NANYANG TECHNOLOGICAL UNIVERSITY

Incineration Bottom Ash Treatment through Accelerated Carbonation

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING

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ABSTRACT

In Singapore, incineration is the main waste management technology used for handling municipal solid waste (MSW), in conjunction with recycling and other waste minimisation policy. After incineration, the volume of waste can be reduced up to 90%, thereby significantly reducing the demand of land space for the final disposal of waste. However, incineration cannot completely eradicate the need for landfill as the end product of incineration, i.e. incineration ash, still has to be disposed of properly in a sanitary landfill. Currently, Singapore's only offshore landfill, Pulau Semakau, is estimated to last till 2035. With a lack of suitable alternative landfill in land scarce Singapore, there is an urgency to utilise incineration bottom ash (IBA), which accounts for 85-95% of the total residues produced after incineration, so as to prolong the lifespan of the landfill. Before IBA can be utilised, it has to be treated to reduce the leaching of heavy metals. This research proposes accelerated carbonation for IBA treatment as it has some advantages over other methods, and has not yet been explored in Singapore. Literature review has also shown this process is sustainable and economically viable.

Before accelerated carbonation was carried out, the physical and chemical characteristics of untreated IBA were studied by collecting and analysing IBA from two incineration plants in Singapore, over a 6 months period. The two incineration plants, i.e. SWTEP and TSIP, were selected based on the types of waste received, which could then produce different mineralogical compositions of IBA. The 6 months sampling period was decided to cover the possible temporal variation of IBA characteristics. This characterisation study showed that the total element contents of IBA from both incineration plants in Singapore are similar to those in other countries reported in literature. However, elements like Cd, Co, Hg, Pb and Se exhibited high variation over the investigated sampling period. Pb showed similar high variation in leaching test.

The accelerated carbonation experiment was divided into two parts. In the first part, the influence of moisture content and temperature on accelerated carbonation was

investigated using the 0-2 mm size fraction of IBA. The optimum operating conditions found in the first part was then applied to other size fractions (i.e. 2-4 mm, 4-20 mm and 20-50 mm) in the second part of the experiment. Results showed that the optimum operating conditions fixed at 20% CO_2 for the two incineration plants were slightly different. For SWTEP, it was 35°C and 15% moisture content. For TSIP, it was 50°C and 15% moisture content. The carbonation duration for both plants was 2 hours. XRD analysis showed slight difference between the mineralogical compositions of the two incineration plants, which could explain the different optimum carbonation temperatures.

Most of the heavy metals (i.e. Pb, Zn, Cu and Cr) were found to reduce in leaching after accelerated carbonation, whereas Mo and Sb leaching increased after carbonation. After sieving, the amount released from untreated IBA decreased as the size fractions increased. The leaching mechanism among the different size fractions was found to be similar. Despite the limitations in reducing the leaching of certain trace elements, accelerated carbonation was able to significantly reduce the amount released of Pb, Zn, Cu and Cr, which were much higher in the amount released, compared to Mo and Sb. On the other hand, accelerated carbonation was found to be ineffective in reducing the leaching of soluble salts.

In conclusion, this research has shown that accelerated carbonation has the potential to treat IBA effectively within a short time frame.

PUBLICATIONS

Manuscript submitted to peer-review journals

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LIST OF ABBREVIATIONS

Abbreviation	Description
CCS	Carbon Capture Storage
DI	Deionised
DOC	Dissolved Organic Carbon
GOF	Goodness of Fit
IBA	Incineration Bottom Ash
IFA	Incineration Fly Ash
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrometry
IC	Ion Chromatography
LOI	Loss of Ignition
MSW	Municipal Solid Waste
SWTEP	Senoko Waste to Energy Plant
TC	Total Carbon
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TSIP	Tuas South Incineration Plant
XRD	X-Ray Diffraction

CHAPTER 1: INTRODUCTION

1.1 Background

Municipal solid waste (MSW) is an inevitable by-product of human lifestyle. The management of MSW has become a challenge as the rate of generation per person per day increases at exponential rate. According to the World Bank report (2012), the world cities are currently generating about 1.3 billion tonnes of solid waste per year, or 1.2 kg per person per day. Ten years ago, it was only 0.64 kg per person per day. And by 2025, it is projected to increase to 2.2 billion tonnes per year. Hence, the management of municipal solid waste has to be efficient and affordable so as to maintain a reasonable level of hygiene for human community.

The common method for waste disposal used worldwide is landfill (World Bank, 2012). In 1999, the European Union (EU) issued a Landfill Directive to reduce the use of landfills and the type of wastes that are acceptable to landfill (CEU, 1999). This means that EU members are encouraged to improve the recycling rate or use alternative waste treatment technology (such as composting and incineration) to reduce the amount of waste needed to be landfilled. However, incineration is not the last step in the treatment of MSW as incineration ash, which is the remains of the non-combustible portion of MSW, is produced. Incineration ash cannot be disposed directly into the landfills without treatment as the council of EU has issued a set of criteria for leaching limits acceptable at landfills for hazardous waste (CEU, 2003).

Incineration is the main technology used for the management of MSW in Singapore. It is the preferential choice for a tiny island like Singapore. Firstly, waste can be disposed of in an efficient and hygienic manner through mass burning, thereby maintaining a high level of cleanliness in the country; secondly, the volume of the waste is reduced by approximately 90% after incineration, so the amount of land needed for the final disposal of ash is greatly reduced. In addition, by providing affordable waste disposal through the extensive use of incineration, Singapore has been able to control illegal dumping. Hence, incineration plants have been playing an important role in Singapore's waste management since the first plant was

commissioned in 1979. However, incineration should not be considered as the final step for waste management as the ash generated still needs to be treated and disposed properly.

Currently in Singapore, all the incineration bottom ash (IBA) and fly ash (IFA) are mixed at the bottom ash pits inside the incineration plants, before they are landfilled in an offshore island, Pulau Semakau. The only resource recovery is done by a magnetic separator placed above the conveyor belt to recover the scrap ferrous metal before the incineration ash reaches the ash pits. Pulau Semakau, the only landfill in Singapore, is estimated to last till 2035. In view of the lack of alternative landfill option in land-scarce Singapore, there is an urgent need to explore ways to utilise the incineration ash. In recent years, Singapore has been exploring ways to utilise IBA as European Waste Catalogue classifies IBA as a non-hazardous waste and hence, can be utilised after proper treatment. A major concern in the utilisation of IBA is the leaching of heavy metals and highly soluble salts, which may occur over the period of utilisation due to the interaction of IBA with water such as rain or groundwater. The dissolved heavy metals pose a risk in polluting the surrounding groundwater to toxic levels while soluble salts such as chloride salts are detrimental to the soundness of structural buildings. Therefore, IBA has to be treated to reduce leaching before utilisation. Some of the treatment technologies include washing, extraction with chelating agents, stabilisation/solidification with cement, and natural weathering (Todorovic and Ecke, 2006).

IBA from burning of MSW undergoes carbonation with atmospheric CO_2 naturally at ambient conditions, due to its metastable state after quenching with water straight after combustion at high temperature (Rendek et al., 2006). This process, known as natural weathering or aging, is beneficial to the quality of IBA as the leaching of certain heavy metals is reduced (Fernández Bertos et al., 2004a; Arickx et al., 2006). Compared to other treatment technologies, aging does not require advance facility and is cost effective. Unlike washing, which produces large volume of wastewater that requires treatment after washing IBA, there are less waste streams to deal with after aging. However, the aging process is slow. In Denmark, IBA are naturally

aged for 2 to 3 months, sometimes up to 12 months, before the leaching is reduced to the limit set in Danish legislation (Astrup, 2007). The long aging process poses a challenge to Singapore due to the lack of available land to hold the IBA. However, it has been demonstrated that the duration of this process can be shortened to complete within hours or days by optimising operating conditions such as the concentration of CO_2, reaction temperature, moisture content of ash, and particle size of ash (Costa et al., 2007). Arickx et al. (2006) compared natural weathering to accelerated carbonation process. The authors reported that by using accelerated carbonation process, the reduction in leaching was achieved in shorter time, from 3 months of natural weathering to 4 weeks of accelerated carbonation. The shorter carbonation period will help to ease the burden of having to set aside a large piece of land to naturally age IBA in land-scarce Singapore.

1.2 Problem statement

For Singapore, where the research on the treatment technologies of IBA is still in its infancy, it is vital to explore various treatment options and accelerated carbonation has been overlooked up till now. Most of the research in Singapore had been focused on using stabilisation/solidification treatment for civil application (Tay, 1988; Tay and Cheong, 1991; Tay and Goh, 1991; Goh et al., 2003). This study aims to fill in this gap by investigating accelerated carbonation process for IBA treatment.

1.3 Objective and scope

The aim of this research is to understand the physicochemical mechanism of accelerated carbonation and its influences on the leaching behaviour of IBA, using leaching tests and analytical methods such as mineralogical characterisation. The following tasks were carried out:

1.3.1 Characterisation of IBA

To understand the physicochemical mechanism of accelerated carbonation, IBA was collected from two incineration plants with different types of waste input – one

receives predominantly household waste and the other receives predominantly industrial waste. This is to determine the influence of mineralogical composition of IBA on accelerated carbonation process. Physical and chemical characterisation of IBA was carried out to compare the similarities and differences of IBA from the two incineration plants. The physical characterisation includes size fraction distribution and density. The chemical characterisation includes total element content, loss of ignition (LOI), total carbon content, and X-ray diffraction (XRD).

1.3.2 Accelerated carbonation of IBA under controlled environment

The accelerated carbonation process was carried out under a controlled environment using a CO_2 incubator. The concentration of CO_2 is fixed at 20% at atmospheric pressure for all the experiments as it would be more realistic than using pure CO_2. The influence of operating conditions, i.e. moisture content and temperature, on the degree of carbonation was investigated using 0-2 mm size fraction of IBA, which was ground to <425 μm. This is to determine the optimum operating condition that can achieve the highest rate of carbonation. The optimum operating condition for the accelerated carbonation process was then applied to other size fractions of IBA, which were also ground to <425 μm to minimise the effect of particle size on carbonation. This is to investigate the response of different size fractions of IBA towards the accelerated carbonation treatment.

1.3.3 Leaching tests

To understand the effect of accelerated carbonation on the leaching behaviour of IBA, two leaching tests were carried out. EN 12457-2 was used to evaluate the leaching behaviour of IBA before and after carbonation. This leaching test was selected for this research as it is developed for determination of waste compliancy with regulated values set by respective European countries such as Finland, France, Germany and Italy. The second leaching test, i.e. CEN/TS 14429, was done to investigate the effect of pH on IBA leaching. This leaching test was carried out to compare the leaching behaviour of IBA as a function of pH due to externally added acid versus the change in pH due to carbonation.

1.3.4 Mineralogical study

To further complement the understanding in the carbonation and leaching mechanism of IBA after accelerated carbonation, mineralogical composition of IBA was analysed using XRD. This study investigated the differences in mineralogical composition in terms of IBA collected from two different incineration plants and the different size fractions of IBA.

1.4 Organisation of report

This report starts with an introduction of the background and the identification of research gap in Chapter 1. Chapter 2 provides the literature review of the characteristics of IBA and the research done previously on accelerated carbonation of IBA. The leaching mechanism of IBA reported by other researches is also discussed here. Chapter 3 describes an overview on the sampling, handling and analysis of IBA for the accelerated carbonation process. To achieve the objective of this study, the research was divided into four experimental works. The characterisation of IBA was discussed in Chapter 4. This chapter summarises the physical and chemical characteristics of IBA collected from two incineration plants over a 6 months period. This study was accepted as a conference paper "Sampling and Characterisation of Singapore's Municipal Solid Waste Incineration Bottom Ash" in Venice Symposium 2014. The accelerated carbonation experiments carried out are described in Chapter 5 and 6. Chapter 5 looks at the influence of moisture content and temperature on the degree of carbonation, using 0-2 mm size fraction of IBA. The optimum operating conditions were then selected and applied to other size fractions, which is detailed in Chapter 6. In both Chapter 5 and 6, the effect of degree of carbonation on leaching behaviour of IBA was investigated using leaching tests. Chapter 5 focuses on discussing factors that play a dominant role in the leaching mechanisms of elements in the 0-2 mm size fraction. Chapter 6 compares the differences in the leaching behaviour in terms of the difference in chemical composition in the four size fractions. The last experimental work used mineralogical characterisation (i.e. XRD) to evaluate and compare the mineralogical composition of untreated IBA from two different incineration plants and among the different size fractions, which is discussed in Chapter 7. Chapter 8

concludes the knowledge gain in this research and discusses the potential of applying this study to treat IBA with recommendation in continuation of this research.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

Incineration is a type of thermal waste treatment technology that combusts the organic portion of the municipal solid waste, and converts the non-combustible portion into by-products such as incineration ash, flue gases and heat. Despite the advantages of incinerating waste, such as volume and weight reduction, and the destruction of pathogens during the combustion of waste, incineration cannot completely eradicate the need for landfills. The production of incineration ash and flue gases are the major concerns that have to be addressed together with the use of incineration plants for MSW management. This literature review covers the characteristics of fresh and naturally weathered IBA, the researches done on accelerated carbonation of IBA and the changes in the leaching behaviour of IBA after carbonation.

2.2 Characteristics of IBA

2.2.1 Physical characteristics

IBA consists of ash that remains unburned from the grate, and includes siftings that fall through the grate. In Singapore, IBA also includes the heat recovery system ash, i.e. the ash that condenses on the walls of the boiler, which is mixed with grate ash and grate siftings before quenching. Upon exiting the quench tank, the water content of IBA ranges from 9.4% to 58.4%, depending on the system used to quench IBA (Chandler et al., 1997). IBA has a wide particle size distribution that makes up a well-gradation of fine to coarse material. By visual inspection, IBA is found to be made up of refractory materials such as glass, ceramic, scrap metals and minerals. These materials are non-combustible and account for 85 to 95% of the total solid by-products (Chandler et al., 1997). Chimenos et al. (1999) conducted a visual sorting of IBA with particle size greater than 1 mm into glass, ceramics, minerals, magnetic metals, diamagnetic metals, and unburned organic matter. Glass was found to be the highest in all the size fractions investigated, ranging from the

lowest 35 wt% in the 1-2 mm size fraction to the highest 68 wt% in the 4-6 mm size fraction from the same incineration plant. Ceramics and minerals were the next two materials most commonly found in IBA. Unburned organic content after incineration is usually low. It is measured by LOI test, where the weight lost is measured after heating dried IBA at 550°C for 2 hours. As LOI gives an indication on the combustion efficiency of the incineration plant, some countries like Spain, regulates the maximum allowable LOI value to be 5% (Izquierdo et al., 2002).

2.2.2 Chemical characteristics

Studies were done to identify the minerals present in IBA, using analytical technique such as X-ray diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS) (Kirby and Rimstidt, 1993; Eighmy et al., 1994; Speiser et al., 2001; Wei et al., 2011). The purpose of these studies is to develop a better understanding in the leaching behaviour of IBA, which determines the treatment needed for IBA and the potential utilisation of IBA. SiO_2 and Ca-based minerals are found to be present in dominant concentrations in IBA (Kirby and Rimstidt, 1993).

In terms of the elemental composition of IBA, silicon is one of the major elements present in IBA. Other elements present in IBA are shown in Table 2-1, which is not exhaustive. These elements had been investigated by Chandler et al. (1997). The data was collected from 39 incineration plants over a 1.5 year period and spanned across 6 different countries. Chandler et al. (1997) classified the elements found in IBA into major (>10,000 mg/kg), minor (1,000 to 10,000 mg/kg) and trace elements (<1,000 mg/kg).

Although IBA can be acid-digested into solution for the analysis of its elemental composition, in reality, such harsh condition is not attainable and IBA is considered to be insoluble in water. The pH of a freshly quenched IBA ranges from 10.5 to 12.2 due to the hydrolysis of CaO (Chandler et al., 1997). IBA is also resistant to slight changes in pH due to its buffering capacity. Johnson et al. (1995) found that fresh IBA have an $ANC_{7.5}$ of 1.2 to 1.7 ± 0.05 meq/g. This means that 1.2

milliequivalent of acid was required to reduce the pH of 1 g of IBA to pH 7.5 from pH 11(Johnson et al., 1995). The endpoint for ANC does not need to be fixed at 7.5.

Table 2-1: Range of composition of elements found in IBA sampled 18 times over a 1.5 year period from Canada, Denmark, Germany, the Netherlands, Sweden and the United States incineration plants (Chandler et al., 1997).

Major Elements (>10,000mg/kg)	
Si	91,000 – 308,000
Fe	4,120 – 150,000
Ca	370 – 123,000
Al	21,900 – 72,800
Na	2,870 – 42,000
K	750 – 16,000
Minor Elements (1,000 to 10,000mg/kg)	
Mg	400 – 26,000
Cl	800 – 4,190
Mn	83 – 2,400
Ba	400 – 3,000
Zn	613 – 7,770
Cu	290 – 8,240
Pb	98 – 13,700
Cr	23 – 3,170
Trace Elements (<1,000mg/kg)	
Sn	2 – 380
Sb	10 – 432
V	20 – 122
Mo	2.5 – 276
As	0.12 – 189
Se	0.05 – 10
Sr	85 – 1,000
Ni	7 – 4,280
Co	6 – 350
Cd	0.3 – 70.5
Ag	0.29 – 36.9
Hg	0.02 – 7.75

2.2.3 Distribution of heavy metals among size fractions

The elemental composition of the different size fractions of IBA were investigated (Chimenos et al., 1999; Baciocchi et al., 2010). These studies have found that certain heavy metals were more abundant in the fine fraction. Chimenos et al. (1999) reported that Pb, Zn and Cu were more concentrated in the 1-2 mm size fraction and their concentrations decreased significantly as the size fraction increased. Baciocchi et al. (2010) found Pb, Cr and Sb to be concentrated in the <0.425 μm size fractions, while Cu, Zn, Ni and V were evenly distributed. The soluble salts were more concentrated in the fine fractions (Baciocchi et al., 2010).

2.3 Utilisation potential of IBA

Although there are concerns of heavy metal leaching from IBA which makes it unattractive for utilisation, IBA has been found to be suitable for civil engineering applications such as aggregate substitute in the sub-base of road paving, partial replacement of raw materials in cement production, and as filler in concrete production (Chandler et al., 1997).

Izquierdo et al. (2002) studied the IBA in Catalonia for use in road sub-base and found that IBA complied with Spanish Specifications for road construction. A similar trial using IBA to replace 50% of aggregate in a binder course asphalt pavement was conducted in New Hampshire by Musselman et al. (1994). The physical properties of IBA was found to meet the requirements of New Hampshire Department of Transportation but the high moisture content of IBA resulted in lower manufacturing throughput of the asphalt.

There are a few problems with using IBA as partial replacement in cement production. Pera et al. (1997) reported gaseous emission during the mixing of IBA and OPC, which resulted in high porosity and low strength material. However, the authors found that this was due to the reaction between metallic Al and OPC, which was resolved by immersing IBA in NaOH solution for 15 days. Filipponi et al. (2003) compared the mineralogy of IBA with that of ordinary Portland cement (OPC), blast furnace slag (BFS) and coal fly ash. They found that IBA has similar

composition with Class F of BFS. BFS has been used as a partial replacement in cement production with improved physical properties. However, upon mixing IBA with OPC, the authors found that the pozzolanic properties of IBA were weak.

In a study conducted using IBA from Singapore, the specific gravity and compacted density of fine IBA fraction was found to be 2.67 and 1.54 mg/m^3 respectively, similar to the typical sand values of 2.65 and 1.90 mg/m^3 respectively (Tay and Goh, 1991). The authors also found that the fine IBA had high permeability, which made it suitable for land reclamation.

2.4 Treatment of IBA – Carbonation

Before the utilisation of IBA, treatment must be done to reduce the leaching of heavy metals. Various treatment technologies are available, such as washing, solidification and carbonation. This research proposes to use accelerated carbonation as the treatment technology for IBA. This is because accelerated carbonation has several advantages over other treatment technologies: carbon neutral, ease of application, and less waste stream produced after carbonation. This section reviews the work done on the carbonation of IBA.

2.4.1 Natural weathering

In nature, rocks and minerals undergo chemical reactions, such as carbonation with atmospheric CO_2 and hydrolysis, to form new or secondary minerals. This process is thermodynamically favoured. However, the kinetics of carbonate formation with appropriate minerals is exceedingly slow at ambient temperatures and pressures, occurring over geologic time frames. It involves reacting CO_2 with abundantly available alkaline rocks. Similarly, IBA undergoes natural weathering or aging at ambient conditions due to its metastable state after quenching straight after combustion at high temperature, but the process is slow. The act of quenching IBA at high temperature resulted in a large proportion of IBA to consist of reactive amorphous materials (Meima and Comans, 1997a). At this stage, freshly quenched IBA has a pH range of 10.5 to 12.2 (Chandler et al., 1997). Its alkaline nature was

reported to be controlled by portlandite ($Ca(OH)_2$) (Meima and Comans, 1997a). Upon carbonation with atmospheric CO_2, the pH of IBA will drop to neutral.

For carbonation of IBA to occur, firstly, CO_2 has to be dissolved in water to form weak carbonic acid. Secondly, the weak acid will react with the dissolved alkaline minerals to form carbonates. Calcite ($CaCO_3$) had been reported to be the principal newly formed mineral after weathering (Piantone et al., 2004). Rendek et al. (2006) provided a simplified chemical expression of the carbonation process:

$$Ca(OH)_{2\,(aq)} + CO_{2\,(aq)} \rightarrow CaCO_{3\,(s)} + H_2O_{\,(l)} \qquad \text{(Equation 2-1)}$$

In the natural weathering process, besides carbonation, many complex reactions, such as hydration/oxidation of metals or metal oxides, corrosion of glassy phase, and dissolution/precipitation of salts, take place at the same time (Speiser et al., 2000).

2.4.2 Accelerated carbonation

Lackner et al. (1995) were one of the pioneers to conduct detailed investigations on accelerating the carbonation of minerals to sequestrate CO_2 into thermodynamically stable carbonate minerals. Their focus was on Ca- and Mg- bearing minerals that are available in abundant quantities. However, the main disadvantage of using minerals for carbon capture storage (CCS) is the transportation of minerals to the CO_2 emission sites. Other disadvantages include the need for mining of such minerals, pre-treatment of minerals and non-ambient conditions during accelerated carbonation, all of which indirectly drives up the cost of using minerals for CCS.

Since the weathering of IBA is based on the same principle of using alkaline earth minerals to react with CO_2, several researchers have been investigating the use of IBA as an alternative material for CCS (Fauth et al., 2002; Rendek et al., 2006; Prigiobbe et al., 2009; Lim et al., 2010). Another important advantage of using accelerated carbonation is to treat IBA as the leaching behaviour of IBA can be improved in a shorter period of time compared to natural weathering, hence

allowing for use in civil engineering applications or for safer final disposal to landfills (Costa et al., 2007).

The main difference between natural weathering and accelerated carbonation is the concentration of CO_2 present during the treatment process. In natural weathering, IBA is left in an open area for aging to take place with atmospheric CO_2. As the reaction is exothermic, there is no need for energy input, except for the occasional turning over the pile of IBA. However, the concentration of CO_2 used in accelerated carbonation is much higher than atmospheric CO_2. Arickx et al. (2006) proposed that the stack gas from incineration plant of around 10% CO_2 can be used as a CO_2 source for accelerated carbonation process. Generally, the rate of carbonation increases with the concentration of CO_2 (Fernandez Bertos et al., 2004b). The rate of carbonation has also been found to increase with the partial pressure of CO_2 but higher partial pressure did not increase the amount of CO_2 sequestrated (Rendek et al., 2006).

Other factors that affect the rate of carbonation are the moisture content of IBA and temperature of carbonation. The presence of moisture in IBA is necessary for the dissolution of CO_2 and Ca minerals for the precipitation of carbonates, as shown in Equation 2-1. Rendek et al. (2006) showed that carbonation did not take place for dry IBA and the optimum moisture content was found to be 15% at room temperature under CO_2 pressure of 2 bar. However, excess moisture retards penetration and diffusion of CO_2 to IBA particle surface, thus reducing the rate of carbonation process (Fernandez Bertos et al., 2004b). Temperature of carbonation does not have a linear relationship with the rate of carbonation either. Although higher temperature results in higher Ca^{2+} dissolution, the solubility of CO_2 in water decreases (Fernandez Bertos et al., 2004b). Costa et al. (2007) summarised the studies done on the operating conditions of accelerated carbonation, and the investigated moisture content and temperature were 5-60% and ambient to 50°C respectively.

Besides the operating conditions that affect the rate of carbonation, the amount of CO_2 sequestrated is dependent on the surface area of IBA available for the carbonation reaction and the chemical composition of IBA. The finer the particle size of IBA, the greater the surface area for carbonation reaction, and the less moisture is needed (Fernandez Bertos et al., 2004b). In terms of the chemical composition of IBA, Baciocchi et al. (2010) studied the effect of the different chemical composition on accelerated carbonation by sieving the IBA into different size fractions and grinding to <425 μm. Under the same operating conditions of 30°C, L/S of 0.3 and 100% CO_2 at 10 bar, the coarse fractions (i.e. >0.425 mm) sequestrated around 4% of CO_2 after 8 hours of carbonation, compared to 14% for the fine fraction (i.e. <0.150 mm). The elemental composition of the different size fractions showed that the fine fraction had higher Ca content than the coarse fraction, which could promote higher CO_2 uptake (Baciocchi et al., 2010).

The most important advantage of accelerated carbonation over natural weathering in IBA is the shorter carbonation period needed for the reduction in certain heavy metals leaching. This will indirectly reduce the need for vast amount of land to store IBA during natural weathering, which is economically unviable for land-scarce Singapore. Arickx et al. (2006) reported that by using accelerated carbonation process, the reduction in leaching was achieved in shorter time, from 3 months of natural weathering to 4 weeks of accelerated carbonation.

2.5 Leaching

Leaching can be described as the dissolution of elements from IBA, when IBA comes into contact with a liquid. In terms of leaching, this liquid is known as the leachant. The leachant can be water, acid or alkaline, or mixed with other chemicals. Although the chemical and mineralogical composition of IBA greatly influences the leaching behaviour of IBA, there are several external factors that also affect the degree of dissolution. This motivates in-depth study of leaching due to concerns over the environmental impact on either the safe disposal of IBA, or during the utilisation of IBA.

2.5.1 Physical aspects of leaching

The main factors that influence the leaching of IBA are particle size and porosity of IBA, degree of mixing between leachant and IBA, and temperature. Dissolution of elements will generally increase with increase in surface area and porosity (Van der Sloot et al., 1997). This is due to the greater contact between the leachant and IBA. In determining the leachability of elements from IBA, the leaching result is more reproducible when equilibrium is reached during the contact between the leachant and IBA. Sufficient contact time for mixing will ensure that equilibrium of the leaching system is reached (Chandler et al., 1997). The presence of mixing will further ensure the homogenisation of the leachant and IBA. However, if the mixing is too aggressive, equilibrium condition may not be achieved in the required time frame. In leaching standards, the contact time is usually specified together with the type of mixing device. And leaching is usually carried out at room temperature.

2.5.2 Chemical aspects of leaching

The difference in pH has been found to affect the leaching behaviour of elements from IBA (Van der Sloot et al., 1997; Chandler et al., 1997). For example, at neutral pH, the leaching of Pb and Zn from IBA is the lowest but increases at low and high pH. This type of element is known as amphoteric element. On the other hand, leaching of soluble salts like NaCl is independent of pH. Therefore, the pH of the leachant used to study the leaching behaviour of IBA will not be comparable to another leachant with a different pH.

Leaching results are also not comparable when leaching tests are performed under different liquid-to-solid (L/S) ratios. When the leachate concentration (expressed in mg/L) is compared to regulatory requirements such as WHO drinking water, confusion arises when different L/S ratios produce different results. This can be resolved by converting the leaching result from element concentration in mg/L to element release in mg/kg, which expresses the mass of element dissolved to per unit dry mass of IBA subjected to leaching. Although this conversion allows the comparison of leaching results done using different L/S ratio, solubility controlled constituents are greatly influenced by the L/S ratio used in leaching tests. For

example in Figure 2-1, Si shows the same leachate concentration for the different L/S ratios investigated (top right graph). However, when the leaching results are expressed in release, Si actually leaches more as the L/S ratio increases (top left graph).

