University of Miyazaki

Doctoral Dissertation

Long-term Leaching Behavior and Geochemical Modeling of Cement Solidified Industrial Waste Incineration Fly Ash

セメント固化産業廃棄物焼却飛灰の長期浸出挙動と地球化学モデリング

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1. Introduction

1.1 Background and Significance

Currently, the increase in population, economic expansion, rapid urbanization, and variation in consumer habits have increased the amount of waste generated worldwide. It is estimated by 2025 and 2050, the global urban solid waste production will reach 2.2 billion tons and 4.2 billion tons, respectively (Cudjoe & Acquah, 2021). Countries worldwide face the challenge of creating environmentally sustainable methods to manage the increasingly complex problem of waste generation. Due to its capacity to significantly reduce the volume, mass, and harmfulness of municipal solid waste (MSW) and industrial solid waste, incineration has become the most common method of treatment in most developed countries. In 2020, 27 European Union countries, treated more than 27% of MSW by incineration (Chen et al., 2023). In the same year, China incinerated around 62% (146 million tons). In other countries such as Denmark and Japan, more than 65% of the MSW generated is treated by incineration. In Japan, about 4 million tons of incineration ashes are generated every year (National Institute for Environmental Studies, 2022). In Europe, around 18.75 million tons of bottom ash and 2.25 million tons of fly ash are generated (Bruno et al., 2021). (National Institute for Environmental Studies, 2022). In addition, incineration of waste including biomass and other industrial waste for energy recovery has become popular because it can replace an equivalent amount of energy generated from fossil fuels and result in greenhouse gas emission savings (Papageorgiou et al., 2009). Furthermore, in the incineration process, different residues are produced, including slags, bottom ash, and different types of air pollution control (APC) residues such as boiler fly ashes. The incinerated residues often contain heavy metals (e.g.; Pb, Zn, Ni, Cd) and organic dangerous substances. For this reason, the incinerated residues are usually treated as hazardous materials and landfilled (Fabricius et al., 2020).

The composition of municipal and industrial solid waste incineration ashes is extremely diverse. It is quite difficult to predict possible contaminants in these complex materials when they are disposed of in landfills or recycling applications. Through the degradation of landfilled waste and infiltration processes, waste incineration ashes threaten to contaminate groundwater and soil, and this causes expressive societal concern. Typically, leachate in landfill sites in developed countries is collected and treated with leachate treatment facilities and discharged into the environment. However, to reduce the risk of leakage of contaminants from landfill sites, several technical applications are applied before disposal have been developed such as washing, cement solidification/stabilization, chelator stabilization, natural weathering, etc. (Du et al., 2018, 2019; Li et al., 2018). Even though these techniques help in the reduction of contaminant release in landfills and reduce the burden of operation of leachate treatment facilities, further studies on alternatives regarding disposal are still necessary. Contrarily to developed countries with advanced waste management and sanitary landfills, in developed countries of Latin America, Asia, and Africa open dumps and non-engineered landfills are common and have a direct impact on public and environmental health (Vaccari et al., 2019). Open dumps and poorly managed landfills pose a risk to health and safety. The risks posed by the leachate, are amplified by the lack of leachate containment systems in many developing countries, leading to high concentrations of organic and inorganic pollutants in the surface and groundwater resulting in both environmental and health hazards (Vaccari et al., 2019). Specifically, leaching heavy metals such as lead reduce the groundwater quality and is toxic to several organisms (Limoli et al., 2019).

In recent years due to the environmental concern and limited landfill space, there is an increasing global interest in the utilization of recycled materials produced from waste incineration ashes in the construction and rehabilitation of the

infrastructure sectors. Studies have focused on the potential of recycling incineration ashes as a replacement for natural aggregates in civil engineering applications such as road construction (Ahmaruzzaman, 2010; Almahayni & Vanhoudt, 2018; Choi et al., 2020; Hjelmar et al., 2007; Zhang et al., 2016). In European countries such as the Netherlands and Denmark, 80% and 90% respectively of municipal incineration bottom ash is reused, predominantly as embankment fill and in pavements (Lynn et al., 2017). Dabo et.al., (2009) evaluated the chemical evolution of leachate and municipal solid waste incineration bottom ash used in a test road site and found that heavy metals leachability drops after the first 2 years. In addition, Izquierdo, et. al., (2008) showed that trace pollutants such as Pb, Zn, or Cd were highly immobile in bottom ash when comparing field test sites and laboratory leaching tests when used as road material. Although considering the strict environmental regulations in the United States, in 2022 projects have been approved to build test roads using ash from Waste-to-Energy facilities (Postbulletin, 2022). The major concern related to the application of incineration ashes in the natural environment is the potential release of contaminants such as high concentrations of soluble salts and heavy metals when the incineration ashes are in contact with water. In that sense, due to the growing concern from society regarding the long-term safety of recycling and utilizing incineration ashes in the natural environment, the demand for research and studies is high at an international level.

Especially, there are very few studies on the long-term evaluation of recycled incineration ash produced from various industrial wastes including waste tires (Dahim et al., 2021; James et al., 2012; Zhou et al., 2020) compared to that of MSW incineration ash and coal ash. In the case of waste tires, there is an alarming concern since as much as 80% of all rubber waste produced in the world comes in the form of used tires and it is estimated that the amount of end-of-life tires is around one billion units per year (Wiśniewska et al., 2022). In addition, due to their physical and chemical characteristics, environmental hazards caused by improper management of waste tires include potential fire hazards and mosquito-derived diseases (Tsai et al., 2017). Consequently, in recent years waste tire incineration has become an attractive fuel for many industries such as cogeneration plants, cement kilns, and paper mills (Feraldi et al., 2013; Pan et al., 2021; Pipilikaki et al., 2005). Utilizing waste tires and other industrial waste as incineration material to produce energy, reduces the scrap tires deposited in landfills, making it a sustainable practice in the long term (Feraldi et al., 2013; Pan et al., 2021; Pipilikaki et al., 2005). However, it has been found that waste tire incineration fly ashes were more enriched with Zn and Cu compared to that other types of incinerated ashes, and very little information was found on the leaching behavior of the heavy metals from the ash (Banar et al., 2015; Hower & Robertson, 2004; Raudonytė-Svirbutavičienė et al., 2022). To recycle the ash in the environment safely, it is important to investigate the behavior of heavy metals from the recycled material using ash-containing waste tires. In Japan, it was recorded that in 2019 around 60% of waste tires are treated by thermal incineration in several different industries such as paper mills and cement factories (JATMA, 2023). For example, Oji Paper CO. Nichinan plant in Miyazaki Prefecture has contributed to the thermal recycling of waste tires from other prefectures in southern Japan (Japan Times, 2007). Although the incineration of waste tires provides a fuel alternative, the presence of heavy metals in waste tires is a concern when treating the ashes after incineration. Furthermore, there is very limited information regarding the characterization of ashes from waste tire incineration. In that sense, it is fundamental to research and characterize waste tire incineration ashes and their leaching behaviors.

Primarily, to understand the leaching dynamics of incineration ashes, the characterization of the physical and chemical properties through various leaching experiments and content analysis is necessary (Dijkstra et al., 2006; Lager et al., 2006;

Luo et al., 2019; Yin et al., 2018). These results are used as a guide to characterize the hazardous level of the incineration ashes for disposal or recycling. On the other hand, to characterize the long-term leaching of incineration ashes, standardized column leaching tests have been applied, but they are costly and time-consuming. In addition, the successful prediction of the amount of leachate and its composition is a highly complex task gaining popularity in the field of waste management and environmental systems. Various numerical models to simulate processes governing leachate occurrence and behavior in landfill and recycle applications have been developed and applied to further understand and predict the evolution of incineration ashes in the natural environment (Fellner et al., 2009; Fellner & Brunner, 2010; Hyks et al., 2009). Recently developed models focus on not only the simulation of leachate quantity but also on estimating leachate quality to control its associated environmental impacts, particularly on groundwater pollution, which guides the design of leachate control, recirculation, and collection systems (Abunama et al., 2019; Almahayni & Vanhoudt, 2018; El-Fadel et al., 1997; Gómez-Puentes et al., 2014; Mukherjee et al., 2015; Yildiz et al., 2004). Understanding leachate formation mechanisms, quantity, quality, and perhaps most importantly, its migration characteristics in relationship to the spatial and temporal variations during landfill operations, closure, and in recycling applications, requires a multidisciplinary approach to confront this problem (El-Fadel et al., 1997).

1.2 Research Objectives

This study investigates the leaching behavior of boiler fly ash and cement-solidified recycled material produced from fly ash, with a focus on their mineral characteristics and pH control. The goal of this research is to provide crucial information that can contribute to the better management and systematization of cement solidification ash recycling. By understanding the minerals that influence pH in incinerated cement-solidified waste tire incineration fly ashes, we can optimize the recycling process and promote sustainable practices in waste management. Additionally, this study aims to validate leaching prediction models, which are essential for assessing the long-term environmental impacts associated with the use of cement-solidified ashes as a road-bed recycled material. This research has broader implications for society, as it helps advance our knowledge of effective strategies for utilizing waste materials, reducing reliance on natural resources, and minimizing environmental harm. Furthermore, by analyzing the performance of cement-solidified materials as road-based aggregate materials, we can evaluate their suitability for infrastructure projects, promoting sustainability in construction practices. Overall, this study addresses important environmental concerns, contributes to the development of recycling practices, and supports the transition toward a more sustainable and resource-efficient society.

1.3 Structure of the study

The outline of this study is presented in Figure 1.1. In Chapter 1, the background of this study was discussed. This chapter shows the significance of this study and the objectives of this study. The significance of ash recycling and especially the necessity of long-term predictions of leachate quality from SFA is also discussed. Chapter 2 is a critical review of the literature concerning waste incineration ashes and geochemical modeling applications with waste disposal and recycling. The literature review attempts to provide an assessment of the current state of knowledge in this field, supported by a comprehensive list of modeling methodologies relevant to various types of waste incineration ashes including municipal residue and industrial. Chapter 3 describes the mineral and chemical characteristics of BFA and SFA by various batch leaching tests and mineral analysis. In this chapter, heavy metals such as lead, and zinc were contained in BFA and SFA

and the significance of the stabilization of these metals was discussed. A column leaching test was conducted on fresh SFA samples in Chapter 4. By analyzing the long-term evolution of pH and major component release in saturated conditions it was concluded that the mineral and chemical composition of the SFA material contributes to maintaining an alkaline environment. The alkalinity of the material prevents any major release of heavy metals even after 100 years of leaching. The results of the column leaching tests are simulated in Chapter 5. Using the geochemical model HYDRUS-1D and its HP1 component, an adequate fit between modeled and measured data was obtained for pH and major components. Finally, the conclusions regarding the characteristics and modeling of the SFA material are presented in Chapter 6.

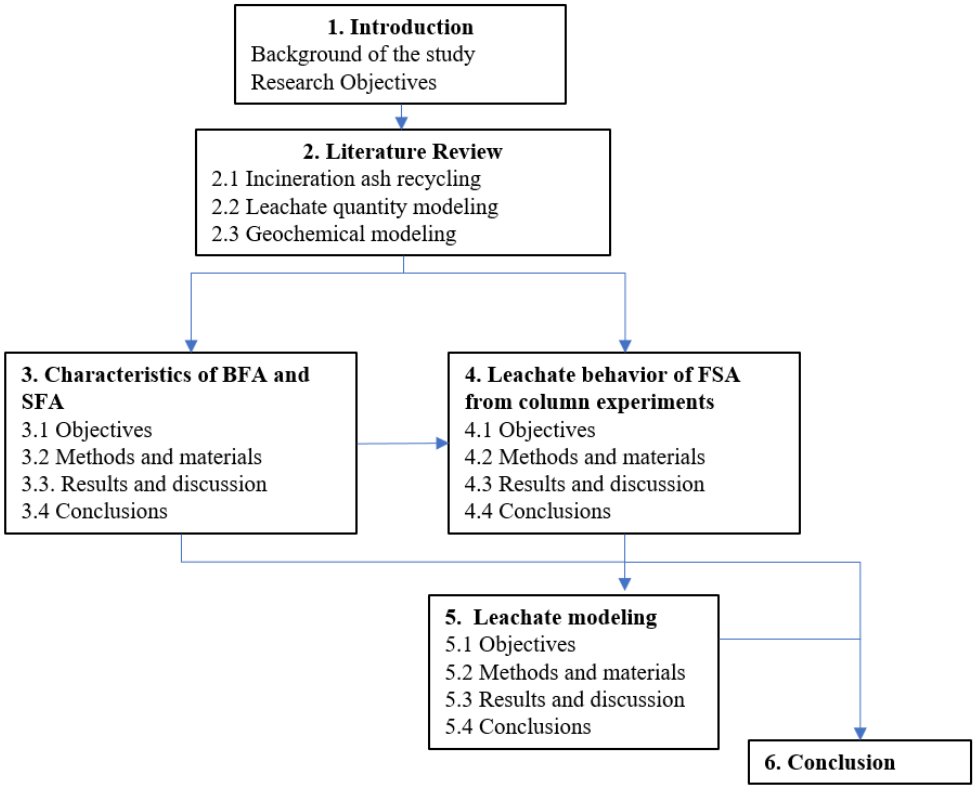

Figure 1.1. Outline of the study

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2. Literature review

2.1 Incineration ash recycling

Over the past decades, extensive studies on waste incineration ashes have been performed to develop more effective recycling technologies and waste management. However, still large amounts of incineration bottom and fly ashes from waste incineration facilities and energy recovery facilities are disposed of in landfill across the world. For example, in Japan, approximately only 30% of municipal solid waste incineration ash (MSW ash) has been recycled as civil engineering materials, a source of cement, and a source of metal recovery (Sakanakura, 2018). On the other hand, the recycling of incineration ashes in the civil engineering sector as a replacement for raw materials is one of the most promising options because of the potential for its large consumption. Table 2.1 shows study examples of waste incineration ash recycling and elution of substances from the recycled material. In general, bottom and fly ashes from municipal solid waste incineration show great potential in the utilization as road base aggregate materials. Furthermore, due to the composition of ashes, the mineral contents are suitable for incorporation as roadbed material.

Although heavy metal content is a concern, various studies have shown that the leaching potential from these types of materials is low in the short term. However, further studies are still necessary to determine the safety of the material in the long term.

