.35	61.87	--
IGN-250	0.31	17.12	3.91	4.94	43.87	52.52	--
IGN-330	0.06	8.93	3.21	0.25	70.73	60.97	--
IGN-430	0.05	7.62	2.93	0.09	75.01	64.35	42.78
IGN-550	0.06	12.68	3.54	0.11	58.42	56.98	26.04
IGN-700	0.07	17.90	3.91	0.15	41.30	52.44	4.04
Ctrl. *	0.01	30.50	8.23	0.15	--	--	--

* Ctrl. (control group): concentration in the leachate of fly ash (without fishbone) after a 6 h-leaching process (*Plan A*)

-- : value could not be calculated

4.3.7 Effectivity of ignited fishbone on the stabilization of heavy metals in MSWI fly ash during leaching process (*Plan CA*)

The effectivity of ignited Eso fishbone on the stabilization of Pb in MSWI fly ash during leaching process was conducted for a 6 h-leaching process under different fishbone doses. The fishbone/fly ash ratios were set as 10%, 20%, 30%, 50%, 70% and 100% (test groups) by weight. The control group was designated as the original concentration in the leachate of fly ash (fishbone absent) after a 6 h-leaching process (*Plan A*). The concentration of target elements (Pb, Cu, Zn and P) in the leachates was identified by ICP-AES. The Pb removal efficiency in the leachate was calculated by Equation 4-5. The comparisons of Pb removal efficiency and the concentration of P, Pb, Cu, Zn and total metal in the leachates at the presence of natural or IGN-430 Eso fishbone were shown in Figure 4-9 and Table 4-10.

$$\text{Metal removal efficiency (\%)} = \left(1 - \frac{C(\text{Metal in IGN - 430 test group})}{C(\text{Metal in control group})} \right) \times 100 \quad 4-5$$

Where Metal is the target heavy metal (Pb, Zn, Cu) or total heavy metal (Pb+Zn+Cu).

It was shown in Figure 4-9 that Pb removal efficiency was improved by 20% when using IGN-430 Eso fishbone instead of the natural one, and the release of P from fishbone was reduced to a considerate low concentration concurrently. The highest Pb removal efficiency could reach 79% at the ignited fishbone dosage of 100%. The comparison of P concentration implied that the release of P was related to the non-HAP fraction in fishbone, but it was not related to the Pb stabilization. It was observed that P was released and then involved into the reformation process with the contact time expending in *Plan A* (see Figure 3-7 on Page 55), thus it was inferred that the reaction of Pb and HAP was followed as a dissolution-precipitation mechanism. Therefore, what was observed in *Plan CA* suggested that the non-HAP fraction might hinder the combination of Pb and HAP maybe by covering the HAP surface.

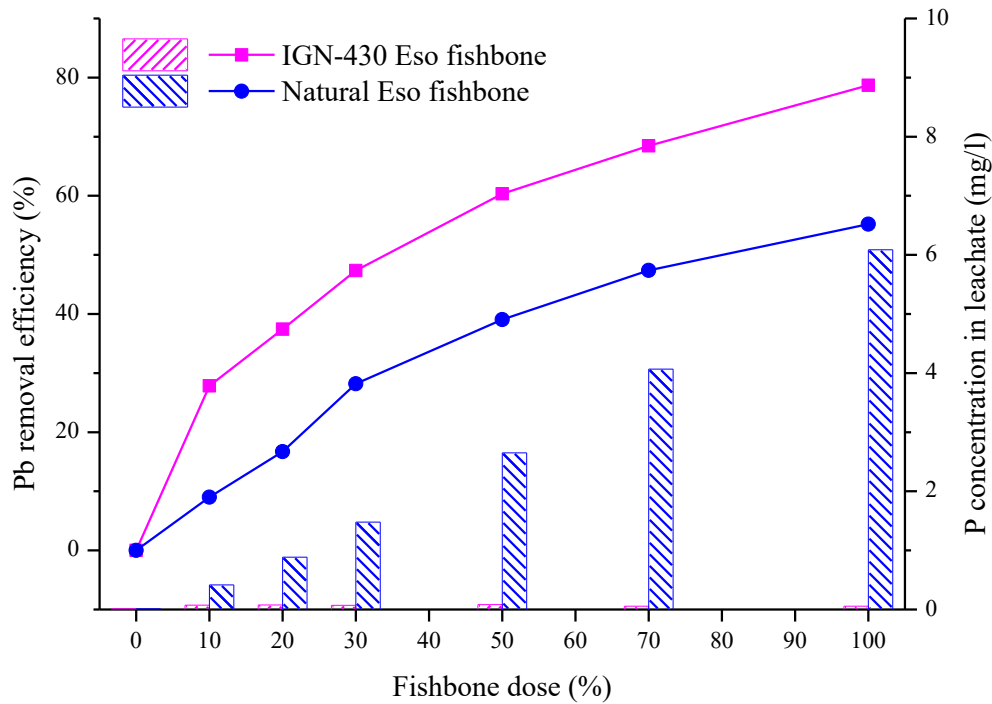


Figure 4-9 Pb removal efficiency (solid lines) and P concentration in the leachates (vertical bars) at the presence of natural or ignited Eso fishbone under various doses after a 6 h-leaching process

The concentration of heavy metals shown in Table 4-10 indicated that ignited fishbone could co-stabilize Pb and Zn during leaching process. Additionally, the release of Cu was well controlled by adopting ignited fishbone, which implied that the non-HAP fraction induced the additional release of Cu from fly ash. Thanks to this conversion, the technique that using fishbone on the stabilization of heavy metals (primary Pb) in MSWI fly ash could reduce the risk of a secondary environmental problem.

Table 4-10 Concentration of heavy metals in the leachate at the presence of ignited or natural Eso fishbone under various doses after a 6 h-leaching process

Fishbone dose (%)	Pb (mg/l)		Zn (mg/l)		Cu (mg/l)		Total metal* (mg/l)	
	IGN-430	Natural	IGN-430	Natural	IGN-430	Natural	IGN-430	Natural
0	30.50		8.23		0.15		38.88	
10	22.01	27.75	7.04	8.75	0.12	0.66	29.16	37.16
20	19.08	25.40	7.20	8.25	0.10	1.24	26.39	34.89
30	16.05	21.90	6.87	7.65	0.10	1.93	23.02	31.47
50	12.09	18.59	6.53	7.50	0.11	3.17	18.74	29.26
70	9.62	16.05	6.22	7.66	0.14	4.23	15.98	27.94
100	6.50	13.66	5.56	8.20	0.17	5.40	12.23	27.27

*Total heavy metal = Pb + Zn + Cu

It was mentioned in *Plan A* that natural fishbone could be separated from fly ash after the treatment by centrifugation owing to the differences of the two materials in particle size and density. However, this separation becomes impossible if using ignited fishbone in this scenario, because the ignited fishbone could be easily ground into tiny powder and totally mixed with fly ash. It should be considered when using ignited fishbone for the stabilization of heavy metals in fly ash as a pre-treatment for the utilization of fly ash.