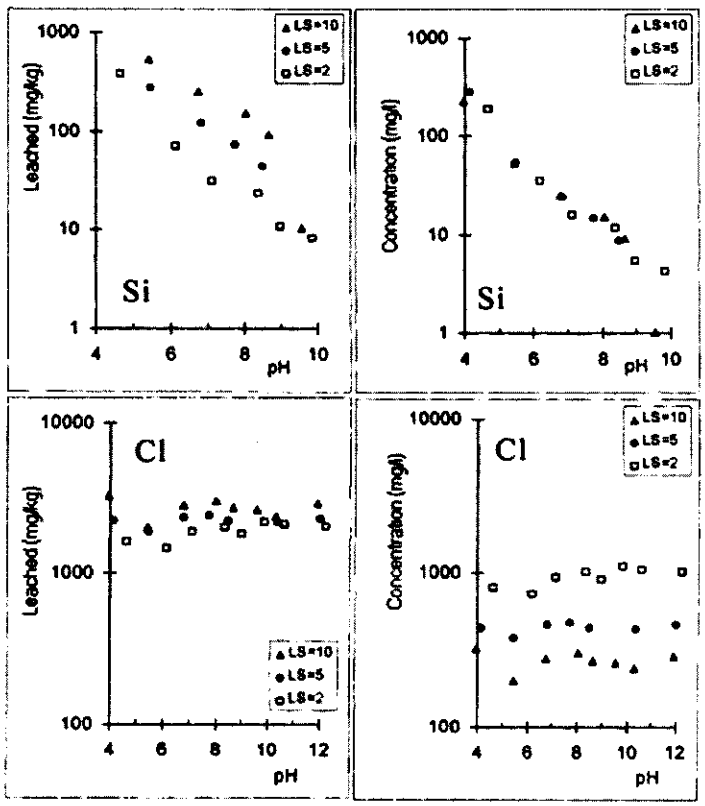


Figure 2-1: Illustration of solubility versus availability control of leaching. Data expressed in mg/kg reflect availability control, when data for different L/S ratios coincide (e.g. Cl). Data expressed in mg/L reflect solubility control when data for different L/S ratios coincide (e.g. Si) (Van der Sloot et al., 1997)

2.5.3 Leaching tests

Leaching standards were developed in recognition of the influences from the external factors discussed earlier. To ensure the leaching data done by different laboratories are comparable, leaching tests are standardised so as to minimise the influence from external factors. This allows the leaching results to be compared and the analysis will then be solely based on the intrinsic leaching behaviour of IBA. However, due to the presence of several leaching factors, numerous leaching tests

were developed to cover all aspects of leaching. Two leaching standards are chosen for this research to evaluate the effect of accelerated carbonation on the leaching of IBA.

Batch leaching test: EN 12457-2

This European standard uses deionized water as the leachant at L/S 10. The pH of the leachate will then be the inherent pH of IBA. The requirement for the particle size of IBA is less than 4 mm. The portion of the IBA with particle size larger than 4 mm is allowed to be crushed but not finely ground. The mixing device is recommended to be rotating at 360° and at 10 rpm. The mixing duration is set at 24 hours, as this has been validated that near-equilibrium condition is reached between the leachant and IBA.

This European standard was developed as a compliance test. Hence, this leaching test is simple and takes shorter time to conduct, compare to other leaching tests which may simulate the actual condition during the utilisation of IBA. Toxicity characteristic leaching procedure (TCLP) was developed by US EPA and like EN 12457-2, it is a batch leaching test. However, the leachant for TCLP is acetic acid, which is to simulate leaching of IBA if it were mixed with food waste in a landfill. Since the purpose of this study is to evaluate the changes in leaching behaviour of IBA after accelerated carbonation, and IBA will not be mixed with food waste or be in extreme acidic condition, EN 12457-2 is chosen over TCLP.

pH-static test: CEN/TS 14429

This European standard evaluates the influence of pH on the leaching behaviour of IBA, so at least 8 bottles with different pH are tested at the same time. The L/S is fixed at 10 but the concentration of the acid or base used to reach the different pH for the 8 bottles are pre-determined. The total mixing duration is 48 hours, rotating at 360° and at 10 rpm. To ensure that equilibrium condition is reached within this time frame, the recommended particle size is less than 1 mm.

Unlike EN 12457-2, pH-stat test falls under the category of basic characterisation. This means that this leaching test is not used to determine whether the IBA complies with a certain regulation or criteria. It is done to understand the fundamental leaching behaviour of IBA as affected by pH and the acid/base consumption to reach the required pH.

2.6 Effect of carbonation on leaching

Some researchers used material analytical techniques and mineralogical studies to examine IBA in greater detail to understand the possible carbonation mechanisms (Zevenbergen et al., 1996; Piantone et al., 2004; Wei et al., 2011), and the relationship between carbonation and leaching (Eighmy et al., 1994; Arickx et al., 2008; Bayuseno and Schmahl, 2010).

During natural weathering of IBA, the first observable change is the release of heat as the hydrolysis of metal oxides is an exothermic reaction (Chandler et al., 1997). The pH will then decrease from alkaline range to neutral range, due to the reaction between CO_2 and the alkaline metals, thus reducing the concentration of hydroxides (Rendek et al., 2006). This is then followed by the formation of new minerals, such as carbonates, and dissolution of minerals. All these changes have been found to change the leaching behaviour of IBA and these are discussed in details in the following, in terms of the heavy metals.

The leaching of IBA is a very complex system to study due to the heterogeneous nature of the material. The relationship between the factors affecting the leachability of IBA can be inter-related, and Figure 2-2 has summed up the complexity in a simple diagram.

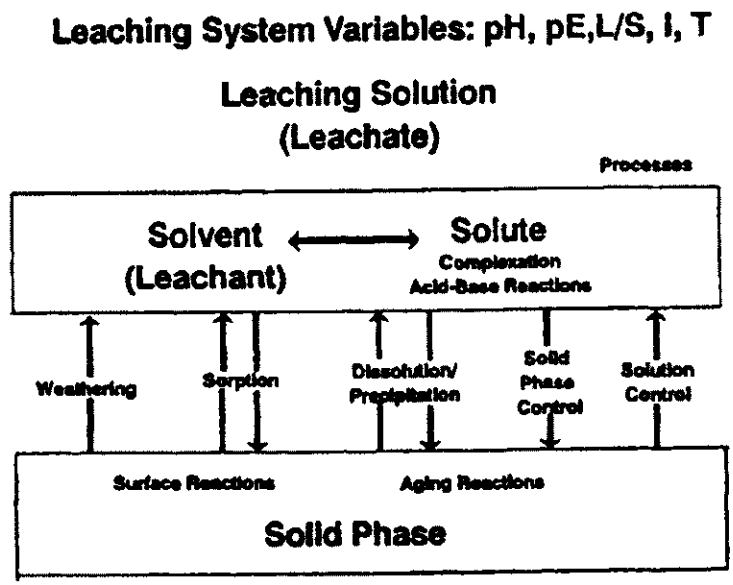


Figure 2-2: Simplified leaching system that shows the inter-relationship between the different factors (Chandler et al., 1997).

2.6.1 Ca

Although Ca is not considered a heavy metal, the leaching behaviour of Ca was studied as it is one of the major constituents leached from IBA. Comans and Meima (1994) found that Ca-minerals played a dominant role in controlling the pH of IBA, which then indirectly influenced the leaching of other trace elements from IBA. As IBA forms carbonates during natural weathering, Comans and Meima (1994) proposed that heavy metals such as Cd, may be sorbed on the newly formed calcite, thus reducing Cd leaching.

2.6.2 Pb and Zn

Accelerated carbonation of IBA was reported to be beneficial to both Pb and Zn by several papers (Freyssinet et al., 2002; Fernández Bertos et al., 2004a; Arickx et al., 2006). Table 2-2 summarises some of the studies done. The studies showed that regardless of the operating conditions used for accelerated carbonation and the leaching tests used to evaluate the efficiency of carbonation treatment, the reduction in Pb and Zn leaching can be up to two orders of magnitude. Meima and Comans (1999) suggested two possible reasons for the reduction in the leaching of Pb and Zn: firstly, it was due to the drop in pH after IBA carbonated as the solubility of Pb

and Zn in IBA were dependent on pH; secondly, Pb and Zn had high affinity for sorbent minerals that were precipitated during carbonation.

Table 2-2: Summary of reduction in Pb and Zn leaching from IBA after accelerated carbonation.

Reference	**Conc. of CO_2**	**Leaching test**	**Effect**
Fernández-Bertos et al. (2004a)	100%	EN 12457-2	Pb: 50-100mg/kg → <1mg/kg Zn: 10mg/kg → <1mg/kg
Arickx et al. (2006)	10%	EN 12457-2	Pb: 7.62mg/kg → 0.60mg/kg Zn: 3.76mg/kg → 1.63mg/kg
Freyssinet et al. (2002)	aging	Collection of leachate	Pb: 9.6mg/L →<25µg/L Zn: 0.8mg/L → <25µg/L

2.6.3 Cr and Cu

The reduction in the Cr leaching after accelerated carbonation was not significant and may be dependent on the degree of carbonation. Todorovic et al. (2006) reported a slight decrease in Cr leaching after moderate carbonation but Cr leaching increased if severe carbonation was used. On the other hand, Van Gerven at al. (2005) reported an increase in Cr leaching after a short period of carbonation but decreased with increasing carbonation duration.

Generally, most literature found that the leaching of Cu has been improved after carbonation. The mechanism for the reduction in Cu leaching has been widely studied (Meima et al., 2002; Van Zomeren and Comans, 2004; Dijkstra et al., 2006; Arickx et al., 2010). Meima et al. (2002) suggested that the reduction in Cu leaching after carbonation could be due to the sorption of Cu onto Al-minerals that precipitated during carbonation. Similarly, Dijkstra et al. (2006) and Arickx et al. (2010) proposed that secondary minerals formed after carbonation played a role in the reduction of Cu but found that the reduction was indirectly due to the sorption of fulvic acid to Fe/Al (hydr)oxides (secondary minerals formed after carbonation). Since many researchers have suggested that the presence of fulvic acid increased the solubility of Cu due to the formation of organic complexes (Van Zomeren and

Comans, 2004; Olsson et al., 2007), the reduction in the mobility of fulvic acid after carbonation would also contribute to the reduction of Cu leaching.

2.6.4 Other trace elements

Some trace elements, such as As, Mo and Sb, are capable of forming oxyanions (negatively charged species containing O), which are more soluble than their cationic species (Cornelis et al., 2008). Similar to Cu, the reduction in mobility of As, Mo and Sb have been reported to be due to the adsorption to ferric oxide at high pH, but competing anions like carbonate would result in desorption (Cornelis et al., 2008). Cornelis et al. (2006) also suggested that ettringite acts as a sink for Sb and further carbonation will increase Sb mobility due to the dissolution of ettringite.

2.6.5 Highly soluble salts

According to Kirby and Rimstidt (1994), highly soluble salts exhibit rapid dissolution during leaching tests and the concentration drops only after depletion of the soluble phase. Components that constitute highly soluble salts include Na, K, Ca, SO_4^{2-}, and Cl^-, of which Ca and SO_4^{2-} have the highest concentration in the leachate (Chandler et al., 1997). It has been reported that the carbonation of IBA has no effect on the leaching behaviour of Cl^- (Todorovic et al., 2006). A direct and inexpensive method to improve the leaching concentration of Cl^- is to wash IBA with water (Todorovic and Ecke, 2006b). The leaching trend of SO_4^{2-} after carbonation was observed to be different from Cl^-. Meima and Comans (1997) found that carbonation may have caused the decomposition of ettringite in IBA to form soluble gypsum, resulting in increased SO_4^{2-} leaching.

CHAPTER 3: MATERIALS AND METHODS

3.1 Sampling of IBA

All the IBA used in this research was collected from Tuas South Incineration Plant (TSIP) and Senoko Waste-to-Energy Plant (SWTEP). TSIP is Singapore's largest incineration plant, with a capacity of handling 3,000 tonnes of MSW per day, while SWTEP is designed to handle 2,100 tonnes per day. These two incineration plants were selected for this research as the plants receive slightly different composition of waste. TSIP receives predominantly industrial waste, in addition to residential waste, while SWTEP receives mostly residential waste.

IBA was collected at a location along the conveyor belt before the magnetic separator. To ensure a representative sample was collected, the sampling location was selected based on both the recommendation from Chandler et al. (1997) and the incineration plants' layout. For TSIP, IBA was collected from a falling stream (Figure 3-1a). The sampling tool used to collect the IBA from the falling stream was custom made to be as long as the width of the conveyor belt. For SWTEP, there is no standing platform next to a falling stream. So IBA was collected by shoveling a full cross-section cut from a moving stream (Figure 3-1b). Around 50 kg of wet IBA was collected. IBA was not sampled directly from bottom ash pits because freshly quenched IBA eventually become mixed with IFA at the bottom ash pits. However, due to the design of both incineration plants, freshly quenched IBA still consists of grate siftings, boiler and economiser ash.

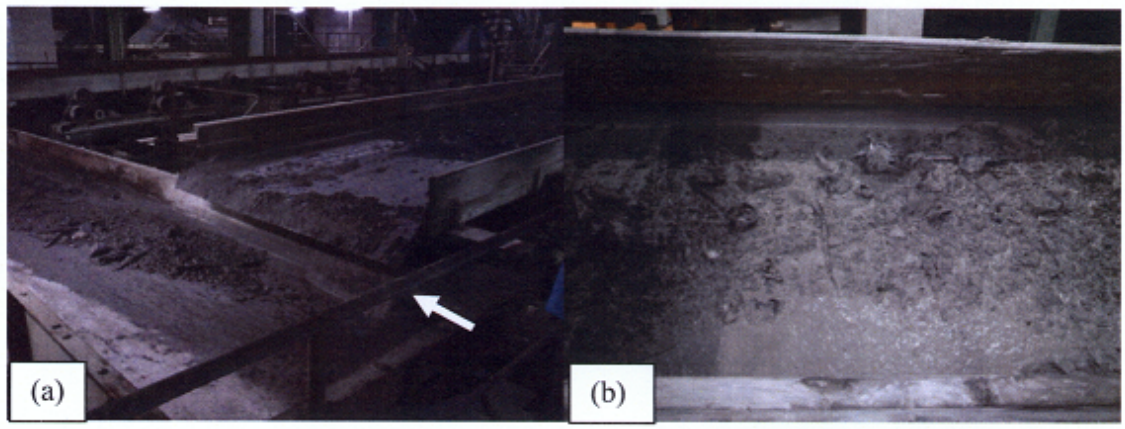


Figure 3-1: IBA sampling location within (a) TSIP (white arrow indicates the IBA falling stream) and (b) SWTEP.

3.2 Handling of IBA

Immediately upon collection, IBA was dried in oven at 40°C for 3 days to minimise further weathering and leaching from taking place. The dried IBA was then sieved into four size fractions: 0-2 mm, 2-4 mm, 4-20 mm and 20-50 mm. The weight of each size fraction was recorded, including the oversized fraction, i.e. >50 mm. However, the oversized fraction was not included in this research. Ferrous and non-ferrous metals were manually removed from all the size fractions, except 0-2 mm, and their weight was recorded. All the size fractions were further crushed and ball-milled to <425 μm. This is to minimise the effect of different surface area on carbonation efficiency.

3.3 Analysis

3.3.1 Total element content

Untreated IBA was analysed for total element content by digesting IBA with aqua regia followed by HF acid. The solution was then analysed for cations using Inductively Coupled Plasma – Mass Spectrometer (ICP-MS Nexlon 300D, Perkin Elmer) and anions using Ion Chromatography (IC 882 Compact IC Plus, Metrohm).

3.3.2 Total inorganic carbon content

The amount of carbonate content in IBA was determined by Analytik Jena Multi N/C 2100/2100S analyser (solid module). To obtain total carbon content (TC), a small amount of the sample was weighed onto the quartz boat and combusted at 900°C. The amount of CO_2 released during the combustion was detected by nondispersive infrared sensor in the analyser. To obtain total organic carbon (TOC) of IBA, the sample was acidified using 2M HCl to remove the inorganic carbonate content before combustion. The total inorganic carbon (TIC) content of IBA was obtained by subtracting TOC from TC. TC and TOC analysis were conducted in triplicates. The absolute increase in TIC is defined as the degree of carbonation (Equation 3-1), which is determined by subtracting TIC of the untreated sample from the TIC at the sampling time t.

$$\text{Degree of carbonation (mg/g)} = TIC_t - TIC_{untreated} \quad \text{(Equation 3-1)}$$

3.4 Leaching Tests

Two leaching tests were used to study the leaching behaviour of IBA. After leaching, the leachates were filtered through 0.45 μm nylon membrane and analysed for pH, dissolved organic carbon (DOC), heavy metals and soluble salts. The pH of the leachate was measured by Mettler-Toledo G20 Compact Titrator. The Analytik Jena Multi N/C 2100/2100S (liquid module) was used to determine the DOC content. The concentrations of heavy metals were determined using Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) from Perkin Elmer Optima 8300. Soluble salts were analysed by Dionex ICS-1100 RFIC Ion Chromatography (IC) System.

3.4.1 EN 12457-2

15 ± 0.02 g of dried IBA was mixed with 150 ± 1 ml of deionised (DI) water in a 250 ml polypropylene bottle to obtain a liquid to solid ratio (L/S) of 10 L/kg. The capped bottle was then clamped in a rotary device and agitated in 360° for 24 hours. Triplicate leaching was carried out for each sample.

3.4.2 CEN/TS 14429 (pH-static test)

8 portions of IBA, each weighing 15 ± 0.02 g, were leached with leachants containing different amount of acid to reach an end pH value ranging from around 4 to 12. The last pH value was based on the inherent pH of IBA. No base was added to further increase the pH. The L/S ratio was fixed at 10 L/kg. A preliminary leaching test was first carried out to determine the amount of acid was required to add to IBA to reach the relevant pH values. The total contact time between the leachant and IBA was 48 hours, mixed in a rotary device.

CHAPTER 4: CHARACTERISATION OF IBA

4.1 Introduction

In Singapore, incineration of MSW is used in parallel with recycling. For household waste, recycling is on volunteering basis. After the recyclables are segregated, most incineration plants burn waste in the as-received condition, i.e. no further sorting is done before incineration. Hence, this gives rise to a highly heterogeneous waste input to the incineration plants.

IBA accounts for 85-95% of all the residues generated after MSW incineration (Chandler et al., 1997). Depending on the waste that is fed into the incineration plants and the different combustion conditions of individual plants, the physical and chemical characteristics of IBA varies among countries and seasons. IBA can be considered a heterogeneous material, consisting of fine powder-like particles to coarse remains of incombustible MSW such as glass, ceramics, minerals and unburned organic matter (Chimenos et al., 1999).

Before IBA can be utilised in an environmentally safe manner, the physical and chemical characteristics of IBA must be clearly investigated. This includes monitoring the variation of IBA characteristics with time. This study aims to evaluate the statistical characteristics of Singapore's IBA, so as to provide a knowledge base for effective IBA treatment. To determine the temporal variation on the characteristics of IBA in Singapore, IBA was collected over a 6 months period in 2013.

4.2 Materials and Methods

The procedure for the sampling and analysis of IBA was as detailed in Chapter 3. The sampling of IBA was carried out over a 6 months period in 2013 for both incineration plants. In the first month, IBA was collected daily, except on weekends. For the rest of the five months, IBA was collected once a week. The procedure for the handling of IBA for this study is shown in the schematic diagram (Figure 4-1).

After removing the ferrous and non-ferrous metals, the size fractions greater than 4 mm was crushed using a jaw crusher to <4 mm. After crushing, the four size fractions were recombined according to their original percentage into subsamples for further testing. The characterisation of IBA includes moisture content, particle size distribution, LOI, TOC, total element content and leaching test based on EN 12457-2.

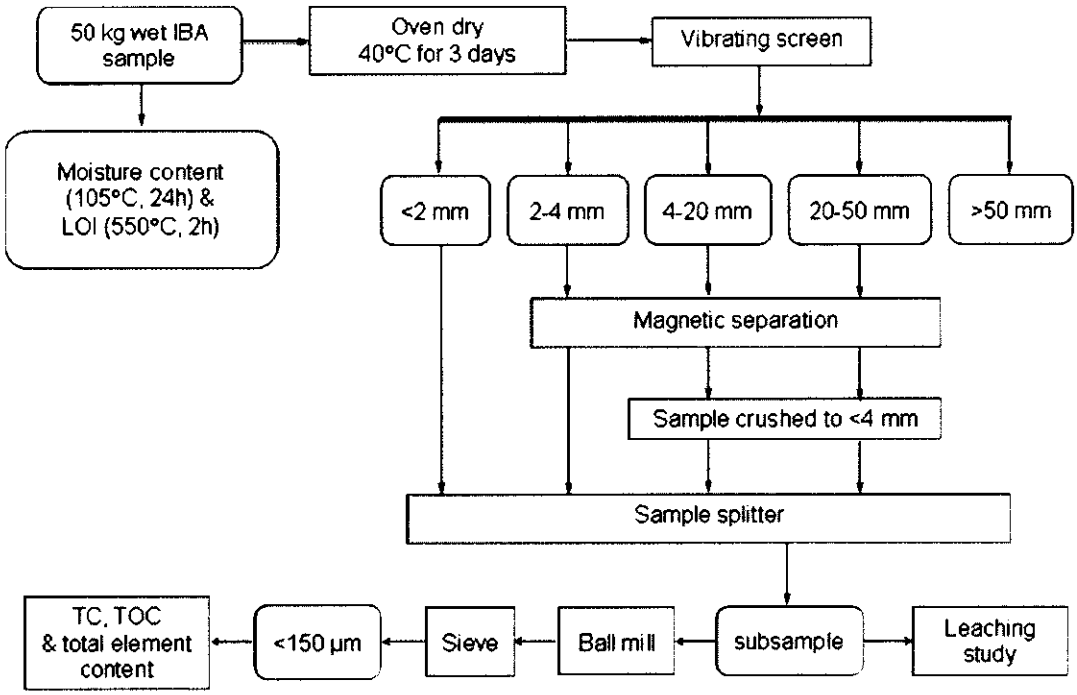


Figure 4-1: Sample preparation process of IBA for characterisation.

4.3 Results and Discussion

4.3.1 Physical characteristics

Figure 4-2 shows the particle size distribution of IBA collected from TSIP and SWTEP. The particle size distribution from both incineration plants were found to be mostly concentrated in the 0-2 mm and 4-20 mm size fractions, where their weight percentage ranged from 30.6-31.6% and 38.0-47.9% respectively.

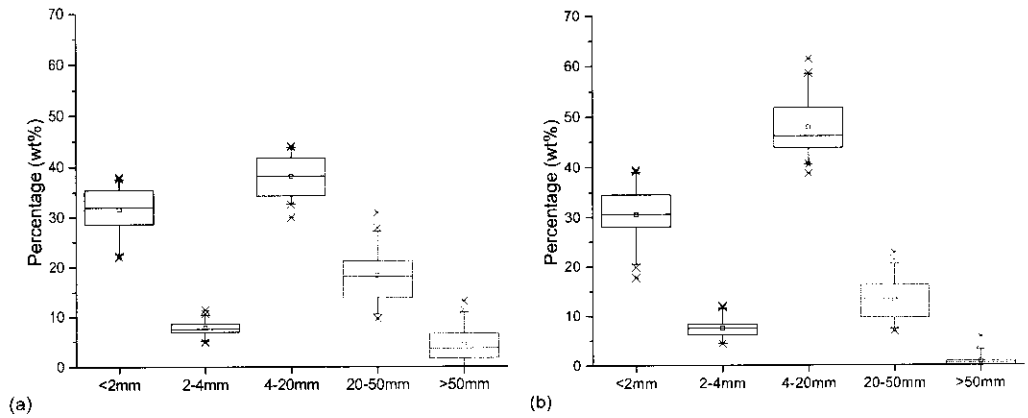


Figure 4-2: Particle size distribution of (a) TSIP, and (b) SWTEP. The bottom and top of the box are 25 and 75 percentile respectively. The band inside the box is the median and the tiny box is mean. The end of the whiskers are 5 to 95 percentile. The cross is the outliers and the stars represent the minimum to maximum values.

LOI values give an indication on the combustion efficiency of incineration plants. In Singapore, the LOI value is required to be less than 3%, which explains the average low readings (Table 4-1) compared to reported values from other incineration plants, such as 2.1-9.8% for Catalonia in Spain (Izquierdo et al., 2002), and 5.5% and 7.2% for VALOR-SUL and LIPOR II in Portugal, respectively (Monteiro et al., 2008). As some factors unrelated to organic content could contribute to mass loss in the LOI test, another test was performed to evaluate the organic carbon content in finely ground IBA and the average TOC for the two plants was 0.73% and 0.64%. This is also found to be lower than those reported by Rendek et al. (2007) where the lowest TOC value was 0.88%.

Table 4-1: Physical characteristics of IBA samples.

	Number of samples	TSIP		SWTEP	
		Range	Average	Range	Average
Moisture content (%)	40	11.9-20.9	16.2	15.0-25.1	18.6
Ferrous content (wt%)	40	6.9-15.3	11.2	6.3-11.9	10.0
LOI (%)	35	0.29-2.12	1.09	0.50-4.65	1.15
TOC (%)	40	0.48-1.91	0.73	0.30-1.34	0.64

4.3.2 Total element content

Table 4-2 shows the average total element content of Singapore's IBA (n=40) compared with other countries (Chandler et al., 1997). Generally, both incineration plants produced IBA with similar composition, except for elements like Cd, Mn, Pb and Sb, whereby the average differed by an order of magnitude. Cd, Pb and Sb were present in higher concentration in SWTEP than TSIP IBA. These elements are commonly used in batteries, a common household waste, which could explain their higher concentration in SWTEP as SWTEP receives predominantly household waste while TSIP receives more industrial waste. Mn is used mainly as an alloy for metallurgy, which could be contributed from steel related waste from industry, resulting in higher concentration in TSIP IBA. Overall, the tested elements are found to fall into the range reported by Chandler et al. (1997).

Table 4-2: Comparison of Singapore's IBA composition with other countries.

Element (mg/kg)	TSIP	SWTEP	Range reported by Chandler et al., 1997
Ag	4.04	4.31	0.29-36.9
As	34.38	28.57	0.12-189
B	244.04	285.32	38-510
Ba	2207.37	1615.38	400-3,000
Be	1.15	0.95	-
Cd	5.19	28.61	0.3-70.5
Co	26.67	40.55	6-350
Cr	177.75	160.79	23-3,170
Cu	1463.23	1373.43	190-8,240
Hg	0.48	0.23	0.02-7.75
Mn	1228.18	706.69	83-2,400
Mo	44.97	13.86	2.5-276
Ni	133.87	113.36	7-4,280
Pb	688.23	1384.61	98-13,700
Sb	98.53	147.53	10-432
Se	0.36	0.71	0.05-10.0
Sn	103.70	175.90	2-380
Sr	366.96	675.50	85-1,000
Tl	0.18	0.15	-
V	41.38	23.32	20-122
Zn	2398.44	2260.93	613-7,770

Most of the elements showed narrow variation over the 6 months sampling period. The possible reasons could be that the volume and chemistry of waste feedstock containing these elements was fairly consistent and the mixing of waste in the holding bunker before incineration was helpful in homogenizing the waste to some extent. However, certain elements like Cd, Co, Hg, Pb and Se displayed high coefficient of variation, as can be seen in Figure 4-3.