Typically, the waste incineration ashes contain leachable hazardous heavy metals such as Pb, Cd, Zn, and Hg. Therefore, various technologies have been developed to control the release of hazardous heavy metals. Cement solidification/ stabilization is a common method to reduce the mobility of heavy metals for MSW incineration ashes, specifically, MSW fly ashes. Due to its fine powder characteristics and pozzolanic reactions of MSW fly ashes, taking advantage of the cement hydration reaction to produce a high-strength solidified body for physical encapsulation and chemical stability of heavy metals (Du et al., 2018; Tang et al., 2016). Du et.al., (2019a) have extensively studied cement-solidified MSW incineration fly ash and focused on the long-term characterization of the material. Various treatments, including chelate agent solidification, vitrification, and washing, are employed to effectively minimize the presence of soluble salts and the leachability of heavy metals. Research studies have demonstrated the successful reduction of heavy metal leaching through the vitrification process, which transforms bottom and fly ashes from waste incineration into solid, crystallized residues (Wong et al., 2021; Z. Zhang et al., 2016). Similarly, the utilization of chemical chelate solidification has been proven to enhance the stability of heavy metals in MSW fly ashes (Du et al., 2019a, p. 201; Li et al., 2019). Additionally, washing has proven to be an effective technique, facilitating the removal of significant amounts of soluble salts such as Cl, Na, K, and Ca from fly ashes generated by MSW incineration (Bogush et al., 2019; Yan et al., 2022).

As the above discussion, the popularity of using waste incineration ashes has been slowly increasing currently in the world. However, few researchers have made efforts to describe the long-term evolution of incineration ashes used in road base applications. For example, Dabo et al., (2009), analyzed a ten-year chemical evolution of leachate and MSW incineration bottom ash used in a test road site. Results of the study suggest that the leachate pH and concentration in major elements such as Ca, Na, and Cl as well as in Al and heavy metals (Cu, Pb, Zn) quickly drops during the first two years and reach a set of minimum values over 10 years. Furthermore, Hjelmar et al., (2007) compared eluates from laboratory leaching tests and observations of the leachate from a road construction test site using MSW incineration bottom ash as a sub-base

material as a function of L/S and concluded a fairly good agreement for salts (Cl and SO_4) but less agreement for some trace elements. As shown by the mentioned studies, there is a concern regarding the mobility of heavy metals in the long term when utilizing MSW incinerated ashes.

Even though extensive research has focused mainly on MSW incineration ash recycling, there is still a large research gap on various industrial wastes such as tire waste, woody biomass, sewage sludges, and oil incineration (Dahim et al., 2021; James et al., 2012; Ramachandran et al., 2017; Zhou et al., 2020). In the case of tire waste, there is an alarming concern since as much as 80% of all rubber waste produced in the world comes in the form of used tires and it is estimated that the amount of end-of-life tires is around one billion units per year (Wiśniewska et al., 2022). The moisture content of tires is relatively low compared to alternative energy such as MSW or biomass, which makes it an attractive fuel for many industries. Utilizing waste tires to produce electricity also reduces the scrap tires deposited in landfills (Pan et al., 2021). Some studies have shown great potential in the production of energy through industrial waste incineration such as woody biomass. Currently, power generation using biomass, which is a renewable energy source, is attracting significant attention. As such, the exploitation of biomass is being considered worldwide as an avenue for the reduction of environmental emissions (Lee et al., 2021). On the other hand, biomass ash research related to its utilization is not widely reported. However, several research efforts are underway for applications such as adsorbent, raw material for ceramics, cement, concrete additive, material recovery, etc. based on its characteristics (Ahmaruzzaman, 2010). In addition, characteristics of ashes from biomass and industrial waste incineration are varied significantly depending on facilities because compositions of the biomass and industrial waste incinerated are widely varied. Consequently, individual investigation to propose suitable treatment of ash from biomass and industrial waste is required.

2.2 Leachate quantity modeling

In the field of waste management, leachate modeling simulates the movement and transport of contaminants through the environment, typically in water, soil, and through waste material. The prediction of leachate amounts is elementary in sustainable waste management and leachate treatment processes, before discharging to the surrounding environment (Abunama et al., 2019). The prediction is largely based on various factors such as waste composition, hydraulic characteristics of waste, meteorological data, etc. (Abunama et al., 2019; Yildiz et al., 2004). Extensive research has been conducted in the modeling of leachate quantity from landfill sites of MSW waste and MSW incineration ash by applying mechanistic and stochastic models (Mukherjee et al., 2015). The use of models has gained further development attributed to understanding the leaching of solutes in a landfill and incineration ash recycling applications (Almahayni & Vanhoudt, 2018; Cetin et al., 2012; Fellner & Brunner, 2010; Hyks et al., 2009). On the other hand, further research is required before the validation of these models can lead to a reliable simulation of leachate composition. Examples of studies focusing on the modeling and prediction of leachate quality from landfill sites are shown in Table 2.2. Although there is extensive research on studies modeling the leachate of various porous media such as landfill materials and soils, far less work has been performed on the modeling of cement solidified and stabilized wastes. Consequently, the studies are limited only to cement solidified MSW incineration bottom and fly ashes, and studies focusing on cement stabilized biomass and waste tire incineration ashes are almost nonexistent.

In landfill simulation scenarios, researchers have focused on quantifying the water infiltrating and discharge coming out as leachate using meteorological data that accounts for the precipitation and evapotranspiration for water mass balance calculations (Fellner & Brunner, 2010; Gómez-Puentes et al., 2014; Hartmann et al., 2004). Johnson et al., (2001) simulated the discharge of drainage from MSW incineration bottom ash landfill using various modeling approaches by HYDRUS5 and MACRO (version 4.0). In his study, the models showed the possibility of the model to predict the quantity of leachate by considering preferential flow and inverse modeling. Hartmann et al. (2004) also validated the MACRO model through different scenarios to describe water transport in a landfill with MSW incineration bottom ash. This research shows that it was possible to achieve a reasonable correspondence between measured and calculated leachate flow through a series of calibrations using physically reasonable parameter values, using the hydraulic structure of the landfill including total porosity, the ratio of macropore to micropore porosity, saturated and micropore hydraulic conductivity and meteorological data. Furthermore, a review study by El-Fadel (1997) states that the predominant approach for modeling the water flow process in solid waste media assumes a homogenous porous media. However, generally, water flows through waste incineration ashes and cement-solidified wastes are not uniform.

2.3 Geochemical modeling

Geochemical modeling has been developed in the field of soil contamination and solute movement in agriculture fields and other porous mediums. Table 2.2 shows the summary of studies on the prediction of leachate quality from various waste incineration ashes including municipal and industrial incineration residues. Jalali et.al. (2022), was able to simulate potassium and phosphorous in leaching from agricultural soils by different rates of fertilizer application utilizing the geochemical model PHREEQC. Blackmore et.al. (2018) evaluated the release of Bromide and Chloride tracers from heterogeneous waste-rock piles. Through solute transfer parameter calibration and different porosity, models obtained comparable fitting breakthrough curves between measured and modeled results. Another application of geochemical modeling is the ability to model mineral speciation. Tahervand and Jalali (2016) used the software MINTEQ (version 2.30) to estimate the speciation and saturation index (SI) of Cd, Ni, and Fe in solution phases of calcareous soils.

Geochemical modeling also plays an important function in modeling solute movement from waste (Araujo et al., 2020). For example, geochemical modeling can simulate the chemical reactions that occur in landfills and environments, including the dissolution, precipitation, and complexation of minerals and other substances found in waste incineration ashes (Hyks et al., 2007; Jankowski et al., 2006; Meima & Comans, 1997). Waste incineration ashes have been considered mineral assemblages, similar to rocks and soils, which allows using of geochemical knowledge to characterize incineration wastes (Meima & Comans, 1997). Recent research shows that dissolution/precipitation reactions control the leaching of major elements from MSW bottom and fly ashes, and coal fly ashes (Dijkstra et al., 2008; Hareeparsad et al., 2011; Meima & Comans, 1997). Although geochemical models have identified the leaching processes in MSW incineration ash in batch experiments, further research on the dynamic modeling of leachate from waste materials is relatively scarce (Dijkstra et al., 2008). Additionally, chemical speciation obtained by geochemical modeling helps to determine the most important mineral phases that act in the cement matrix and control the mobility of heavy metals. Du et al. (2019b) used Leach XS geochemical modeling to fit the heavy metal leaching concentrations with the change of pH in the leachate from pH-dependent leaching tests. Mineral phases controlling the release of heavy metals in the long term were successfully determined. Researchers

have also included the site-specific environmental conditions such as climate and hydrogeology to further interpret the geochemical model with realistic data input (Dabo et al., 2009; Fellner & Brunner, 2010; Hartmann et al., 2004; Hjelmar et al., 2007; Johnson et al., 2001; Ludwig et al., 2000).

2.4 pH modeling

Predicting pH levels in waste incineration ashes is essential for multiple reasons. It helps assess and mitigate environmental risks associated with the disposal or use of these types of ashes, particularly in terms of leaching harmful substances into the environment (Beyer et al., 2009). Predicting pH aids in proper waste management and determining suitable handling and treatment methods. It also enables the identification of potential resource recovery opportunities by assessing the ashes' suitability for various applications (Mbugua et al., 2014). Lastly, predicting pH ensures compliance with regulations and guidelines governing waste management, safeguarding environmental and public health (Hyks et al., 2009).

To understand the effects of the mineral composition in incineration ashes on the leachate quality and quantity, it is important to understand that pH is a major factor to control reactions in incineration ashes. Various studies have concluded that the pH value of leachate can significantly change the leaching behavior of heavy metals in MSW incineration bottom and fly ashes (Araujo et al., 2020; Astrup, Mosbæk, et al., 2006; Dijkstra et al., 2008; Van Herck et al., 2000; H. Zhang et al., 2008; Y. Zhang, Cetin, et al., 2016). For example, Ca minerals in MSW incinerated bottom ashes and fly ashes mainly control leachate pH, which in turn has been identified as a major parameter controlling the leaching of heavy metals (Astrup, Mosbæk, et al., 2006; Dijkstra et al., 2008; Hyks et al., 2009; Meima & Comans, 1997). Typically fly ashes are characterized by having very high pH values, typically in the order of pH 11-13 (Astrup, Mosbæk, et al., 2006) Due to their compositions of Ca minerals such as $Ca(OH)_2$ and $CaCO_3$. In the case of cement solidified and stabilized fly ash, the by-product of minerals produced in the cementing process maintains an alkaline condition. This alkaline condition keeps controlling heavy metal release from the ashes. However, generally, the mobility of heavy metals increases at low pH conditions, and the risk of environmental contamination increases.

Taking into consideration the chemical and mineralogical composition of incineration ashes, a popular approach is to determine the most important mineral phases affecting the composition of the leachate. This is done through the utilization of geochemical modeling software. The approach utilizes elemental content data, mineralogical investigation data, literature information, and qualitative information from acid neutralization capacity test results. (Astrup, Mosbæk, et al., 2006; Dijkstra et al., 2008; Gómez-Puentes et al., 2014; Gonzalez et al., 2019; Hareeparsad et al., 2011; Hyks et al., 2009; Y. Zhang, Soleimanbeigi, et al., 2016). Recent efforts have been made to apply geochemical modeling in cement matrices and cement-solidified MSW incineration ashes (Martens et al., 2010; Santiago et al., 2022).

2.5 HYDRUS-1D and HP1

Hydrus-1D represents a significant advancement in the field of hydrological modeling, offering a public-domain comprehensive software package for simulating the intricate movement of water, heat, and solutes within variably saturated porous media. Specifically designed to investigate flow and transport phenomena in soils, sediments, and geological materials, this numerical simulation tool combines sophisticated algorithms with the governing equations of water flow (Richard’s equation), heat transfer (conduction-convection equation), and solute transport (advection-dispersion equation)

in one-dimensional soil profiles. By considering the influence of soil properties, boundary conditions, and external factors, Hydrus-1D provides researchers, hydrologists, agronomists, and environmental scientists with a robust platform to analyze critical processes such as water infiltration, evaporation, plant water uptake, and pollutant dispersion (Haws et al., 2005; Jacques et al., 2008; Leterme et al., 2014; Šimůnek & Genuchten, 2008). Moreover, this software empowers users to evaluate the impact of irrigation and drainage practices, enabling informed decision-making in the domains of water resource management, agriculture, and environmental protection. In essence, Hydrus-1D exemplifies an invaluable tool that enhances our understanding of subsurface dynamics, facilitating the formulation of effective strategies and policies toward sustainable utilization and conservation of vital natural resources. Furthermore, researchers have studied the possibility of using HYDRUS-1D in simulating water and solute transport in other porous media other than soils such as cementitious materials, MSW, coal fly ashes wood chips (Almahayni & Vanhoudt, 2018; Fellner & Brunner, 2010; Pontedeiro et al., 2018; Subroy et al., 2014).

HYDRUS-1D also incorporates a model coupled with the PHREEQC geochemical code (Parkhurst & Appelo, 1999) to create the simulation tool HP1(Jacques & Šimůnek, 2005; Šimůnek et al., 2006). This code contains modules simulating transient water flow, the transport of multiple components, mixed equilibrium/kinetic biogeochemical reactions, and heat transport in one-dimensional variably saturated porous media. HP1 is a significant expansion of the individual Hydrus-1D and PHREEQC programs by preserving most of their original features. The code still uses the Richards equation for simulating variably saturated water flow and advection-dispersion type equations for heat and solute transport. However, the loosely coupled program can also simulate a broad range of reactions in water, the vadose zone, and in groundwater systems, including interactions with minerals, gases, exchangers, and sorption surfaces based on thermodynamic equilibrium, kinetic, or mixed equilibrium-kinetic reactions (PC-progress, 2021). The model capabilities show the potential to numerically simulate the water content and the evolution of pH and solute concentrations leached out in column leaching experiments using cement-solidified incineration ashes. To the best of our knowledge, no study has yet simulated column leaching experiments using cement-solidified boiler fly ash containing waste tire incineration and biomass fly ashes, and only a few have estimated the mineral phases via geochemical modeling.

Table 2.1. Studies evaluating the recycling of incineration ashes.