4.3.8 Effectivity of ignited fishbone on the stabilization of heavy metals in MSWI fly ash under various L/S conditions (*Plan CB*)

The effectivity of ignited Eso fishbone on the stabilization of Pb in MSWI fly ash under various L/S conditions were conducted for a 24 h-settlement period with the fishbone dose of 50%. The L/S ratios were set as 10, 5, 3, 1.5, 1 and 0.5 ml/g, thus the mixtures presented a high L/S (>3) or low L/S (<1.5) state. The control group was designated as the original concentration in the leachate of fly ash (without fishbone) after a 6 h-leaching process (*Plan A*). The concentration of target elements (Pb, Cu, Zn and P) in the leachates was identified by ICP-AES. The Pb removal efficiency in the leachate was calculated by Equation 4-5 (*on Page 90*). The comparisons of Pb

removal efficiency and the concentration of P, Pb, Cu, Zn and total metal in the leachates at the presence of natural or IGN-430 Eso fishbone were shown in Figure 4-10 and Table 4-11.

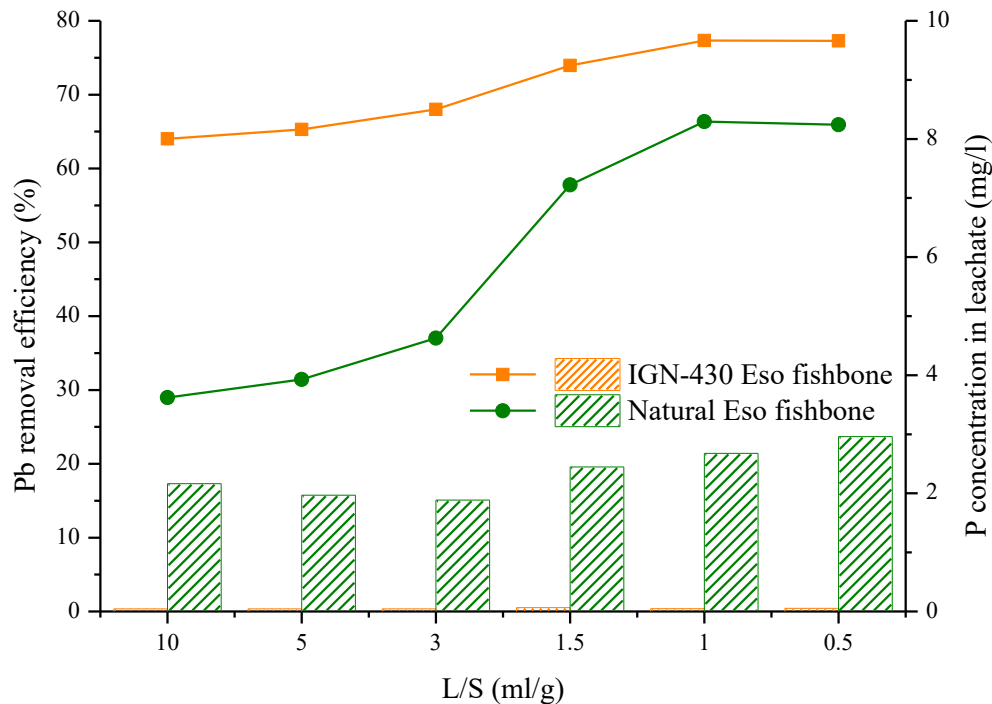


Figure 4-10 Pb removal efficiency (solid lines) and P concentration in the leachate (vertical bars) with the presence of ignited or natural Eso fishbone under various L/S conditions for the settlement period of 24 h

It was shown in Figure 4-10 that Pb removal efficiency was improved when using IGN-430 Eso fishbone instead of the natural one; however, the improvement was more obvious at higher L/S conditions. Pb removal efficiency was not affected so dramatically with the decreasing of L/S as that in the natural fishbone cases. In *Plan B*, that the Pb removal efficiency was increased with the decrease of L/S was attributed to the rich supply of Pb ions supplied to fishbone HAP. What was observed in *Plan CB* also indicated that the non-HAP fraction in fishbone might be hindering the contact of Pb ions and HAP via covering on the surface of fishbone, as what was assumed in *Plan CA*. The release of P was reduced to a considerate low concentration in the cases of ignited fishbone. The highest Pb removal efficiency could reach 77% at the L/S of 1 ml/g. The comparison

of P concentration implied that the release of P was related to the non-HAP fraction in fishbone, but it was not related to the Pb stabilization.

Table 4-11 Concentration of heavy metals in the leachate at the presence of ignited or natural Eso fishbone under various L/S conditions for the settlement period of 24 h

L/S (ml/g)	Pb (mg/l)		Zn (mg/l)		Cu (mg/l)		Total metal* (mg/l)	
	IGN-430	Natural	IGN-430	Natural	IGN-430	Natural	IGN-430	Natural
Ctrl.	30.50		8.23		0.15		38.88	
10	10.97	21.66	7.41	11.21	0.13	3.40	18.51	36.27
5	10.59	20.91	6.31	9.93	0.13	3.60	17.02	34.44
3	9.75	19.20	4.91	7.36	0.11	3.58	14.78	30.14
1.5	7.94	12.87	3.62	3.62	0.10	3.61	11.66	20.10
1	6.92	10.26	3.03	3.14	0.10	2.70	10.05	16.10
0.5	6.93	10.39	3.13	3.09	0.12	1.90	10.18	15.38

*Total heavy metal = Pb + Zn + Cu

Ctrl. (control group): concentration in the leachate of fly ash (without fishbone) after a 6 h-leaching process (*Plan A*)

The concentration of heavy metals in the leachate shown in Table 4-11 indicated that ignited fishbone could co-stabilize Pb and Zn in the way of *Plan B* and *Plan CB*. When ignited fishbone was used instead of natural fishbone, the stabilization of Pb and Zn was both improved. From the viewpoint of removal efficiency, the improvement of Zn was bigger than Pb, which indicated that Zn got more opportunities to combine with fishbone HAP in the ignited fishbone case. In addition, the same as in *Plan CA*, Cu was no need to be worried for the unexpected leaching out when use ignited fishbone instead of the natural one.

Comparing *Plan CA* and *Plan CB*, the highest Pb removal efficiency was both reached 80%. Therefore, based on that ignited fishbone could not be separated with fly ash after the treatment, *Plan CB* was recommended when ignition pretreatment was adopted, for it could save water, time and energy consumption.

4.3.9 Comparison of the capacities of natural and ignited fishbone on stabilization of heavy metals in MSWI fly ash

The capacity of fishbone on the stabilization of heavy metals was also employed to describe the effectivity of unit fishbone by Equation 4-6, where the control group was designated as the original concentration in the leachate of fly ash (fishbone absent) after a 6 h-leaching process (*Plan A*). The results of the capacities on Pb and total metal of ignited fishbone in *Plans CA* and *CB*, as well as the corresponding value tested in natural fishbone case, were listed in Table 4-12 and Table 4-13.

$$\text{Capacity on M stabilization (mg/g)} = \left(1 - \frac{C(\text{M in IGN - 430 test group})}{C(\text{M in control group})} \right) \times 0.1 \div m(\text{fishbone}) \quad 4-6$$

Where M is the target heavy metal (Pb, Zn, Cu) or total heavy metal (Pb+Zn+Cu), and 0.1 is the volume of leachant (super-pure water, 100 ml).