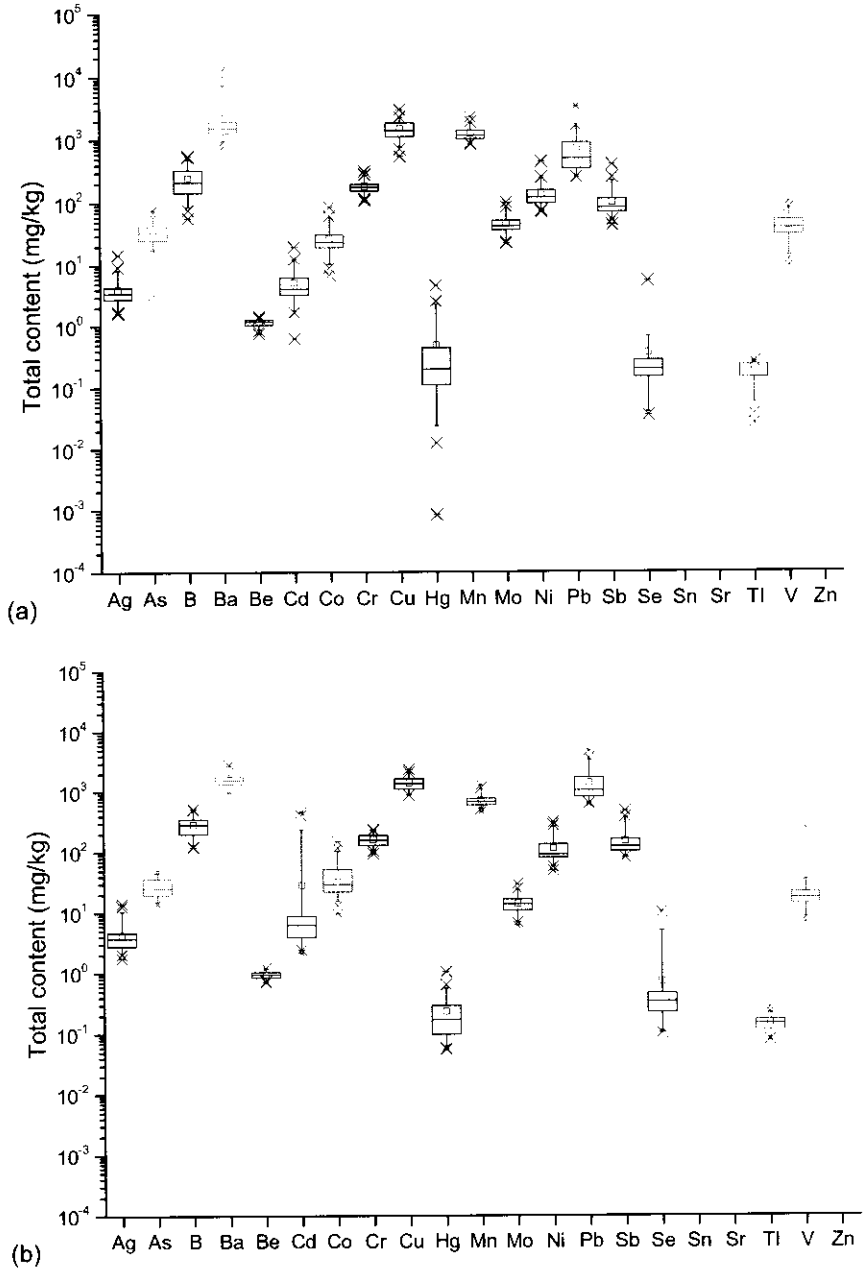


Figure 4-3: Total element contents of 6 months' IBA from (a) TSIP; and (b) SWTEP in Singapore. The bottom and top of the box are 25 and 75 percentile respectively. The band inside the box is the median and the tiny box is mean. The end of the whiskers are 5 to 95 percentile. The cross is the outliers and the stars represent the minimum to maximum values.

4.3.3 Leaching

Leaching test was conducted based on EN 12457-2 for all the IBA collected (n=40).

The leaching behavior of untreated IBA and its variation with time are shown in Figure 4-4. A number of trace elements of concerns for their toxcitiy were analysed but only seven of them were within the detection limits of ICP-OES. The trace element concentrations for SWTEP are mostly higher than TSIP, which is surprising as TSIP receives more industrial waste. For example, the leachable Pb from SWTEP had a significantly higher average and broader data dispersion than TSIP.

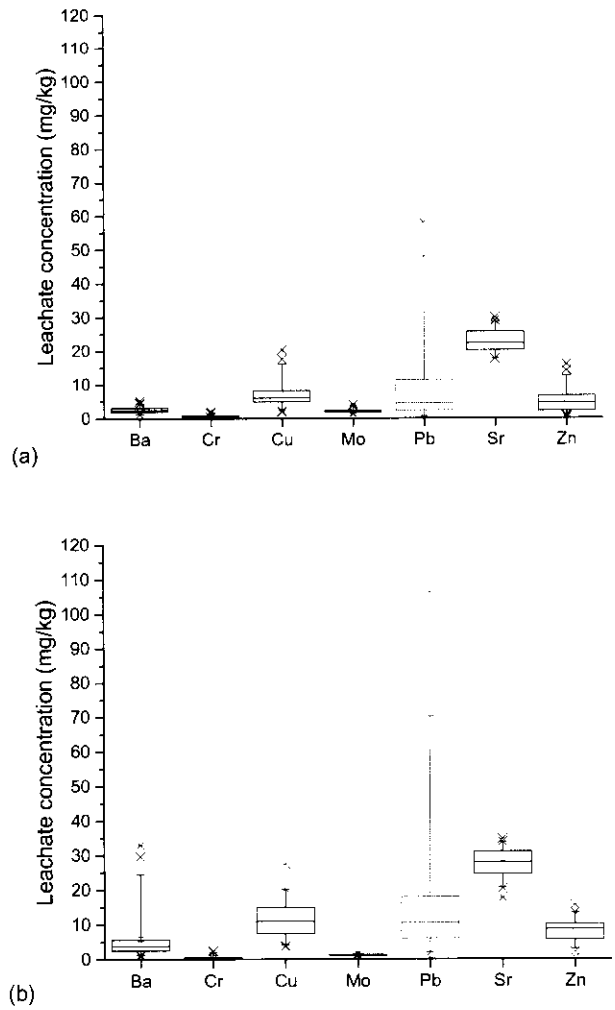


Figure 4-4: (a) TSIP and (b) SWTEP leaching test results based on EN12457-2. The bottom and top of the box are 25 and 75 percentile respectively. The band inside the box is the median and the tiny box is mean. The end of the whiskers are 5 to 95 percentile. The cross is the outliers and the stars represent the minimum to maximum values.

4.4 Conclusion

The characteristic of Singapore's IBA was evaluated in this study. The results discussed here are a summary of data obtained through a deliberate sampling and testing done over a 6 months period in 2013. The total element content was found to be within the range of several other countries reported in literature. However, elements like Cd, Co, Hg, Pb and Se exhibited high variation over the investigated sampling period. Pb showed similar high variation in leaching test.

ACKNOWLEDGEMENT

This research work on characterisation of IBA was funded by National Environment Agency (NEA) of Singapore.

CHAPTER 5: INVESTIGATION OF MOISTURE CONTENT AND TEMPERATURE ON THE EFFICIENCY OF ACCELERATED CARBONATION OF IBA

5.1 Introduction

Natural weathering, a simple IBA treatment process, is one of the treatment technologies commonly used in countries that utilise IBA (Chandler et al., 1997). However, natural weathering is a slow process that takes months to complete. In view of the difficulty of finding a sufficient large space to naturally weather IBA in land-scarce Singapore, accelerated carbonation would be a more attractive alternative treatment method. The natural weathering process can be shortened through optimising operating conditions, such as concentration of CO_2, pressure, moisture content, and temperature (Costa et al., 2007), to accelerate the carbonation process.

The influence of these operating conditions on the kinetics of accelerated carbonation has been studied individually. However, the range of the optimum operating conditions is still wide and varies across studies. Fernández Bertos et al. (2004a) found that the optimum moisture content was 30-40% for IBA size fraction <710 μm. Van Gerven et al. (2005) carried out accelerated carbonation treatment on 0.1-2 mm size fraction of IBA. In terms of leaching results, the optimum moisture content and temperature was 13-25% and 50°C, respectively. Rendek et al. (2006) reported the optimum moisture content for <4 mm IBA was 15% at a pressure of 2 bar using pure CO_2. The reasons for the slight difference in the optimum moisture content reported in these studies could be attributed to the different IBA size fractions and temperature studied. Furthermore, although steps were taken to ensure that the moisture content remained unchanged in these studies, Van Gerven et al. (2005) showed that moisture content decreased over the carbonation period. This would have an impact on the efficiency of carbonation.

The objective of this study is to investigate the influence of operating conditions on the degree of carbonation and the leaching behaviour as a function of carbonation time. This investigation was carried out using IBA size fraction 0-2 mm to obtain the optimum operating condition for further study on other size fractions (discussed in Chapter 6). Since industrial emission with 10-20% CO_2 has been suggested to be the source of CO_2 for accelerated carbonation (Arickx et al., 2006), this study used 20% CO_2 at atmospheric pressure as it would be more realistic than using pure CO_2. The study on the factors influencing the degree of carbonation was chosen to focus on moisture content and temperature. These operating conditions, i.e. fixed CO_2 concentration, varying moisture content and temperature, were selected for this study in consideration of minimising energy and cost of the process. Lastly, this study aims to address the possible factors influencing the leaching mechanism by investigating leaching as a function of carbonation time.

5.2 Materials and Methods

5.2.1 Incineration bottom ash

The IBA used for the accelerated carbonation experiment was the same as those discussed in Chapter 4. A single day was randomly chosen from the IBA collected in the first month from SWTEP and TSIP. For this study, only the size fraction 0-2 mm ball-milled to <425 μm was used.

5.2.2 Accelerated carbonation experiment

The accelerated carbonation process was carried out in CO_2 incubator (Sanyo MCO-18AIC). 20% CO_2 at 1 atm was used for all the experiments. The nominal moisture contents were set at 5, 15, 18.8 and 25% in weight percentage. The investigated temperatures were 35, 42.5 and 50°C. In total, 9 sets of experiment were conducted for the investigated nominal moisture content and temperature, as shown in Table 5-1. DI water was added to the dried IBA to obtain the required moisture content. A tray of DI water was placed at the bottom of the incubator to maintain a constant atmospheric humidity. IBA sample was spread on plastic petri dishes to no more

than 2 mm thick. Samples were collected after different carbonation durations at 2, 4, 6, 8, 24, and 168 hours, and the actual moisture content was measured.

Table 5-1: Abbreviation of the 9 sets of carbonation experiment carried out under different operating conditions.

Moisture content \ Temp	**35°C**	**42.5°C**	**50°C**
5%	35C5MC	42.5C5MC	50C5MC
15%	35C15MC	42.5C15MC	50C15MC
18.8%	-	42.5C18.8MC	-
25%	35C25MC	-	50C25MC

5.2.3 Analysis

The analysis for this study was as detailed in Chapter 3. Both EN 12457-2 and CEN/TS 14429 leaching tests were used for this study.

5.2.4 Linear correlation coefficient

The relationship between leachability and its possible influencing factors was evaluated by calculating the linear correlation coefficient, i.e. Pearson's R. Pearson's R is a measure of the strength of the relationship between two random variables. The value of the correlation coefficient varies between -1 to +1, whereby ±1 means the two variables have absolute positive or negative correlation, and 0 means no correlation. The Pearson's R was calculated using Originlab software.

5.3 Results and Discussion

5.3.1 Total element content

Table 5-2 shows the total element content of IBA from the two incineration plants. Generally, both plants had similar elemental composition in the 0-2 mm size fraction, except for Cd, Fe, Mn, Mo, Sb, Sn and Cl, which differed by an order of magnitude. This observation is similar to the average total element content, which consists of all the four size fractions, results discussed in Chapter 4.

Table 5-2: Total element content (mg/kg) of 0-2 mm size fraction of IBA from incineration plants SWTEP and TSIP.

Element (mg/kg)	SWTEP	TSIP
	0-2 mm	0-2 mm
Ag	19	18
Al	32,467	32,033
As	20	64
Ba	81	65
Be	0.9	1.2
Ca	180,333	139,667
Cd	11	5.3
Co	52	48
Cr	235	206
Cu	2,453	2,437
Fe	51,467	111,000
K	9,270	9,857
Mg	10,113	10,633
Mn	895	1,600
Mo	17	121
Na	15,333	13,067
Ni	183	169
Pb	611	199
Sb	246	85
Sn	161	95
Sr	340	327
Ti	6,720	5,267
V	27	55
Zn	3,073	4,050
Cl	11,200	5,900
SO_4	8,307	6,987

5.3.2 Degree of carbonation as a function of time

Figure 5-1 shows the degree of carbonation under different operating conditions, as a function of carbonation time. Samples with 5% and 15% moisture content both showed significant increase in the degree of carbonation after 2 hours of carbonation, regardless of temperature and source of IBA. After 2 hours of carbonation, the increase in degree of carbonation was minimal. 18.8% moisture content showed similar trend at 42.5°C. Only samples with 25% moisture content showed an initial lag in carbonation degree. But they subsequently caught up with other samples with lower moisture content after 8 hours of carbonation, and reached a plateau thereafter. The onset of plateau in the degree of carbonation implies that the samples had reached saturation in carbonation under the given operating conditions. With prolonged carbonation, i.e. 1 week of carbonation, the IBA from the same plant reached similar degree of carbonation under different operating conditions. This could be associated with the amount of Ca available for carbonate formation. The total Ca content for 0-2 mm size fraction of SWTEP and TSIP samples were 180,333 mg/kg and 139,667 mg/kg respectively (Table 5-2), which corresponds to higher degree of carbonation attained by SWTEP sample.

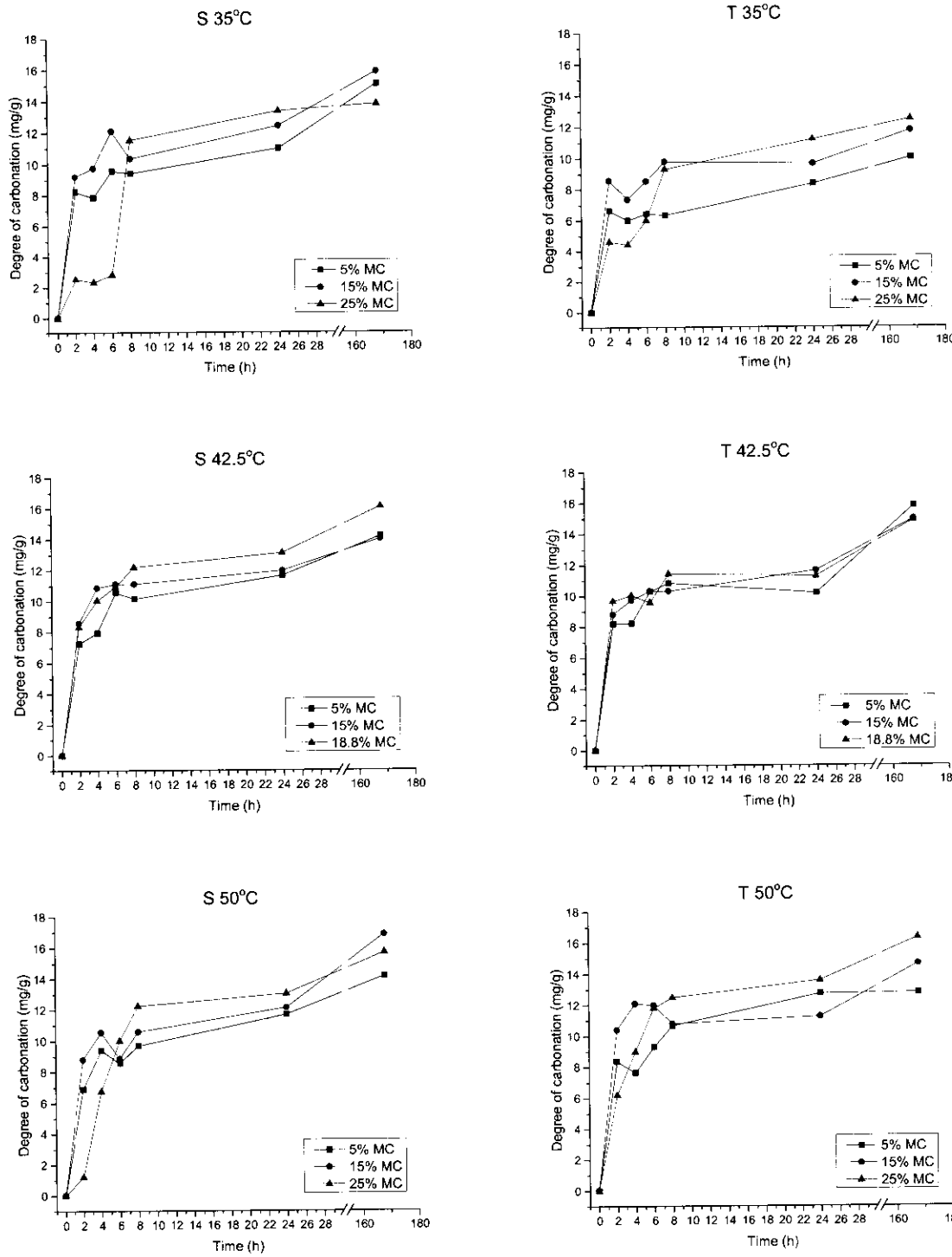


Figure 5-1: Degree of carbonation as a function of time for SWTEP and TSIP samples at various operating conditions.

Our study has shown that 2 hours of carbonation was sufficient for the samples to reach a relatively high degree of carbonation that was close to the endpoint

observed after 1 week of carbonation. This can be achieved by selecting the optimum moisture content and temperature. Figure 5-2 shows that both SWTEP and TSIP samples had the highest degree of carbonation at 15% moisture content. However, the optimum temperature for SWTEP and TSIP was different, at 35°C and 50°C respectively.

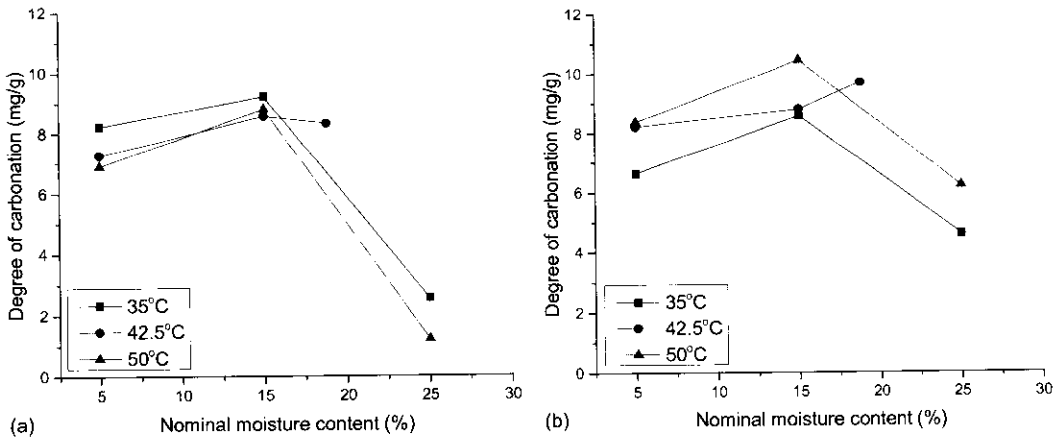


Figure 5-2: Comparison of degree of carbonation for (a) SWTEP and (b) TSIP samples after 2 hours of carbonation.

Baciocchi et al. (2010) reported that the significant carbonate increase lasted 8 hours and the finest size fraction (<0.150 mm) had approximately 14% of CO_2 uptake. In the study done by Van Gerven et al. (2005) on IBA size fraction 0.1-2 mm, the significant increase in carbonate content occurred in the first 6 hours of carbonation with an increase of around 100%. Compared with other studies, we observed the steep increase in degree of carbonation after only 2 hours of carbonation, followed by a plateau. Furthermore, our study showed the highest gain in degree of carbonation after 2 hours of carbonation was 128%, at the operating condition of 50°C and 15% moisture content for TSIP sample.

5.3.3 Effect of actual moisture content on rate of carbonation

The initial retardation in carbonation for samples with 25% moisture content showed that 25% moisture content was too high for effective carbonation to take place for IBA with particle size <425 μm. The duration of lag for 35°C lasted longer

than 50°C, for both SWTEP and TSIP samples. The initial retardation and the difference in the lag period for 25% moisture content can be explained by observing the actual moisture content of the samples. It was found that the moisture content changed throughout the carbonation period (Figure 5-3).

Generally, moisture content decreased during the first 8 hours of carbonation, except for samples with 5% moisture content of which moisture was gained. As a tray of DI water was placed inside the incubator, the evaporation of water had resulted in an atmosphere saturated with moisture within the enclosed environment. Moisture was then gained by samples with low moisture content, i.e. 5%, but not by samples with higher nominal moisture content. At 50°C, the rate of moisture gain for 5% moisture content was the slowest while the rate of moisture loss for 25% moisture content was the highest. This is logical since at 50°C, water tends to evaporate. After 8 hours of carbonation, all the samples approached similar moisture content with respect to their temperatures. This equilibration in moisture content continued to the end of 1 week of carbonation. Again, at 50°C, the actual moisture contents after 24 hours of carbonation for all the three nominal moisture contents were the lowest among the three temperatures.

This change in the moisture content during carbonation had an impact on the initial rate of carbonation. Our study has shown that significant carbonation will only take place after the moisture content has decreased to a certain threshold. For 35°C, the sharp increase in degree of carbonation for 25% moisture content occurred between 6 to 8 hours, which corresponded to actual moisture content decrease from 17.1% to 11.6% for SWTEP sample, and from 20.3% to 17.7% for TSIP sample. As for 50°C, the increase in degree of carbonation started after 2 hours of initial lag, whereby the actual moisture content had decreased to 14.0% and 21.4% for SWTEP and TSIP samples respectively. Thus, for significant carbonation to take place, the actual moisture content range should be 12-17% for SWTEP sample and 18-21% for TSIP sample. This observation is in agreement with samples with 18.8% moisture content, whereby the carbonation did not display an initial lag like those with 25% moisture content. Hence, 18.8% moisture was still effective as nominal moisture content for

significant carbonation to take place. However, after factoring in the change in moisture content, the carbonation experiment has shown that the best nominal moisture content for the highest rate of carbonation was 15% for IBA of size particle <425 μm.

This study has shown that the initial rate of carbonation was strongly dependent on the nominal moisture content of IBA. The rate of moisture loss or gain seems to be affected by the carbonated temperature, which in turn indirectly affects the rate of carbonation. The implication of this study is that the carbonation temperature may be determined by the flue gas used as the source of CO_2 for the accelerated carbonation process. If the temperature of the flue gas is high, e.g. >50°C, higher moisture content would have to be used to compensate for the decrease in moisture. The disadvantage is the lag in the initial rate of carbonation. However, this study has shown that with time, the moisture content will decrease to the optimum threshold and significant carbonation will take place.

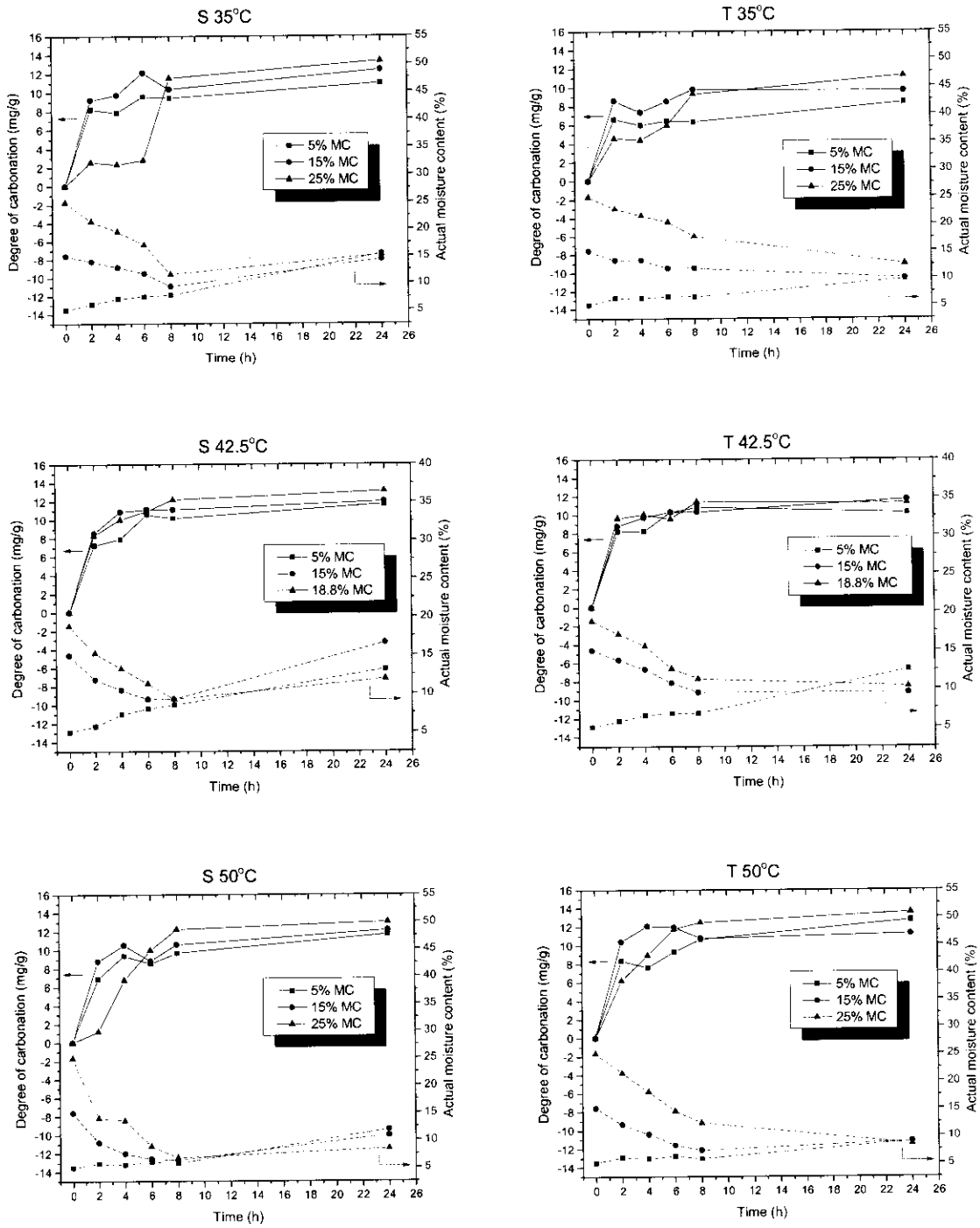


Figure 5-3: Degree of carbonation and corresponding actual moisture content for SWTEP and TSIP samples at various operating conditions.

5.3.4 pH profile as a function of time

Figure 5-4 shows the change in pH as a function of carbonation time. The pH of untreated IBA was found to be 12.4 and 12.6 for SWTEP and TSIP samples

respectively. There was a significant decrease in pH for most of the samples during the first 2 hours of carbonation period, at least 1 to 2 units of reduction. The pH continued to decrease with carbonation time, reaching as low as pH 8.5 at the end of 1 week of carbonation for both sources of IBA.

The decrease in pH was dependent on the degree of carbonation for the different operating conditions investigated, as shown by the high correlation coefficient in Figure 5-5. This observation shows that a lower pH can be achieved by applying the optimum operating conditions to obtain the highest degree of carbonation.