Wastes incinerated	**Types of ash**	**Recycled materials**	**Treatment**	**Substances surveyed**	**Endpoints**	**Reference**
MSW	bottom ash	Aggregates	No treatment	Not applicable	Physical and mechanical properties	Huang et al., (2020)
MSW	bottom ash	Cement base Road base materials	Mixture with limestone aggregates	Not applicable	Compression strength	Tang et al., (2018)
MSW	Bottom ash	Permeable subgrade material	No treatment	Organic pollutants	Adsorption of organic pollutants	Tian et al., (2021)
MSW	Bottom ash	Glass ceramics for construction materials	Dried and pulverized, vitrification	Mineral phases	Melting points for vitrification	Monteiro et al., (2008)
MSW	Bottom ash	Roadbed materials	Natural maturation	Heavy metals	Compressive strength	Becquart et al., (2009)
Not specified	Incineration ashes	eco cement	Not specified	Alkali reactions	Chemical composition and physical properties	Torii et al., (2003)
MSW	Bottom ash	Road construction materials	Mixed with Portland cement and lime and slag	Aluminum reactions	Swelling and expansion	Pecqueur et al., (2001)
MSW	Bottom ash	Aggregate substitute for pavement	No treatment	Trace elements	Geotechnical properties	Izquierdo et al., (2002)
MSW	Bottom ash	Sand replacement	Washing, magnetism, eddy current, and crushing	Heavy metals	Physical properties	Wu et al., (2016)
Sugar cane bagasse	Fly ash	Cement mortars	Cement solidification	Not applicable	Physical and moisture properties	Wyrzykowski et al., (2016)
MSW	Bottom ash	Aggregate materials	Metal and chloride removal, immobilization	Heavy metals	Geotechnical properties	Verbinnen et al., (2017)

Table 2.1. *cont.*

Wastes incinerated	**Types of ash**	**Recycled materials**	**Treatment**	**Substances surveyed**	**Endpoints**	**Reference**
MSW	Bottom ash	Roadbed	Quenching and air drying	Heavy metals and organic compounds	Leaching depletion of heavy metals	Izquierdo et al.,(2008)
MSW	Bottom and fly ash	Hot mix asphalt	Hot asphalt Mixtures	Heavy metals	Physical properties	Cho et al., (2020)
MSW	Bottom ash	road base aggregate	Blending with natural and recycled aggregates	Heavy metals	Chemical speciation Long-term leachability	Gonzalez et al., (2019)
Tire derived fuel	Fly ash	Filler in hot mix asphalt	Hot asphalt Mixtures	Pb, Cu, As, Hg, Cr(VI), Cd, and Oil	Physical and mechanical properties	Choi et al., (2020)
Sewage sludge	Incinerated ash	Cementitious binder	Mixture of lime and ordinary Portland cement	Heavy metals	Physical-chemical characterization	Zhou et al., (2020)
Solid waste	Bottom ash and fly ash	Pavement base layer	Cement treatment	Heavy metals	Leaching of heavy metals	Cai et al., (2004)
Wood waste and refused-derived fuel	Fresh and aged fly ash	Embankment fill material	No treatment	Heavy metals	Geotechnical properties	Zhang et al., (2016)
MSW	Bottom ash	Stone mastic asphalt	Mixture with mineral filler and asphalt	Heavy metals	Physical and chemical properties	Xue et al., (2009)
MSW	Bottom ash	Road base material	Metal removal	Not applicable	Physical and mechanical properties	Spreadbury et al., (2021)

Table 2.2 Studies evaluating modeling applications with incineration ashes.

Materials of study	Main parameters investigated	Modeling software	Experimental condition	Remarks	Reference
Household waste landfill sections	Hydraulic conductivity	HYDRUS 2D	Saturated and unsaturated	Laboratory scale column test, Dual porosity.	Fellner & Brunner, (2010)
Municipal solid waste	Hydraulic parameters	HYDRUS-1D	Saturated and unsaturated conditions	Laboratory scale, lysimeters tests, water flow.	Taheri Soudejani et al., (2020)
Air pollution control residues	Mineral concentrations	PHREEQC	Saturated conditions	Laboratory scale column test, mineral dissolution.	Hyks et al., (2009)
Municipal solid waste bottom ash	Mineral speciation	PHREEQCI (version 3.3)	Sequential chemical extraction and Batch leaching test	Determined mineral phases based on saturation indices and pH conditions.	Gonzalez et al., (2019)
Air pollution control fly ashes	Mineral speciation and concentrations determination	PHREEQC-2	Sequential batch leaching tests	Column transport modeling with a mineral assemblage and concentration amounts.	Astrup et al., (2006)
MSW incineration bottom ash	Solute transport model, hydraulic parameters, adsorption, diffusion	Brinkam equation and COMSOL Multiphysics 5.5	Subgrade under asphalt	Organic pollutants	Tian et al., (2021)
Cement solidified MSW ashes	Mineral speciation	Model LeachXS	Batch leaching pH-stat	Heavy metal speciation in cement solidified ashes	Du et al., (2018)
Plaster and Mortar covered panels	Mineral phases, diffusion	PHREEQC using LNLL data base	Vertical test panels exposed to real weather conditions and leaching tests	Qualitative and quantitative leaching modeling	Vega-Garcia et al., (2021)
Coal fly ash and MSW bottom ash	Soil transport parameters	ECOSAT	Laboratory column leaching tests	Modeling of pH and heavy metals	Schreurs et al., (2000)
Soil contaminated by swine slurry	Root growth and water uptake	HYDRUS-1D	Zn and Cu	Prediction of Cu concentrations into soil	Mallmann et al., (2017)

Table 2.2 *cont.*

Materials of study	**Main parameters investigated**	**Modeling software**	**Experimental condition**	**Remarks**	**Reference**
River sediment and mine tailing dumps	Flow and transport parameters	HYDRUS-1D	Sample digestions and extractions	Prediction of leachate quality	Aghili et al., (2018)
Untreated MSW	Hydraulic parameters	HYDRUS-1D, Dual porosity	Full-scale landfill	Prediction of leachate from a landfill site	Feng et al., (2018)
MSW incineration ash, blast furnace slag, and demolition waste.	Flow and transport parameters	GeoSys and SMART	Tracer experiments	Prediction of leachate quality	Beyer et al., (2009)
Solidified/stabilized waste	Porosity and effective diffusion coefficient	HYTEC	Batch leaching tests	Modeling leaching of Pb and major components	De Windt and Badreddine (2007)
MSW bottom ash	Element concentrations and reactive surfaces	ORCHESTRA, MINTEQA2 V 4.0, NICA -Donann model, Two-layer model	Column percolation	Leaching and reactive transport of major elements and heavy metals	Dijkstra et al., (2008)
Landfill site	Chemical speciation water evaporation process	PHREEQC	Soil and monitoring well sample	Heavy metal leaching	Gomez-Puentes et al., (2014)
Wood combustion ashes	Mineral dissolution	ORCHESTRA, MINTEQA2, NICA-Donann model	Column leaching tests	Heavy metal leaching	Maresca et al., (2018)
Carbonated and uncarbonated cement mortars with MSW bottom ash	Sorption sites of Al and Fe phases	PHREEQC	Single extraction tests and diffusion tests conducted on samples	Leaching of major elements and Pb	Martens et al. (2010)
MSW fly ash	Thermodynamic equilibrium	PHREEQC, diffuse layer model	Batch leaching test	Adsorption of CO_2 and heavy metal speciation	Wang et al., (2016)

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3. Characteristics of BFA and SFA

3.1 Objectives

In order to ensure the safe recycling and utilization of incineration boiler fly ash as a civil engineering material in the natural environment, it is essential to evaluate the leachability of heavy metals. This chapter aims to characterize both the raw boiler fly ash and a cement-solidified recycled material made from the fly ash. The analysis includes examining the total content, mineral composition, and behavior of heavy-metal leaching in the samples. The boiler fly ash used in the study was obtained from the incineration of industrial waste that included waste tires. Additionally, a cement-solidified boiler fly ash was produced to assess the effects of cement solidification on reducing heavy metal leachability. Furthermore, cement-solidified samples, which were used in a road test pilot site, were obtained from an aggregate-producing company, and analyzed to investigate changes in the solubility of heavy metals and the chemical composition evolution of the recycled roadbed material.

3.2 Research method and materials

3.2.1 Raw boiler fly ash

The original raw boiler fly ash (BFA) sample was obtained from a paper mill plant in 2016 in Nichinan City, Japan. To generate energy for the paper production processes, the plant incinerates 4 different types of waste such as woody biomass, scrap tires, refuse paper, and plastic fuels. The plant utilizes a fluidized bed boiler with a steam production capacity of 100 T/H and power generation of 25 MW. The total waste composition and its source ratios are described in Table 3.1. Originally the fly ash was landfilled in industrial waste landfills before recycling.

3.2.2 Preliminary test for determination of mixing design for production of solidified boiler fly ash

To utilize the BFA as a recycled material, fresh solidified boiler fly ash (SFA-F) was produced by mixing cement, fine sand, and water. Focusing on Pb, which is the BFA heavy metal that causes the greatest concern due to its high solubility compared to that of other heavy metals, different mixing ratios were tested. To determine the optimal mixing ratio of source materials for the prevention of Pb leaching from SFA-F material, the lead leachability of the mortar bar with 7 different mixing ratios was evaluated using a batch leaching test (JLT-46). A total of 2.0 kg. of materials were used for the experiment, following the mixing ratios as provided in Table 3.2. To ensure consistency, water was added in the proportion of 48.6% for all mixing ratios. For the mixing process, a cement mortar mixer was employed. Mortar bar samples of 4 x 4 x 16 cm in size were produced. The mortar sample was then aged for 7 and 28 days to allow for proper curing. After the curing period mortar samples were then crushed and sieved for analysis. A visual representation of the BFA and SFA-F after mortar crushing is shown in Figure 3.1.

Table 3.3 shows the Pb concentrations of the mortar samples after 7 and 28 days of curing. The regulatory concentration value of lead is below 0.010 mg/L as specified by the Japanese environmental quality standards for soil pollution. Although it was determined that a larger BFA addition percentage is favorable to reduce the disposal, it showed slightly larger leachability from the SFA after 7 days of curing. Therefore, sample mixtures of mortar 3040 were selected for the following study.

3.2.3 Production of SFA

With the optimal mixing ratios established, The SFA was produced by an aggregate-material-producing company located in Miyakonojo City, Japan. The process consists of mixing cement, fine sand, and water followed by BFA in a mixer (2.217 t/batch). The sample used for this study has a mixing ratio as described in Table 3.3.

A pilot test road site was constructed in 2017 depicted in Figure 3.1. The site was divided into three equal sections, each measuring 5 meters in width and 12 meters in length. The first (SFA-O) and second (SFA-D) sections have a 15 cm layer of SFA-F, followed by a 5 cm layer of open-graded asphalt and dense-graded asphalt, respectively. The third section (SFA-N) has the same 15 cm layer of SFA-F but without any asphalt cover layer, allowing the material to be exposed to the natural environment. Samples from the SFA-O and SFA-D sections were obtained by digging a hole to a depth of approximately 10 cm. In contrast, samples from the SFA-N section were taken directly without any digging. All samples were collected and subsequently oven-dried and sieved before their corresponding analysis.

3.2.4 Chemical and mineralogical analysis

The bulk chemical composition and the major mineral phases of BFA, SFA-F, SFA-O, and SFA-N were analyzed using XRF (Shimadzu, EDX-720) and XRD (PANalytical X'pert PRO MRD diffractometer), respectively. To determine the total concentrations of the major elements (Ca, Na, K, Mg, Al, Fe, and Si) and trace heavy metals (Pb, As, Cu, Cd, T-Cr, Ni, and Zn) in all the sample materials, the samples were pulverized into a fine powder consistency. Next, 2 g of the sample was put into a beaker with an acid mixture solution of HCl and HNO3 (3:1) at 150 °C. The solid and liquid were separated by a glass filter (1.00 µm) and the major element and trace heavy metal concentrations in the solution were measured using inductively coupled plasma mass spectrometry (ICP-MS; Agilent Mass Hunter 5.1).

3.2.5 Batch leaching tests

The Japanese batch leaching test method (JLT-46) was conducted on dry samples of SFA-F, SFA-O, and SFA-N. Samples sizes of 2 mm or less were put in a sealed PE bottle in contact with distilled water at a liquid-to-solid (L/S) ratio of 10 and shaken at a constant rate of 200 rpm for 6 h. The solutions were filtered with a 0.45 µm membrane filter and subjected to pH measurement. Filtered solutions were analyzed for major elements and trace heavy metal concentrations (ICP-MS; Agilent Mass Hunter 5.1).

The pH-stat leaching test was performed on samples SFA-F, SFA-D, and SFA-N, with a sample size of 2 mm or less to evaluate the solubility of major elements and heavy metal solubility release as a function of pH. The method consisted of 20 g of sample in 200 ml of distilled water. The sample was constantly stirred in open beakers for 24 h with specific pH values of 2, 4, 6, 8, 10, and 12. To maintain a constant 10 L/S ratio, the pH of the solutions was controlled with an automatic titration system (902 Metrohm) by adding highly concentrated HNO3 and NaOH solutions which did not increase the liquid volume substantially. To reduce the leaching error between samples due to an increase in solution volume, the L/S ratio increase of samples and solutions was kept in the range of 10-12 L/S for all samples. The batch samples were conducted in triplicates and at the end of each pH-stat test, the solutions were filtered through a 0.45 µm membrane filter. The major elements and trace heavy metals were measured by ICP-MS.

3.3 Results and Discussion

3.3.1 Characterization of BFA, SFA-F, and road test samples

The total elemental content determined by acid digestion for the BFA, source materials, SFA-F, SFA-O, SFA-D, and SFA-N samples is presented in Table 3.5. The variability of the mass balance might be attributed due to incomplete mixing during the production of SFA and the inhomogeneous characteristics of the BFA composition. Furthermore, future studies that identify the evidence of the errors using various BFA samples will be needed. The heavy metal content in BFA and SFA had the following order: Zn > Cu > Ni > T-Cr > Pb > As > Cd. In general, the decrease in contents between SFA-F and the road test samples could be attributed to the readily soluble mineral phases and soluble chloride salts during natural leaching processes (Du et al., 2018a). Specifically, the contents of Na in the road test samples were lower than that in the fresh SFA-F sample. Alkaline metals such as Ca, K, and Mg show no significant reduction between fresh and weathered samples attributed to their low solubility provided by the alkaline conditions of the cement matrix (Glasser, 1997). Although no significant reduction of the contents of heavy metals between SFA-F and the road test samples; Pb, Cd, and T-Cr levels exhibited a slight reduction, particularly in the case of the SFA-N sample. This reduction can be attributed to a "wash-off" mechanism on the material's surface, which appears to have had the greatest impact on Cd and T-Cr levels in the SFA-N sample (Liu et al., 2022). Although Sample SFA-F showed some inconsistencies in total content compared to that of SFA-O and SFA-D, there was no major release of Zn. In the case of SFA-N, The dissolution of Zn might be due to the carbonation processes of Zn in the field, which could affect the precipitation and dissolution process of silicate hydrate aluminum phases adsorbing Zn (Du et al., 2018b).