As the most toxic heavy metal in MSWI fly ash, the capacity of fishbone on Pb was primarily focused on. It was indicated in Table 4-12 and Table 4-13 that ignition pretreatment on fishbone was improved the capacity on Pb stabilization in both scenarios, and the improvement in *Plan CA* was obvious than that in *Plan CB*. In *Plan CA*, higher capacity on Pb stabilization was obtained at lower doses of ignited fishbone, similar as what happened in natural fishbone case. This indicated that the rich supply of Pb ions benefited the combination with fishbone HAP. Comparing the increment of capacity on Pb stabilization by ignition pretreatment, it could be found that much more obvious improvement was obtained in the cases of lower doses, which implied that non-HAP fraction might be the main barrier that hindered the combination between Pb ions to fishbone HAP. In *Plan CB*, the capacities of ignited fishbone on Pb stabilization was higher than the maximum obtained from natural fishbone cases; there was still an increasing trend in the capacities with the decreasing of L/S, but the increment was not so significant as what was observed in the cases of the natural fishbone. This indicated that 0.4-0.5 mg/g might be the biggest capacity of fishbone HAP on Pb stabilization under the given conditions. Ignition pretreatment may accelerate the combination between Pb ions and fishbone, but not benefit to higher capacity. Without ignition pretreatment, the possible combinations could be also conducted when given long enough contact time, and 24 h was sufficient for getting maximum value.

When calculating the share of Pb in the total metal (Pb+Zn+Cu) that stabilized by ignited fishbone, they were all at over 80% in both scenarios.

Table 4-12 Capacities of ignited and natural fishbone on the stabilization of Pb and total heavy metal under various doses after a 6 h-leaching process

Fishbone dose (%)	Capacity on Pb (mg/g)		Capacity on total heavy metal* (mg/g)	
	IGN-430	Natural	IGN-430	Natural
10	0.85	0.27	0.97	--
20	0.57	0.25	0.62	--
30	0.48	0.29	0.53	--
50	0.37	0.24	0.40	--
70	0.30	0.21	0.33	--
100	0.24	0.17	0.27	--

*Total heavy metal = Pb + Zn + Cu

-- : value could not be calculated (Cu/Zn was leached out instead of stabilized in *Plan A*)

Table 4-13 Capacities of ignited and natural fishbone on the stabilization of Pb and total heavy metal under various L/S conditions for the settlement period of 24 h

L/S (ml/g)	Capacity on Pb (mg/g)		Capacity on total heavy metal* (mg/g)	
	IGN-430	Natural	IGN-430	Natural
10	0.39	0.18	0.41	--
5	0.40	0.19	0.44	--
3	0.41	0.23	0.48	--
1.5	0.45	0.35	0.54	--
1	0.47	0.40	0.58	--
0.5	0.47	0.40	0.57	--

*Total heavy metal = Pb + Zn + Cu

-- : value could not be calculated (Cu/Zn was leached out instead of stabilized in *Plan B*)

4.4 Section summary

The feasibility of natural fishbone on the stabilization of Pb, which was the most leachable and toxic element in MSWI fly ash, has been proved via directly added into the leaching process of fly ash. Higher capacity of natural fishbone on Pb stabilization was obtained at lower fishbone doses, which might be attributed to the relatively rich supply of Pb ions to fishbone HAP. Therefore, the effectivity of fishbone on the stabilization of heavy metals under various L/S conditions was taken into account.

Natural fishbone was involved in the stabilization of heavy metals under various L/S conditions. Generally, the lower L/S condition was much more beneficial for Pb stabilization by fishbone in MSWI fly ash. When L/S was lower than 1 ml/g, the leaching out of Cu would be suppressed effectively by either L/S ratio or by settlement period. The increasing trend of Zn concentration at fishbone presence could be totally convert to decreasing when L/S was lower than 3 ml/g, and the stabilization of Zn were facilitated visibly both by L/S and by settlement period in the low L/S condition ($L/S < 1.5$).

In addition, Zn and Cu in the leachates were found in an increasing trend at the presence of natural fishbone. The additional release of Zn and Cu might be from MSWI fly ash on the effect of the non-HAP fraction (mainly organic residues) in the fishbone. Therefore, ignition pretreatment on natural fishbone for purified HAP was taken into account.

TG-DTA was launched in order to select the candidate temperatures for the ignition pretreatment on fishbone. Accordingly, 250, 330, 430, 550 and 700 °C were considered. The ignited fishbone from different temperatures were respectively involved in the stabilization of heavy metals in MSWI in the two scenarios that natural fishbone was subjected. Accordingly, 430 °C was the undisputed optimal temperature for the ignition pretreatment on fishbone among the candidates, which provided the best effectivity of fishbone on Pb stabilization with totally hindering the additional leaching of Cu and P, and did not bring negative impact on Zn stabilization. The ignited fishbone at 430 °C (IGN-430 Eso fishbone) was also subjected the batching leaching test via directly added in the leaching process or under various L/S conditions. Ignited fishbone brought a preferred increase of Pb stabilization in *Plan CA*, the increment was almost 20% at each dosage than that of natural fishbone. And the leaching of P and Cu were well controlled to a considerate low concentration. In *Plan CB*, the enhancement by ignition of fishbone on Pb

stabilization was not so high, especially in the low L/S conditions. The mass loss and XRD patterns indicated that the ignition could remove the non-HAP fraction in fishbone, and synchronously improve the crystallinity of HAP, which was in contract not benefit the stabilization of heavy metals.

Chapter 5 Conclusions and recommendation

5.1 Conclusions

Municipal solid waste incineration (MSWI) fly ash is one of the main solid residues derived from the incineration process, which is classified as hazardous waste worldwide owing to the relatively high concentration of heavy metals, which require further treatment before the final disposal in landfill sites. There have been many technologies for the stabilization of heavy metals in MSWI fly ash, most of which were too complicated or expensive to be practically accepted. The most common technique currently is cement treatment which is relatively simple in operation, but the biggest problem was that the volume of the final products were almost doubled. This research was conducted with the aim of stabilizing the heavy metals in MSWI fly ash by waste fishbone as an environmental-friendly technique for final disposal or utilization.

Fishbone is a common type of waste generated from the food and especially fish processing industries. As a bio-waste, fishbone or fish waste were usually treated as the source of organic matters for the by-production. In addition, fishbone is an enriched natural source of hydroxyapatite (HAP). As an inorganic substance, HAP is reported to possess a strong ability on the stabilization of heavy metals by producing metal-HAP bonding. Ample efforts have been conducted for using fishbone on the stabilization of heavy metals in the contaminated environments, while there is no practical investigation for heavy metal stabilization in MSWI fly ash. In addition, MSWI fly ash may provide an extreme environment and relatively low concentration for the reaction of the stabilization, which were different with many previous researches.

Fly ash is discharged as a part of air pollution control (APC) residues that contain pure fly ash and alkaline salts for the adsorption of acid gases. The APC residue has been vastly used to investigate the behavior of heavy metals in fly ash. In the present research, the MSWI fly ashes from three plants in Japan and various types of fishbone from the market were used. Considering that the heavy metals are essentially derived from fly ash, the term APC residue is considered equal with the term fly ash in most cases. The collected fly ash materials were firstly subjected to different tests for characterization. Fly ash is composed of fine particles that produces highly alkaline solution when discharged in the water. The major elements in the fly ash samples were

Ca and Cl. Among the heavy metals, Zn and Pb were the top two elements in the fly ash samples; while after the leaching process, Pb was the most abundant heavy metal in the leachate followed by Zn. Therefore, Pb was primarily focused on in the stabilization process as a significantly toxic element in the soluble form. X-Ray diffraction (XRD) analysis was performed to identify the mineralogical composition of fly ash. This technique determined both major and minor mineral species, however, it was almost impossible to identify any heavy metal related components possibly due to the peak position overlap by the peaks of major phases.