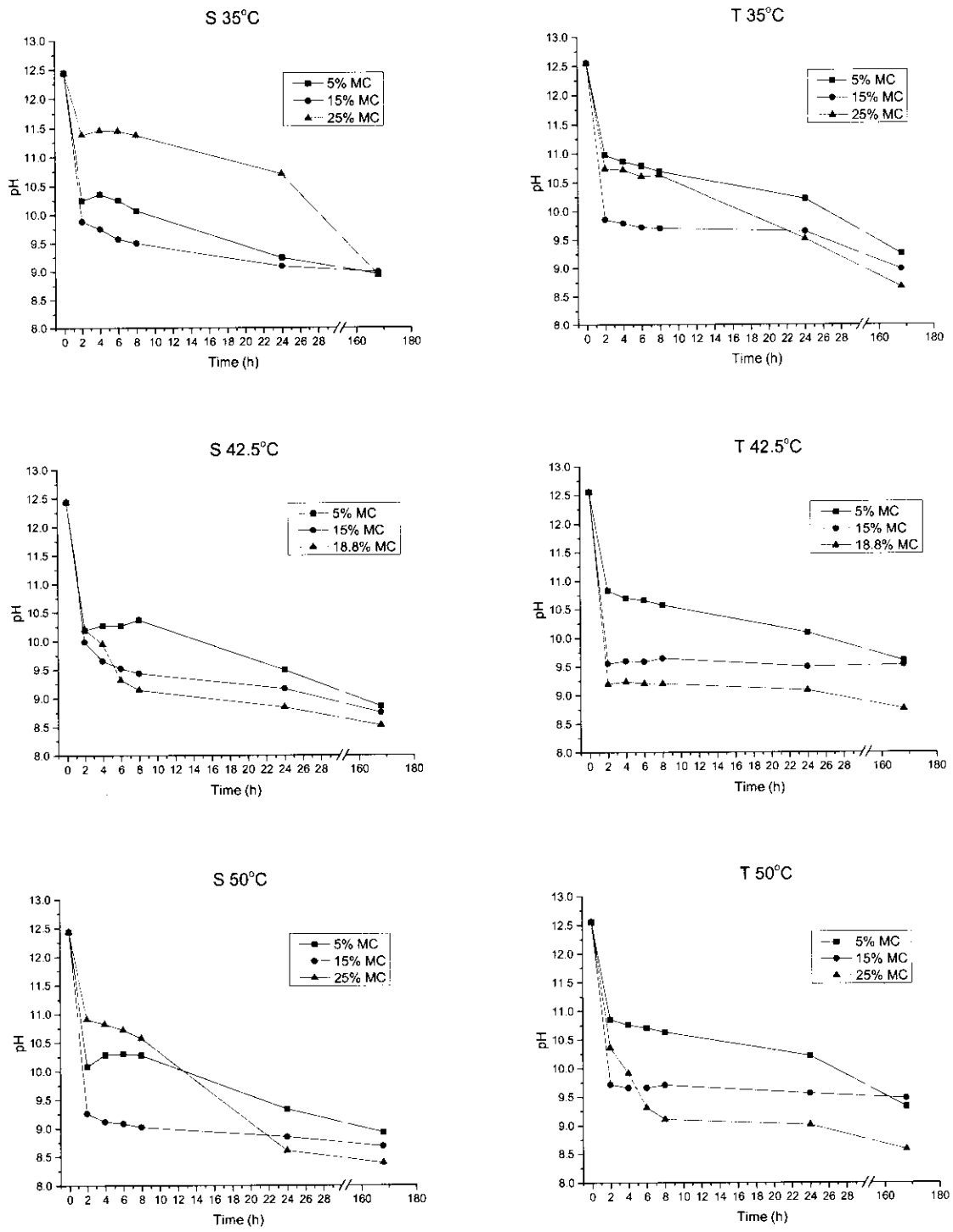


Figure 5-4: pH as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

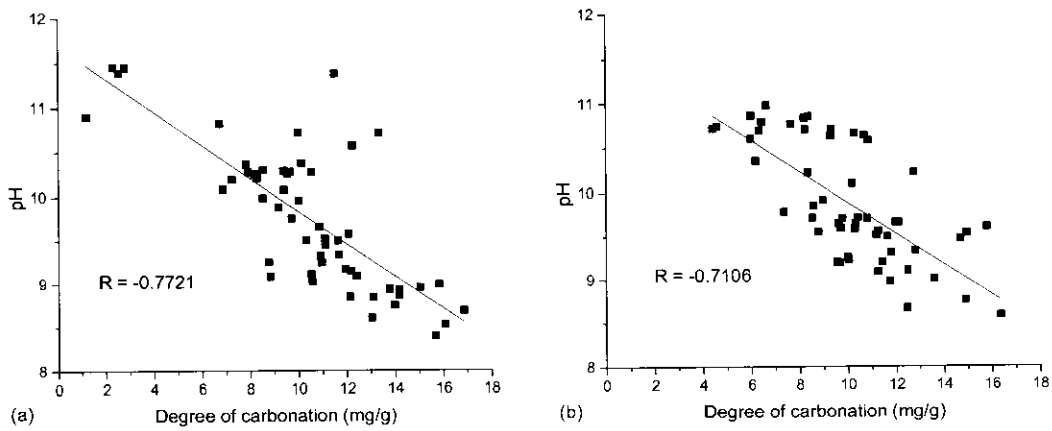


Figure 5-5: Correlation between pH and degree of carbonation for (a) SWTEP and (b) TSIP samples.

5.3.5 Leaching profile as a function of time

The evolution of leaching as a function of carbonation time was monitored by carrying out leaching tests at each sampling time. Most of the trace elements were found to be below the detection limit by ICP-OES. Therefore, only certain trace elements are discussed here as these are regulated in most countries that utilise IBA.

Pb and Zn

Both Pb and Zn showed the most significant reduction in leaching after carbonation. In untreated SWTEP and TSIP samples, the release of Pb was 30.05 mg/kg and 0.36 mg/kg respectively, which coincides with the higher total Pb content in SWTEP sample. After only 2 hours of carbonation, Pb was below the detection limit in the leachate (i.e. <50 µg/L), regardless of the degree of carbonation. Zn leaching was reduced by ~97% in the same period of carbonation. The reduction in the leaching of Pb and Zn could be due to the decrease in pH after carbonation, as suggested by Meima and Comans (1999). The pH for both SWTEP and TSIP samples decreased from an average of 12.5 to 10.2 after 2 hours of carbonation. The pH-static tests of SWTEP and TSIP samples have shown that Pb and Zn leaching were not detectable below pH 11.

Cu and DOC

Similar to Pb and Zn, Cu leaching decreased significantly after just 2 hours of carbonation and reached a plateau with further carbonation (Figure 5-6), regardless of the operating conditions. A possible reduction mechanism in Cu leaching could be degree of carbonation, which results in the formation of less soluble carbonate, as shown from the high correlation coefficient in Figure 5-7 (a, c). The Cu leaching as a function of measured pH from carbonated samples were also compared to the pH-static leaching of untreated samples (Figure 5-7 (b, d)). It can be seen that below pH 10, Cu leaching continued to decrease for the carbonated samples whereas under the influence of pH, Cu leaching has increased. This decrease in Cu leaching as pH decrease with carbonation time showed the possibility of Cu forming a less soluble mineral (such as carbonate) during the carbonation process. Hence, pH did not contribute significantly to the decrease in Cu leaching. Van Gerven et al. (2005) had reported similar findings.

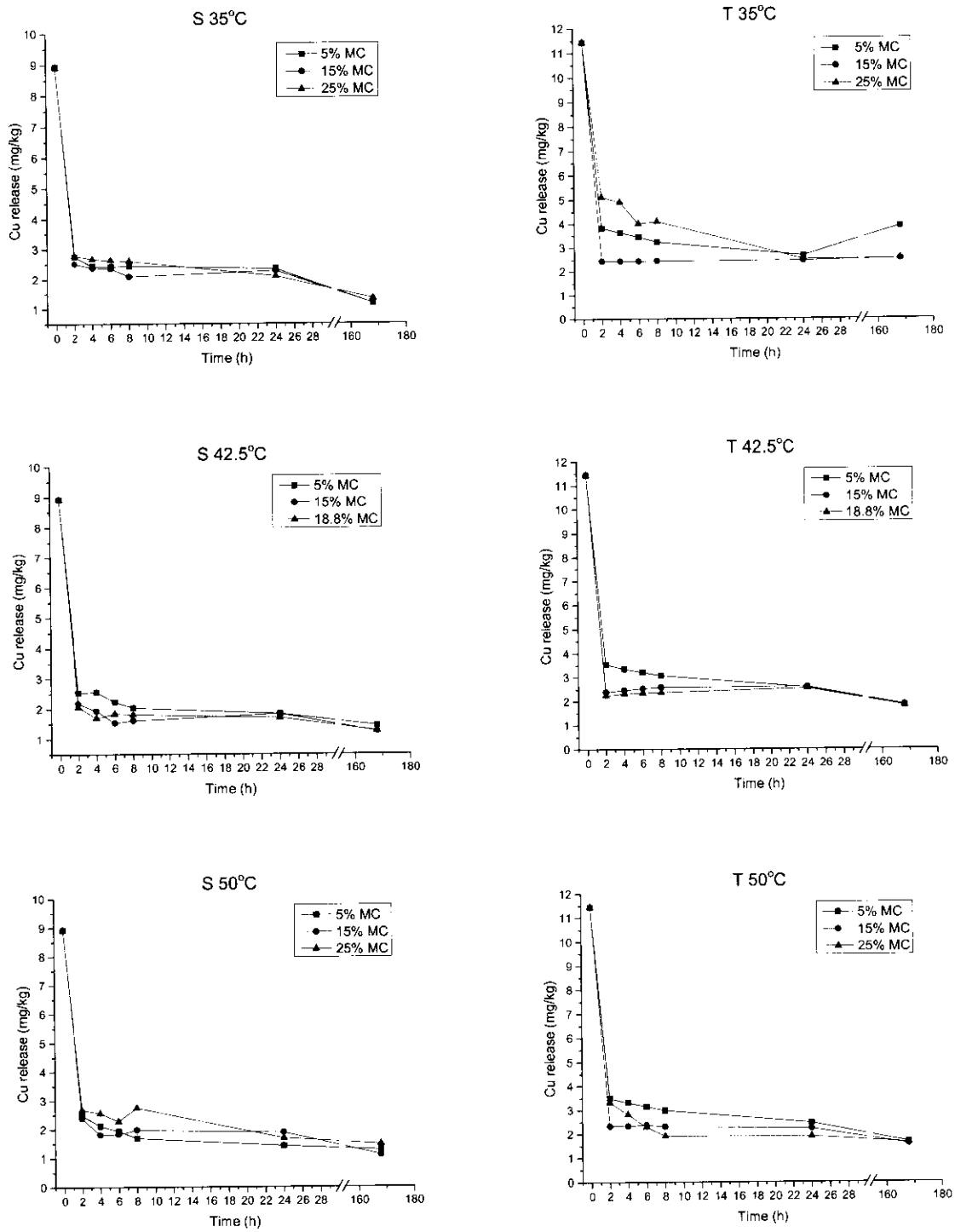


Figure 5-6: Cu release (mg/kg) as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

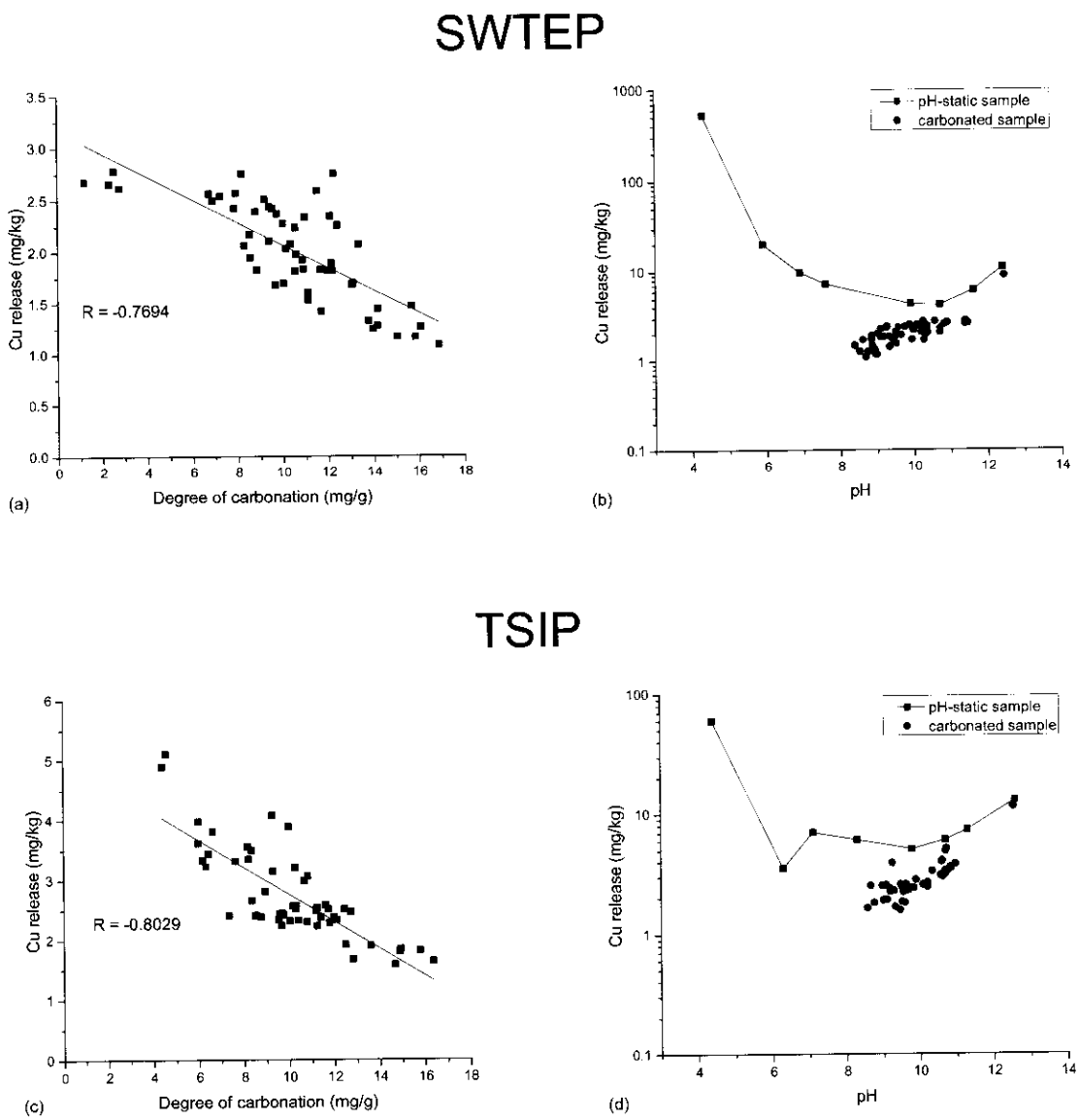


Figure 5-7: Correlation between Cu leaching and degree of carbonation for (a) SWTEP and (c) TSIP samples. Cu leaching as a function of measured pH for carbonated sample and pH-static leaching of untreated (b) SWTEP and (d) TSIP samples.

Many researches had suggested the leaching behaviour of Cu was affected by the presence of DOC in IBA due to Cu affinity to form organic ligands, which increase Cu solubility (Van Zomeren and Comans, 2004; Olsson et al., 2007). Hence, DOC leaching as a function of carbonation time was investigated. Generally, DOC leaching decreased with carbonation time, as shown in Figure 5-8. It is likely that

the decrease in DOC leaching could be due to the adsorption to Fe/Al (hydr)oxides formed during carbonation, as reported by Arickx et al. (2010). Figure 5-9 compares the DOC leaching as a function of measured pH from carbonated samples to the pH-static leaching of untreated samples. Similar to Cu, the decrease in DOC leaching was not due to the decrease in pH.

The contribution from both DOC and degree of carbonation would have affected the Cu leaching, however, to different extent. For SWTEP sample, the contribution from DOC (Figure 5-10a) and degree of carbonation (Figure 5-7a) seems to affect Cu leaching equally as the R values were high for both factors. For TSIP sample, the contribution from degree of carbonation (Figure 5-7c) seems to be higher than that of DOC (Figure 5-10b), based on the high R value between leaching and degree of carbonation and low R value between leaching and DOC. This difference in the contributing factors could be due to the different source and mineralogy of IBA.

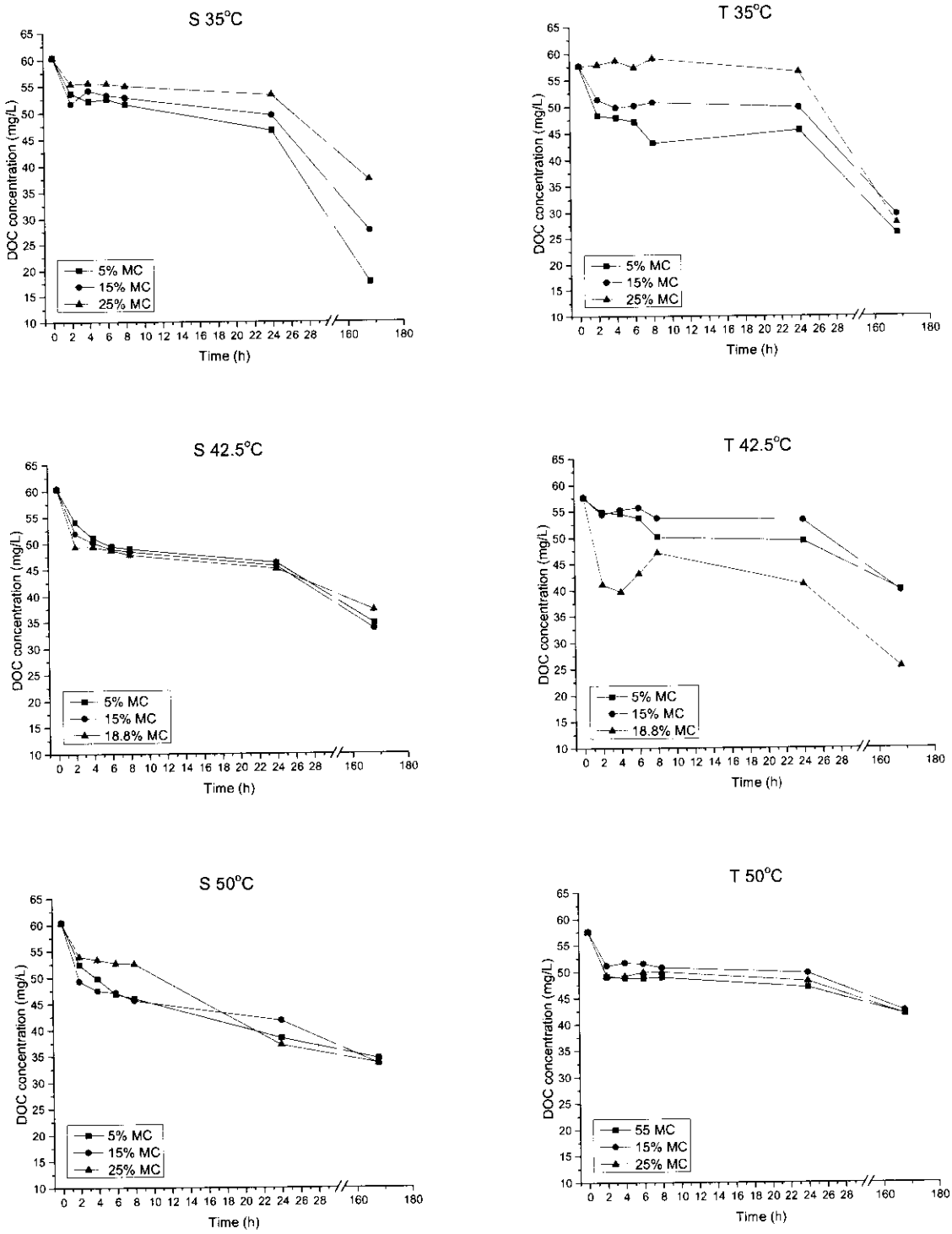


Figure 5-8: DOC leaching (mg/L) as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

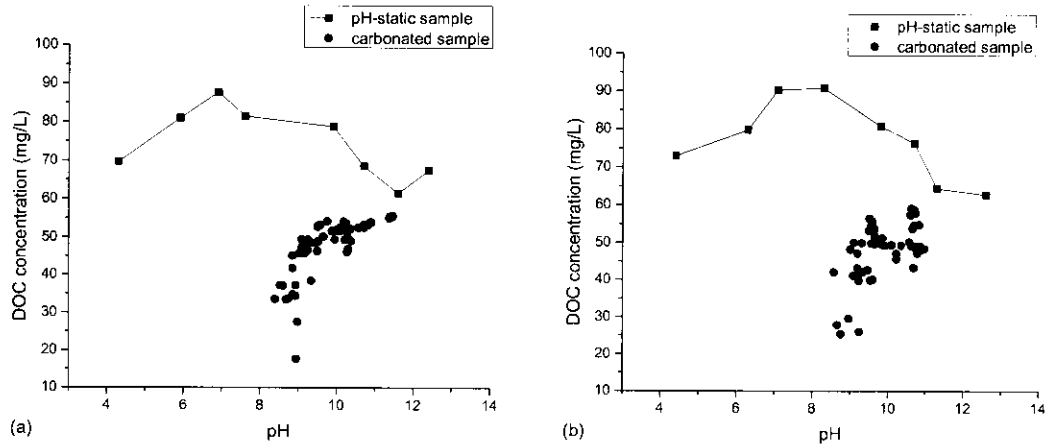


Figure 5-9: DOC leaching as a function of measured pH for carbonated sample and pH-static leaching of untreated (a) SWTEP and (b) TSIP samples.

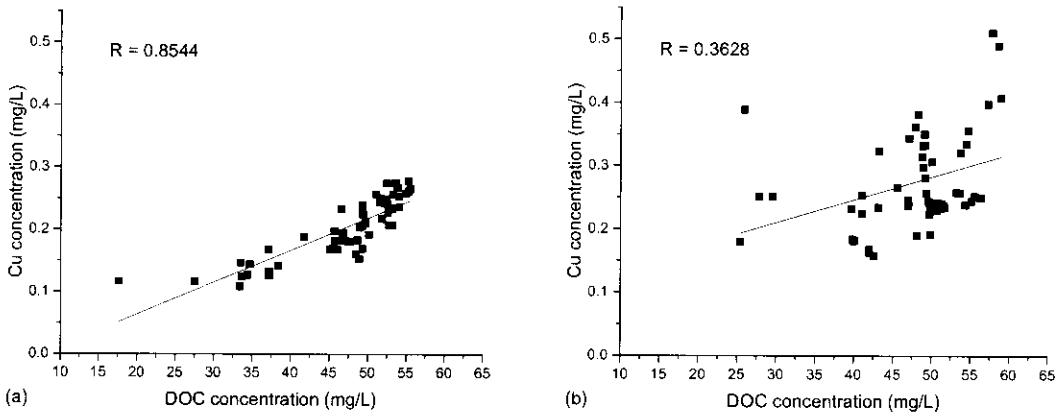


Figure 5-10: Correlation between Cu and DOC leaching for (a) SWTEP and (b) TSIP samples.

Oxyanions

Oxyanions refer to elements that form negatively charged species, such as As, Cr, Mo, Sb, Se, V and W (Cornelis et al., 2008). The leaching behaviour of these elements from IBA is not as well studied in literature due to the much lower total element content compared to other elements with higher total element content like Cu, Pb and Zn (Cornelis et al., 2008). However, these elements are now regulated in Europe for the acceptance of waste at landfills (CEU, 2003). Hence, this study discusses the effect of accelerated carbonation on Cr, Mo and Sb as the rest of the

oxyanion forming elements is below the detection limit of ICP-OES in the leachate of untreated IBA.

Cr leaching was slightly higher for untreated SWTEP sample than untreated TSIP sample at 3.59 mg/kg and 2.30 mg/kg respectively (Figure 5-11). Unlike Cu, Cr leaching did not decrease for all the operating conditions. Samples with 15% moisture content consistently showed the most significant decrease in leaching for all the investigated temperatures. However, Cr leaching increased for SWTEP and TSIP samples with 25% and 5% moisture content respectively, which corresponded to lower degree of carbonation. After 1 week of carbonation, Cr leaching decreased for all the samples to concentration below the untreated samples, including those samples that showed an initial increase in leaching. This finding was similar to studies done by Van Gerven et al. (2005), who reported a decrease in Cr leaching with prolong carbonation. Cornelis et al. (2008) suggested that the decrease in Cr leaching could be due to the exchange of SO_4^{2-} in ettringite with CrO_4^{2-}.

Figure 5-12 shows the relationship between Cr leaching with two other factors, i.e. degree of carbonation and pH. The correlation coefficient between Cr leaching and degree of carbonation were relatively low at R = -0.5765 and -0.5500 for SWTEP and TSIP samples respectively. Figure 5-12 (b, d) shows that the leaching mechanism of Cr could be more dependent on pH, instead of the formation of carbonate. This is supported by the similarity in the measured pH profile of carbonated sample and pH-static leaching of untreated sample. Furthermore, Figure 5-12 (b, d) shows that Cr leaching increased initially during carbonation due to the slight decrease in pH. After prolonged carbonation, the pH decreased further to around pH 9, whereby the solubility of Cr becomes lower. Hence, to reduce Cr leaching significantly, the pH of carbonated IBA has to reach pH 7, which is the minimum solubility of Cr based on the pH-static leaching test.