The compositions of the major chemicals in their oxide forms present in the BFA, SFA-F, and road test samples as determined by XRF are shown in Table 3.6. For BFA and SFA-F, both samples had high levels of CaO, SiO_2, and Al_2O_3. After the solidification process, the SiO_2 content in the SFA-F more than doubled from 17.5% to 40%. Although the content of Al_2O_3 had a percentage increase, the total content of Al in SFA-F did not follow the same order of increase. With the current results and analysis, these findings can only be described by sampling error and incomplete digestion of amorphous aluminosilicate phases (Akinyemi et al., 2020). The SFA-F became a complex material in which the ash–cement mixture contained CaO, SiO_2, and Al_2O_3. These determine the main mechanical and physical properties of the materials and serve as sources of oxides that can react with each other and generate calcium-silicate-hydrates (C-S-H) and amorphous ettringite phases to facilitate the ability to fix heavy metals (Hareeparsad et al., 2011; J. Li et al., 2018; Yakubu et al., 2018).

The mineralogical composition of the BFA shows major peaks attributed to Ca-containing minerals such as anhydrite ($CaSO_4$) and calcium silicate in crystal forms (Figure 3.2). The minerals in common cement such as portlandite ($Ca(OH)_2$) and calcium aluminum oxide ($Ca_3Al_2O_6$) were also identified in BFA due to the similarity to the elemental composition of mineral phases determined by XRD in MSWI fly ash from China, Denmark, and France (Dabo et al., 2009; Du et al., 2018b; Hyks et al., 2009; J. Li et al., 2018; Luo et al., 2020). The XRD data facilitates comparisons of the minerals newly formed following solidification. The main crystallized minerals such as calcite ($CaCO_3$), quartz (SiO_2), calcium aluminate silicate hydrates ($CaAl_2Si_2O_8{\cdot}4H_2O$), and gypsum ($CaSO_4{\cdot}2H_2O$) were identified in SFA-F (Figure 3.2).

The addition of BFA to cement affects the mineralogy of the hydrate cement products and the chemical properties of the system, which are dominated by the more rapid hydration reactions of C-S-H. Thus, the calcium silicate gel is the principal conditioning phase with a broad spectrum of cement and blended cement compositions (Glasser, 1997). Furthermore, Calcium aluminate hydrates and aluminosilicates (i.e. $(KAl_2(AlSi_3O_{10})(OH)_2)$ were also identified in the SFA-F sample. There were only slight discrepancies in the identification of mineral phases between SFA-F and road test samples, except for an increase in the calcite peak intensity in the SFA-N sample. The increase of calcite in the SFA-N is probably due to the initial stages of maturation that result from the carbonation process, which may have been accelerated by atmospheric carbon dioxide. As described by Li et al. (2020), indirect carbonation can enrich the surface of fly ash matrices by promoting the formation of amorphous or mineral carbonate. Furthermore, the carbonation reaction of Portland cement-based materials has been assumed primarily by the conversion of calcium hydroxide ($Ca(OH)_2$) to calcium carbonate by the decalcification of CSH minerals (Garrabrants et al., 2004; W. Li et al., 2020).

3.3.2 Compliance batch leaching test: JLT-46

The test results are presented in Table 3.7. In Japan, the BFA is classified as industrial waste and can be disposed of in industrial waste landfills. The Pb concentration seen here (0.01 mg/L) exceeded the regulatory value of 0.010 mg/L specified by the Japanese environmental quality standards for soil pollution. The heavy metals of concern found in SFA-F and road test samples had concentrations well below the regulatory limits except for total chromium (T-Cr). The T-Cr concentration of SFA was 0.073 mg/L, which is higher than the Japanese environmental quality standard value (0.05 mg/L of Cr(VI)). To confirm that the concentration of Cr(VI) was below the standard value, the concentration of Cr(VI) in SFA-F was measured via the diphenylcarbazide method. The results indicated that the concentration of Cr(VI) in SFA-F was below the Japanese environmental quality standard value. In alkaline cement environments, Cr(VI) compounds appear in the form of a chromate anion (CrO_4^{2-}), which is highly soluble and makes the application of the cement solidification/stabilization technique quite challenging (Bakhshi et al., 2019). Yamaguchi et. al (2006), reported that 50–80% of T-Cr in ordinary Portland cement typically appears as Cr(VI). In contrast, cement hydration products contain octahedrally coordinated Al that can be easily replaced by Cr(III). Therefore, the chemical immobilization of T-Cr is due to the formation of calcium aluminate hydrate phases, which are insoluble in the cement matrix (Glasser, 1997). The levels of T-Cr in the road test samples were below the permissible limits, suggesting that the dissolution reactions of organic chlorides and $CaCrO_4$ may facilitate the washing out of Cr(VI) from the cement matrix in these samples.

3.3.3 pH-stat Leaching test

The mass release of major elements and heavy metals in BFA, SFA-F, SFA-D, and SFA-N at various pH values is shown in Figures 3.3 and 3.4. The leaching of Ca and Mg exhibited a strong pH dependence, as represented by its cationic leaching pattern for BFA and SFA-F (Komonweeraket et al., 2015). The solubility process promotes the release of these elements and is inversely proportional to the pH values. In extremely acidic conditions (pH 2), the Ca leaching rate from SFA-F compared with the total content determined by acid digestion was 93%. Calcite minerals, C-S-H, and calcium hydroxides formed in the hydration and solidification process of cement created a highly alkaline condition, which has a high resistance to acid attack (Du et al., 2019; Fan et al., 2018a; X. Li, 2001). The leaching rate of Mg in BFA at pH 2 was only 53%. In BFA and SFA-F, the concentration amounts of K and Na were the highest at pH 2, but after pH 4, the release was constant,

and the solubility of these elements had weak pH dependence. In general, no major differences were identified in leaching behavior between SFA-F and road test samples other than the difference in available concentrations released during the test.

The largest mass concentration of all heavy metals is released at pH 2. On the other hand, the cement solidification demonstrated favorable fixation and effective control of Pb and Zn at pH 12, with less than 1% release of total Pb and Zn contents in SFA-F and road test samples. The solubility of Pb in samples SFA-F, SFA-D, and SFA-N exhibited an amphoteric behavior with a solubility minimum between pH 6 and 8 in SFA-F and pH 10 in SFA-N. On the other hand, Pb in BFA followed a cationic leaching behavior with minimal leaching concentrations detected. The lower solubility of Pb at pH levels greater than 10 could be regulated by the precipitation of various lead-bearing compounds, including $Pb(OH)_2$, $CaPb(OH)_6$, and $CaPb_2(OH)$, as well as by the adsorption of calcium silicate hydrate (CSH) (Garrabrants et al., 2004; J. Li et al., 2018; Pandey et al., 2012; Shao et al., 2016). In contrast, achieving a greater release of Pb at pH levels below 4 is possible due to the reversal of lead adsorption and the promotion of the solubility of reactive surfaces such as hydrous ferric oxides and hydrous aluminum oxides (Du et al., 2019). The leaching behavior of Zn showed an amphoteric curve according to the pH for all the samples. For all samples, Zn had the highest concentration release at pH 2 compared to the rest of the heavy metals. Li et al. (2020), suggest that acid-leaching environments (pH 3) strongly contribute to the dissolution of the carbonate layer found in MSWI fly ashes. Both BFA and SFA-F XRD results show the detection of calcium carbonate ($CaCO_3$) and further confirm the high release of Pb and Zn by the solubility processes. Moreover, in the natural environment, the leaching of Zn in carbonated phases from SFA-N was enhanced due to exposure to atmospheric CO_2 (W. Li et al., 2020). Consequently, the phases that regulated the release of Zn at a pH of 10 were already depleted, resulting in the absence of detectable concentrations.

The concentrations of Cu and Ni showed a cationic leaching behavior with relatively low concentrations or no detection in the high alkaline range in SFA-F. The cement solidification has a strong stabilizing effect on BFA, specifically Ni and Cu in alkaline pH from 10-12 and pH 8-12. At pH 2, 60% of the total Cu in BFA was detected, compared to that of SFA-F and SFA-D with 30% and 40%, respectively. In SFA-F from pH 8-12, no concentration of Cu was detected compared to that of SFA-D and SFA-N. $Cu(OH)_2$ and surface complexation to Fe and Al hydroxides are potential Cu-controlling phases at pH above 8. The control of solubility at this pH range could be further enhanced by the cement solidification in the SFA-F material (Dijkstra et al., 2008; Hyks et al., 2009; Quina et al., 2009). On the other hand, in the pH range of 8-12, Cu shows poor pH dependency in BFA, SFA-D, and SFA-N. Studies evaluating incineration ashes show similarly shaped leaching curves for Cu where carbonation processes control the solubility of Cu binding phases (Costa et al., 2007).

The release behavior of Cd followed a cationic leaching pattern in samples SFA-F and SFA-D, stabilizing Cd in the pH range of 10-12. However, sample BFA and SFA-N showed an amphoteric pattern at pH 12, which could be due to the carbonation process weakening the fixing ability of Ca-carbonated minerals for Cd (W. Li et al., 2020; Yin et al., 2017). The release of Cd from SFA-F and SFA-D was in the range of 40-46% of the total content of Cd, while BFA and SFA-N had a higher release of more than 97% at pH 2. The high percentage of release of Cd in an acidic environment might be due to the weak ability of amorphous carbonates to resist acid dissolution (W. Li et al., 2020). A similar release trend of T-

Cr in the pH range of 8-12 was observed with 0.6 mg/kg of mass release and this was 2% of the leaching ratio of total T-Cr contents in samples SFA-F, SFA-D, and SFA-N. This result represents an oxyanionic leaching pattern with a maximum release at neutral to mildly alkaline pH (van der Sloot, 2002).

Concentrations of As in BFA showed a cationic leaching pattern, whereas those in SFA-F and road test samples showed a weak amphoteric leaching pattern. Differences in leaching patterns can be the result of the sorption of anions on mineral surfaces. The increased concentration of As at alkaline pH in the case of SFA has been observed in other studies on leaching from coal fly ash and various stabilized wastes (Komonweeraket et al., 2015). It could be assumed that amorphous Fe hydroxides and amorphous Al hydroxides, which are known to have a strong affinity for surface complexation with As could be present in the cement matrix of SFA-F, allowing the amphoteric movement similar to that of Fe and Al. Thus, the increase of As at alkaline pH can be explained (Fan et al., 2018b). There was no significant difference in the release of As between SFA-F and road test samples. At pH 2, the largest releasing ratio was approximately 10% of the total content of As for these samples. Arsenic adsorption to metal oxide surface such as iron and aluminum oxides in near neutral pH range has been well investigated establishing an oxyanion leaching pattern (Garrabrants et al., 2004). Findings by Garrabrants et al. (Garrabrants et al., 2004) suggest that the release of As(V) in fly ash matrices has been linked to adsorption and co-precipitation mechanisms involving Ca-bearing cement mineral phases, particularly at pH values greater than 11. Furthermore, the substitution of anions such as AsO_4^{3-} into ettringite phases, would control the dissolution of As in the form of “free” ions at high pH levels (Hyks et al., 2009).

The results provided are useful information to define the optimal utilization environment for the SFA material in the pH range of 10-12. It is an important notice to the fact that all heavy metals were mobile at pH $\leq$ 4, and as a result leached out of the SFA material. Based on the previous findings, it is highly recommended to carry out further long-term studies to guarantee the safe utilization of the material in the environment. It is important to highlight that a decline in pH levels corresponds to an increase in the leachability of heavy metals. Therefore, it becomes crucial to determine the precise moment when the SFA-F pH buffer capacity weakens, leading to a drop in pH. In contrast, it has been demonstrated through pH-stat experiments that maintaining an alkaline condition effectively diminishes the leachability of heavy metals.

3.4 Conclusions

Cement solidification is a proven and sustainable technique known for its efficient heavy-metal-binding effect, effectively preventing the release of hazardous heavy metals from boiler fly ashes (BFA). Extensive leaching assessments have confirmed the remarkable heavy metal binding capability of the SFA-F material. The leaching observed in SFA-F can be primarily attributed to the solubility of minerals present in the cement matrix. This study's results strongly support the recommended mixing ratio method for SFA production, emphasizing its suitability for safe disposal in non-hazardous waste landfills and even recycling applications. Furthermore, the SFA-F material holds great promise for utilization in roadbed construction, offering an opportunity to reduce the reliance on natural aggregates. The combination of cement mixing and the pozzolanic properties of BFA enhances the immobilization capacity of heavy metals by facilitating the formation of hydration products and secondary minerals. Besides the leaching characterization conducted in this study, further investigations using geochemical modeling techniques have the potential to assess and predict the leaching potential of

SFA recycling and long-term disposal scenarios. These insights will contribute to the future management of incinerated materials, including fly ash from waste tire incineration.

Table 3.1. Waste composition and their proportions incinerated at the paper mill plant.

Waste	Proportion (t/day)
Waste tires	240
Waste wood	196
Paper mill sludge	214
Others	24.0
Total	674

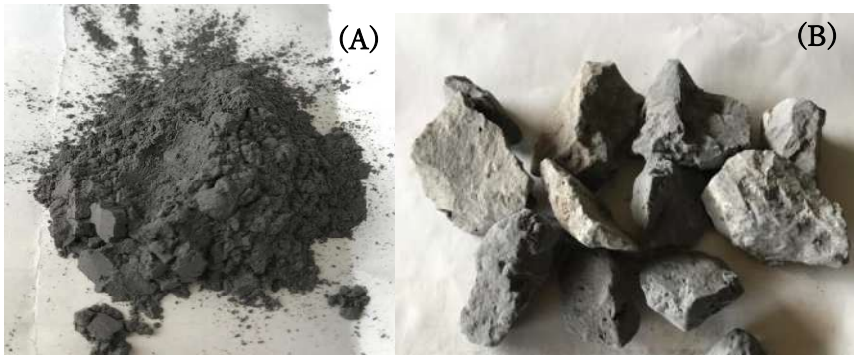


Figure 3.1. BFA (A) and SFA-F (B) samples

Table 3.2. Mixing ratios of dry powders (dry weight %)

Mortar sample	BFA	Cement	Fine sand
2030	20	30	50
3020	30	20	50
3030	30	30	40
3040	30	40	30
4020	40	20	40
4030	40	30	30
4040	40	40	20

Table 3.3. Lead concentration from SFA after the curing period.