The feasibility of natural fishbone on the stabilization of heavy metals in MSWI fly ash was verified by directly adding natural fishbone powder into the solution during the leaching process (*Plan A*). Three types of fishbone were used in the experiments. The results indicated that natural fishbone could sequester Pb from the leachate, and there were few differences in the effectivities on the stabilization of heavy metal brought by different fishbone species. The tests of the chemical and mineral composition indicated that fishbone was the natural source of HAP and HAP was the only mineral phase in it. When the stabilization of heavy metals was conducted via adding fishbone during the leaching process of fly ash, either longer contact time or higher fishbone dosage benefited the stabilization; while contact time was also not so effective on improving the Pb removal efficiency comparing with adding fishbone dosage. The highest Pb removal efficiency 59.31% at the Eso fishbone dosage of 100% after a 72 h leaching process. However, Zn and particularly Cu were encouraged to leach out rather than to stabilize at the presence of fishbone. The behaviours of Zn and Cu were in different patterns; Zn was increased mildly, while the increment of Cu was noticeable as a function of either fishbone dosage or contact time, and the influence of contact time was bigger. Divalent metal of Cu and Zn was supposed to be stabilized together with P, thus the impact of non-HAP fraction in fishbone was considered. Besides, higher capacity of fishbone on Pb stabilization was obtained at lower dosage. This implied that the relatively abundant supply of heavy metal ions might facilitate the stabilization reactions. Therefore, the influence of liquid/solid (L/S) condition in the stabilization of heavy metals by fishbone was taken into account. Other elements that detected in the leachate were not obviously changed at the presence of fishbone. The pH of the leachate was quite high and was slightly decreased at the presence of fishbone in higher dosage.

Accordingly, two approaches was taken into account for improving the effectivity of fishbone on the stabilization of heavy metals in MSWI fly ash, which were providing various L/S conditions

and taking ignition pretreatment on natural fishbone. Generally, the preferred effectivity on Pb stabilization could be obtained at low L/S conditions. However, Pb removal efficiency could not be enhanced after certain L/S ratios. When L/S was lower than 1 ml/g, the leaching out of Cu would be suppressed effectively by either L/S ratio or by settlement period. The increasing trend of Zn concentration at fishbone presence could be totally convert to decreasing when L/S was lower than 3 ml/g, and the stabilization of Zn were facilitated visibly both by L/S and by settlement period in the low L/S condition ($L/S < 1.5$).

TG-DTA was conducted on fishbone in order to select the candidate temperatures for the ignition based on the potential phase transformation. Accordingly, 250, 330, 430, 550 and 700 °C were chosen as the candidates. Then the ignited fishbone was involved into the stabilization process by directly added during the leaching process (*Plan CA*) and under various L/S conditions (*Plan CB*). Fishbone ignition at 430 °C was chosen as the optimal temperature for the pre-treatment of fishbone, because it could improve the Pb stabilization, and prevent the leaching out of Cu and P into the leachate, and did not bring negative impact on Zn stabilization. Then the ignited fishbone at 430 °C (IGN-430) was also subjected the tests in *Plan CA* and *Plan CB*. In *Plan CA*, ignited fishbone brought a preferred increase of Pb stabilization, and the increment was almost 20% at each dosage than that of natural fishbone. And the leaching of P and Cu were well controlled to a considerate low concentration. In *Plan CB*, the enhancement by ignition of fishbone on Pb stabilization was not so high, especially in the low L/S conditions. The ignition pretreatment not only removed the non-HAP fraction of fishbone but also promoted the crystallinity of HAP, while the latter was not beneficial to the stabilization of heavy metals in MSWI fly ash.

5.2 Recommendation

As a technique that using waste material for the treatment of contamination, fishbone was worth to being considered, especially for the coastal areas or regions. However, based on the extreme environments (high pH and high salinity) provided by MSWI fly ash, the effectivity might be not that high as that obtained in the experiments conducted in lab or controlled environments. In this case, it is better to adding the dosage of fishbone prior to consuming additional chemicals for modifying the properties of sample (like change the pH of MSWI fly ash, etc.)

The non-HAP fraction (mainly organic matters) seems to impact on the heavy metal behavior in leaching process, thus the ignition pretreatment on fishbone was taken into account. However,

ignition did not bring the good results as expected, which means that ignition actually destroyed part of the preferred HAP structure. Therefore, the pretreatment at room temperature for better separation of non-HAP and HAP fraction should be of concerns.

If not used in this way, fishbone may be composted, or used in food industry for animals, and so on. But it should be noticed that fishbone HAP was still the waste even in the by-production which were mainly recovering the organic fraction. So fishbone HAP was originally a part of landfill. The technique we want to develop is not adding new items in landfill sites for the final disposal but just rearrangement. And maybe there are more waste holding this kind of potentials, which might be the path that reduce the pressure of the landfilling.

References

- Admassu, W., Breese, T., 1999. Feasibility of using natural fishbone apatite as a substitute for hydroxyapatite in remediating aqueous heavy metals. *J. Hazard. Mater.* 69, 187–196. doi:10.1016/S0304-3894(99)00102-8
- Aklil, A., Mouflih, M., Sebti, S., 2004. Removal of heavy metal ions from water by using calcined phosphate as a new adsorbent. *J. Hazard. Mater.* 112, 183–90. doi:10.1016/j.jhazmat.2004.05.018
- Alcantara, R., Amores, J., Canoira, L., Fidalgo, E., Franco, M.J., Navarro, A., 2000. Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow. *Biomass and Bioenergy* 18, 515–527. doi:10.1016/S0961-9534(00)00014-3
- Arvanitoyannis, I.S., Kassaveti, A., 2008. Fish industry waste: Treatments, environmental impacts, current and potential uses. *Int. J. Food Sci. Technol.* 43, 726–745. doi:10.1111/j.1365-2621.2006.01513.x
- Bayuseno, A.P., Schmahl, W.W., Müllejans, T., 2009. Hydrothermal processing of MSWI Fly Ash-towards new stable minerals and fixation of heavy metals. *J. Hazard. Mater.* 167, 250–259. doi:10.1016/j.jhazmat.2008.12.119
- Bin, M.I., Dara, A., Sontang, M., Zuha, R., Nina, A., 2013. Fish Bone Waste Utilization Program for Hydroxyapatite Product: a Case Study of Knowledge Transfer From a University To Coastal Communities. *J. Environ. Res. Dev.* 7, 1274–1281.
- Brown, R., Dykstra, J., 1995. Systematic errors in the use of loss-on-ignition to measure unburned carbon in fly ash. *Fuel* 74, 570–574. doi:10.1016/0016-2361(95)98360-Q
- Burris, S.C., Li, D., Riley, J.T., 2005. Comparison of Heating Losses and Macro Thermogravimetric Analysis Procedures for Estimating Unburned Carbon in Combustion Residues. *Energy & Fuels* 19, 1493–1502. doi:10.1021/ef049668f
- Chen, W.-S., Chang, F.-C., Shen, Y.-H., Tsai, M.-S., Ko, C.-H., 2012. Removal of chloride from MSWI fly ash. *J. Hazard. Mater.* 237–238, 116–120. doi:10.1016/j.jhazmat.2012.08.010
- Chen, X., Wright, J. V., Conca, J.L., Peurrung, L.M., 1997. Effects of pH on Heavy Metal Sorption