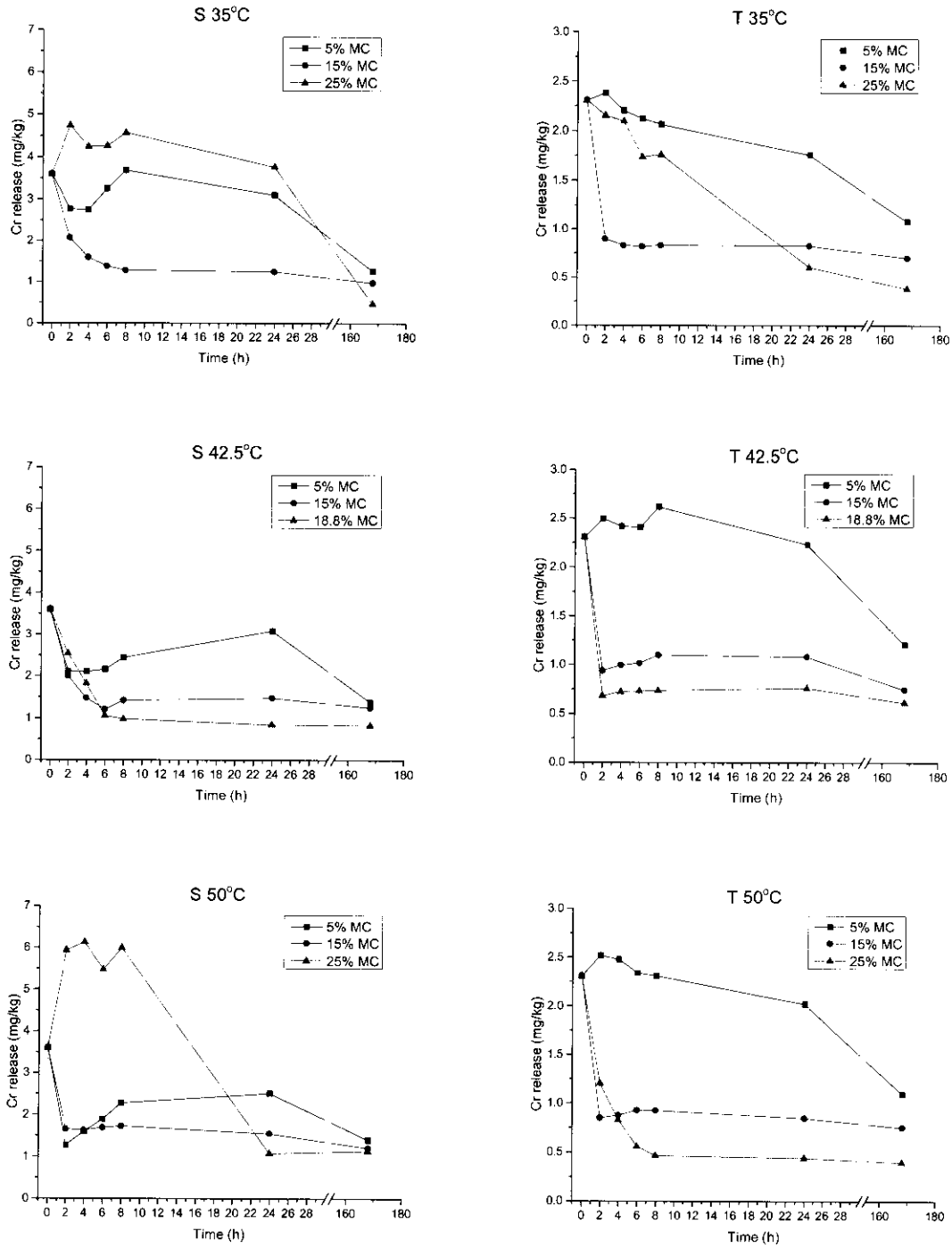


Figure 5-11: Cr release (mg/kg) as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

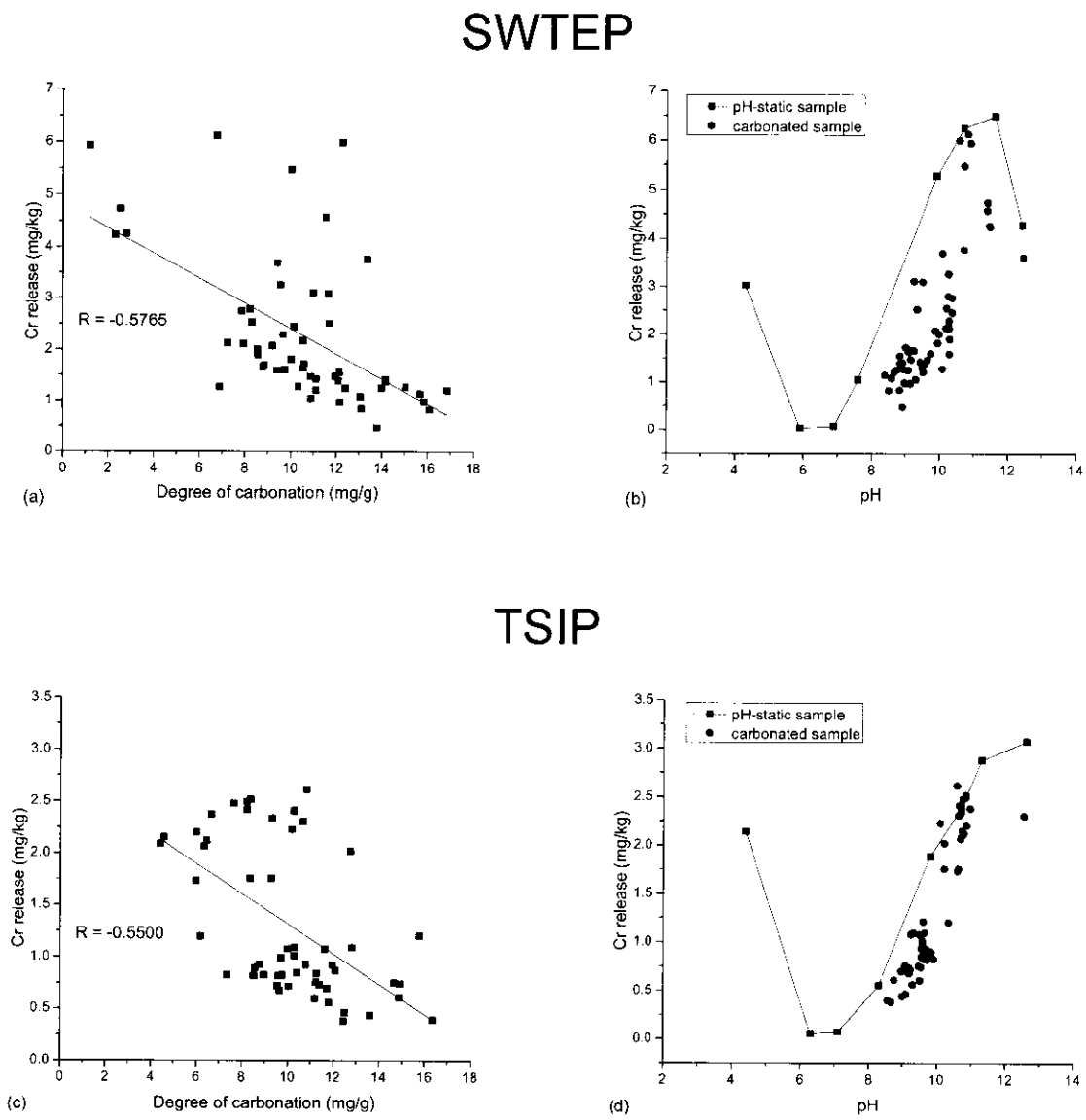


Figure 5-12: Correlation between Cr leaching and degree of carbonation for (a) SWTEP and (c) TSIP samples. Cr leaching as a function of measured pH for carbonated sample and pH-static leaching of untreated (b) SWTEP and (d) TSIP samples.

Mo leaching from untreated TSIP sample was about 6 times higher than that from untreated SWTEP sample (Figure 5-13). This could be due to the higher total Mo content in TSIP sample. Generally, Mo leaching increased during the first 24 hours of carbonation. Similar to Cr, Mo showed signs of decrease in leaching after prolong carbonation, i.e. 1 week of carbonation. However, the decrease in leaching

was not significant for SWTEP sample. Regardless of operating conditions, Mo leaching decreased to around the same level as untreated SWTEP sample. In contrast, TSIP sample had greater reduction in Mo leaching after 1 week of carbonation, especially for operating condition 50°C with 25% moisture content.

Figure 5-14 (a, c) shows the correlation between Mo leaching and degree of carbonation was poor, i.e. R = -0.0706 and -0.1541 for SWTEP and TSIP samples respectively. However, pH seems to be the determinant factor in Mo leaching mechanism. The pH-static test suggests that the maximum solubility of Mo occurs around pH 8-10, which is around the pH of carbonated samples in this study (Figure 5-14 (b, d)). Hence, based on this finding, to reduce Mo leaching using accelerated carbonation would be difficult since the minimum solubility of Mo occurs around pH 4, which is not attainable through carbonation.

Figure 5-15 shows Sb leaching as a function of carbonation time. The concentration of Sb in untreated TSIP sample was below the detection limit of ICP-OES (i.e. <10 μg/L) while untreated SWTEP sample released 0.16 mg/kg of Sb. The readings that were found to be below the detection limit were represented by a zero value in the graphs. TSIP samples carbonated at 35°C were not presented here as they were below the detection limit too. Similar to Mo, Sb leaching increased during the first 24 hours of carbonation and decreased to untreated level after 1 week of carbonation.

The correlation between Sb leaching and degree of carbonation was poor and inconsistent, i.e. a positive relationship for SWTEP but negative for TSIP, as shown in Figure 5-16 (a, c). The pH-static result and trend of Sb leaching for carbonated sample was found to be similar to Mo. Hence, it is possible the mineralogy of Mo and Sb are similar, and their leaching mechanisms are not positively affected by carbonation, possibly due to the dominant role pH plays in Sb leaching mechanism. This finding is similar to (Cornelis et al., 2012).

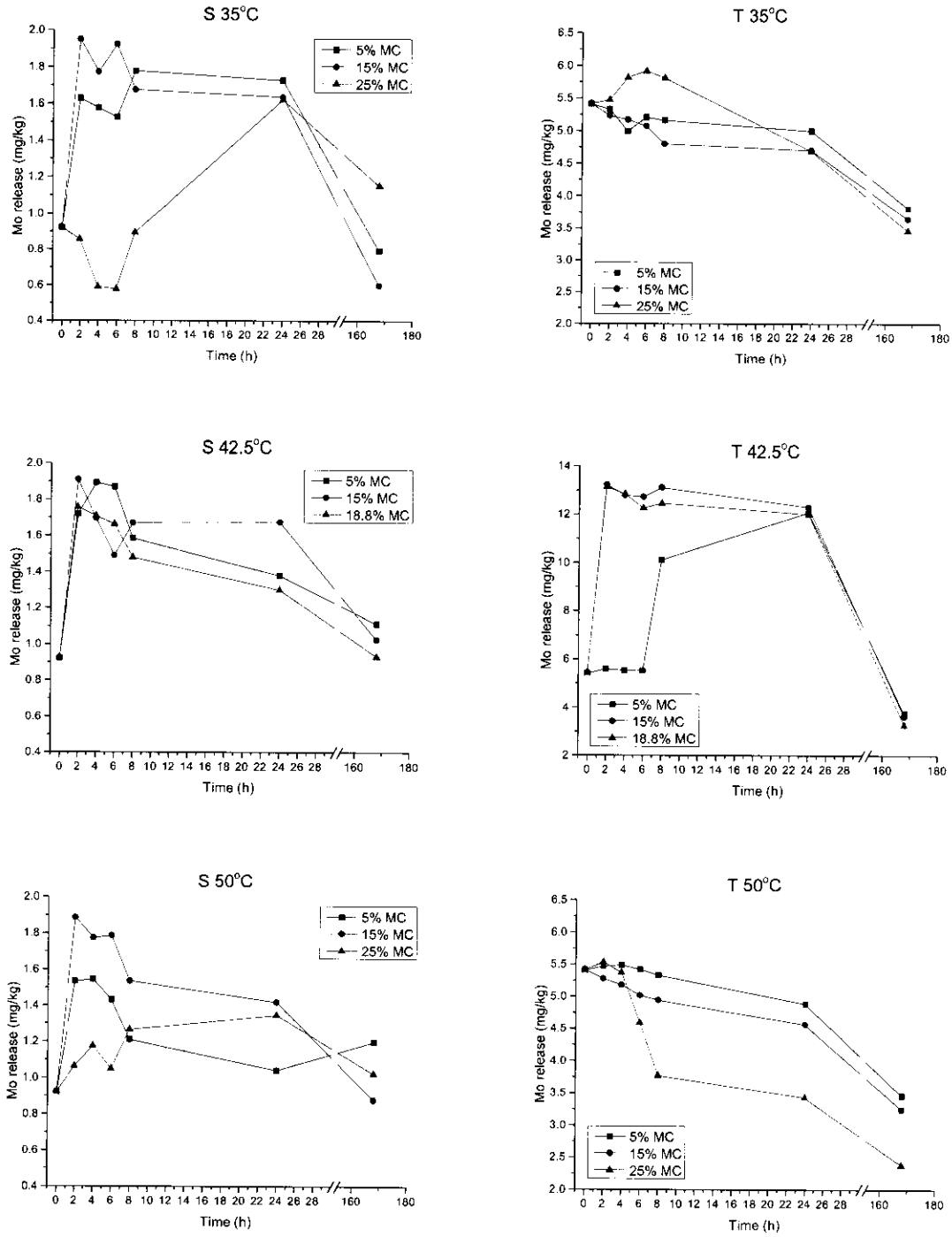


Figure 5-13: Mo release (mg/kg) as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

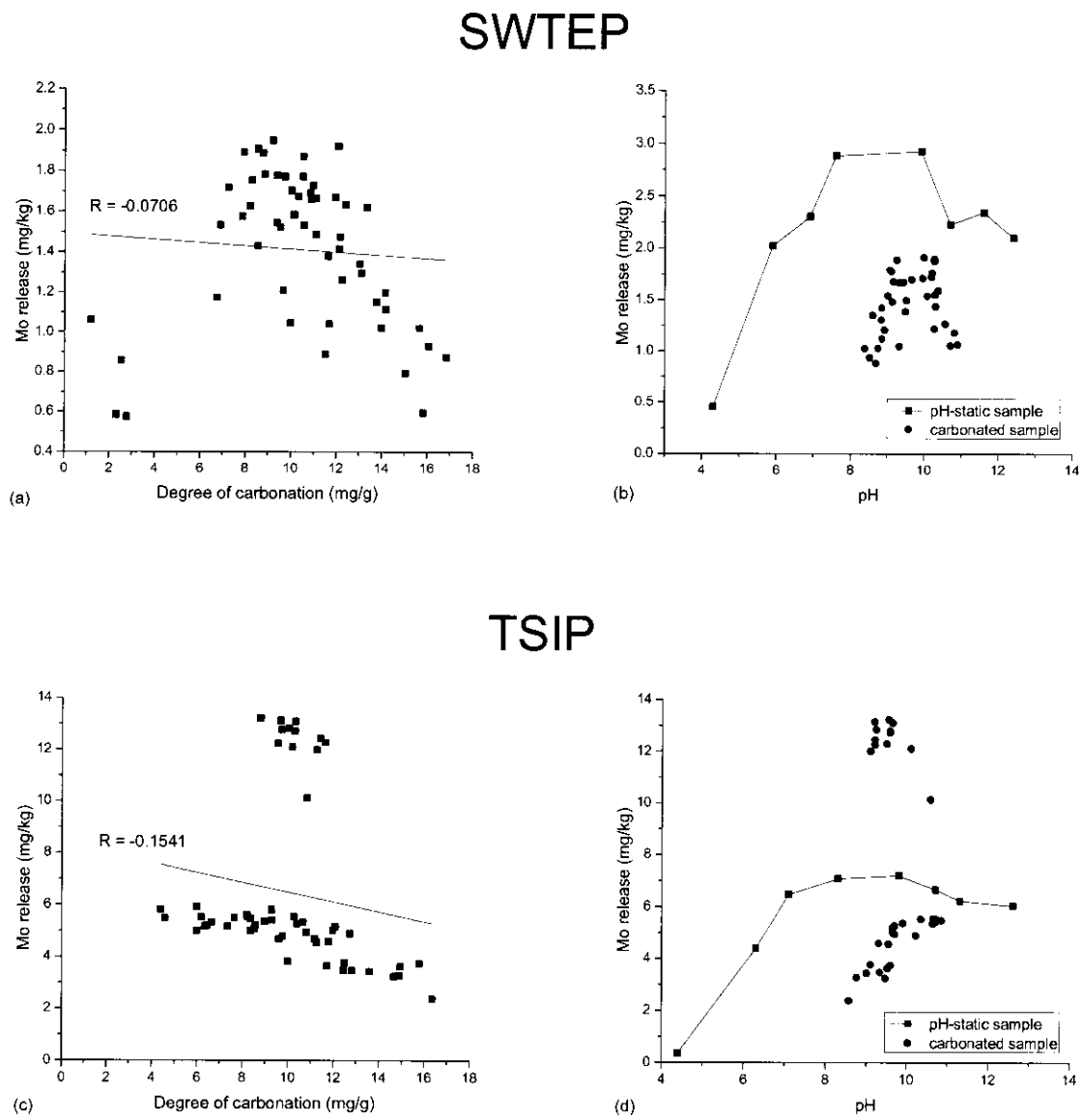


Figure 5-14: Correlation between Mo leaching and degree of carbonation for (a) SWTEP and (c) TSIP samples. Mo leaching as a function of measured pH for carbonated sample and pH-static leaching of untreated (b) SWTEP and (d) TSIP samples.

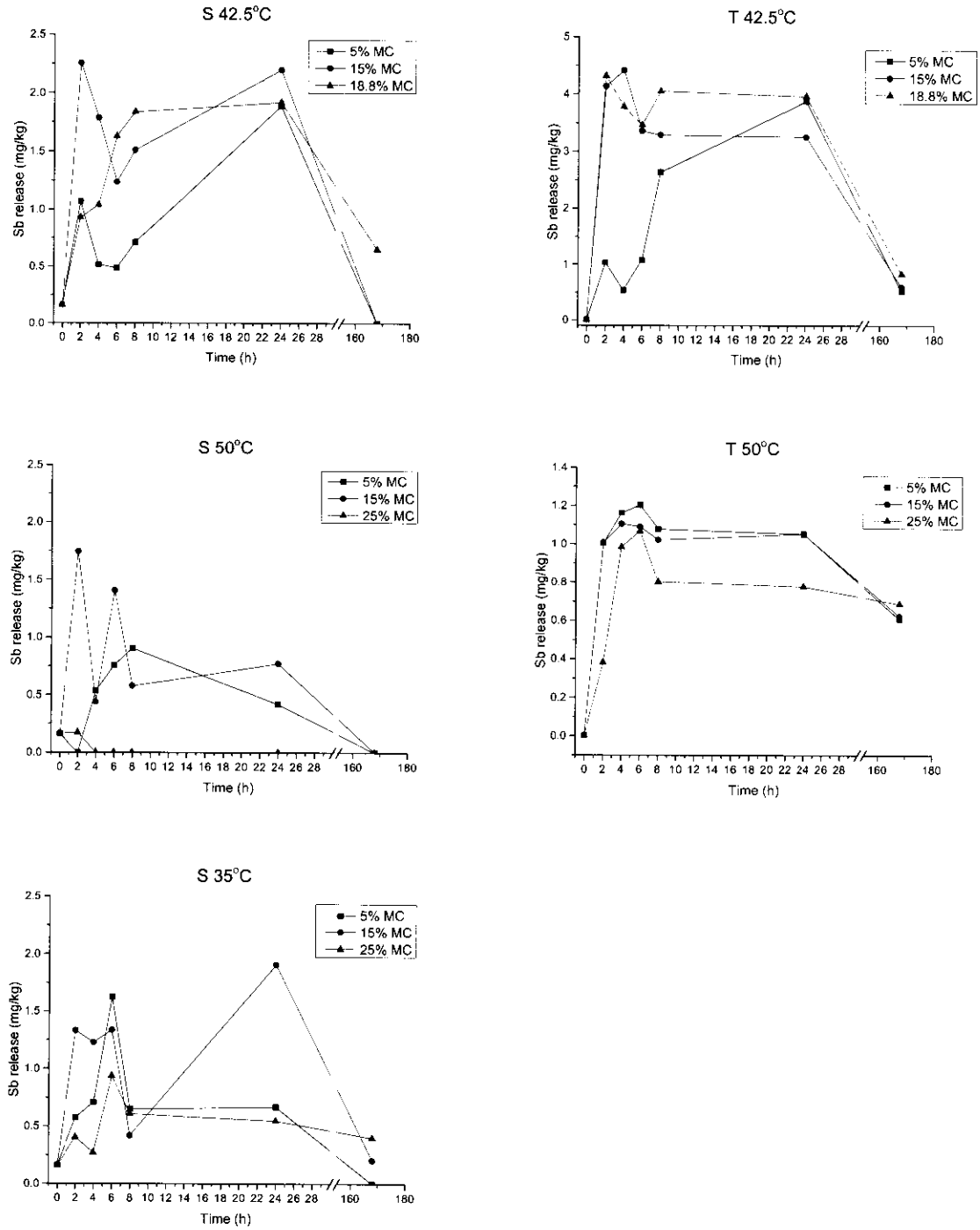


Figure 5-15: Sb release (mg/kg) as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

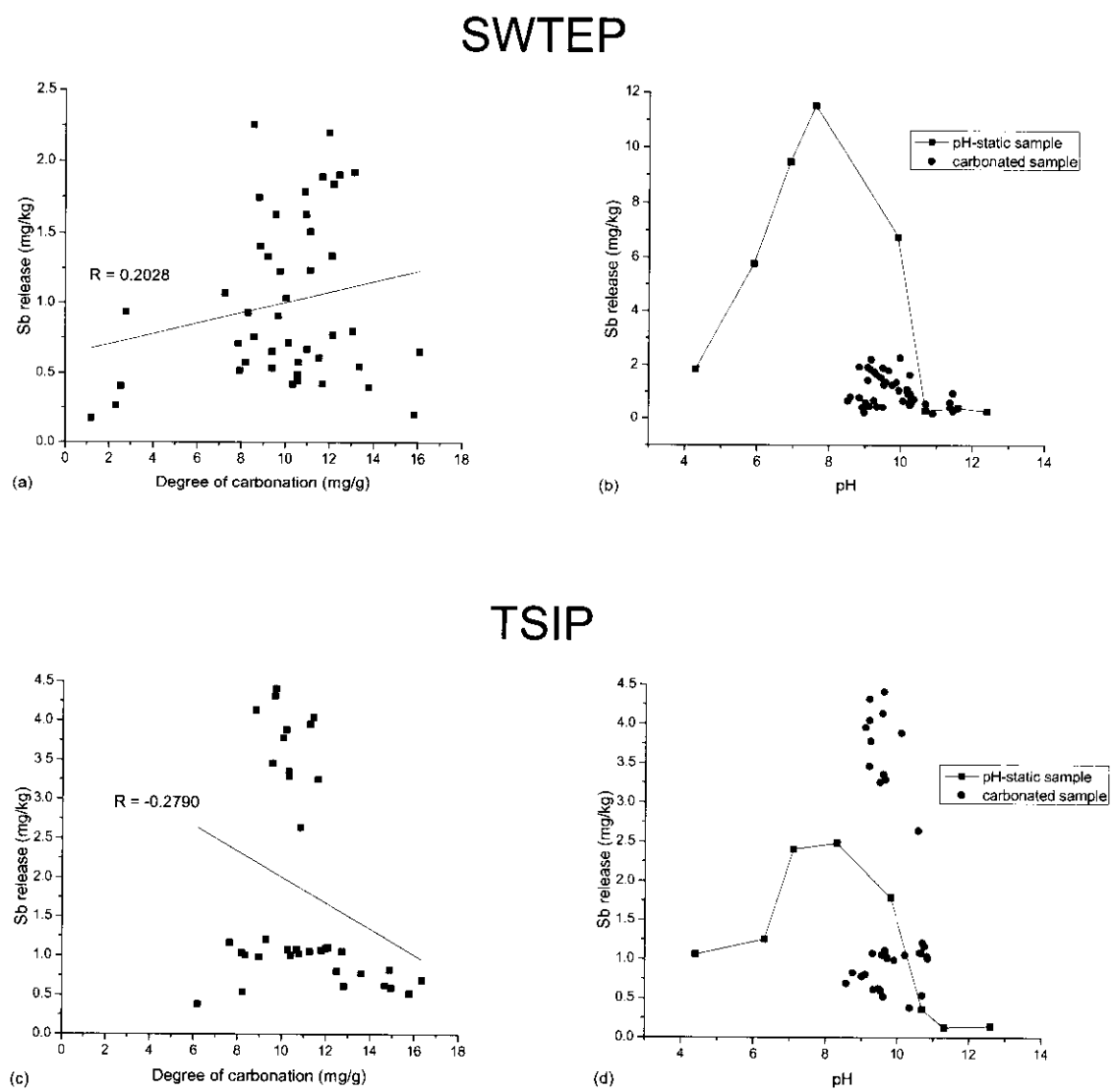


Figure 5-16: Correlation between Sb leaching and degree of carbonation for (a) SWTEP and (c) TSIP samples. Sb leaching as a function of measured pH for carbonated sample and pH-static leaching of untreated (b) SWTEP and (d) TSIP samples.

Cl^- and SO_4^{2-}

Cl^- leaching did not show obvious trend of increasing or decreasing after carbonation at various operating conditions, only showing a slight decrease after 1 week of carbonation for certain operating conditions (Figure 5-17). Due to the high release of Cl^-, the highest reduction in Cl^- leaching was only 13.1% for SWTEP sample and 6.7% for TSIP sample. It has been reported that carbonation has

minimal effect on the immobilisation of Cl^- leaching (Todorovic and Ecke, 2006a). This study reports similar findings as Figure 5-18 shows the correlation coefficient between Cl^- leaching and degree of carbonation were relatively low at R = 0.2508 and 0.4201 for SWTEP and TSIP samples respectively.

SO_4^{2-} leaching was found to have increased for all samples after 2 hours of carbonation, regardless of operating conditions (Figure 5-19). The amount of leaching corresponded to the degree of carbonation for SWTEP sample but not TSIP sample. Figure 5-20 shows that R = 0.7000 and 0.0653 for SWTEP and TSIP samples respectively. The high R value for SWTEP sample suggests the SO_4^{2-} leaching has strong dependence on the degree of carbonation, which could be explained by the dissolution of ettringite while $CaCO_3$ precipitates (Meima and Comans 1997b). On the other hand, the increase in SO_4^{2-} leaching for TSIP sample could be contributed from the replacement of SO_4^{2-} with CrO_4^{2-} (Cornelis et al., 2008), where Cr leaching was found to be more dependent on pH than degree of carbonation.

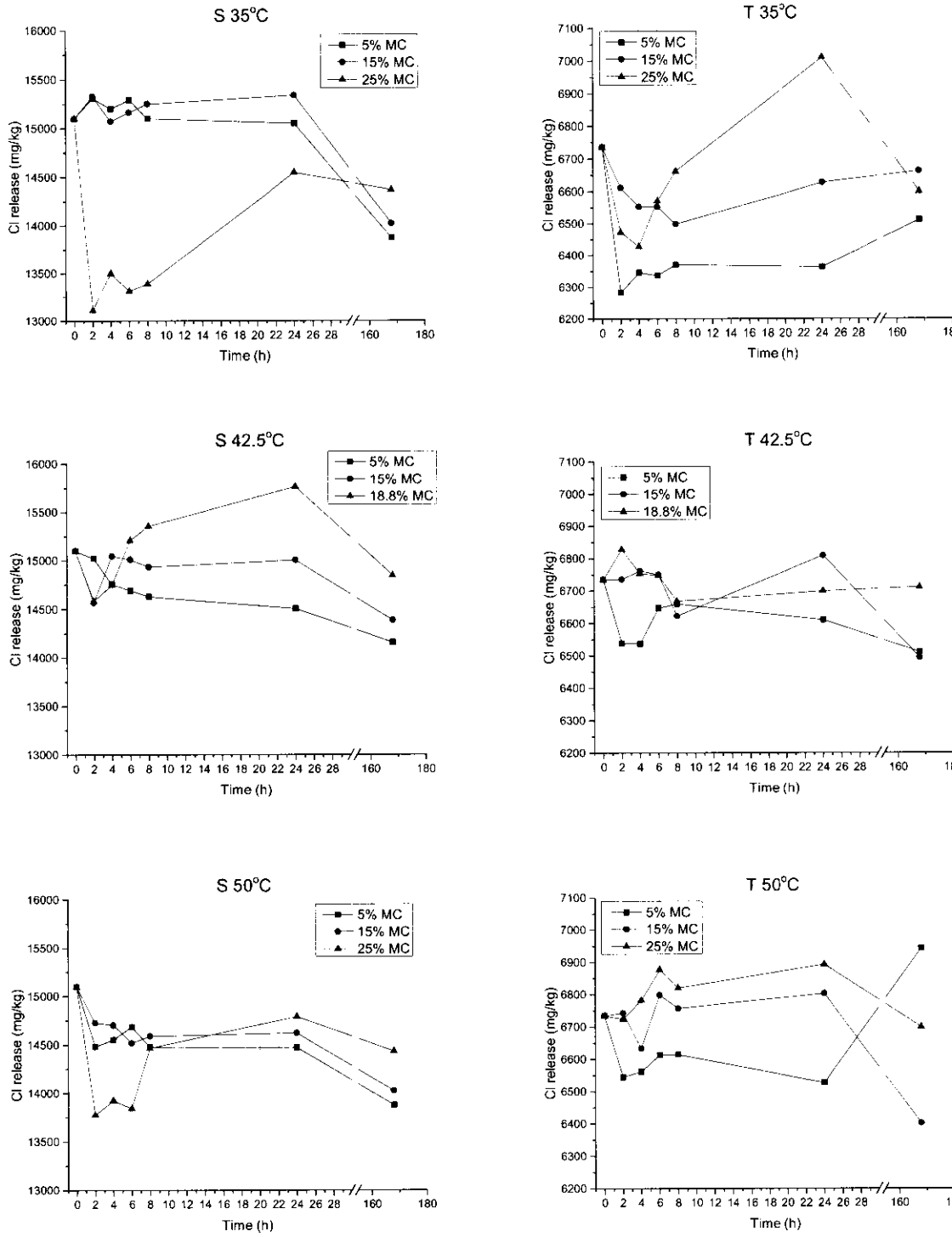


Figure 5-17: Cl^- release (mg/kg) as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

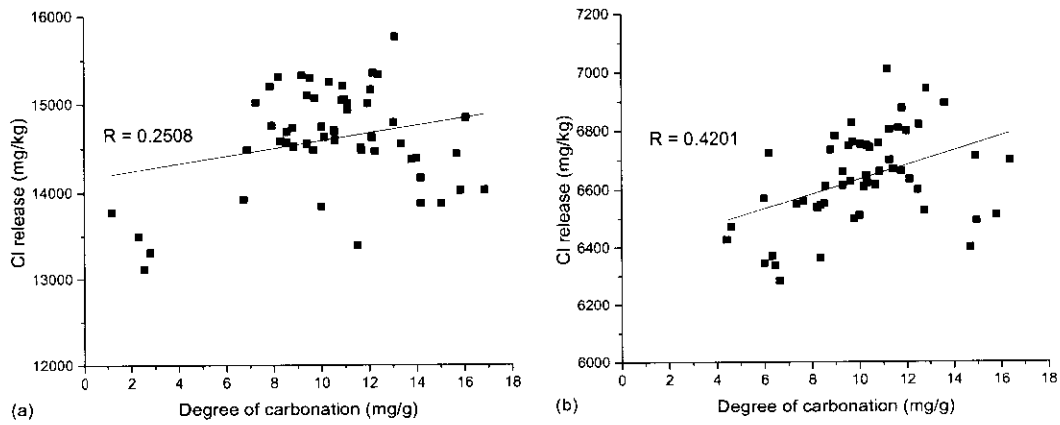


Figure 5-18: Correlation between Cl^- leaching and degree of carbonation for (a) SWTEP and (b) TSIP samples.