Mortar sample	After 7 days of aging (μg/L)	After 28 days of aging (μg/L)
2030	>2.00	>2.00
3020	>2.00	>2.00
3030	2.28	3.36
3040	>2.00	2.16
4020	2.91	>2.00
4030	>2.00	>2.00
4040	3.80	2.08

Table 3.4. Optimal mixing ratios of SFA-F.

Solid content mass ratio			Moisture (%)
BFA (%)	Cement (%)	Fine sand (%)	
30.0	30.0	40.0	48.6

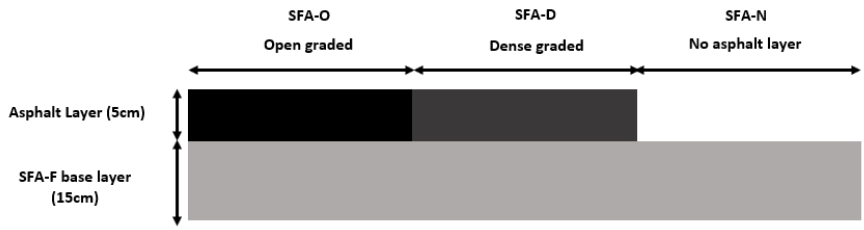


Figure 3.2. Schematic transversal cross-section of the road test site

1-SiO_2 2-$KAl_2(AlSi_3O_{10})(OH)_2$ 3-$CaAl_2Si_4O_{12} \cdot 4H_2O$ 4-$CaCO_3$ 5-$CaSO_4 \cdot 2H_2O$

6-$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ 7-$CaSO_4$ 8-$Ca(OH)_2$

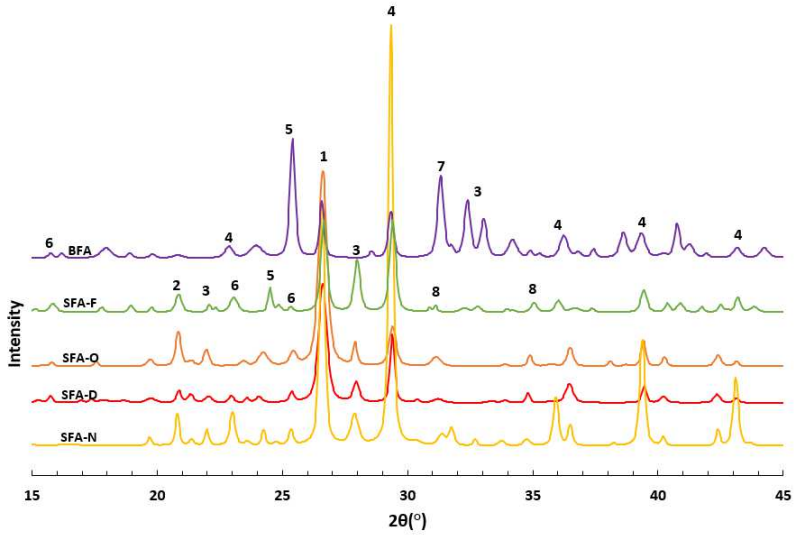


Figure 3.2. XRD analysis of identified mineral phases of BFA (purple), SFA-F (green), SFA-O (orange), SFA-D (red), and SFA-N (yellow).

Table 3.5. Total elemental content (mg/kg) of BFA, fine sand, cement, SFA-F, and road test site samples by acid digestion.

Element	BFA	Fine sand	Cement	SFA-F	SFA-O	SFA-D	SFA-N
Ca	157,000	16,790	670	160,000	136,047	136,046	157,785
Na	260	63.7	100	174	54.8	60.0	61.4
K	4,750	2,940	2,240	5,000	2,482	1,872	1,734
Mg	11,033	3,564	6,580	9,300	10,500	9,970	10,600
Al	37,400	12,865	24,700	26,000	34,200	30,400	18,400
Fe	12,600	2,000	20,000	13,600	16,170	14,200	9,600
Zn	25,000	100	200	8,320	9,975	9,027	5,503
Cd	1.78	<0.002[a]	1.31	1.17	1.41	1.32	1.24
Pb	51.4	23.1	34.3	40.6	38.1	36.2	35.0
As	7.44	5.94	25	7.86	6.75	6.35	6.33
T-Cr	71.4	14.0	50.0	51.2	30.1	28.8	26.1
Cu	480	16.0	250	170	190	180	160
Ni	121	15.8	24.3	37.3	34.0	31.1	30.0

Table 3.6. Bulk chemical composition of BFA, fine sand, cement, SFA-F and road test site samples determined by XRF.

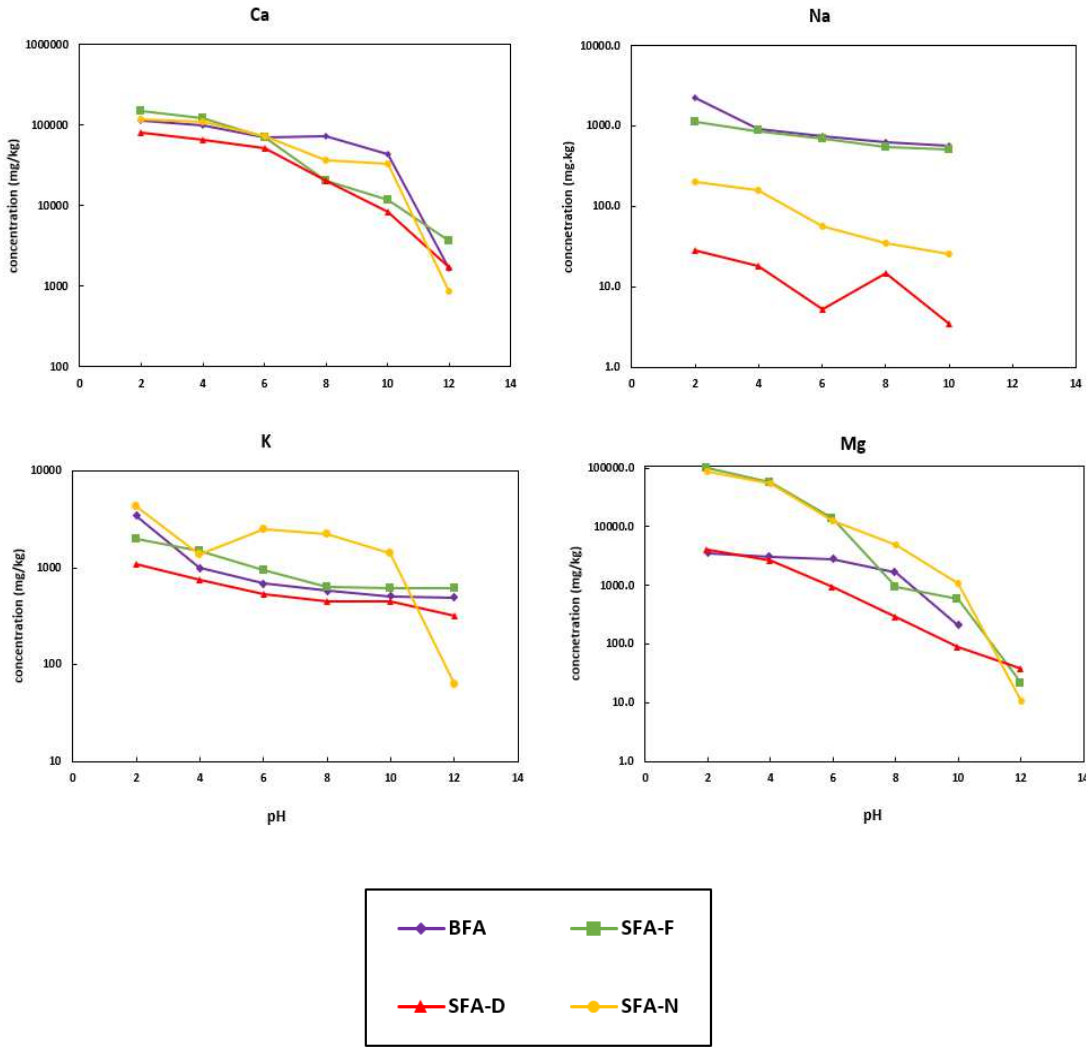
Component (%)	BFA	Fine sand	Cement	SFA-F	SFA-O	SFA-D	SFA-N
CaO	44.6	3.37	70.0	38.0	35.6	35.9	36.3
SiO_2	17.5	60.0	16.5	40.0	32.5	31.8	32.6
Al_2O_3	9.11	24.3	4.00	11.1	11.6	11.4	12.5
SO_3	17.0	0.290	5.60	9.20	9.35	10.1	7.52
Fe_2O_3	2.32	5.18	3.35	3.41	3.54	3.25	3.57
MgO	2.10	2.55	--	2.55	2.96	3.15	3.22
ZnO	5.70	0.0160	--	2.58	2.31	2.37	2.13
K_2O	0.714	3.93	0.511	1.51	1.36	1.31	1.39

Table 3.7. Japanese batch leaching test (JLT-46) results for BFA, SFA-F, SFA-O, SFA-D, SFA-N.

Sample	Pb (mg/L)	T-Cr (mg/L)	As (mg/L)	Cd (mg/L)
BFA	0.0141	0.0311	<0.001[a]	<0.001[a]
SFA-F	0.00304	0.108	<0.001[a]	<0.001[a]
SFA-O	<0.001[a]	0.0300	<0.001[a]	<0.001[a]
SFA-D	<0.001[a]	0.0240	<0.001[a]	<0.001[a]
SFA-N	<0.001[a]	0.0413	<0.001[a]	<0.001[a]
Limit values	0.01	0.05[b]	0.01	0.01

[a] Below limit of determination, <0.001 mg/L, as measured by ICP-MS.

[b] The Japanese environmental quality standards for soil pollution only considers Cr(VI) and not total Cr (T-Cr).


Ca
Na
K
Mg
concentration (mg/kg)
concnetration (mg,kg)
pH
BFA
SFA-F
SFA-D
SFA-N

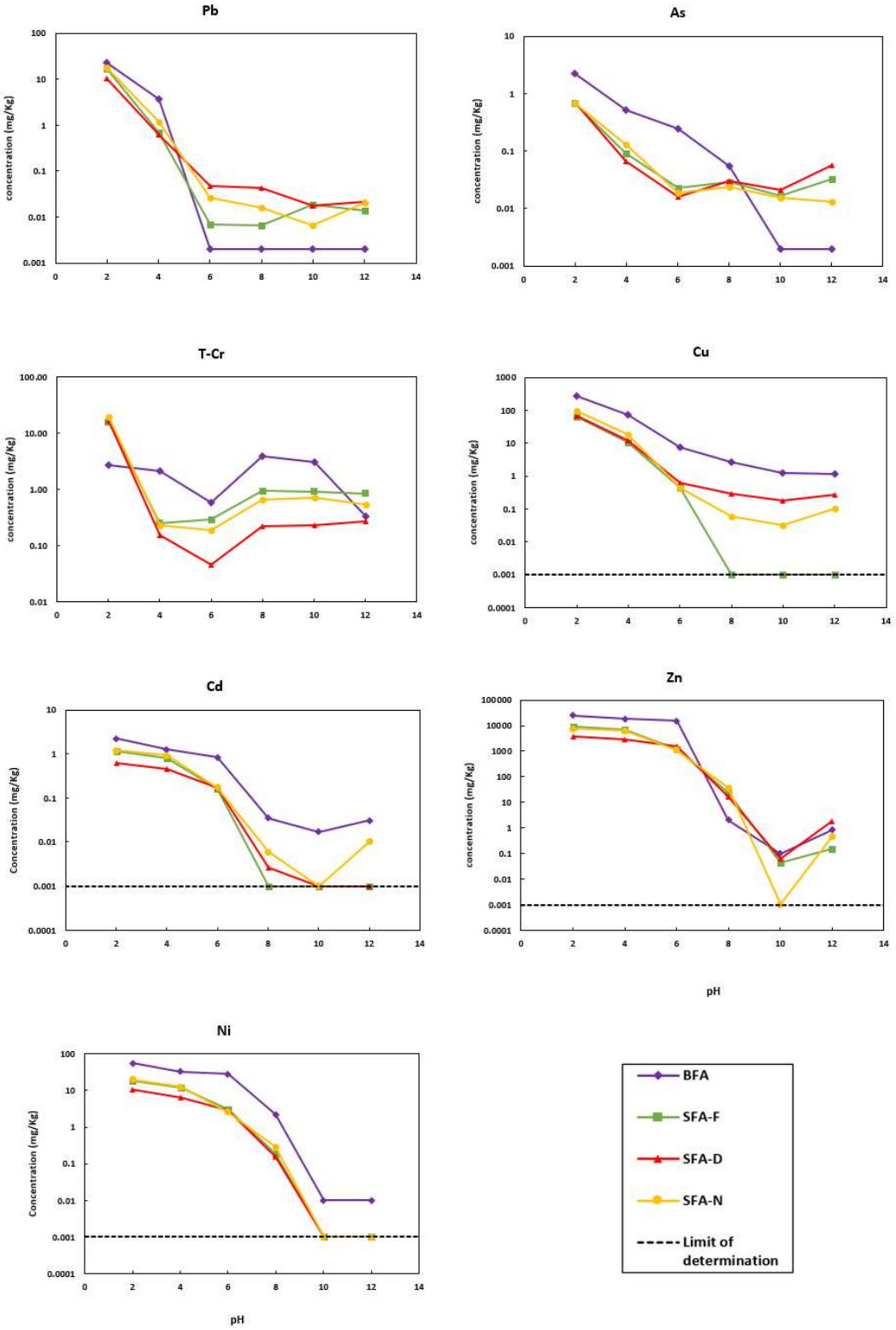


Figure 3.4 Mass of released heavy metals at various pH values. The limit of determination by ICP-MS (0.001 mg/Kg) is shown by the dotted line.

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4. Column leaching tests

4.1 Objective

The aim of this chapter is to monitor the long-term leaching of major components and heavy metals from SFA-F. This will be accomplished by conducting column leaching experiments over 20 months. The significance of these experiments lies in acquiring concentration data of major components in the leachate throughout the entire testing period. Such data is essential for observing the leaching behavior of SFA-F and its ability to sustain alkaline conditions over an extended period and prevent the heavy metal release. Subsequently, the obtained results will be compared to modeling and simulations, enabling a comprehensive description of the leaching process occurring in the saturated column conditions using numerical modeling.

4.2 Research method and materials

4.2.1 Solidified boiler fly ash

Fresh Solidified boiler fly ash (SFA-F) was produced as a recycled material by mixing cement, fine sand, and water with BFA. An aggregate-material-producing company in Miyakonojo City, Japan, was responsible for producing the SFA-F. The SFA-F sample was produced by mixing 30% BFA, 40% fine sand, 30% cement, and 49% water toward solid in a mixer with a capacity of 2.217 tons per batch. This mixing ratio to prevent the leaching of soluble Pb from the SFA-F was determined by a preliminary experiment.