- on Mineral Apatite. *Environ. Sci. Technol.* 31, 624–631. doi:10.1021/es950882f
- Chimenos, J., Segarra, M., Fernández, M., Espiell, F., 1999. Characterization of the bottom ash in municipal solid waste incinerator. *J. Hazard. Mater.* 64, 211–222. doi:10.1016/S0304-3894(98)00246-5
- Choi, S., Jeong, Y., 2008. The removal of heavy metals in aqueous solution by hydroxyapatite/cellulose composite. *Fibers Polym.* 9, 267–270. doi:10.1007/s12221-008-0042-0
- Cinquepalmi, M.A., Mangialardi, T., Panei, L., Paolini, A.E., Piga, L., 2008. Reuse of cement-solidified municipal incinerator fly ash in cement mortars: Physico-mechanical and leaching characteristics. *J. Hazard. Mater.* 151, 585–593. doi:10.1016/j.jhazmat.2007.06.026
- Colangelo, F., Cioffi, R., Montagnaro, F., Santoro, L., 2012. Soluble salt removal from MSWI fly ash and its stabilization for safer disposal and recovery as road basement material. *Waste Manag.* 32, 1179–1185. doi:10.1016/j.wasman.2011.12.013
- Collettini, C., Viti, C., Tesei, T., Mollo, S., 2013. Thermal decomposition along natural carbonate faults during earthquakes. *Geology* 41, 927–930. doi:10.1130/G34421.1
- Corami, A., D’Acapito, F., Mignardi, S., Ferrini, V., 2008. Removal of Cu from aqueous solutions by synthetic hydroxyapatite: EXAFS investigation. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 149, 209–213. doi:10.1016/j.mseb.2007.11.006
- del Valle-Zermeño, R., Formosa, J., Chimenos, J.M., Martínez, M., Fernández, A.I., 2013. Aggregate material formulated with MSWI bottom ash and APC fly ash for use as secondary building material. *Waste Manag.* 33, 621–7. doi:10.1016/j.wasman.2012.09.015
- del Valle-Zermeño, R., Romero-Güiza, M.S., Chimenos, J.M., Formosa, J., Mata-Alvarez, J., Astals, S., 2015. Biogas upgrading using MSWI bottom ash: An integrated municipal solid waste management. *Renew. Energy* 80, 184–189. doi:10.1016/j.renene.2015.02.006
- Dybowska, A., Manning, D.A.C., Collins, M.J., Wess, T., Woodgate, S., Valsami-Jones, E., 2009. An evaluation of the reactivity of synthetic and natural apatites in the presence of aqueous metals. *Sci. Total Environ.* 407, 2953–65. doi:10.1016/j.scitotenv.2008.12.053
- Ecke, H., Sakanakura, H., Matsuto, T., Tanaka, N., Lagerkvist, A., 2000. State-of-the-art treatment

- processes for municipal solid waste incineration residues in Japan. *Waste Manag. Res.* 18, 41–51. doi:10.1177/0734242X0001800106
- Esteban, M.B., García, A.J., Ramos, P., Márquez, M.C., 2007. Evaluation of fruit-vegetable and fish wastes as alternative feedstuffs in pig diets. *Waste Manag.* 27, 193–200. doi:10.1016/j.wasman.2006.01.004
- Feng, Y., Gong, J.-L., Zeng, G.-M., Niu, Q.-Y., Zhang, H.-Y., Niu, C.-G., Deng, J.-H., Yan, M., 2010. Adsorption of Cd (II) and Zn (II) from aqueous solutions using magnetic hydroxyapatite nanoparticles as adsorbents. *Chem. Eng. J.* 162, 487–494. doi:10.1016/j.cej.2010.05.049
- Ferreira, C., Ribeiro, A., Ottosen, L., 2003. Possible applications for municipal solid waste fly ash. *J. Hazard. Mater.* 96, 201–216. doi:10.1016/S0304-3894(02)00201-7
- Forteza, R., Far, M., Seguí, C., Cerdá, V., 2004. Characterization of bottom ash in municipal solid waste incinerators for its use in road base. *Waste Manag.* 24, 899–909. doi:10.1016/j.wasman.2004.07.004
- Gabrielsen, B.O., Austreng, E., 1998. Growth, product quality and immune status of Atlantic salmon, *Salmo salar* L., fed wet feed with alginate. *Aquac. Res.* 29, 397–401. doi:10.1046/j.1365-2109.1998.00215.x
- García-Lodeiro, I., Carcelen-Taboada, V., Fernández-Jiménez, A., Palomo, A., 2016. Manufacture of hybrid cements with fly ash and bottom ash from a municipal solid waste incinerator. *Constr. Build. Mater.* 105, 218–226. doi:10.1016/j.conbuildmat.2015.12.079
- Ghabbour, E.A., Davies, G., Cuzzo, N.P., Miller, R.O., 2014. Optimized conditions for determination of total soil organic matter in diverse samples by mass loss on ignition. *J. Plant Nutr. Soil Sci.* 177, 914–919. doi:10.1002/jpln.201400326
- Gupta, N., Kushwaha, A.K., Chattopadhyaya, M.C., 2012. Adsorptive removal of Pb²⁺, Co²⁺ and Ni²⁺ by hydroxyapatite/chitosan composite from aqueous solution. *J. Taiwan Inst. Chem. Eng.* doi:10.1016/j.jtice.2011.07.009
- Hammoumi, A., Faid, M., El yachoui, M., Amarouch, H., 1998. Characterization of fermented fish waste used in feeding trials with broilers. *Process Biochem.* 33, 423–427. doi:10.1016/S0032-9592(97)00092-7

- Hartmann, S., Koval', L., Krobankova, H., Matysek, D., Winter, F., Purgar, a., 2015. Possibilities of municipal solid waste incinerator fly ash utilisation. *Waste Manag. Res.* doi:10.1177/0734242X15587545
- Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments: reproducibility and comparability of results. *J. Paleolimnol.* 25, 101–110. doi:10.1023/A:1008119611481
- Hoogsteen, M.J.J., Lantinga, E.A., Bakker, E.J., Groot, J.C.J., Tittonell, P.A., 2015. Estimating soil organic carbon through loss on ignition: effects of ignition conditions and structural water loss. *Eur. J. Soil Sci.* 66, 320–328. doi:10.1111/ejss.12224
- Hoorweg, D., Bhada-Tata, P., 2012. What a waste: A global review of solid waste management, Urban development series; knowledge papers no. 15. World Bank, Washington, DC.
- Hu, Y., Zhang, P., Li, J., Chen, D., 2015. Stabilization and separation of heavy metals in incineration fly ash during the hydrothermal treatment process. *J. Hazard. Mater.* 299, 149–157. doi:10.1016/j.jhazmat.2015.06.002
- Huang, C.-M., Yang, W.-F., Ma, H.-W., Song, Y.-R., 2006. The potential of recycling and reusing municipal solid waste incinerator ash in Taiwan. *Waste Manag.* 26, 979–987. doi:10.1016/j.wasman.2005.09.015
- Husillos Rodríguez, N., Martínez-Ramírez, S., Blanco-Varela, M.T., Donatello, S., Guillem, M., Puig, J., Fos, C., Larrotcha, E., Flores, J., 2013. The effect of using thermally dried sewage sludge as an alternative fuel on Portland cement clinker production. *J. Clean. Prod.* 52, 94–102. doi:10.1016/j.jclepro.2013.02.026
- Ibáñez, R., Andrés, A., Viguri, J., Ortiz, I., Irabien, J., 2000. Characterisation and management of incinerator wastes. *J. Hazard. Mater.* 79, 215–227. doi:10.1016/S0304-3894(00)00268-5
- Islam, K.M.N., 2016. Municipal Solid Waste to Energy Generation in Bangladesh: Possible Scenarios to Generate Renewable Electricity in Dhaka and Chittagong City. *J. Renew. Energy* 2016, 1–16. doi:10.1155/2016/1712370
- Karak, T., Bhagat, R.M., Bhattacharyya, P., 2012. Municipal Solid Waste Generation, Composition, and Management: The World Scenario. *Crit. Rev. Environ. Sci. Technol.* 42, 1509–1630. doi:10.1080/10643389.2011.569871