Cl^- and SO_4^{2-} leaching are not considered toxic to human health. However, the high leachability of Cl^- is one of the main considerations preventing the use of IBA in concrete as Cl^- is detrimental to the structural soundness of building due to corrosion of steel reinforcement in concrete. Cl^- leaching from IBA usually exceeds the maximum allowable concentration in cement mixtures, which is set at 4,000 mg/kg (Boghetich et al., 2005). Similarly, SO_4^{2-} leaching from IBA leads to loss of integrity of concrete due to gypsum formation. However, several authors have reported the increase in SO_4^{2-} leaching after carbonation (Meima and Comans 1997b; Bodénan et al., 2000; Polettini and Pomi, 2004), as this study has shown.

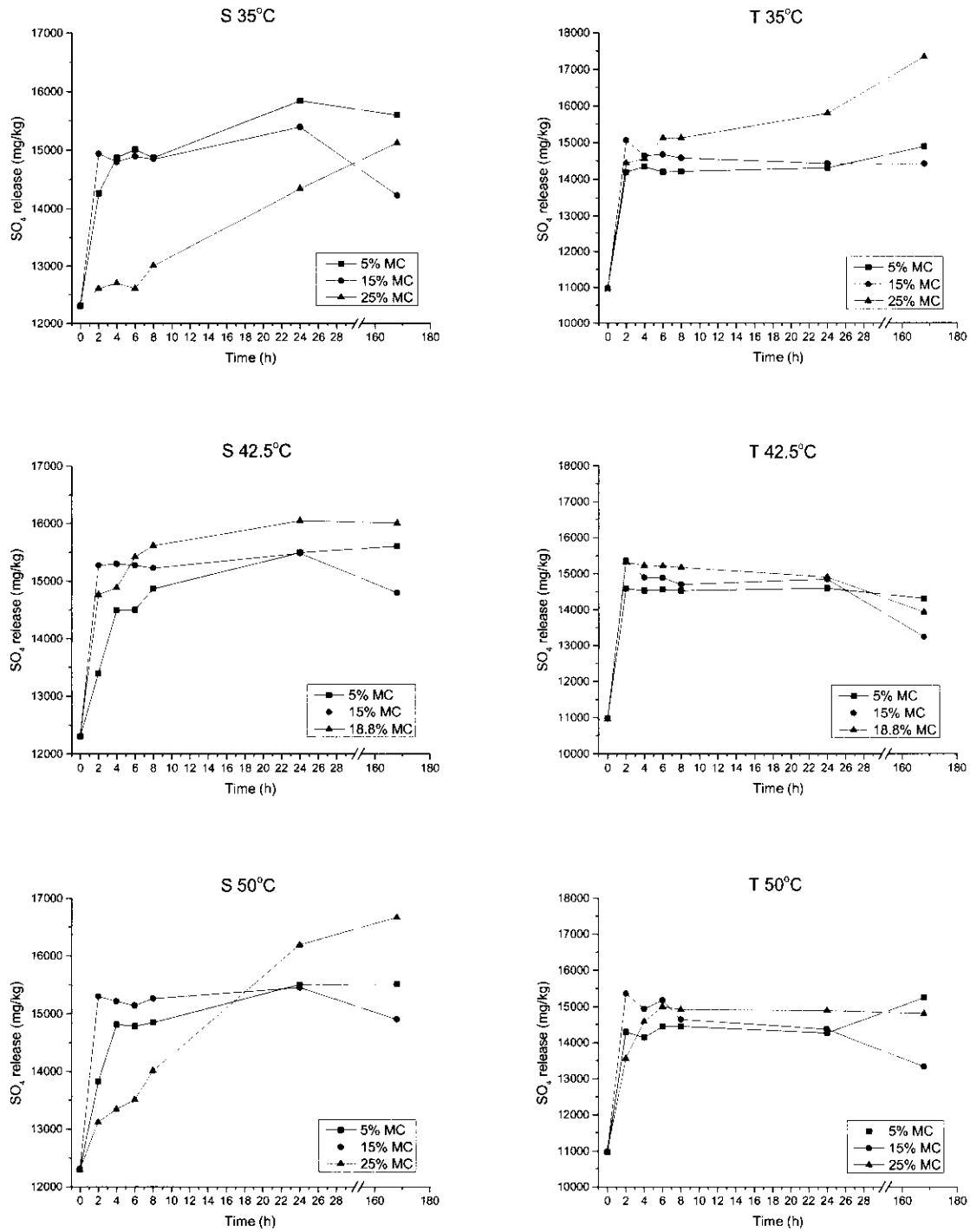


Figure 5-19: SO_4^{2-} release (mg/kg) as a function of carbonation time for SWTEP and TSIP samples at various operating conditions.

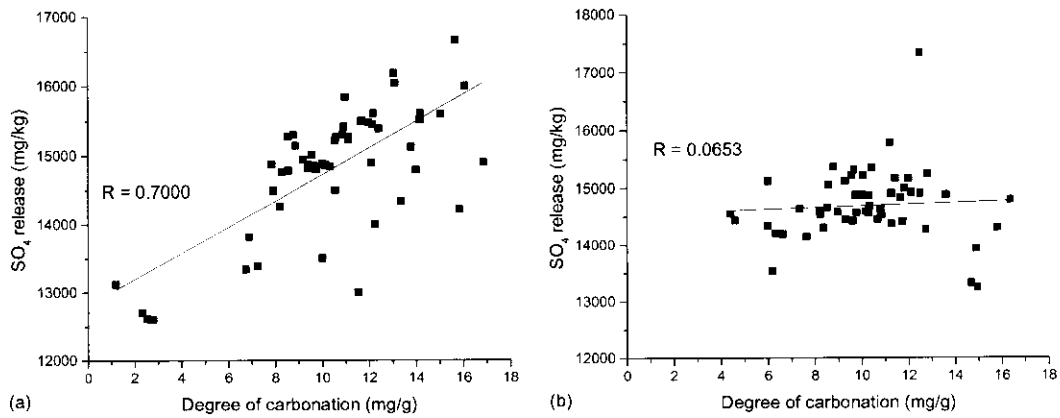


Figure 5-20: Correlation between SO_4^{2-} leaching and degree of carbonation for (a) SWTEP and (b) TSIP samples.

5.4 Conclusion

This study aims to address two issues pertaining to treatment of IBA by accelerated carbonation: the influence of operating conditions on the degree of carbonation, and possible factors influencing the leaching mechanism.

In this study, the moisture content was found to strongly affect the initial rate of carbonation. At IBA particle size <425 μm, 15% nominal moisture content achieved the highest degree of carbonation after 2 hours of carbonation. The actual moisture content was found to change during carbonation. The rate of moisture loss and gain was dependent on the carbonated temperature, which indirectly affected the initial rate of carbonation. The optimum temperature was found to differ for the two incineration plants, i.e. 35°C and 50°C for SWTEP and TSIP samples respectively.

Based on the findings on the optimum operating conditions for SWTEP and TSIP samples, besides the factor of degree of carbonation, there are a few factors that were found to contribute to the leaching mechanism of Pb, Zn, Cu, Cr, Mo and Sb after carbonation. For Pb and Zn, pH plays a dominant role on the significant reduction in leaching. For Cu leaching, the contributing factors are degree of carbonation and DOC. The R values for the two incineration plants did not agree with each other, whereby the dominant contributing factors for Cu leaching after

carbonation were different. For SWTEP sample, degree of carbonation and DOC seems to affect Cu leaching equally. However, for TSIP sample, the contribution from degree of carbonation seems to be higher than that of DOC. pH did not play a significant role in Cu leaching from carbonated samples. As for Cr, pH seems to affect Cr leaching more than the degree of carbonation. This is similar for the other two oxyanions forming elements, i.e. Mo and Sb. However, accelerated carbonation did not significantly reduce Mo and Sb leaching as the pH of carbonated samples was around 9, which coincides with the maximum solubility of Mo and Sb. For the highly soluble salts, i.e. Cl^- and SO_4^{2-}, carbonation did not affect Cl^- leaching significantly while SO_4^{2-} leaching increased significantly.

Through the investigation of leaching as a function of carbonation time, our study reveals that many factors, e.g. temperature, moisture content, pH, DOC and source of IBA, contribute to the leaching level of each element to different extent.

CHAPTER 6: EFFECT OF ACCELERATED CARBONATION ON DIFFERENT SIZE FRACTIONS OF IBA

6.1 Introduction

Sieving of IBA is a mandatory pre-treatment step in countries, such as Denmark and the Netherlands, which utilise IBA (Chandler et al., 1997). The common applications of IBA include use as aggregate for road base construction, as a fill for embankments and as an amendment for Portland cement concrete. The need to sieve IBA arises from the engineering requirement when utilising IBA in the applications as mentioned. From the engineering viewpoint, the total percentage of fine size fraction (<60 μm) in IBA for use as asphalt pavement or structural fill has to be less than 10% as the fine size fraction has high absorption for water, which compromises durability due to freeze-thaw susceptibility (Chandler et al., 1997). Furthermore, sieving of IBA is essential for the removal of oversized fraction (i.e. >50 mm) and metallic materials. Non-ferrous metals in IBA, such as Al, are detrimental to the structural integrity due to the evolution of H_2 when IBA comes into contact with water (Chandler et al., 1997).

In terms of treatment of IBA, sieving of IBA has several advantages. Firstly, sieving IBA in different size fractions improves the precious metals recovery (Muchova et al., 2008), which has the additional benefit of generating revenue during IBA treatment. Secondly, by sieving IBA into different size fractions, the leachability of trace elements were found to improve as the size fractions increased (Stegemann and Schneider, 1991). This will help to reduce the treatment cost of IBA by reducing the volume of IBA that needs to be treated.

The focus of this study is to explore the use of sieving before the accelerated carbonation treatment and its effect on improving leaching. The optimum operating conditions obtained from Chapter 5 was used for all the size fractions in this study. This is to investigate the differences in the chemical composition among the size fractions and its effect on the degree of carbonation and leaching behaviour. The

motivation of this study is to minimise the cost and duration of carbonation treatment of IBA.

6.2 Materials and Methods

6.2.1 Incineration bottom ash

The IBA used for this accelerated carbonation experiment was from the same samples as discussed in Chapter 5. The sampling and handling of IBA was as detailed in Chapter 3. A portion of the wet IBA was tested for moisture content and the dried IBA was then tested for LOI at 550°C. The rest of the dried IBA was sieved to obtain four size fractions: 0-2 mm (S0-2 and T0-2), 2-4 mm (S2-4 and T2-4), 4-20 mm (S4-20 and T4-20) and 20-50 mm (S20-50 and T20-50). The ferrous and non-ferrous metals which could not be crushed were removed and weighed. All the size fractions were further ball-milled to pass through a 425μm stainless steel sieve. This is to minimise the effect of difference in surface areas on the efficiency of carbonation.

6.2.2 Accelerated carbonation experiment

The accelerated carbonation process was carried out in CO_2 incubator (Sanyo MCO-18AIC), using 20% CO_2 at 1 atm for all the experiments. A tray of DI water was placed at the bottom of the incubator to maintain a constant atmospheric humidity. The optimum operating conditions from Chapter 5 using 0-2 mm was applied to other size fractions: 35°C and 50°C at 15% moisture content. The required moisture content was obtained by adding DI water to dried IBA. IBA was spread on plastic petri dishes to no more than 2 mm thick. The carbonation was stopped after 2 hours. The actual moisture remained in the petri dish was monitored.

6.2.3 Analysis

The analysis for this study was as detailed in Chapter 3. Both EN 12457-2 and CEN/TS 14429 leaching tests were used for this study. In addition, the following analysis was carried out for this study. The density of each size fraction was

measured by automatic density analyser (Ultrapyc 1200e). The surface area after grinding each size fraction separately before accelerated carbonation was determined by Brunauer-Emmett-Teller (BET) test (Quadrasorb SI, Quantachrome Instruments).

6.3 Results and Discussion

6.3.1 Characteristics of IBA

Table 6-1 shows the characteristics of IBA collected from the two incineration plants. The high moisture content (16.8% for SWTEP and 15.5% for TSIP) was due to the sampling of IBA near to the exit of the quenching tank for both incineration plants. The LOI values for both plants (0.59% for SWTEP and 1.51% for TSIP) were found to be much lower than mean values reported in Canada, Denmark and United States (Chandler et al., 1997). The oversize fraction of >50 mm was not used in this study but their weight percentages were noted as 4 wt% and 13 wt% from SWTEP and TSIP respectively. Both plants showed higher weight percentages for 0-2 mm and 4-20 mm size fractions than other fractions. The TOC, which measures the organic carbon remaining in IBA after combustion, was observed to decrease as the size fraction increase. The density was found to increase as the size increased for TSIP samples but not for SWTEP. The density for the different size fractions of SWTEP samples was quite close to one another. This could be due to the difference in waste input for SWTEP and TSIP, whereby the higher density for the coarser size fraction in TSIP may be contributed from industrial waste. After ball-milling, the same size fraction from the two incineration plants was able to achieve a relatively similar surface area.

Table 6-1. Characteristic of IBA collected from incineration plants SWTEP (S) and TSIP (T).

Incineration plant	**SWTEP**		**TSIP**	
Moisture content (%)	16.8		15.5	
LOI (%)	0.59		1.51	
Ferrous (wt%)	12.1		8.3	
Non-ferrous (wt%)	0.8		1.2	
Size fraction	**0-2 mm**	**2-4 mm**	**4-20 mm**	**20-50 mm**
Particle size distribution (wt%)	34.2 (S) 29.7 (T)	8.6 (S) 7.3 (T)	38.7 (S) 29.9 (T)	14.5 (S) 20.1 (T)
TOC (mg/g)	5.86 (S) 9.98 (T)	4.45 (S) 10.30 (T)	3.01 (S) 5.73 (T)	1.78 (S) 1.63 (T)
Density (kg/m^3)	2,782 (S) 2,928 (T)	2,822 (S) 2,997 (T)	2,766 (S) 3,023 (T)	2,772 (S) 3,099 (T)
BET (m^2/g) *After ground to <425 μm	4.34 (S) 4.70 (T)	3.63 (S) 4.95 (T)	2.46 (S) 2.42 (T)	3.07 (S) 2.74 (T)

The total element contents for the four size fractions are shown in Table 6-2. Only the total concentrations of Ca, Cd, Co, Sb, Cl^- and SO_4^{2-} were observed to decrease as the size increased for both incineration plants. Cr was found to decrease in SWTEP sample as the size increased but increase in TSIP sample as the size increased. For Cu, it was found to be most concentrated in S2-4 and T0-2. For Mn and Pb, the highest concentrations were found in 2-4 mm size fraction of both SWTEP and TSIP samples while Zn was mostly concentrated in 0-2 mm for both plants. For Mo, the concentration in TSIP sample was significantly higher than in SWTEP sample for all the size fractions. The trend of total element content of Ca, Pb and Zn as a function of the size fractions was similar to those reported by (Chimenos et al., 2003).

Table 6 ntent (mg/kg) for the four size fractions from incineration plants SWTEP and TSIP.

Elen (mg/	SWTEP			TSIP			
	2-4 mm	4-20 mm	20-50 mm	0-2 mm	2-4 mm	4-20 mm	20-
A	13	9	9	18	19	7	
A	33,767	30,600	62,900	32,033	37,867	36,667	4(
A	24	37	17	64	63	38	
B	57	41	52	65	74	66	
B	1.2	1.5	3.4	1.2	1.4	1.7	
C	132,000	108,000	84,067	139,667	108,667	103,267	9
C	2.1	1.4	0.58	5.3	1.8	1.1	<
C	34	30	17	48	41	33	
C	216	184	140	206	210	248	
C	3,513	1,703	733	2,437	2,070	2,243	1
F	59,067	56,700	51,067	111,000	117,333	133,667	14
K	9,447	8,977	14,500	9,857	10,467	9,970	9
M	9,723	11,133	8,217	10,633	10,300	11,367	1
M	1,030	679	718	1,600	2,127	1,987	1
M	14	11	8	121	96	85	
N	22,700	41,667	19,033	13,067	17,100	25,967	1
N	140	92	88	169	172	130	
P	1,717	1,133	145	199	294	288	
S	153	131	84	85	59	57	
S	130	99	113	95	94	63	
S	388	521	736	327	348	502	
T	5,297	3,450	3,350	5,267	6,163	5,527	5
V	30	24	40	55	53	49	
Z	2,387	1,523	1,900	4,050	2,953	2,147	1
C	6,493	3,877	1,887	5,900	3,687	1,940	1
SC	6,440	4,890	1,880	6,987	5,320	3,143	1

6.3.2 Degree of carbonation of different size fractions

Based on the study discussed in Chapter 5, the optimum operating conditions were 2 hours of carbonation at 15% moisture content, 35°C and 50°C for S0-2 and T0-2 samples respectively. Both 35°C and 50°C were used for carbonating the four size fractions of SWTEP and TSIP samples for comparison on the difference in degree of carbonation (Table 6-3). Generally, the degree of carbonation for the four size fractions decreased as the size fractions increase. This decrease in the degree of carbonation corresponded to the decrease in the total Ca content as the size fractions increase. This result echoed the findings of Baciocchi et al. (2010) and demonstrated that the amount of CO_2 sequestrated by IBA is strongly dependent on the total Ca content. The operating conditions only influenced the initial rate of carbonation but not the capacity.

In terms of the optimum operating conditions, SWTEP samples carbonated more effectively at 35°C, 15% moisture content, except for S20-50 sample. The same trend was observed for TSIP samples for operating conditions 50°C, 15% moisture content, except for T4-20 sample. However, the differences in the degree of carbonation for the exceptions were not great. In fact, there was very minute difference in degree of carbonation for 4-20 mm and 20-50 mm size fractions. This suggests that the coarse size fractions were not as sensitive to the difference in operating conditions.

Lastly, the actual moisture content remained after 2 hours of carbonation was observed to be similar with respect to the carbonated temperatures, regardless of the source of IBA. The actual moisture content of all the size fractions from both plants had an average value of 14.3% at 35°C, while the average value at 50°C was 10.6%. This shows that the temperature used for carbonation would result in some loss of moisture with time. Furthermore, the effect of moisture content on the degree of carbonation was more pronounced for the 0-2 mm and 2-4 mm size fractions only.

Table 6-3. The degree of carbonation (mg/g) of the respective size fractions and the actual moisture content (%) remained after 2 hours of carbonation.

Operating conditions	Degree of carbonation (mg/g)	Actual moisture content (%)
S0-2		
35C15MC	9.20	14.00
50C15MC	8.79	9.58
S2-4		
35C15MC	4.34	15.18
50C15MC	3.78	11.25
S4-20		
35C15MC	3.55	14.31
50C15MC	3.26	11.00
S20-50		
35C15MC	4.42	14.75
50C15MC	4.47	10.75
T0-2		
35C15MC	8.56	13.31
50C15MC	10.41	12.03
T2-4		
35C15MC	4.89	14.31
50C15MC	6.53	10.50
T4-20		
35C15MC	4.15	14.09
50C15MC	4.11	9.75
T20-50		
35C15MC	2.51	14.53
50C15MC	2.86	9.75

6.3.3 Effect of accelerated carbonation on pH

Figure 6-1 shows the pH before and after carbonation at 35°C and 50°C, 15% moisture content. For the untreated SWTEP samples, the pH did not vary much among the four size fractions, from pH 12.4 to 12.1 (i.e. from finest to coarsest). However, the pH was found to decrease slightly from pH 12.6 to 11.9 as the size increased for the untreated TSIP samples. After 2 hours of carbonation, the pH of S0-2 and T0-2 decreased to an average of 9.6 and 9.8 respectively. The average refers to the average pH of two carbonation temperatures. For the other size

fractions, the pH reduced more, the lowest observed pH was 9.0 for S4-20 sample carbonated at 50°C and 15% moisture content. It was noted that the reduction in pH of T20-50 sample was slower than that of S20-50 sample, from 11.9 to an average of 9.4 compared to 12.1 to an average of 9.3. The lower pH obtained by other size fractions after 2 hours of carbonation shows that the optimum operating conditions selected based on the 0-2 mm size fraction was able to efficiently carbonate the other size fractions too.

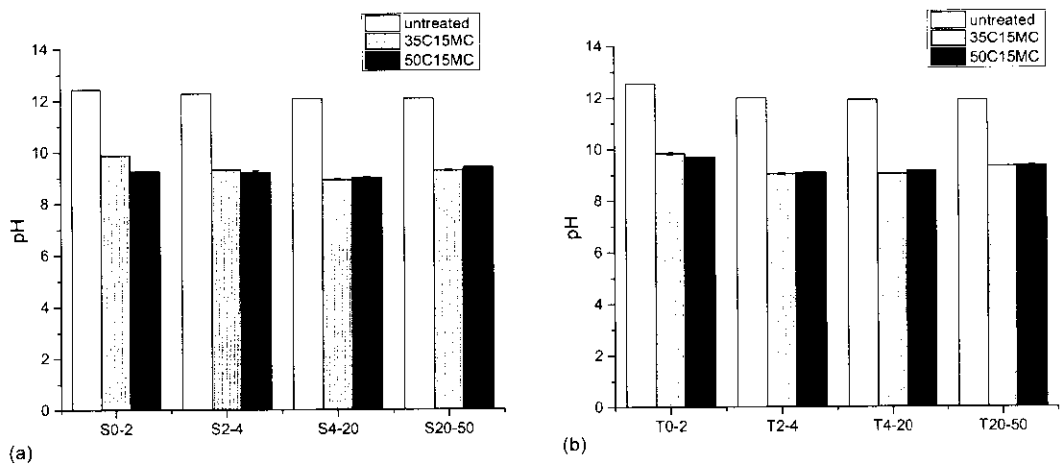


Figure 6-1: The pH of the different size fractions showing untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

6.3.4 Effect of accelerated carbonation on leaching

Pb and Zn

The leaching trend of Pb from untreated SWTEP and TSIP samples was observed to be significantly different. Untreated S2-4 had the highest Pb released at 73.1 mg/kg but Pb leaching was below the detection limit (i.e. <50 µg/L) for the same size fraction of untreated T2-4. In fact, only untreated T0-2 was found to leach slightly at 0.36 mg/kg and the rest of the untreated size fractions of TSIP samples were undetectable in Pb leaching. In contrast, for SWTEP samples, only untreated S20-50 was undetectable in Pb leaching. However, accelerated carbonation was found to be very effective in reducing Pb leaching. Regardless of the initial concentration leached from the untreated samples and operating conditions of carbonation, Pb was

undetectable after carbonation in all the leachates. The reduction in Pb leaching could be due to the lower pH reached after carbonation, as discussed in Chapter 5.

Figure 6-2 shows Zn leaching from untreated and carbonated IBA as a function of size fractions. The amount of Zn released from untreated SWTEP and TSIP samples decreased as the size increased. Generally, all the size fractions from untreated TSIP sample showed significantly less Zn leaching compared to those from untreated SWTEP sample. After carbonation, only S0-2 and T0-2 samples still had slight Zn leaching while Zn leaching in the rest of the size fractions were below the detection limit of ICP-OES (i.e. <5 μg/L). Similar to Pb, the reduction in Zn leaching could be due to the lower pH reached after carbonation.

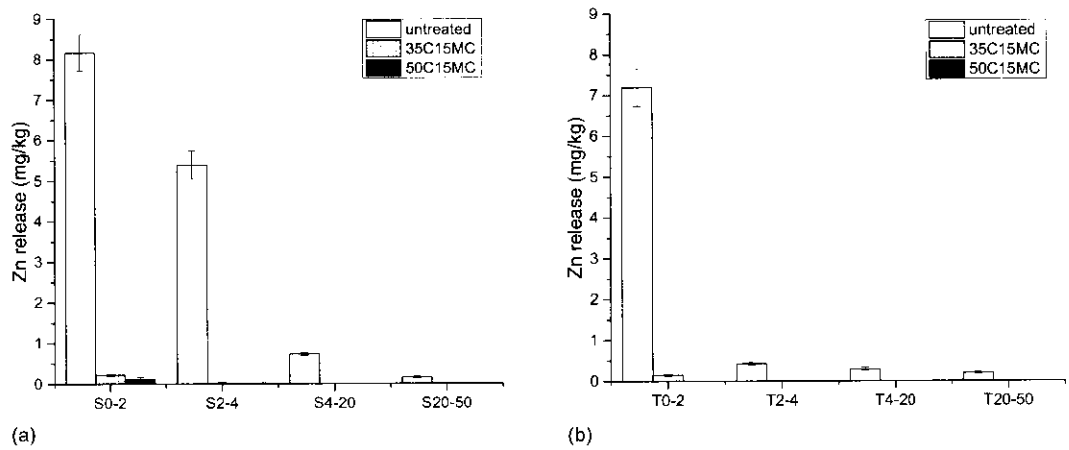


Figure 6-2: Zn release (mg/kg) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

Cu

Figure 6-3 shows Cu leaching decreased as the size increased for the untreated samples. After carbonation, the percentage reduction in Cu leaching ranged from 64.8 to 85.3% for SWTEP samples and 69.5 to 82.4% for TSIP samples. As discussed in Chapter 5, the leaching mechanism of Cu in 0-2 mm size fraction was affected by DOC and degree of carbonation, however, to different extent for the two types of IBA. Degree of carbonation was found to affect Cu leaching in T0-2 more

than DOC, while both factors affect Cu leaching in S0-2 equally. As for the different size fractions, only TSIP samples were consistently affected by the difference in carbonated temperatures, which leads to a lower Cu leaching for samples carbonated at 50°C (i.e. the optimum temperature for TSIP), as can be seen in Figure 6-3b. This finding is in agreement with the earlier findings in Chapter 5.