4.2.2 Column leaching experiments

Column leaching experiments consisted of evaluating the release of heavy metals and major ion components of the SFA-F sample with a particle size of less than 2 mm. The SFA-F material was layered successively and gently rammed in acrylic columns with a height of 25 cm and an inner diameter of 4.6 cm as shown in Figure 4.1. The average height and weight of the packed sample inside the columns were approximately 20 cm and 300 g-dry sample. The setting condition is shown in Table 4.1. The test was conducted on a set of three columns. HNO_3 acidified water with pH 4 was used for the inflowing solutions, which were pumped in an up-flow direction with an initial outflow rate of 30 mL/h. The leachates from the columns were collected at a cumulative L/S with an initial L/S ratio of 0.5. Shortly after each L/S ratio was reached, the pH was measured and samples were taken and filtered through a 0.45-µm membrane filter and major elements (Ca, Na, K, Mg), trace heavy metals (Pb, T-Cr, As, Cd, Cu, and Zn) and anion (Cl and SO_4) concentrations were measured by ICP-MS (Agilent ICP-MS MassHunter 5.1) and ion chromatography (Thermo Scientific; DIONEX ICS-1100), respectively.

4.3. Results and discussion

4.3.1 Column leaching test

Figure 4.1 shows the pH and major element concentrations in leachate from the column. The high concentrations of Ca, Na, and K were observed until 50 of L/S due to a “first flush”. The rapid decrease pattern of SO_4 until L/S 50 could be attributed to the rapid dissolution of gypsum ($CaSO_4 \bullet 2H_2O$) and anhydrite ($CaSO_4$) phases (Lager et al., 2006; Li et al., 2018). A pH decrease was observed between L/S 75 and 150 because sampling of leachate was conducted after almost one-week generation of leachate and the dissolving of carbon dioxide in leachate might lower the pH. To address this issue, pH measurements after L/S 150 were conducted immediately to prevent the dissolution of carbon dioxide. Once the L/S ratio

reached 300, the concentration of Ca appeared to stabilize, because the Ca minerals in the sample could reach a state of equilibrium along with a stable pH value of 10.0-10.5. This sustained alkalinity of the leachate can be attributed to soluble Ca minerals that act as pH-buffering agents (Dijkstra et al., 2006; Hareeparsad et al., 2011; Hyks et al., 2007, 2009). Furthermore, ettringite in the SFA-F could be a pH buffer mineral and maintain stable values of pH in the range of 10-10.5 after L/S 200 (Astrup et al., 2006; Dabo et al., 2009; Gonzalez et al., 2019). SO_4 is an abundant anion in the cement matrix and is a major constituent of their structure during the hydration and hardening process of cement (Karamalidis & Voudrias, 2009). The stable concentrations of SO_4 from L/S 100 to around 400 of L/S were due to the dissolution of cement-type minerals such as ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) (Li et al., 2018; Meima & Comans, 1997).

The release of Na, K, and Cl leaching curve until L/S 100 is mainly attributed to readily soluble compounds. Researchers have found a large correlation between the temporary increase in pH values due to the release of Na and K in the form of soluble chloride salts such as sylvite (KCl) and halite (NaCl), which have a weak fixation effect of cement (Hyks et al., 2009; Li et al., 2018). In regards to cement performance, alkalis (Na_2O and K_2O) are the most soluble constituents and are assumed to leach relatively early, leaving $Ca(OH)_2$ and/or C-S-H gel to buffer the aqueous pH (Glasser, 1997). Contrarily to Na, the higher concentrations of K could be a result of cation exchange processes or the dissolution of aluminosilicate minerals (Ex: K-mica for K). Furthermore, a relationship between organic chlorides such as NaCl and CaCl should be considered in the initial stages of leaching as studies have shown that their dissolution increases the leaching rate of Cr, further supported by the relatively large initial release of T-Cr at L/S 0.5 of around 1.40 mg/L, and then quickly decreasing to minimal amounts (Yin et al., 2017).

The relatively high initial release of T-Cr was observed, and the concentration was approximately 1.40 mg/L at an L/S ratio of 0.5. This might be explained by the rapid dissolution of soluble salts such as NaCl, KCl, and $CaCl_2$ during early leaching stages (Yin et al., 2017). Dissolution promotes the decomposition of hydration products, encouraging solidified Cr to redissolve into leachate, resulting in high T-Cr concentrations initially (Wang et al., 2022). As shown in Figure 2, the major concentration release of other heavy metals was observed in the initial L/S ratios and subsequently decreased relatively small and below the limits of detection (0.1 μ g/L). In contrast, Pb and Zn showed occasional concentration increases from L/S 100 to L/S 900. It is important to note that while heavy metal concentrations were released, the concentrations can be diluted in the natural environment during rainfall events, reducing the risk of groundwater contamination (Ahmed et al., 2019; Boum-Nkot et al., 2023; Karunanidhi et al., 2022). An analysis of the rain intensity and equivalent water injection rate into the column revealed that at L/S 1000, approximately 170 years' worth of water had flowed through the column. Based on the results of our experiment, the leaching ratios of T-Cr, Pb, Zn, and Cu from SFA-F material used as road base was found to be 12%, 27%, 0.1%, and 5%, respectively. With the SFA-F material used as a road base maintaining alkaline conditions, it is expected that heavy metal concentrations will not be significantly released even after 170 years of use.

4. Conclusions

This chapter investigated the long-term evolution of leachate characteristics and heavy metal fixation of recycled roadbed material using ash from industrial waste incineration of waste tires and biomass (SFA-F). The SFA-F material exhibited a

strong heavy metal binding effect, confirmed through the low leaching rates in the long term according to the column leaching test. To further reduce the release of hazardous heavy metals, a pre-washing step is recommended before utilization. Further studies are needed to evaluate its sustainability as a safe aggregate resource by considering the numerical simulation of hydraulic parameters and contents of mineral phases required for a prediction of leachate quality from recycled materials.

Table 4.1. SFA-F column leaching test setting conditions.

Average Dry weight	[gr]	300
Average height	[cm]	20
Bulk density in Column	[gr/cm^3]	1.09
True density	[gr/cm^3]	0.97
Initial Flow speed	[ml/hr]	30

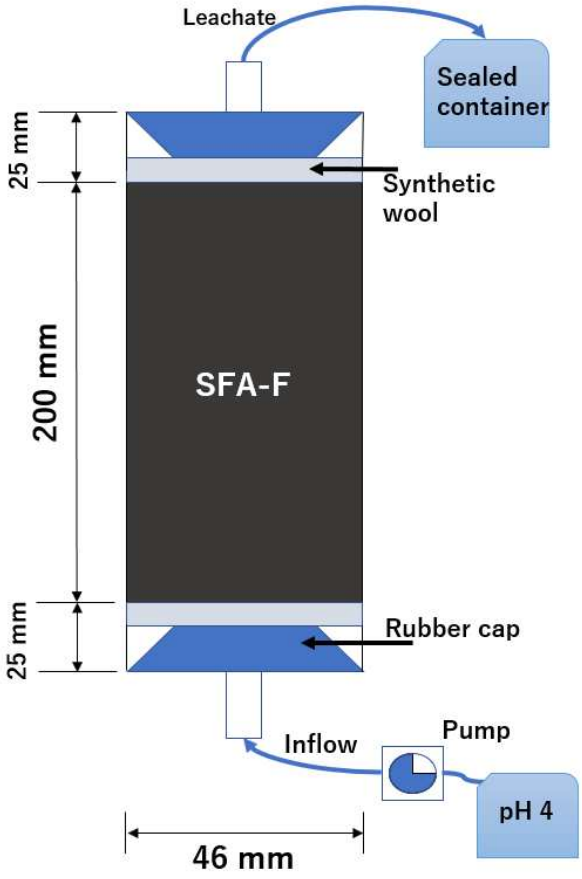

Figure 4.1. Visual description of the column setup with SFA-F

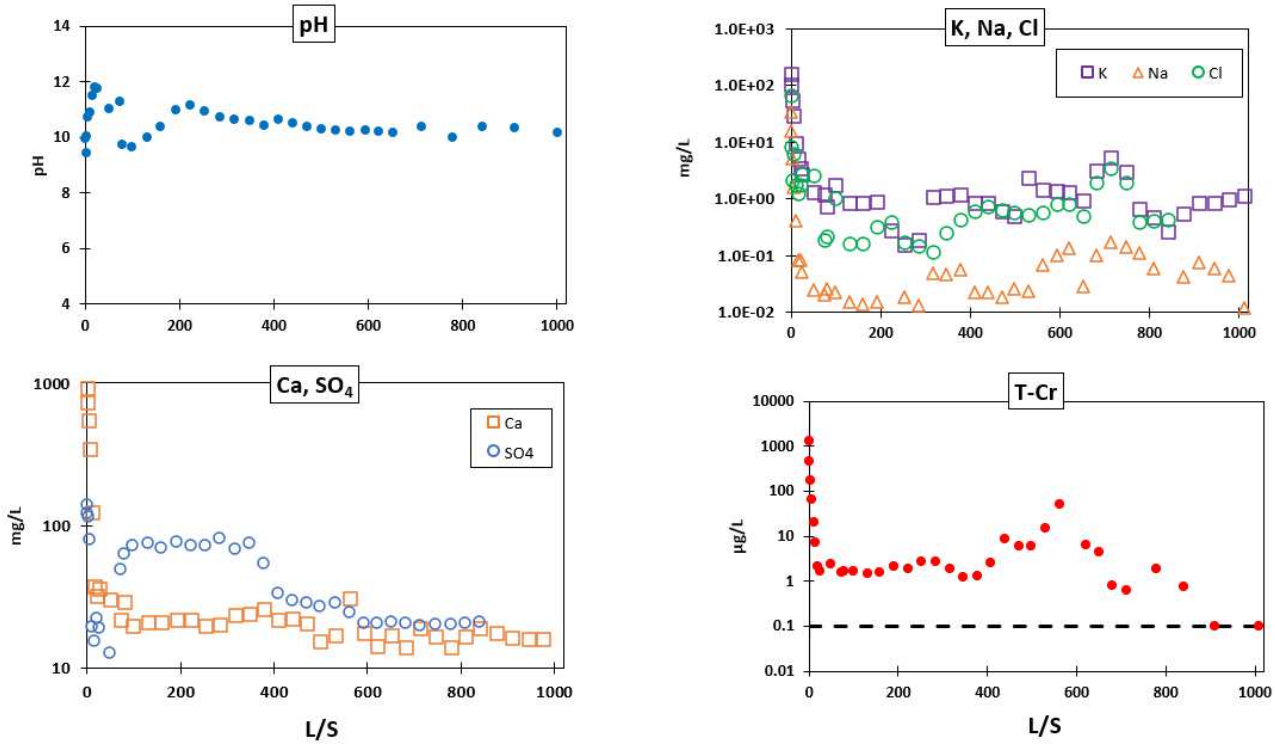

Figure 4.2. pH, and solution concentrations of Na, K, Cl, Ca, SO4, and, T-Cr, as a function of L/S ratio measured from the SFA-F column leaching test. The limit of detection by ICP-MS (0.1 μg/L) is represented by the dotted line.

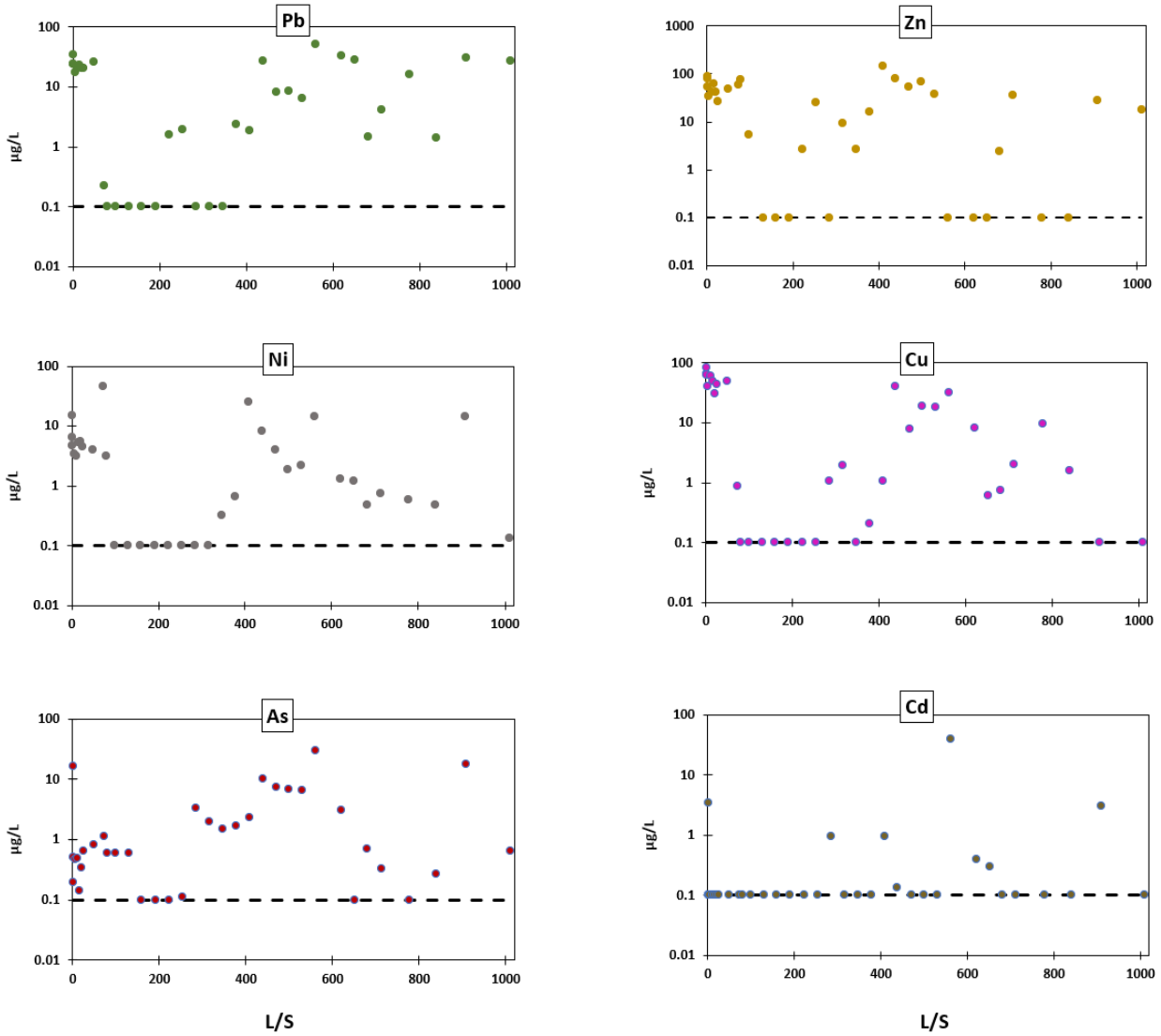

Figure 4.3. Concentrations of heavy metals as a function of L/S ratio measured from the SFA-F column leaching test. The limit of detection by ICP-MS (0.1 μ g/L) is represented by the dotted line.