- Kato, S., Kunisawa, K., Kojima, T., Murakami, S., 2004. Evaluation of ozone treated fish waste oil as a fuel for transportation. *J. Chem. Eng. Japan* 37, 863–870. doi:10.1252/jcej.37.863
- Khan, M.A.A., Hossain, M.A., Hara, K., Osatomi, K., Ishihara, T., Nozaki, Y., 2003. Effect of enzymatic fish-scrap protein hydrolysate on gel-forming ability and denaturation of lizard fish *Saurida wanieso* surimi during frozen storage. *Fish. Sci.* 69, 1271–1280. doi:10.1111/j.0919-9268.2003.00755.x
- Kiattikomol, K., Jaturapitakkul, C., Songpiriyakij, S., Chutubtim, S., 2001. A study of ground coarse fly ashes with different finenesses from various sources as pozzolanic materials. *Cem. Concr. Compos.* 23, 335–343. doi:10.1016/S0958-9465(01)00016-6
- Kim, M.-R., Jang, J.-G., Lee, S.-K., Hwang, B.-Y., Lee, J.-K., 2010. Correlation between the ash composition and melting temperature of waste incineration residue. *Korean J. Chem. Eng.* 27, 1028–1034. doi:10.1007/s11814-010-0156-0
- Kizilkaya, B., Tekinay, A.A., Dilgin, Y., 2010. Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones. *Desalination* 264, 37–47. doi:10.1016/j.desal.2010.06.076
- Kizilkaya, B., Tekinay, A.A., 2014. Utilization to Remove Pb (II) Ions from Aqueous Environments Using Waste Fish Bones by Ion Exchange. *J. Chem.* 2014, 1–12. doi:10.1155/2014/739273
- Konen, M.E., Jacobs, P.M., Burras, C.L., Talaga, B.J., Mason, J.A., 2002. Equations for Predicting Soil Organic Carbon Using Loss-on-Ignition for North Central U.S. Soils. *Soil Sci. Soc. Am. J.* 66, 1878–1881. doi:10.2136/sssaj2002.1878
- Kotzamanis, Y.P., Alexis, M.N., Andriopoulou, A., Castritsi-Cathariou, I., Fotis, G., 2001. Utilization of waste material resulting from trout processing in gilthead bream (*Sparus aurata* L.) diets. *Aquac. Res.* 32, 288–295. doi:10.1046/j.1355-557x.2001.00042.x
- Kristinsson, H.G., Rasco, B.A., 2000. Fish Protein Hydrolysates: Production, Biochemical, and Functional Properties, *Critical Reviews in Food Science and Nutrition*. TAYLOR & FRANCIS. doi: 10.1080/10408690091189266
- Lam, C.H.K., Ip, A.W.M., Barford, J.P., McKay, G., 2010. Use of incineration MSW ash: A review. *Sustainability* 2, 1943–1968. doi:10.3390/su2071943

- Lei, Y., Dang, Y., Lan, Z., Sun, D., 2016. Effects of multiple inhibitory components on anaerobic treatment processes in municipal solid waste incineration leachate. *Appl. Microbiol. Biotechnol.* 100, 5123–5130. doi:10.1007/s00253-016-7341-y
- Li, X.-G., Lv, Y., Ma, B.-G., Chen, Q.-B., Yin, X.-B., Jian, S.-W., 2012. Utilization of municipal solid waste incineration bottom ash in blended cement. *J. Clean. Prod.* 32, 96–100. doi:10.1016/j.jclepro.2012.03.038
- Lim, H.K., Teng, T.T., Ibrahim, M.H., Ahmad, A., Chee, H.T., 2012. Adsorption and Removal of Zinc (II) from Aqueous Solution Using Powdered Fish Bones. *APCBEE Procedia* 1, 96–102. doi:10.1016/j.apcbee.2012.03.017
- Lin, R.-B., Shih, S.-M., Liu, C.-F., 2003. Structural Properties and Reactivities of Ca(OH)₂ /Fly Ash Sorbents for Flue Gas Desulfurization. *Ind. Eng. Chem. Res.* 42, 1350–1356. doi:10.1021/ie020289o
- Lindberg, D., Molin, C., Hupa, M., 2015. Thermal treatment of solid residues from WtE units: A review. *Waste Manag.* 37, 82–94. doi:10.1016/j.wasman.2014.12.009
- Lundtorp, K., Jensen, D.L., Sørensen, M. a, Christensen, T.H., Mogensen, E.P.B., 2002. Treatment of waste incinerator air-pollution-control residues with FeSO₄: concept and product characterisation. *Waste Manag. Res.* 20, 69–79. doi:10.1177/0734242X0202000108
- Massaccesi, L., Bardgett, R.D., Agnelli, A., Ostle, N., Wilby, A., Orwin, K.H., 2015. Impact of plant species evenness, dominant species identity and spatial arrangement on the structure and functioning of soil microbial communities in a model grassland. *Oecologia* 177, 747–759. doi:10.1007/s00442-014-3135-z
- Morimura, S., Nagata, H., Uemura, Y., Fahmi, A., Shigematsu, T., Kida, K., 2002. Development of an effective process for utilization of collagen from livestock and fish waste. *Process Biochem.* 37, 1403–1412. doi:10.1016/S0032-9592(02)00024-9
- Nagai, T., Suzuki, N., 2000. Isolation of collagen from fish waste material — skin, bone and fins. *Food Chem.* 68, 277–281. doi:10.1016/S0308-8146(99)00188-0
- Narasaraju, T.S.B., Phebe, D.E., 1996. Some physico-chemical aspects of hydroxylapatite. *J. Mater. Sci.* 31, 1–21. doi:10.1007/BF00355120