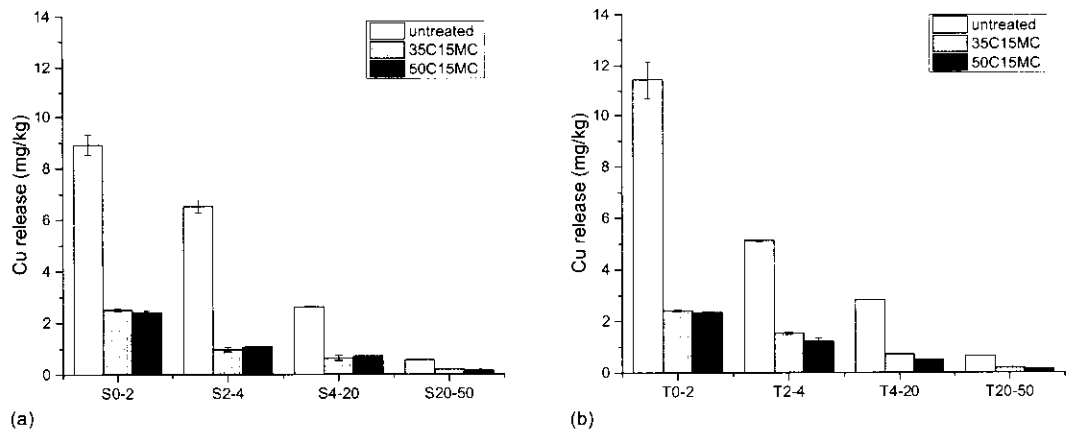


Figure 6-3: Cu release (mg/kg) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

Cr, Mo and Sb

The amount of Cr released from untreated TSIP samples decreased as the size increased but SWTEP samples did not show the same trend as Cr leaching from untreated S2-4 sample was exceptionally low (Figure 6-4). After carbonation, S0-2 sample had an average of 48.3% reduction in Cr leaching while the other size fractions of SWTEP samples had more significant reduction in Cr leaching, ranging from 63.1 to 92.9%. Similarly, the reduction in Cr leaching for T0-2 samples was an average of 62.2%, which was less significant compared to other size fractions (i.e. 83.0 to 94.9%). It was discussed in Chapter 5 that pH plays a dominant role in Cr leaching. In this study, after carbonation, the final pH of 0-2 mm size fractions was slightly higher than other size fractions (Figure 6-1). Therefore, the lower pH has contributed to the lower Cr leaching in the rest of the size fractions.

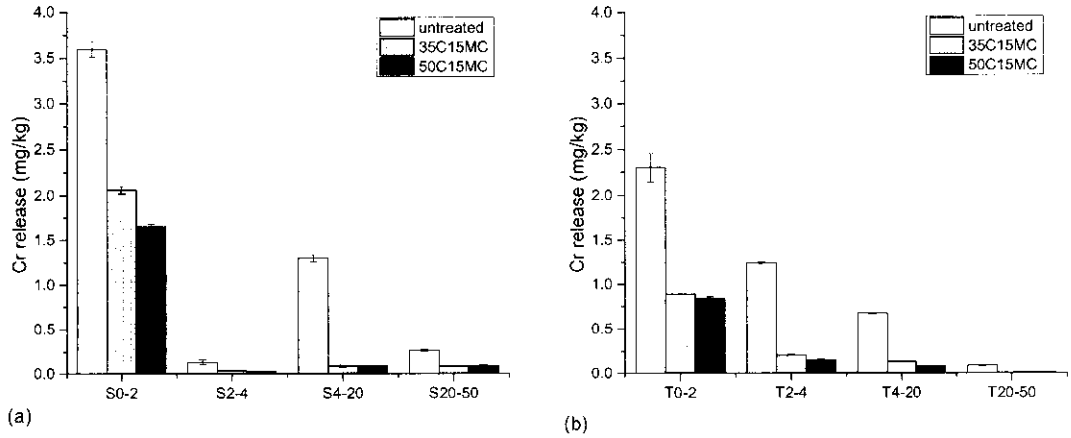


Figure 6-4: Cr release (mg/kg) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

The amount of Mo released from untreated TSIP samples were significantly higher than that from SWTEP samples (Figure 6-5). Coincidentally, the total Mo content in all the size fractions of TSIP was an order of magnitude higher than SWTEP, which could be a possible reason for the higher leaching from untreated TSIP samples. The leaching behaviour after carbonation was totally different for the two types of IBA. Most of SWTEP samples showed an increase in Mo leaching after carbonation while TSIP samples showed varying levels of reduction. Mo leaching was discussed in Chapter 5 to be affected by pH. However, the pH after carbonation was not sufficiently low for Mo to reach its minimum solubility, which is around pH 4 as shown in Figure 5-14 (b, d). Therefore, the decrease in Mo leaching for the rest of size fractions of TSIP samples could be due to the difference in mineralogical composition in the other size fractions, as can be seen from the similar leaching trend in Figure 6-5b. However, this finding is not conclusive as more research is needed to investigate other factors contributing to the leaching mechanism of Mo.

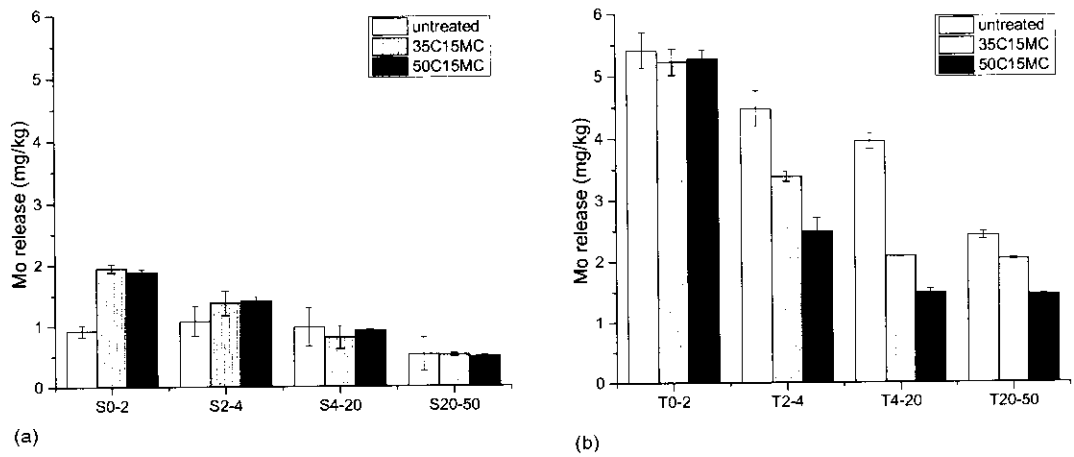


Figure 6-5: Mo release (mg/kg) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

The leachates from untreated SWTEP and TSIP samples were found to be below the detection limit of Sb (i.e. <10 μg/L), except for S0-2 (Figure 6-6). The values that were below the detection limit were represented by zero in the graphs. After carbonation, all the samples show drastic increase in Sb leaching. Similar to Mo, accelerated carbonation would not favour the reduction in Sb leaching as the final pH after carbonation coincides with the maximum solubility of Sb (Figure 5-16 (b, d)). Unlike Mo, the effect of pH as the dominant factor contributing to the increase in Sb leaching seems to explain the phenomenon observed for the different size fractions. However, the reason for the difference in the increment of leaching between SWTEP and TSIP samples after carbonation is unclear at this point.

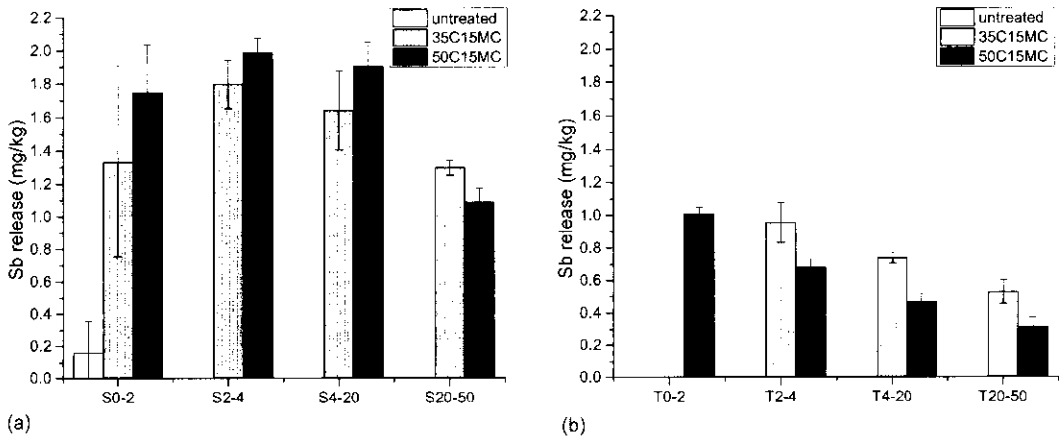


Figure 6-6: Sb release (mg/kg) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

DOC, Cl^- and SO_4^{2-}

DOC displayed similar reduction in leaching for the untreated samples as the size increased (Figure 6-7). After carbonation, DOC leaching decreased but did not differ much within the same size fractions of the same source of IBA. This shows that the degree of carbonation did not have much effect on the DOC leaching reduction. The percentage reduction for DOC ranges from 11.0 to 32.3% for all the size fractions.

For soluble salts Cl^- and SO_4^{2-}, the amount of soluble salts released from untreated samples decreased as the size increased. The difference between them is that Cl^- did not show reduction in leaching after carbonation (Figure 6-8), while SO_4^{2-} leaching increased after carbonation (Figure 6-9). These findings are in agreement with the discussion in Chapter 5.

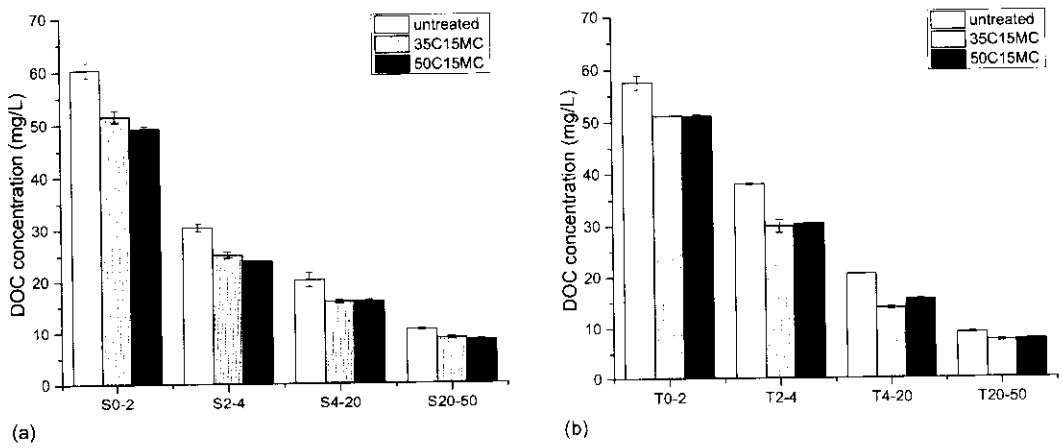


Figure 6-7: Concentration of DOC (mg/L) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

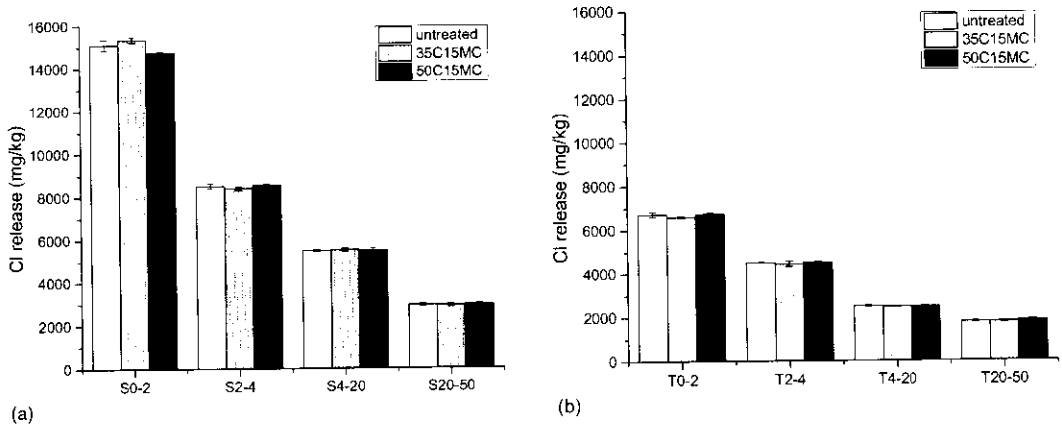


Figure 6-8. Cl^- release (mg/kg) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

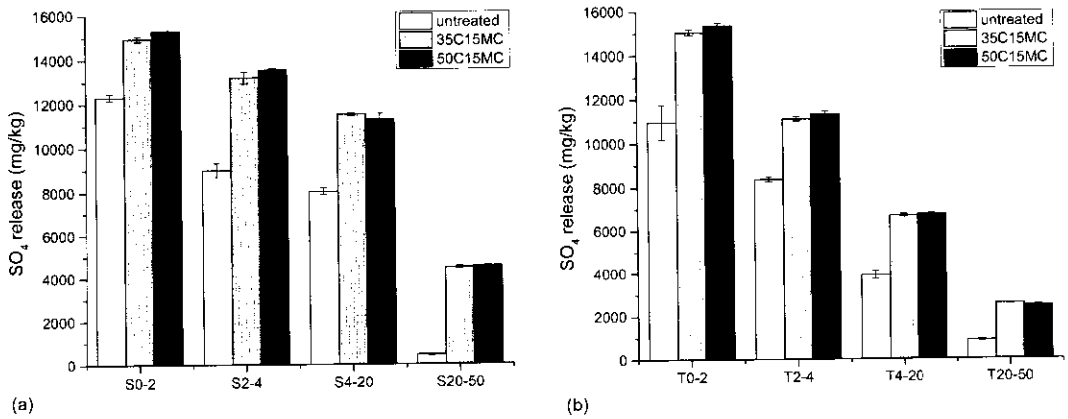


Figure 6-9. SO_4^{2-} release (mg/kg) as a function of size fractions for untreated (a) SWTEP and (b) TSIP samples, and after carbonation.

6.3.5 Effect of different size fractions on pH-static leaching

The acid neutralising capacity (ANC) of the different size fractions was investigated (Figure 6-10). The ANC for both SWTEP and TSIP samples was observed to decrease as the size increased. However, the ANC of 0-2 mm size fractions for both SWTEP and TSIP samples was significantly higher than the rest of the size fractions. Both S0-2 and T0-2 samples required approximately 1.33 mol H^+/kg of acid to reduce the pH from the initial of around 12 to 10. This amount of acid required was about 2 to 3 times higher than those required by other size fractions to reach a pH of 10. In fact, at around pH 10, the pH of other size fractions were found to decrease significantly from pH 10 to 7 with just an addition of 0.5 to 1 mol H^+/kg of acid. The implication of this result in terms of carbonation is that 0-2 mm size fraction requires more CO_2 uptake (i.e. higher CO_2 percentage or longer carbonation duration) to reduce the pH from alkaline to neutral and the other size fractions requires less. Since 0-2 mm size fraction was effectively carbonated after 2 hours when the optimum operating conditions were used, and this duration was applied to the other size fractions in this study, the ANC results imply that the other size fractions can be effectively carbonated in even shorter period than 2 hours.

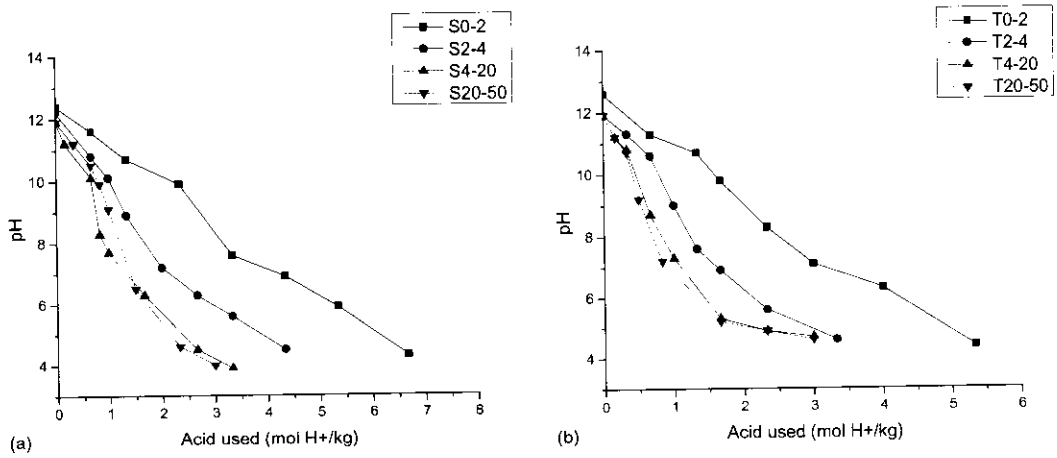


Figure 6-10: The acid neutralising capacity (ANC) of the different size fractions of untreated (a) SWTEP and (b) TSIP samples.

The leaching behaviours of Pb, Zn, Cr and Cu in response to an externally added acid are shown in Figures 6-11 to 6-14. Leachate samples from this pH-static leaching test were analysed by ICP-MS as the concentrations of most elements were below the detection limit of ICP-OES. The concentration of some elements was also below the detection limit of ICP-MS and the representative values in the graphs were explained under the figures' captions.

Generally, the leaching trend as a function of pH for the individual elements was similar for all the different size fractions. Comparing between untreated SWTEP and TSIP, the leaching trend was also similar, except for Cu, which showed two minimum solubility ranges for TSIP samples (Figure 6-13b). This similarity in the pH dependency leaching among the different size fractions explains the similarity in leaching behaviour for the different size fractions discussed earlier, as pH plays a dominant role in the leaching mechanism for most of the elements.

It was also observed that for the elements discussed here, the amount released in the pH-static leaching test decrease as the size fractions increase. This is in contrast to the trend in the total element content of the different size fractions (Table 6-2). For example, the total Pb content was more concentrated in the 2-4 mm and 4-20 mm. For Cr, the total Cr content decrease as size fractions increase for SWTEP samples

but increase with the size fractions for TSIP samples. However, both SWTEP and TSIP samples showed similar pH dependence leaching trend in Figure 6-14. This has further showed that coarse size fraction has lower release of elements and hence, requires less extensive treatment before utilisation. However, the pH-static leaching test would have to be carried out on more samples to ensure that this observation is statistically repeatable.

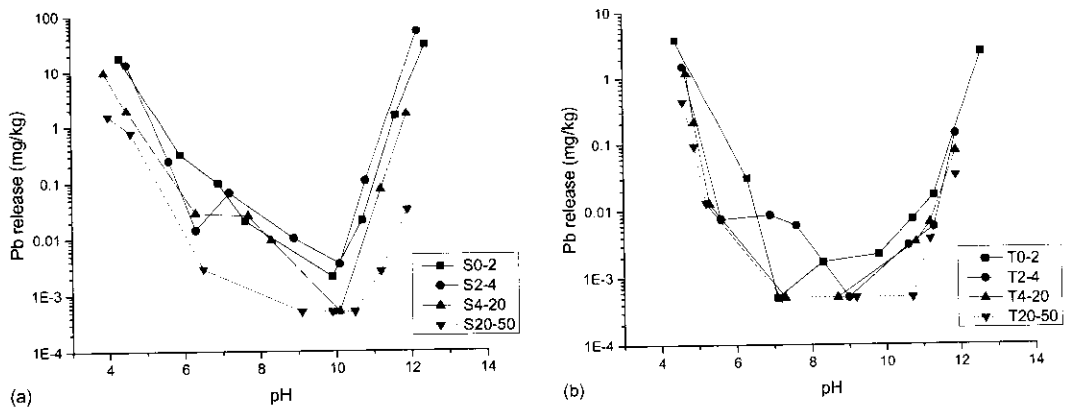


Figure 6-11: Pb leaching from different size fractions of untreated (a) SWTEP and (b) TSIP samples as a function of pH based on CEN/TS 14429 leaching test. The detection limit of ICP-MS for Pb is 0.1 µg/L. The represented value used here is 5 x 10^{-4} mg/kg.

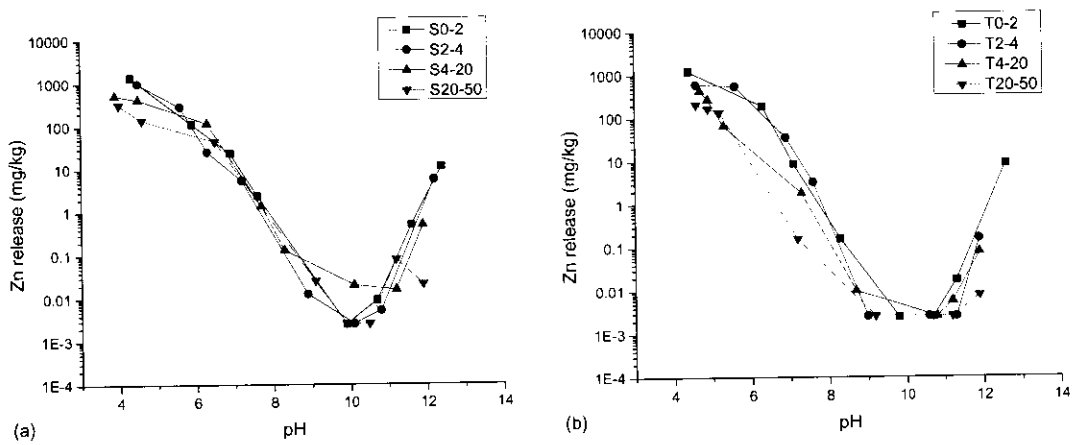


Figure 6-12: Zn leaching from different size fractions of untreated (a) SWTEP and (b) TSIP samples as a function of pH based on CEN/TS 14429 leaching test. The detection limit of ICP-MS for Zn is 0.5 µg/L. The represented value used here is 2.5 x 10^{-3} mg/kg.

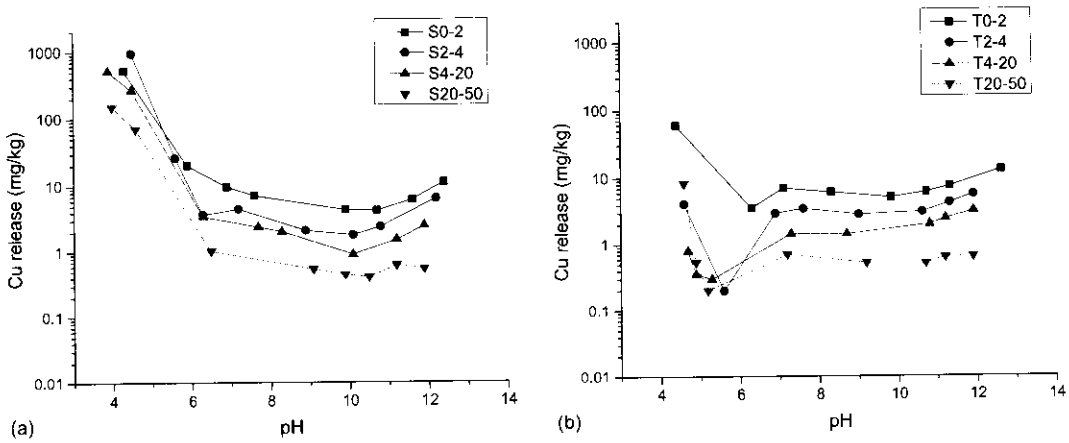


Figure 6-13: Cu leaching from different size fractions of untreated (a) SWTEP and (b) TSIP samples as a function of pH based on CEN/TS 14429 leaching test.

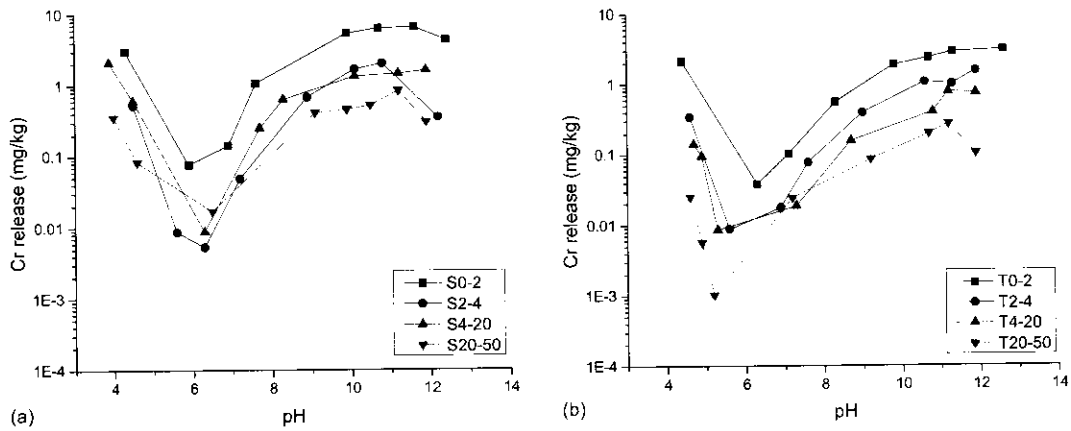


Figure 6-14: Cr leaching from different size fractions of untreated (a) SWTEP and (b) TSIP samples as a function of pH based on CEN/TS 14429 leaching test.

6.4 Conclusion

This study has shown through the leaching of untreated samples of different size fractions, the quality of IBA can be improved through the simple use of sieving before carrying out carbonation. Most of the elements discussed here showed decrease in leaching for the untreated samples as the size increases. This finding is important especially for highly soluble elements like DOC, Cl^- and SO_4^{2-}, whereby the concentration in the 20-50 mm size fraction was significantly lesser compared to

0-2 mm size fraction. Thus sieving has helped to increase the utilisation potential of IBA for the coarse size fraction as the coarse size fraction can generally be used with less treatment, depending on the regulation of each country. This translates to monetary saving as sieving is simple and inexpensive to carry out. This findings is similar to those reported by (Stegemann and Schneider, 1991).

Generally for the elements discussed here, the leaching mechanism was found to be in agreement with the leaching mechanism discussed in Chapter 5, except for Mo which showed reduction in leaching for TSIP samples in this study. The mineralogical composition between the two different sources of IBA seems to play a role here for Mo only. Further research would have to be carried to ascertain the reason. Otherwise, based on the leaching behaviour of other elements, the mineralogical composition could be quite similar among the different size fractions. This conclusion is further supported by the similarity in the leaching behaviour of the different size fractions as a function of pH done on the untreated IBA. The main difference among the different size fractions were the total element content.

Lastly, ANC results show that 0-2 mm size fraction required more acid to reduce the pH as compared to other size fractions. Thus, the carbonation duration may be further reduced for the coarse size fractions to achieve similar reduction in leaching as discussed in this study.

CHAPTER 7: INVESTIGATION ON THE MINERALOGICAL COMPOSITION OF IBA

7.1 Introduction

The complexity of IBA leaching arises from the heterogeneous nature of IBA, whereby the interaction between the different minerals in IBA and water (or leachant) results in a multiple of dissolution systems. Furthermore, IBA undergoes carbonation with time, either naturally or artificially, resulting in changes to the mineralogical composition of IBA and also the leaching behaviour. Many studies have investigated the mineralogy of naturally weathered IBA in great detail to obtain valuable information on the possible carbonation mechanisms, thus providing a better understanding on how carbonation reduces the leaching of certain heavy metals (Eighmy et al., 1994; Arickx et al., 2008; Bayuseno and Schmahl, 2010; Wei et al., 2011). However, such an analytical approach has not been extensively applied to accelerated carbonated IBA, whereby the process generally uses higher concentration of CO_2 compared to naturally weathered IBA, and may give rise to different mineralogical composition.

XRD is one of the analytical methods that can be used to determine the possible minerals present in IBA. The advantages of using XRD over other similar analytical methods, such as X-ray photoelectron spectroscopy (XRF) and energy-dispersive X-ray spectroscopy (EDX), are the ease of sample preparation for analysis and ease of raw data interpretation. The XRD equipment is also relatively less expensive than other analytical equipment. The minerals found experimentally using XRD in IBA, together with the minerals found geologically on earth, have been compiled into a database for modeling the leaching behaviour of IBA. This information is useful as it can be used to predict the long term leaching behaviour of IBA under different scenarios (Chandler et al., 1997). Besides modeling, understanding the mineralogical composition of IBA enables the evaluation of the suitability of other treatment methods, such as determining the cementitious property of IBA.

This study aims to carry out mineralogical study of IBA using XRD to evaluate and compare the mineralogical composition of untreated IBA from two different incineration plants and among the different size fractions. The minerals identified in IBA were further quantified by Rietveld refinement method. This study also aims to evaluate the mineralogical evolution that takes place in selected IBA samples after accelerated carbonation and investigate the carbonation mechanism for the experiments done in Chapter 5 and 6.

7.2 Materials and Methods

7.2.1 Materials

All the samples discussed in this chapter were selected from carbonated samples carried out per detailed in Chapter 5 and 6.