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5. Modeling

5.1 Objective

This chapter aims to predict the mineral speciation of SFA-F minerals and simulate the pH behavior and the release of major components (Ca, K, Na, and Cl) of the column leaching test results (Chapter 4) with numerical modeling tools. Primarily, the most representative mineral phases of SFA-F were estimated using the geochemical model PHREEQC. Consequently, using HYDRUS 1D software, specifically the HP1 component the water flow and solute transport by mineral dissolution in the column tests was simulated. Two different modeling approaches were evaluated to obtain the fit between measured and simulated data. Additionally, to identify the major component release mechanism in each model three different cases representing a liquid and solid phase were applied. Furthermore, the modeling approach utilizes the results of column leaching experiments, batch leaching tests, and total content to monitor the long-term leaching of major components to assess the heavy metal mobility in SFA-F.

5.2 Research method and materials

5.2.1 Modeling Concept

The approach undertaken in this study aimed at numerically simulating the evolution of pH by considering the solute concentrations leached out during the column leaching test. The calculation code HP1 (v 4.17) which results from the coupling of HYDRUS-1D (Šimůnek and Genuchten, 2008) and PHREEQC (Parkhurst & Appelo, 1999) calculation codes was used. Using HP1 allows the simulation of water flow and solute transport in variably saturated medium and can consider mineral dissolution to represent the column leaching conditions. The geometry of the column was represented using a 1D model, and mineral dissolution along with solute transport was evaluated by a single and dual-porosity model. Modeling of the leaching behavior of ions leached out from the column experiment was evaluated by considering a liquid phase in which ions are already dissolved and a solid phase represented by minerals that when dissolved release ions. In this study, 3 different cases were evaluated. In Case 1, the ions leached out from the column were presented in the initial solution as ions. In Case 2, the ions leached out from the column were presented as mineral phases in the system. In Case 3, the ions leached out from the column were presented evenly between the initial solution and the mineral phases. All 3 cases were applied in both single and dual porosity models. Figure 5.1 shows the visual conceptualization of each case evaluated for the leaching of ions.

5.2.2 Mineral Speciation

Geochemical speciation of the representative mineral phases in the SFA-F sample with the column leaching conditions (Chapter 4) was estimated using PHREEQC. The input concentrations for PHREEQC were determined by considering the pH values and the molar concentrations of Ca, Na, K, Mg, Cl^-, SO_4^{2-}, Si and Al ions leached out by the column experiment at the initial L/S eluate ratio of 0.5. The leached-out amounts were assumed to be in the initial volumetric liquid phase of the column. Potential solubility-controlling minerals and concentrations were selected based on (1) previous modeling studies on raw fly ashes and cement-solidified fly ashes (Astrup et al., 2006; Du et al., 2018; Gonzalez et al., 2019; Hyks et al., 2009; Santiago et al., 2022); (2) mineralogical analysis and batch leaching tests concentration data; (3) mineral saturation indices (SI) computed by PHREEQC; and (4) total content concentration of major components. A manual trial-and-error approach was utilized to obtain the specific amounts of minerals as input in HP1. This involves calibrating the

mineral assemblage and concentration values by modeling the pH evolution of the column leaching test across various L/S ratios.

5.2.3 Reactive transport model in saturated conditions

The following approach was undertaken in this study aimed at numerically simulating the water content and the evolution of solute concentrations in the column leaching test from start to finish. The calculation code HP1 v 4.17 was used (Jacques et al., 2008; Jacques and Šimůnek et al., 2006). The process of mineral dissolution and the movement of solutes were modeled using a single and dual-porosity approach. A single porosity model is based on the description of uniform flow and transport in porous media. In this model, the porous medium is viewed as a collection of impermeable particles, separated by pore or fractures through which flow and transport takes place. Variably saturated water flow through such porous system is usually described using the Richards equation and solute transport using the classical advection-dispersion equation (Šimůnek & Genuchten, 2008). On the other hand, the dual porosity model considers a mobile and immobile phase. The mobile phase represents rapid water flow through the column, whereas the immobile phase depicts a "stagnant flow" component of the column. The solute can move into the immobile phase of the dual porosity model by both molecular diffusion and advection with flowing water and using a first-order rate process (Šimůnek & Genuchten, 2008). Figure 5.2 illustrates the visual representation of the concept of both models. In this study, specifically, the mobile phase accounted for 70% of the column's volume, while the immobile phase was considered to occupy the remaining 30% of the volume of the column (Fellner et al., 2009). The values of mass and water transfer parameters between the immobile and mobile regions were estimated based on values used in previous studies (Ali et al., 2021; Blackmore et al., 2018; Ma & Shao, 2008; Tremosa et al., 2020; Zhang et al., 2013).

5.2.4 Boundary and initial condition parameters

Water flux and boundary conditions were set equal to the inflow solution conditions for the column leaching test. A constant flux in a downward direction of -16277.1 cm/year was set as the upper boundary condition. In simulations with Hydrus, the column profile was represented with 21 nodes of equal length to reduce computation time. To describe saturated conditions from the start of the simulation to the end, a pressure head of -100 was set which equals the measured saturated water content of SFA-F. The concentrations of ions in solution and minerals were given as initial conditions and distributed in all 21 nodes. In the dual porosity model, the values of water transfer parameters were estimated based on values taking taken from the literature (Ali et al., 2021; Blackmore et al., 2018; Ma & Shao, 2008; Tremosa et al., 2020; Zhang et al., 2013). These parameters were estimated based on the difficulty and/or impossibility of direct measurement. The values of the hydraulic parameters for the single and dual porosity are summarized in Tables 5.1 and 5.2.

5.3. Results and discussion

5.3.1 Mineral speciation

The major ion component concentrations as an initial solution input into PHREEQC are described in Table 5.3. The presence of minerals in SFA-F was evaluated with the respective SI (Table 5.4). Ca minerals such as anhydrite ($CaSO_4$), and gypsum ($CaSO_4 \cdot 2H2O$) could exist in SFA and might be important pH-buffering minerals (Hareeparsad et al., 2011; Hyks et al., 2009). In addition, calcite ($CaCO_3$) and K-feldspar $KAlSi_3O_8$ were minerals in SFA. The significantly low

leaching of heavy metals specifically Pb and Cd, in the column leaching test could be attributed to their direct binding to calcium silicate minerals. Chen et al.(2009) reported that heavy metals such as Zn^{2+}, Cd^{2+}, and Pb^{2+} can form hydroxides and can deposit calcium silicate minerals. Calcium aluminum silicate minerals were detected in SFA-F through XRD analysis and leaching concentrations from the column test also show a high probability of the presence of these minerals via estimates of minerals performed with PHREEQC. Although the concentrations of As were detected throughout the entire L/S range, the slow solubility of ettringite, which studies have found to have a strong affinity to oxyanions such as As could explain the binding process into a solid phase. Furthermore, the overall low solubility of heavy metals can be attributed to the precipitation of carbonates, sulfates, and silicates. These species are present in high concentrations in the cement matrix of the SFA-F.

5.3.2 Column leaching modeling results

5.3.2.1 Single porosity model

In general, using case 2 with a solid phase represented by a mineral assemblage provided the best-fitting curves between measured and simulated data for the single and dual porosity models. Cases 1 and 3 were not suitable since HP1 only considers the liquid phase for the calculations and the ions of major components were immediately released from the column. Figure 5.3 shows the results of the three different cases using the single porosity approach to simulate the release of major components and the evolution of pH. The case 2 modeling results showed a reasonable fit between measured and model data for pH, Ca and SO_4 Na, and K. On the other hand, the concentrations of Cl were quickly dissolved, and concentrations of ions were fully depleted from the column at the beginning of the simulation. Table 5.5 shows the mineral assemblage with SI values and concentrations to represent the mineralogy of SFA-F that could control the release of major components through the dissolution process. The Long-term pH buffering mineral identified in case 2 results was mainly Ettringite, other calcite minerals were dissolved.

5.3.2.2 Dual porosity model

Focusing on applying the case 2 approach, the pH behavior was well simulated by applying a dual-porosity modeling approach using portlandite, ettringite, gypsum, and calcite as pH-buffering minerals (Figure 5.4). The leaching behavior of Ca and SO_4 can also be described by the mineral assemblage. Although the levels of K were modeled relatively high to the measured data, an adequate trend was observed. The leaching concentrations of Na followed the simulated curve quite well. Although there is no major difference between mineral assemblage and concentrations the release of Na in single porosity is better described with the addition of Albite which is a hardly soluble phase. In the case of K, it could be contained in more complex minerals or combined with hardly soluble phases present in the cement matrix of the SFA material. Although the information regarding solute transport is scarce and simple values were used, the results provided useful insight into the leaching mechanisms of the SFA material in the long term. Due to the alkalinity of the material being kept at high L/S ratios, significant amounts of heavy metal were immobilized. The mineral assemblage and concentration amounts presented in Table 5.6 indicate a stable dissolution maintaining an alkaline condition for an extended period. Considering the saturated condition and the pH of the inflow solution, the pH is maintained constant for more than 500 years in relationship to the L/S ratio. Modeling results can provide insights into the long-term stability of SFA-F material, and in this case, the depletion of some pH buffering minerals may take more than 500 years in a real-life scenario. Therefore, the model suggests that

SFA-F material can maintain its effectiveness as a pH buffer for an extended period, making it a viable candidate for various environmental applications.

5.4 Conclusions

This chapter explores the long-term evolution of leachate characteristics through numerical modeling of recycled roadbed material using ash derived from the industrial incineration of waste tires and biomass (SFA-F). The elution curves of various major components obtained from column leaching experiments exhibit distinct shapes, but the Dual-porosity approach proves to be a more suitable description of their release compared to the single-porosity approach. The numerical simulation demonstrates that the pH profile is primarily influenced by the dissolution and precipitation of calcium minerals, such as portlandite, ettringite, gypsum, and calcite. The SFA-F material shows great promise as a candidate for roadbed construction, offering potential benefits in terms of reduced reliance on natural aggregates. To further evaluate its sustainability as a safe aggregate resource, additional studies should consider different scenarios in the numerical simulation, including unsaturated conditions. Conducting sensitivity analysis on different combinations of hydraulic parameters and mineral phase contents is necessary to improve the accuracy of leachate quality prediction from recycled materials using HP1.

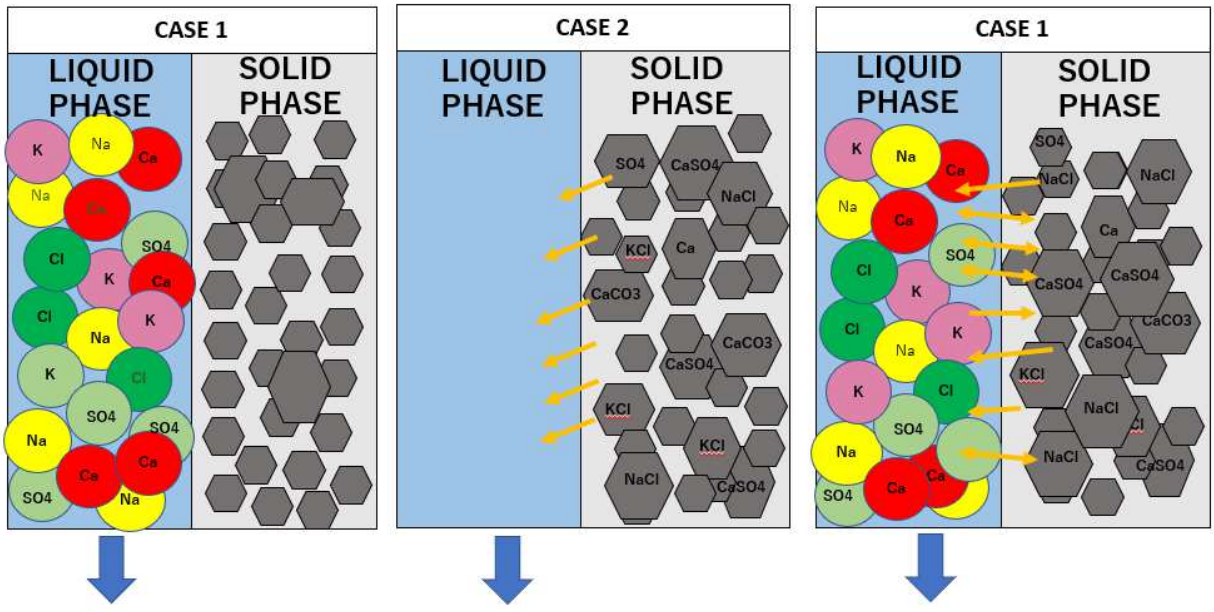

Figure 5.1 Visual conceptualization of the 3 cases representing the leaching mechanisms of ions from the column experiment. Dissolved "free ions" are represented by circles and solid phase (minerals) are hexagonal shapes.

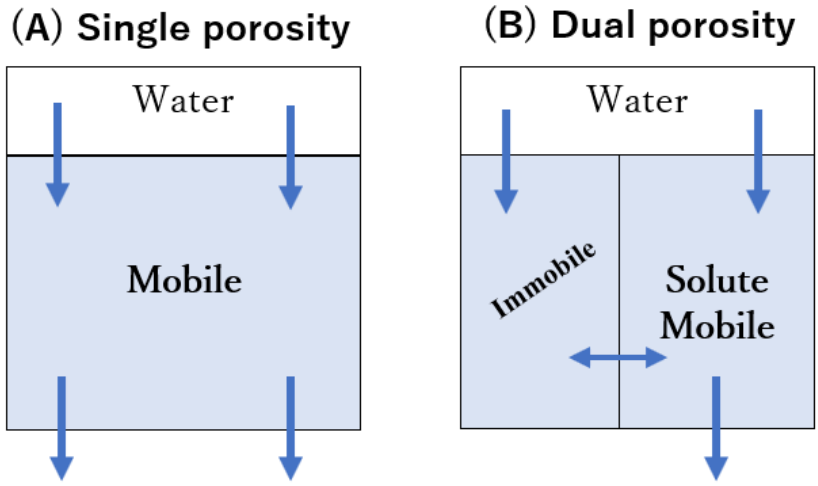

Figure 5.2. Conceptual models of single and dual porosity

Table 5.1. Hydraulic parameters and initial condition of the single porosity model

Water content and retention characteristics				Hydraulic conductivity		Column profile
θ_r [-]	θ_s [-]	α [1/cm]	n [-]	K_s [cm/year]	L [-]	Initial pressure head [-]
0.31	0.54	0.03	2.0563	16277	1	-100

Table 5.2. Calibrated water flow parameters of the mobile and immobile (Im); water and mass transfer.