- Ng, W.P.Q., Lam, H.L., Varbanov, P.S., Klemeš, J.J., 2014. Waste-to-Energy (WTE) network synthesis for Municipal Solid Waste (MSW). *Energy Convers. Manag.* 85, 866–874. doi:10.1016/j.enconman.2014.01.004
- Nixon, J.D., Dey, P.K., Ghosh, S.K., Davies, P.A., 2013. Evaluation of options for energy recovery from municipal solid waste in India using the hierarchical analytical network process. *Energy* 59, 215–223. doi:10.1016/j.energy.2013.06.052
- Nzihou, A., Sharrock, P., 2010. Role of Phosphate in the Remediation and Reuse of Heavy Metal Polluted Wastes and Sites. *Waste and Biomass Valorization* 1, 163–174. doi:10.1007/s12649-009-9006-x
- Oliva, J., Cama, J., Cortina, J.L., Ayora, C., De Pablo, J., 2012. Biogenic hydroxyapatite (Apatite IITM) dissolution kinetics and metal removal from acid mine drainage. *J. Hazard. Mater.* 213–214, 7–18. doi:10.1016/j.jhazmat.2012.01.027
- Oliva, J., De Pablo, J., Cortina, J.-L., Cama, J., Ayora, C., 2010. The use of Apatite IITM to remove divalent metal ions zinc(II), lead(II), manganese(II) and iron(II) from water in passive treatment systems: column experiments. *J. Hazard. Mater.* 184, 364–74. doi:10.1016/j.jhazmat.2010.08.045
- Oliva, J., De Pablo, J., Cortina, J.L., Cama, J., Ayora, C., 2011. Removal of cadmium, copper, nickel, cobalt and mercury from water by Apatite IITM: Column experiments. *J. Hazard. Mater.* 194, 312–323. doi:10.1016/j.jhazmat.2011.07.104
- Orozco, A., Ahmad, M., Rooney, D., Walker, G., 2007. Dilute Acid Hydrolysis of Cellulose and Cellulosic Bio-Waste Using a Microwave Reactor System. *Process Saf. Environ. Prot.* 85, 446–449. doi:10.1205/psep07003
- Ozawa, M., Kanahara, S., 2005. Removal of aqueous lead by fish-bone waste hydroxyapatite powder. *J. Mater. Sci.* 40, 1037–1038. doi:10.1007/s10853-005-6529-9
- Ozawa, M., Satake, K., Suzuki, R., 2003. Removal of aqueous chromium by fish bone waste originated hydroxyapatite. *J. Mater. Sci. Lett.* 22, 513–514. doi:10.1023/A:1022982218727
- Ozawa, M., Suzuki, S., 2002. Microstructural Development of Natural Hydroxyapatite Originated from Fish-Bone Waste through Heat Treatment. *J. Am. Ceram. Soc.* 85, 1315–1317. doi:10.1111/j.1151-2916.2002.tb00268.x

- Palanivel, T.M., Sulaiman, H., 2014. Generation and Composition of Municipal Solid Waste (MSW) in Muscat, Sultanate of Oman. *APCBEE Procedia* 10, 96–102. doi:10.1016/j.apcbee.2014.10.024
- Piantone, P., Bodéan, F., Derie, R., Depelsenaire, G., 2003. Monitoring the stabilization of municipal solid waste incineration fly ash by phosphation: mineralogical and balance approach. *Waste Manag.* 23, 225–243. doi:10.1016/S0956-053X(01)00058-7
- Quina, M.J., Bordado, J.C., Quinta-Ferreira, R.M., 2008a. Treatment and use of air pollution control residues from MSW incineration: An overview. *Waste Manag.* 28, 2097–2121. doi:10.1016/j.wasman.2007.08.030
- Quina, M.J., Bordado, J.C.M.J.C.M., Quinta-Ferreira, R.M., 2010. Chemical stabilization of air pollution control residues from municipal solid waste incineration. *J. Hazard. Mater.* 179, 382–392. doi:10.1016/j.jhazmat.2010.03.016
- Quina, M.J., Santos, R.C., Bordado, J.C., Quinta-Ferreira, R.M., 2008b. Characterization of air pollution control residues produced in a municipal solid waste incinerator in Portugal. *J. Hazard. Mater.* 152, 853–869. doi:10.1016/j.jhazmat.2007.07.055
- Rand, T., Haukohl, J., Marxen, U., 2000. *Municipal Solid Waste Incineration A Decision Maker's Guide*. Washington, D.C. : The World Bank.
- Rocca, S., van Zomeren, A., Costa, G., Dijkstra, J.J., Comans, R.N.J., Lombardi, F., 2012. Characterisation of major component leaching and buffering capacity of RDF incineration and gasification bottom ash in relation to reuse or disposal scenarios. *Waste Manag.* 32, 759–768. doi:10.1016/j.wasman.2011.11.018
- Sabbas, T., Poletini, A., Pomi, R., Astrup, T., Hjelm, O., Mostbauer, P., Cappai, G., Magel, G., Salhofer, S., Speiser, C., Heuss-Assbichler, S., Klein, R., Lechner, P., 2003. Management of municipal solid waste incineration residues. *Waste Manag.* 23, 61–88. doi:10.1016/S0956-053X(02)00161-7
- Saikia, N., Kato, S., Kojima, T., 2007. Production of cement clinkers from municipal solid waste incineration (MSWI) fly ash. *Waste Manag.* 27, 1178–1189. doi:10.1016/j.wasman.2006.06.004
- Sakai, S., Hiraoka, M., 2000. Municipal solid waste incinerator residue recycling by thermal

- processes. *Waste Manag.* 20, 249–258. doi:[http://dx.doi.org/10.1016/S0956-053X\(99\)00315-3](http://dx.doi.org/10.1016/S0956-053X(99)00315-3)
- Santisteban, J.I., Mediavilla, R., López-Pamo, E., Dabrio, C.J., Blanca Ruiz Zapata, M., José Gil García, M., Castaño, S., Martínez-Alfaro, P.E., 2004. Loss on ignition: a qualitative or quantitative method for organic matter and carbonate mineral content in sediments? *J. Paleolimnol.* 32, 287–299. doi:[10.1023/B:JOPL.0000042999.30131.5b](https://doi.org/10.1023/B:JOPL.0000042999.30131.5b)
- Saxena, S., D'Souza, S.F.F., 2006. Heavy metal pollution abatement using rock phosphate mineral. *Environ. Int.* 32, 199–202. doi:[10.1016/j.envint.2005.08.011](https://doi.org/10.1016/j.envint.2005.08.011)
- Shathika Sulthana Begum, B., Gandhimathi, R., Ramesh, S.T., Nidheesh, P. V., 2013. Utilization of textile effluent wastewater treatment plant sludge as brick material. *J. Mater. Cycles Waste Manag.* 15, 564–570. doi:[10.1007/s10163-013-0139-4](https://doi.org/10.1007/s10163-013-0139-4)
- Shekdar, A. V., 2009. Sustainable solid waste management: An integrated approach for Asian countries. *Waste Manag.* 29, 1438–1448. doi:[10.1016/j.wasman.2008.08.025](https://doi.org/10.1016/j.wasman.2008.08.025)
- Singh, R.P., Tyagi, V. V., Allen, T., Ibrahim, M.H., Kothari, R., 2011. An overview for exploring the possibilities of energy generation from municipal solid waste (MSW) in Indian scenario. *Renew. Sustain. Energy Rev.* 15, 4797–4808. doi:[10.1016/j.rser.2011.07.071](https://doi.org/10.1016/j.rser.2011.07.071)
- Song, Y., Li, B., Yang, E.H., Liu, Y., Ding, T., 2015. Feasibility study on utilization of municipal solid waste incineration bottom ash as aerating agent for the production of autoclaved aerated concrete. *Cem. Concr. Compos.* 56, 51–58. doi:[10.1016/j.cemconcomp.2014.11.006](https://doi.org/10.1016/j.cemconcomp.2014.11.006)
- Styszko-Grochowiak, K., Gołaś, J., Jankowski, H., Koziński, S., 2004. Characterization of the coal fly ash for the purpose of improvement of industrial on-line measurement of unburned carbon content. *Fuel* 83, 1847–1853. doi:[10.1016/j.fuel.2004.03.005](https://doi.org/10.1016/j.fuel.2004.03.005)
- Sugiyama, S., Ichii, T., Fujisawa, M., Kawashiro, K., Tomida, T., Shigemoto, N., Hayashi, H., 2003. Heavy metal immobilization in aqueous solution using calcium phosphate and calcium hydrogen phosphates. *J. Colloid Interface Sci.* 259, 408–410. doi:[10.1016/S0021-9797\(02\)00211-4](https://doi.org/10.1016/S0021-9797(02)00211-4)
- Sun, X., Li, J., Zhao, X., Zhu, B., Zhang, G., 2016. A Review on the Management of Municipal Solid Waste Fly Ash in American. *Procedia Environ. Sci.* 31, 535–540. doi:[10.1016/j.proenv.2016.02.079](https://doi.org/10.1016/j.proenv.2016.02.079)