7.2.2 XRD

XRD analysis was performed on selected IBA samples. Before analysis, the samples were further ground using a mortar and pestle. XRD analysis was then performed in Bragg-Brentano geometry (Bruker AXS D8 Advance) with Cu-Kα radiation (λ = 1.54060Å) and fixed receiving slit (2.0 mm). The scan speed was set at 0.3°/min, with a scan step of 0.02° in continuous scan mode. Mineral identification was done by comparing the positions of the measured diffraction maxima with peak positions of possible minerals contained in the ICDD powder diffraction file database (ICDD, 2001). To quantify the minerals, further evaluation of the diffraction patterns by means of the Rietveld method was carried out using the TOPAS software V3.

7.3 Results and Discussion

7.3.1 XRD analysis

The minerals present in the selected IBA samples were identified by XRD and the quantity in weight percent were determined by Rietveld method. The minerals that

may be present in IBA were first identified based on other mineralogical studies done using XRD (Speiser et al., 2000; Bayuseno and Schmahl, 2010; Santos et al., 2013). The minerals were then analysed by adding the minerals one at a time to the Rietveld refinement analysis. Most of the minerals that were quantifiable by the Rietveld method were Ca- and Si- minerals. Compared to other studies (Speiser et al., 2000; Bayuseno and Schmahl, 2010; Santos et al., 2013), the quantity (in wt%) of the minerals in this study were much higher. For example, around 28 wt% of calcite was found for S0-2 sample (Table 7-1) while Santos et al. (2013) only reported 3.5 wt% of calcite in their F sample. Both S0-2 sample in this study and F sample from Santos et al. (2013) study consisted of industrial wastes. The huge difference was due to the high percentage of amorphous material that was included in the analysis done by Santos et al. (2013), which this study has excluded. However, in terms of relative quantity, this study found that the major minerals were calcite, anhydrite and quartz, which were similar to other studies.

The goodness of fit (GOF) describes how well the Rietveld refinement was. It is the ratio between R_{wp} and R_{exp}. A good refinement gives GOF values lower than 2 but it cannot be lower than 1. This study was only able to obtain GOF values of ~4 due to the lack of limitless access to ICDD files for complete matching of peaks. The fitness of the Rietveld calculation can be viewed graphically, as shown in Figure 7-1, which shows the XRD spectrum of untreated T0-2 sample. The blue and red spectra at the top are the experimental data and Rietveld calculated data respectively. The red spectrum shows how well the minerals are matching the experimental data. The grey spectrum in the middle shows the difference between the experimental data and Rietveld calculated data. The grey spectrum should be as flat as possible, if the calculated data fits the experimental data well. The markers at the bottom are the XRD fingerprint of the minerals shown at the top right. As can be seen from Figure 7-1 and GOF values (i.e. ~4), the Rietveld calculated data did not fit the experimental data well as certain peaks were not identified here. If there were limitless access to ICDD files, more minerals (usually the less common ones) can be identified and matched to the remaining peaks in a trial and error process. This will improve the GOF value. However, by adding more minerals, the calculated

quantity of the initially identified minerals will decrease accordingly, as the sum of the weight percentage of all the minerals is fixed at 100%. Hence, under the constraint faced for this study (i.e. the minerals present in IBA were not completely identified), this study selected most of the major and common minerals (i.e. fix the number of minerals at 12) and applied them consistently to the IBA samples so that the trend in the quantification of minerals among the different IBA samples can be compared to another. Table 7-2 only shows 10 minerals as hydroxylapatite and gibbsite were not detectable in TSIP samples and hence, not displayed in the table.

The mineralogical compositions of 0-2 mm size fraction from different incineration plants were found to be different as some minerals were found to be undetectable (Table 7-1). Diopside and ettringite were undetectable in S0-2 sample while hydroxylapatite and gibbsite were undetectable in T0-2 sample. Anhydrite was observed to be present in higher quantity in untreated S0-2 than untreated T0-2. It is possible that anhydrite was involved in the carbonation reaction, together with portlandite as suggested by Rendek et al. (2006). Carbonation of anhydrite takes place at a lower log K (25°C) than portlandite (Bodénan et al., 2000) (Equation 7-1 and 7-2). This could explain the lower optimum carbonation temperature for SWTEP (i.e. 35°C) compared to TSIP (i.e. 50°C).

Portlandite: $Ca(OH)_{2(s)} + CO_{2(aq)} \Leftrightarrow CaCO_3 + H_2O$ $\log K = 14.20$ (Eq. 7-1)

Anhydrite: $CaSO_4 + CO_3^{2-} \Leftrightarrow CaCO_3 + SO_4^{2-}$ $\log K = 4.17$ (Eq. 7-2)

The XRD analysis was also carried out for the different size fractions of untreated samples to determine the difference in mineralogical compositions (Table 7-1). The results show that calcite, anhydrite and magnesium calcite content decreased as the size fractions of TSIP samples increased. In contrast, quartz, gehlenite and diopside content, which contain silicates, increased as the size increased. This observation is consistent with the visual characterisation done by Chimenos et al. (1999), whereby glass was found mostly in the coarse size fraction. Portlandite was observed to be concentrated in the 0-2 mm size fraction of TSIP samples.

Table 7-2 compares the mineralogical composition of TSIP samples after carbonation. Comparing the values in Table 7-1 and 7-2, calcite shows increase in quantity after carbonation while both anhydrite and portlandite decrease in quantity. Although ettringite was known to dissolve after carbonation (Meima and Comans 1997b), the calculated quantity did not show significant decrease after carbonation. Figure 7-2 shows the XRD spectra of the different size fractions of TSIP samples after carbonation. The intensity of the peaks provides a qualitative observation of the decreasing calcite as the size fraction increases.

Table 7 mineralogical composition of the different sources and size fractions of untreated IB/ ined by quantita ıg Rietveld method.

Minera	cal formula	S0-2	T0-2	T2-4	T4-20	
Calcite		28.02	23.22	17.21	9.86	
Anhydı		43.70	30.88	13.77	9.50	
Magne:	$Mg_{0.03}CO_3$	1.70	4.32	2.42	2.06	
Portlan	$)_2$	2.34	2.43	0.69	0.33	
Gehlen	SiO_7	5.47	4.47	10.91	18.81	
Diopsi	$Si_2O_6)$	N.D.	4.18	9.86	11.57	
Hydro›	$)_4)_3(OH)$	2.53	N.D.	N.D.	N.D.	
Quartz		9.28	20.07	25.93	25.12	
Hemati		1.52	5.72	9.16	4.73	
Magne		1.58	4.26	9.43	17.14	
Gibbsi	$)_3$	3.85	N.D.	N.D.	N.D.	
Ettring	$(SO_4)_3(OH)_{12}.26H_2O$	N.D.	0.45	0.61	0.89	
GOF		4.69	5.00	4.70	3.94	
R_{exp}		14.11	13.85	14.82	17.76	
R_{wp}		66.16	69.20	69.65	69.90	

N.D.: n

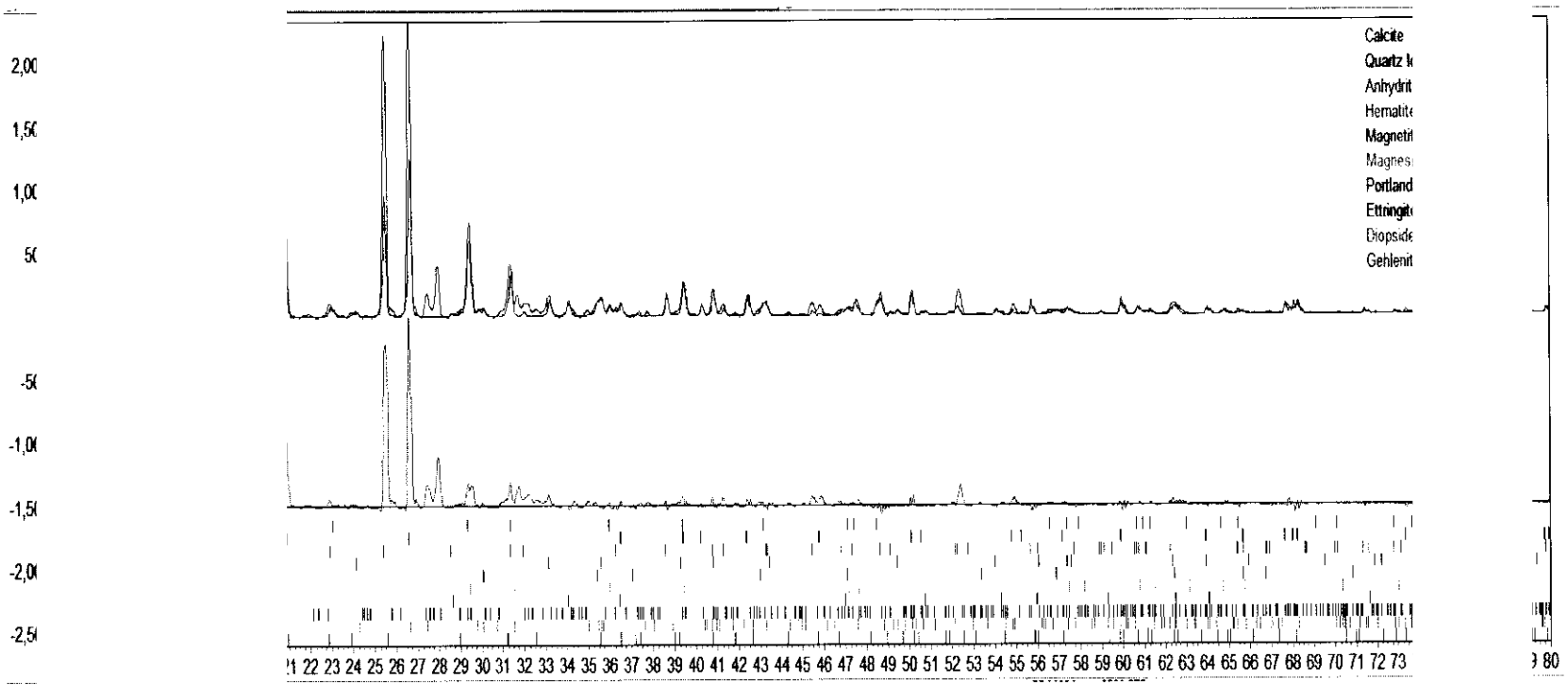
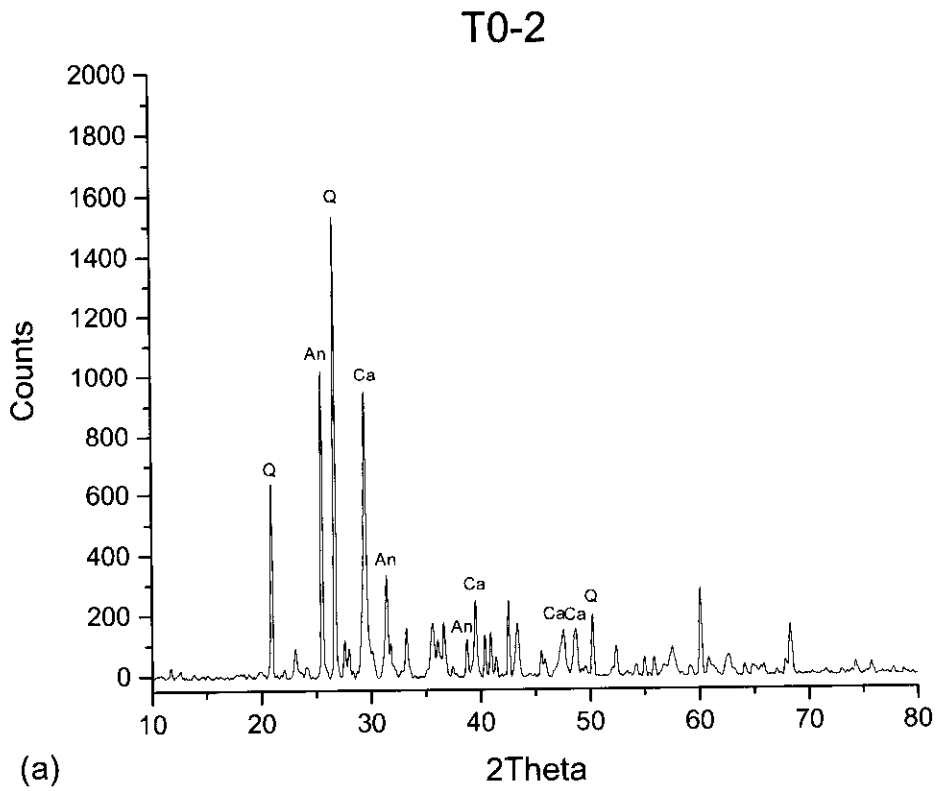


Figure 7-1: XRD spectrum of untreated T0-2 sample.

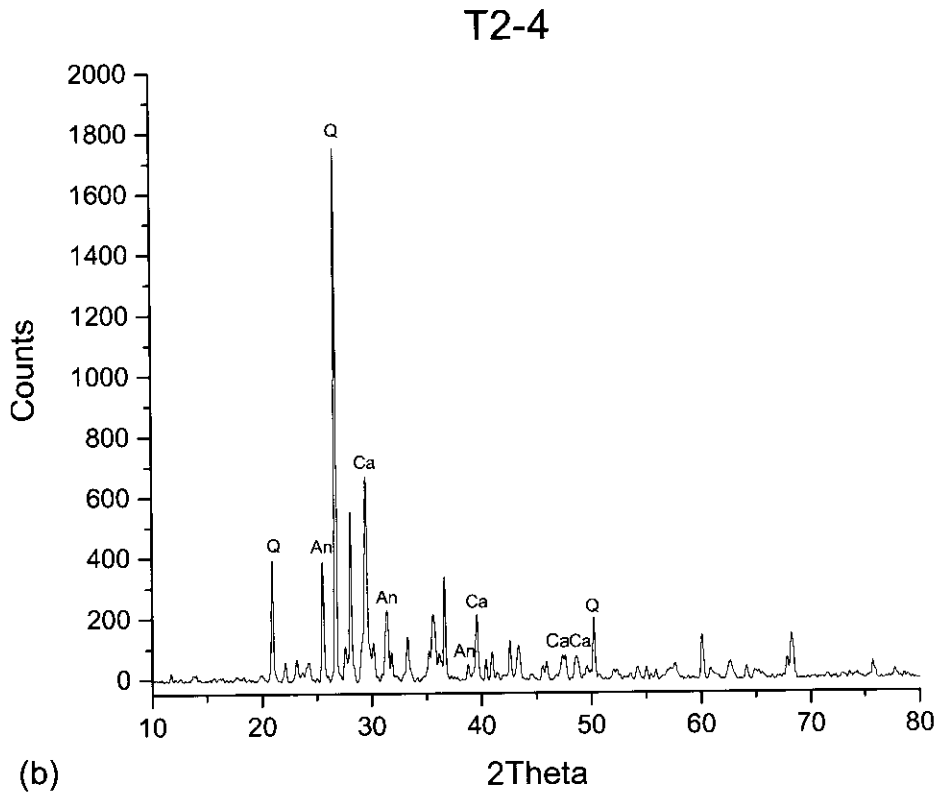
Table 7- ineralogical composition (wt%) after accelerated carbonation at 35°C, 15% moisture conter C, 15% moistur t size fractions, using XRD.

Mineral	la	T0-2		T2-4		T4-20			C15MC
		35C15MC	50C15MC	35C15MC	50C15MC	35C15MC	50C15MC	35C15	
Calcite		40.23	40.16	28.13	30.79	27.53	29.15	16.9	14.57
Anhydri		23.80	21.57	10.79	11.67	4.14	5.42	1.1	1.09
Magnes calcite		1.98	3.44	1.73	0.23	0.44	N.D.	N.I	0.22
Portlanc		0.93	0.41	0.16	0.09	N.D.	N.D.	N.I	N.D.
Gehleni		5.85	7.04	8.23	10.27	15.89	15.23	17.	17.19
Diopsid		1.95	3.17	6.52	8.39	10.99	11.61	20.	22.08
Ettringi	$H)_{12}.26H_2O$	N.D.	N.D.	0.48	0.61	0.38	0.46	0.3	1.28
Quartz		15.63	13.90	29.55	22.36	24.90	21.63	26.	26.81
Hematit		5.49	5.38	7.58	8.98	3.78	3.50	2.5	1.91
Magnet		4.13	4.91	6.82	6.60	11.95	12.99	14.	14.85
GOF		4.33	4.22	4.76	4.22	4.10	3.97	4.8	4.46
R_{exp}		14.21	14.48	14.41	15.49	16.56	16.55	15.	16.07
R_{wp}		61.60	61.05	68.63	65.40	67.85	65.70	73.	71.75

N.D.: n



(a)



(b)

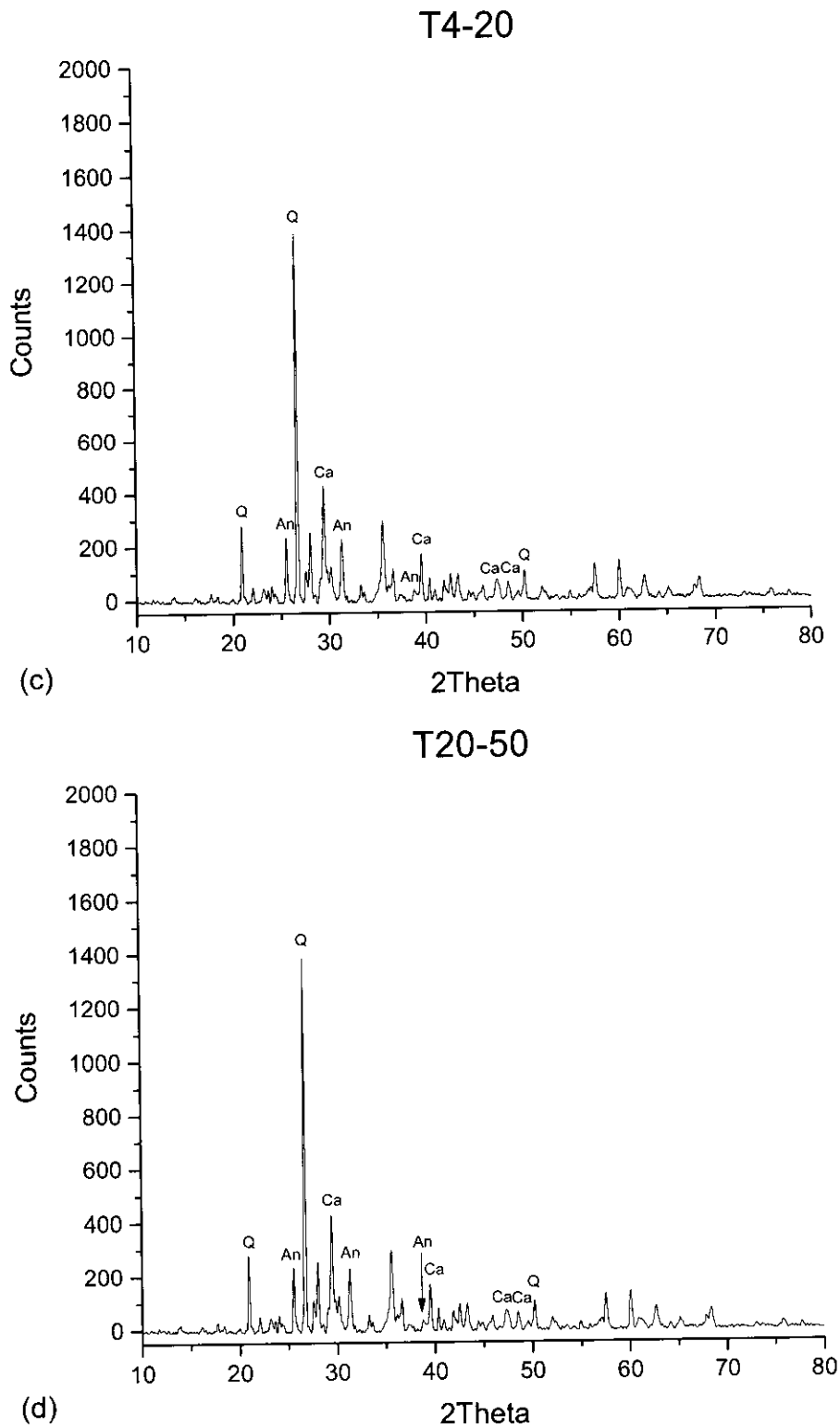


Figure 7-2: XRD spectra of carbonated TSIP samples at 50°C and 15% moisture content for (a) T0-2, (b) T2-4, (c) T4-20 and (d) T20-50. [Ca = calcite, Q = quartz, An = anhydrite]

7.4 Conclusion

XRD analysis was carried out to determine the mineralogical composition of IBA and the Rietveld refinement method was used to quantify the weight percentage of the minerals identified. The GOF was found to be ~4, which is considered unsatisfactory, as certain peaks were not identified due to the limited access to ICDD files. However, this study was able to identify the major minerals and apply them in the Rietveld calculation in a consistent manner. This enables the quantified minerals to be compared among the different source of IBA and size fractions.

The mineralogical compositions of IBA from two incineration plants were compared between untreated S0-2 and T0-2 samples. Diopside and ettringite were undetectable in S0-2 sample while hydroxylapatite and gibbsite were undetectable in T0-2 sample. Anhydrite was observed to be present in higher quantity in untreated S0-2 than T0-2, which could be the reason for the different optimum carbonation temperatures. Among the untreated four size fractions of TSIP samples, calcite, anhydrite and magnesium calcite content decreased as the size increased. In contrast, quartz, gehlenite and diopside content, which contain silicates, increased as the size increased. After carbonation, calcite shows increase in quantity while both anhydrite and portlandite decrease in quantity. Ettringite did not show significant decrease after carbonation in this study, in contrast to those reported in literature.

CHAPTER 8: CONCLUSION AND RECOMMENDATION

8.1 Conclusion

The motivation behind this research is to increase the potential of utilising IBA by offering a treatment method that is sustainable and economically viable. This research explores using accelerated carbonation as a treatment method for IBA in Singapore as it has been overlooked up till now. The approach to this research was firstly, to characterise the IBA in Singapore and compare it with the IBA from other countries through literature review. The accelerated carbonation experiment was then carried out in two parts. In the first part, the influence of moisture content and temperature on accelerated carbonation was investigated using the 0-2 mm size fraction of IBA. The optimum operating conditions found in the first part was then applied to other size fractions (i.e. 2-4 mm, 4-20 mm and 20-50 mm) in the second part of the experiment. By sieving the IBA into different size fractions before accelerated carbonation, the different chemical compositions of the different size fractions can provide an insight into the carbonation mechanism of the accelerated carbonation process. In terms of utilisation, sieving is a simple and inexpensive method to separate IBA into the size fractions as required in different construction applications. Lastly, XRD was used to analyse the mineralogical composition of IBA.

This research has shown through the characterisation of IBA collected over a 6 months period that the total element contents of IBA from both incineration plants in Singapore are similar to those in other countries reported in literature. However, elements like Cd, Co, Hg, Pb and Se exhibited high variation over the investigated sampling period. Pb showed similar high variation in leaching test.

For the accelerated carbonation experiments, a sample was randomly selected from the 6 months' collection of each incineration plant. The results of the accelerated carbonation experiments are summarised as below:

- The actual moisture content was found to change during carbonation, which affected the initial rate of carbonation. The rate of moisture loss and gain was dependent on the carbonation temperature.
- The optimum operating conditions for 0-2 mm size fraction (ground to <425 μm) at 20% CO_2, was 35°C and 15% moisture content for SWTEP sample; and was 50°C and 15% moisture content for TSIP sample. The carbonation duration was 2 hours.
- Under the optimum operating conditions, pH decreased around 2.5 units for both incineration plants after 2 hours of carbonation.
- Pb, Zn and Cu showed significant reduction in leaching after carbonation. Cr leaching initially increased but eventually decreased after 1 week of carbonation. Mo and Sb leaching increased after carbonation. Cl^- leaching was not significantly affected by carbonation, but SO_4^{2-} leaching increased significantly after carbonation.
- The leaching mechanisms of these elements were affected by different factors. For Pb, Zn, Cr, Mo and Sb, pH was the dominant factor. After 2 hours of carbonation at the optimum operating conditions, the pH of S0-2 sample reduced to 9.9 while T0-2 sample reduced to 9.7. For Pb and Zn, this pH coincides with their minimum solubility. However for Mo and Sb, this pH coincides with an increase in solubility. The minimum solubility of Cr occurs at around pH 7, which was not reached even after 1 week of carbonation (pH of S0-2 sample was 9.0 and pH of TSIP sample was 9.5), although Cr leaching showed reduction after 1 week of carbonation.
- For Cu leaching, the contributing factors are degree of carbonation and DOC. For S0-2 sample, degree of carbonation and DOC seems to affect Cu leaching equally. However, for T0-2 sample, the contribution from degree of carbonation seems to be higher than that of DOC. pH did not play a significant role in reducing Cu leaching from carbonated samples.
- The degree of carbonation seems to play a significant role in the leaching of SO_4^{2-} for S0-2 sample but not for T0-2 sample.
- After sieving, for the untreated samples, most of the elements showed decrease in leaching as the size increased.

- The leaching mechanism among the different size fractions was found to be similar, except for Mo which showed reduction in leaching for TSIP samples. The difference in mineralogical composition between the two sources of IBA seems to play a role in terms of the amount of leaching after carbonation for Mo only.
- Otherwise, the mineralogical composition should be quite similar among the different size fractions due to the similar pH dependency leaching observed among the different size fractions.
- XRD analysis showed slight difference between the mineralogical composition of S0-2 and T0-2 samples, which could explain the different optimum carbonation temperatures.

This research has shown that accelerated carbonation of IBA was able to reduce the leaching of certain elements only (i.e. Pb, Zn, Cu and Cr). However, Mo and Sb leaching increased after carbonation. Accelerated carbonation was also found to be ineffective in reducing the leaching of soluble salts. This is one of the limitations of this treatment process due to the different leaching mechanisms of the elements, as discussed in this research. However, accelerated carbonation shows great potential as a treatment for IBA as the leaching concentrations of Pb, Zn, Cu and Cr, which were much higher compared to Mo and Sb before treatment, were reduced significantly after carbonation. This is important as Pb was observed to exhibit high variation in the leaching test of untreated IBA during the 6 months characterisation. For Cr, longer carbonation duration (such as 1 week) may have to be used for 0-2 mm size fractions, in order to reduce Cr leaching significantly. However, 2 hours of carbonation is sufficient for other size fractions. Other elements that increased in leaching after carbonation would have to be treated by other methods, such as washing.

In conclusion, the objective of understanding the physicochemical mechanism of accelerated carbonation and its influences on the leaching behaviour of IBA has been achieved in this research, thereby providing an alternative treatment process to enhance the utilisation potential of IBA in Singapore.

8.2 Recommendation

This research has shown that accelerated carbonation has the potential to treat IBA within a short time frame. However, the research carried out here was focused on understanding the carbonation and leaching mechanism, hence the different size fractions were ground to <425 μm. This is to minimise the effect of different surface area of each size fraction on accelerated carbonation. However, grinding IBA into fine powder would not be practical in real application. Therefore, in continuation to this research, it is proposed that investigation on the leaching behaviour of the different size fractions of untreated IBA be carried without grinding or with minimal size reduction to the particle size required in a specific application. Size reduction of IBA increases the surface area in contact with the leachant, which may increase the leachability of some elements. As this research has shown, most of the elements showed decrease in leaching for the untreated IBA as the size increases. The carbonation duration for the coarser size fractions may be further reduced, if the leaching of untreated IBA without size reduction is lower than that with grinding.

There are other leaching mechanisms of IBA, like sorption on neoformed minerals after carbonation, which were cited from literature and discussed here, but not verified experimentally. These are important research areas that can be explored further.

Another possible future study is to carry out the accelerated carbonation in a continuous gas flow column system, instead of the current enclosed batch system. Factors such as the gas flow rate and packing density would have to be investigated, on top of the knowledge gained from this research.

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