Water content and retention characteristics						Hydraulic conductivity		Water and mass transfer		Column profile
θ_r [-]	θ_s [-]	θ_r Im [-]	θ_s Im [-]	α [1/cm]	n [-]	K_s [cm/year]	L [-]	Omega [1/year]	Γ_s [T^1]	Initial Pressure Head [-]
0	0.378	0	0.16	0.03	2.0563	16277	1	1	1	-100

Table 5.3. Initial solution concentrations of major element components for the column leaching mineral speciation input solution in PHREEQC.

Element	Ca	Na	K	Mg	Cl	SO_4	Si	Al
Concentration (mmol/kgw)	21.0	1.32	3.66	3.03×10^{-3}	1.70	1.32	2.20×10^{-1}	9.0×10^{-4}

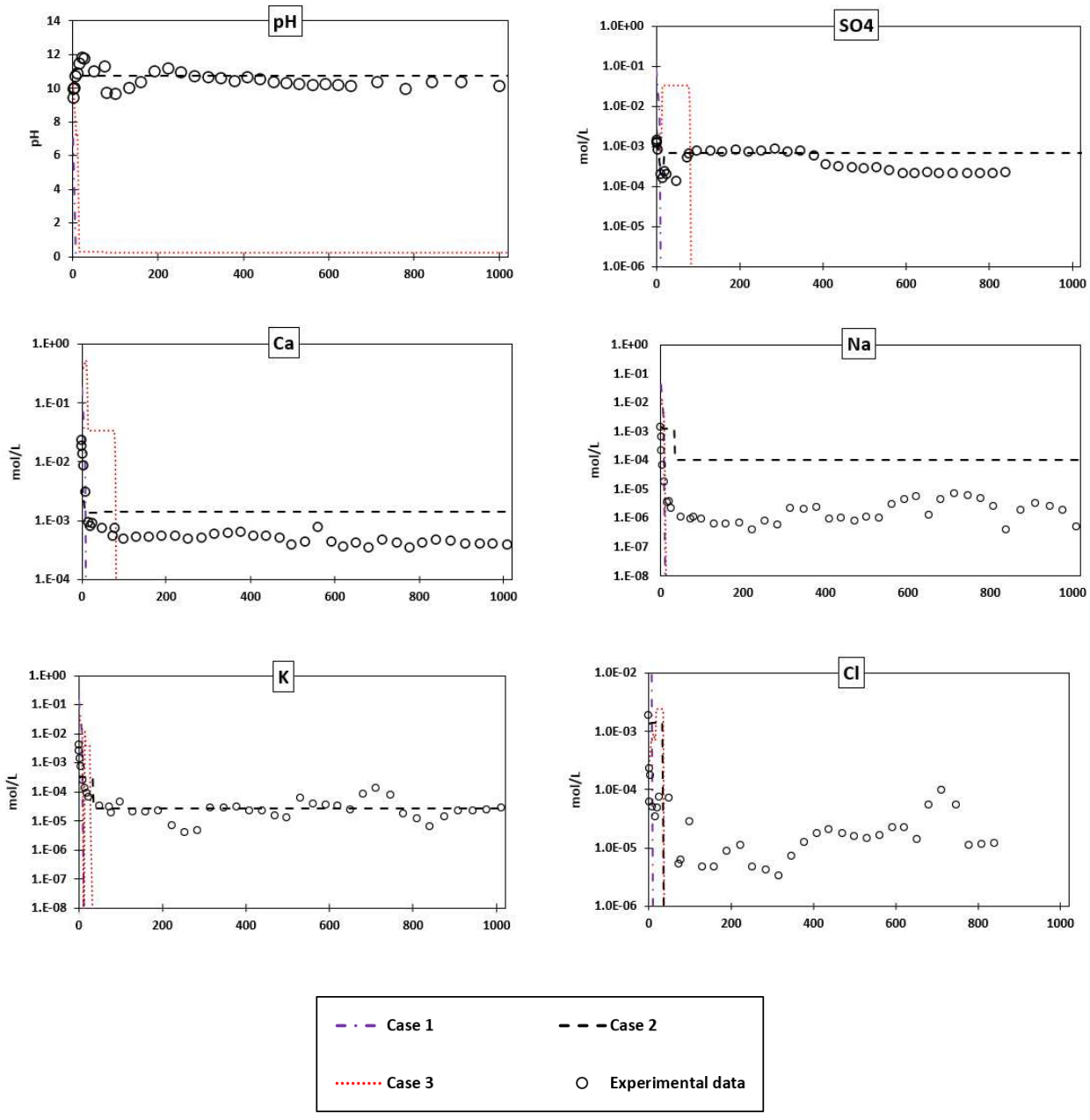

Figure 5.3. Modeling results of single porosity modeling using three different cases. Experimental data in figures are represented by points while model simulations are expressed in the form of associated lines (see legend).

Table 5.5. Mineral assemblage, saturation indices (SI) and concentration amounts input into HP1 for the single porosity model.

Mineral phase	Chemical formula	SI	Concentration (mmol/cm^3)
Halite	NaCl	-7.39	$9.2x10^{-3}$
Sylvite	KCl	-6.21	$3.3x10^{-2}$
Gypsum	$CaSO_4 \cdot 2H_2O$	-0.91	$1.4x10^{-3}$
Calcite	$CaCO_3$	-0.89	$1.9x10^{-1}$
Portlandite	$Ca(OH)_2$	-3.34	$9.8x10^{-3}$
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	-8.89	$8.1x10^{-1}$
Antarcticite	CaCl2:6H2O	-11.81	$1.9x10^{-6}$
K-Feldspar	$KAlSi_3O_8$	1.14	$3.4x10^{-1}$
Albite	$NaAlSi_3O_8$	-2.33	$3.7x10^{-1}$

Table 5.6. Mineral assemblage, saturation indices (SI) and concentration amounts input into HP1 for the dual porosity model.

Mineral phase	Chemical formula	SI	Concentration (mmol/cm^3)
Halite	NaCl	-7.39	$2.9x10^{-2}$
Sylvite	KCl	-6.21	$3.2x10^{-2}$
Gypsum	$CaSO_4 \cdot 2H_2O$	-0.91	$8.1x10^{-3}$
Calcite	$CaCO_3$	-0.89	$1.7x10^{-1}$
Portlandite	$Ca(OH)_2$	-3.34	$8.8x10^{-3}$
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$	-8.89	$7.9x10^{-1}$
Antarcticite	CaCl2:6H2O	-11.81	$8.5x10^{-3}$
K-Feldspar	$KAlSi_3O_8$	1.14	$3.3x10^{-1}$

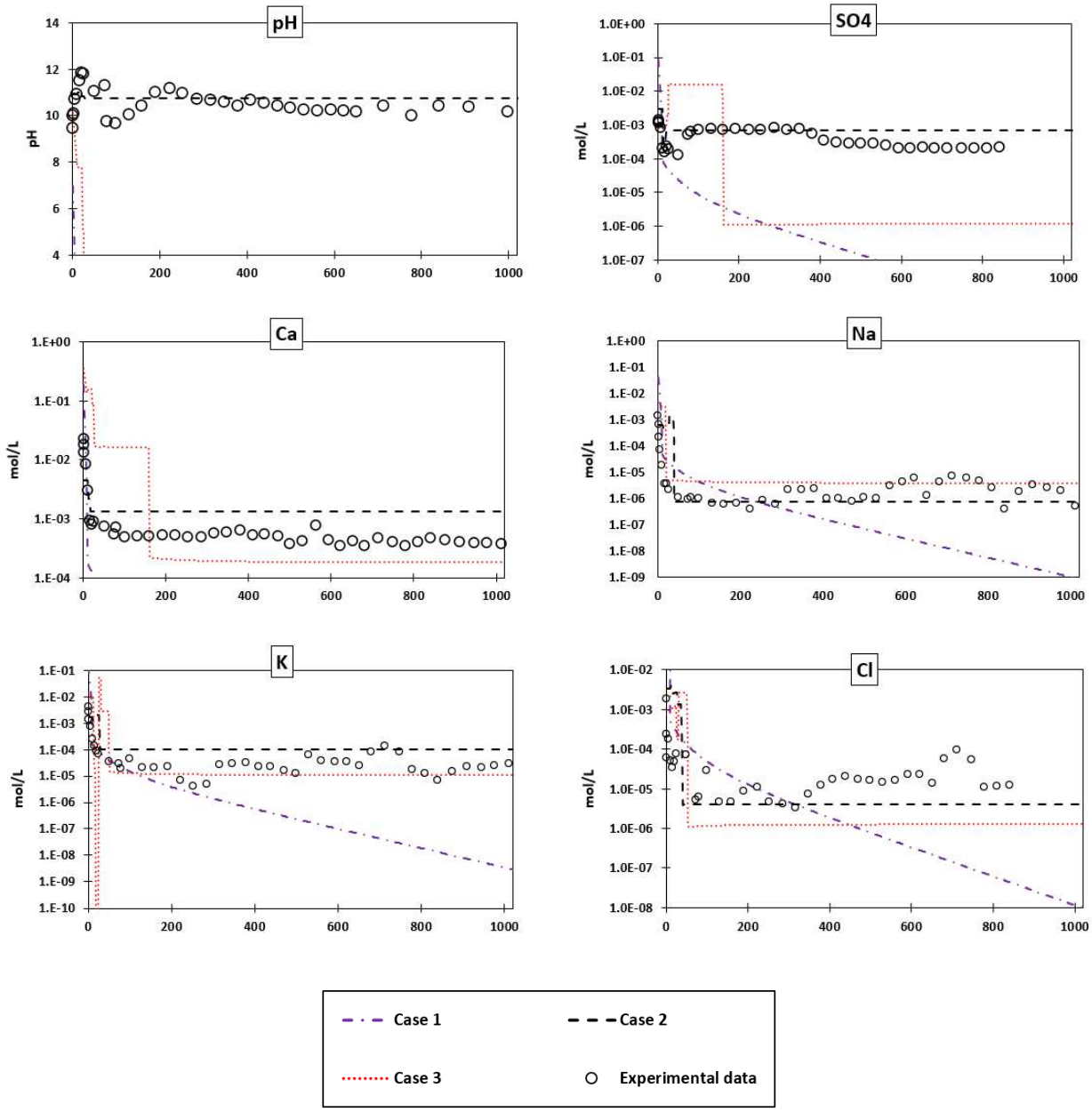

Figure 5.4. Modeling results of dual porosity modeling using three different cases. Experimental data in figures are represented by points while model simulations are expressed in the form of associated lines (see legend).

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6. Conclusions

This study deals with the evaluation of a recycled material composed of industrial waste incineration boiler fly ash solidified with cement. The findings of this study are presented in 5 chapters. Chapters 1 and 2 discuss the importance of this study and by conducting an extensive literature review, it was determined that although waste incineration ashes are suitable for recycling in civil engineering applications, there is a need to study the long-term effects of using the materials in the natural environment regarding heavy metal pollution. In this study, we investigated the long-term evolution of leachate chemistry, mineralogical transformation, and heavy metal fixation performance of recycled roadbed material using ash from industrial waste incineration of waste tires and biomass (SFA). Additionally, field samples from a 5-year pilot test site utilizing SFA were also investigated. The change in mineral composition, element content, and leachability of heavy metals between the SFA and field samples was determined. Furthermore, a column leaching experiment was conducted for over 20 months to monitor the long-term leaching of major components and heavy metals from SFA. Finally, profiles of pH and major ions in leachate from the column leaching experiment were simulated by HYDRUS HP1.

Chapter 3 discusses the effectiveness of cement solidification in preventing the release of hazardous heavy metals from boiler fly ashes (BFA). The study confirms that the fresh solidified fly ash (SFA-F) material has a strong binding capability for heavy metals, primarily due to the solubility of minerals in the cement matrix. The recommended mixing ratio for SFA production is supported, suggesting its suitability for safe disposal in non-hazardous waste landfills and recycling applications. Additionally, the SFA-F material shows potential for use in roadbed construction, reducing the need for natural aggregates. The combination of cement mixing and the pozzolanic properties of BFA improves the immobilization of heavy metals. Further investigations, such as geochemical modeling, are recommended to assess the leaching potential of SFA recycling and long-term disposal scenarios. These findings will aid in the management of incinerated materials, including fly ash from waste tire incineration.

Chapter 4 focuses on investigating the long-term behavior of leachate characteristics and heavy metal fixation in recycled roadbed material made with ash from industrial waste incineration of waste tires and biomass (SFA-F). The study confirms the strong binding effect of SFA-F on heavy metals through low leaching rates observed in long-term column leaching tests. The paragraph also suggests that a pre-washing step is recommended to further reduce the release of hazardous heavy metals. The need for further studies is emphasized to assess the sustainability of SFA-F as a safe aggregate resource, considering numerical simulations of hydraulic parameters and mineral phase contents to predict leachate quality from recycled materials.

Finally, chapter 5 explores the long-term evolution of leachate characteristics in recycled roadbed material made with ash from the industrial incineration of waste tires and biomass (SFA-F) through numerical modeling. The elution curves obtained from column leaching experiments suggest that the Dual-porosity approach is more appropriate for describing the release of major components compared to the single-porosity approach. The numerical simulation highlights the significance of calcium minerals, such as portlandite, ettringite, gypsum, and calcite, in influencing the pH profile. The SFA-F material is considered a promising option for roadbed construction, offering potential advantages in reducing the

reliance on natural aggregates. To further assess its sustainability as a safe aggregate resource, additional studies should incorporate different scenarios in the numerical simulation, including unsaturated conditions. Conducting sensitivity analysis on various combinations of hydraulic parameters and mineral phase contents is necessary to enhance the accuracy of predicting leachate quality from recycled materials using HP1.