- Sutherland, R.A., 1998. Loss-on-ignition estimates of organic matter and relationships to organic carbon in fluvial bed sediments. *Hydrobiologia* 389, 153–167. doi:10.1023/A:1003570219018
- Suzuki, T., Hatsushika, T., Hayakawa, Y., 1981. Synthetic hydroxyapatites employed as inorganic cation-exchangers. *J. Chem. Soc. Faraday Trans. 1* 77, 1059–1062. doi:10.1039/f19817701059
- Tan, E., Kizilkaya, B., Ucyol, N., Ormanci, H.B., Oral, A., 2014. Surface modification with P-aminohippuric acid on biogenic apatite (fish bones) particles. *Mar. Sci. Technol. Bull.*
- Tavares, J.F., Baptista, J.A., Marcone, M.F., 1997. Milk-coagulating enzymes of tuna fish waste as a rennet substitute. *Int. J. Food Sci. Nutr.* 48, 169–76.
- Thipse, S.S., Schoenitz, M., Dreizin, E.L., 2002. Morphology and composition of the fly ash particles produced in incineration of municipal solid waste. *Fuel Process. Technol.* 75, 173–184. doi:10.1016/S0378-3820(02)00007-3
- Vandenberghe, R.E., de Resende, V.G., da Costa, G.M., De Grave, E., 2010. Study of loss-on-ignition anomalies found in ashes from combustion of iron-rich coal. *Fuel* 89, 2405–2410. doi:10.1016/j.fuel.2010.01.022
- Vemic, M., Bordas, F., Guibaud, G., Joussein, E., Labanowski, J., Lens, P.N.L., van Hullebusch, E.D., 2015. Mineralogy and metals speciation in Mo rich mineral sludges generated at a metal recycling plant. *Waste Manag.* 38, 303–311. doi:10.1016/j.wasman.2014.12.021
- Vila, M., Sánchez-Salcedo, S., Vallet-Regí, M., 2012. Hydroxyapatite foams for the immobilization of heavy metals: From waters to the human body. *Inorganica Chim. Acta* 393, 24–35. doi:10.1016/j.ica.2012.06.027
- Walter E. Dean, 1974. Determination of Carbonate and Organic Matter in Calcareous Sediments and Sedimentary Rocks by Loss on Ignition: Comparison With Other Methods. *J. Sediment. Res.* 44, 242–248.
- Wang, B.C., Chang, E., Lee, T.M., Yang, C.Y., 1995. Changes in phases and crystallinity of plasma-sprayed hydroxyapatite coatings under heat treatment: A quantitative study. *J. Biomed. Mater. Res.* 29, 1483–1492. doi:10.1002/jbm.820291204

- Wang, D., Guan, X., Huang, F., Li, S., Shen, Y., Chen, J., Long, H., 2016. Removal of heavy metal ions by biogenic hydroxyapatite: Morphology influence and mechanism study. *Russ. J. Phys. Chem. A* 90, 1557–1562. doi:10.1134/S0036024416080069
- Wang, J.-P., Wang, X.-J., Zhang, J., 2013. Evaluating loss-on-ignition method for determinations of soil organic and inorganic carbon in arid soils of northwestern china. *Pedosphere* 23, 593–599. doi:10.1016/S1002-0160(13)60052-1
- Wang, K.-S., Chiang, K.-Y., Perng, J.-K., Sun, C.-J., 1998. The characteristics study on sintering of municipal solid waste incinerator ashes. *J. Hazard. Mater.* 59, 201–210. doi:10.1016/S0304-3894(97)00147-7
- Wang, L., Jin, Y., Nie, Y., 2010. Investigation of accelerated and natural carbonation of MSWI fly ash with a high content of Ca. *J. Hazard. Mater.* 174, 334–343. doi:10.1016/j.jhazmat.2009.09.055
- Wang, Q., Li, Y., Wang, Y., 2011. Optimizing the weight loss-on-ignition methodology to quantify organic and carbonate carbon of sediments from diverse sources. *Environ. Monit. Assess.* 174, 241–257. doi:10.1007/s10661-010-1454-z
- Yaacoubi, H., Zidani, O., Mouflih, M., Gourai, M., Sebti, S., 2014. Removal of Cadmium from water using Natural phosphate as Adsorbent, in: *Procedia Engineering*. Elsevier, pp. 386–393. doi:10.1016/j.proeng.2014.09.039
- Yang, S., Saffarzadeh, A., Shimaoka, T., Kawano, T., 2014. Existence of Cl in municipal solid waste incineration bottom ash and dechlorination effect of thermal treatment. *J. Hazard. Mater.* 267, 214–220. doi:10.1016/j.jhazmat.2013.12.045
- Yousuf, T. Bin, Rahman, M., 2007. Monitoring quantity and characteristics of municipal solid waste in Dhaka City. *Environ. Monit. Assess.* 135, 3–11. doi:10.1007/s10661-007-9710-6
- Zacco, A., Borgese, L., Gianoncelli, A., Struis, R.P.W.J., Depero, L.E., Bontempi, E., 2014. Review of fly ash inertisation treatments and recycling. *Environ. Chem. Lett.* 12, 153–175. doi:10.1007/s10311-014-0454-6
- Zayed, E.M., Sokker, H.H., Albishri, H.M., Farag, A.M., 2013. Potential use of novel modified fishbone for anchoring hazardous metal ions from their solutions. *Ecol. Eng.* 61, 390–393. doi:10.1016/j.ecoleng.2013.09.010

- Zhang, D.Q., Tan, S.K., Gersberg, R.M., 2010. Municipal solid waste management in China: Status, problems and challenges. *J. Environ. Manage.* 91, 1623–1633. doi:10.1016/j.jenvman.2010.03.012
- Zhang, H., Zhao, Y., Qi, J., 2011. Utilization of municipal solid waste incineration (MSWI) fly ash in ceramic brick: product characterization and environmental toxicity. *Waste Manag.* 31, 331–41. doi:10.1016/j.wasman.2010.10.017
- Zhang, W., Honaker, R., 2015. Studies on carbon flotation from fly ash. *Fuel Process. Technol.* 139, 236–241. doi:10.1016/j.fuproc.2015.06.045
- Zhang, Z., Li, A., Wang, X., Zhang, L., 2016. Stabilization/solidification of municipal solid waste incineration fly ash via co-sintering with waste-derived vitrified amorphous slag. *Waste Manag.* doi:10.1016/j.wasman.2016.07.002