Study on volume reduction and leaching of plastic-related waste treated by pyrolysis technology

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A dissertation submitted to the Faculty of Engineering of

Kyoto University in partial fulfillment of the requirements for

Doctoral Degree in Urban Management

by

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Kyoto University, Japan
2023

Abstract

As a result of global development in every aspect of life, generated amount of waste is increasing day by day which is challenging. Moreover, the composition of waste is getting more complex with technology development on modern materials. Consequently, each section of waste field contains various plastics and generates problems in waste management. This is not the only issue, but volume of these types of plastic-related wastes is increasing due to the consumer demand. It is impossible to landfill all these wastes due to the space limitations. There are various types of challenging plastic-related wastes however because of the time restrictions for the research, only three types of plastic-related wastes were chosen from different waste streams, namely, industrial, disaster and municipal waste streams. First of all, industrial mixed plastic waste is the major concern for many companies that manufacture furniture, home appliances, vehicle and electronics that contain various additives and polymers which makes plastic difficult to recycle and significant amount of industrial mixed plastic waste is annually generated due to the modern consumption pattern of people. Secondly, post-natural disaster waste is significantly considered in Japan since 2011 earthquake of the Pacific coast of Tohoku and subsequent tsunami. As a result of natural disasters, significant amount of mixed waste is generated in a very short time which requires proper waste management. Lastly, disposable diapers for children and adults are popular among parents and nursing houses due to its convenience. In Japan, used diapers are discarded as municipal solid waste and it generates dioxins during combustion which is more dangerous. Increase in Japanese production of disposable diapers due to the increased average life expectancy indicates the importance of handling used diaper waste in a sustainable way. Therefore, plastic-related wastes such as mixed plastic, soil mixed with waste and disposable diaper were chosen as materials of interest due to their generated significant volume and environmental impacts.

Respectively, various technologies are developed in order to manage waste in a proper way. Even though every method has its advantages, there is a negative impact on the environment by the same method. Landfilling does not require much effort on treatment; however, landfilling is uncommon practice in many countries with limited space due to dense population. Incineration is strong method to sanitize and reduce volume of waste material while harmful emissions such as dioxins and carbon dioxide are the great concern. Among all methods existing today, recycling is the best option in terms of environmental sustainability; however, it is expensive and labor consuming compared to the quality of gained recycled materials and not every material can be recycled. Therefore, it is very important to practice sustainable waste treatment method that reduces environmental impacts of harmful emissions, decreases waste volume in the landfills and decomposes plastic forever. Thus, recently, significant attention is directed towards pyrolysis. Pyrolysis technology is a promising thermal method with the complete decomposition of plastic waste without harmful emissions while significantly reducing volume of waste without sorting and cleaning. Previous studies pointed out that carbon dioxide emission during pyrolysis is twice smaller than incineration which indicates its superiority over incineration. Moreover, as a results of pyrolysis thermal treatment, energy is generated in the forms of pyrolysis oil and gas. Generated pyrolysis oil can be used for plastic production as a feedstock and also used for the next pyrolysis treatments that helps to preserve natural fuel resources which is one of the main advantages of pyrolysis. In addition to pyrolytic oil and gas, waste plastic pyrolysis also yields solid char, as a by-product, which does not find wide applications and is simply ignored. Previous studies focused on the effects of operation temperature, heating rate, and catalysts on the pyrolysis oil yield. However, there is a gap on investigations of pyrolytic char from plastic wastes and its utilization. Therefore, it is very important to investigate pyrolysis ash and its possible utilizations. In this study, char yielding pyrolysis method on three types of plastic-related wastes were considered in this research with the aim of reducing amount of plastic waste that going to landfills.

Most of the time even treated materials end up at landfills which leads to the next challenge of treated waste material utilization. A key issue related to this is leaching behavior of thermally treated waste materials during utilization. Leaching characterization is very important when treated waste material is used as geo-material that has direct contact with soil and groundwater. Therefore, the main purpose of this study is investigating volume reduction and leaching characteristics of three plastic-related waste materials treated with pyrolysis technology with the aim of eliminating amount of plastic waste that going to landfill.

In case of the mixed plastic, high-temperature steaming was used as pretreatment for pyrolysis technology in order to separate metal parts from main plastic. Then, all three samples were thermally treated with pyrolysis technology at 600°C for 3 hours. Weight and volume reduction of the samples were investigated. Volume and weight of mixed plastic were reduced by 6 times. Volume of soil mixed with waste was reduced by 3/10 while weight was reduced by 3/7 which were the least reduction ratios among the samples due to the soil contained in the waste. The highest reduction ratio was occurred in disposable diaper both in volume and weight that are 7/1000 and 3/200, respectively.

Since chemical changes occur in the materials due to the high temperature and chemical reactions during pyrolysis treatment, pyrolyzed materials were subjected to basic mechanical property tests, thermogravimetric and compositional analysis in order to study effectiveness of pyrolysis technology. Regarding with the sieve analysis results, waste materials, industrial mixed plastic and soil mixed with waste, were classified as sandy soil with fine fractions and represent gap graded grain size distribution curve. However, fine particle fraction of disposable diaper is significantly high in thermally treated disposable diaper sample, which is equal to 90.4%. Compaction characteristics of samples are similar to previously utilized fly ash and bottom ash resulted from coal and municipal solid waste incineration by other scientists.

From thermal analysis it was found out that all three samples have different pattern of thermal degradation. According to the TG-DTA curves it was determined that mixed plastic contains PVC. Values of residual weight fractions for mixed plastic and disposable diaper were calculated to be about 20% and for soil mixed with waste is 75%. From XRF data, in all three samples high decrease of carbon is observed due to decomposition of polymer molecules. However, carbon is the component with highest concentration compared to the other elements.

Batch leaching test results indicated that leached concentrations of Cd, Cr and Pb are very low. Cd was not detected in disposable diaper, while Cr and Pb were not detected in mixed plastic and soil mixed with waste samples due to the detection limits of ICP-MS. However, As and Se leaching amounts in mixed plastic and disposable diaper waste materials are higher than JLT-46 limit values. Also noticed that leaching amounts of As and Se for both samples are higher than JLT-46 limit values in all pH range as well.

Titration of samples with acid or base showed disposable diaper sample represents higher acid neutralizing capacity compared to other two samples. It was concluded with the higher concentrations of alkali metals (Na, K) and alkaline earth metal (Ca) contents. Ca and Cd leaching behavior as a function of pH represents a cationic pattern where the solubility gradually decreases as pH increases. Leaching amount and total content of cadmium in soil mixed with waste and disposable diaper waste are smaller than the JLT-46 limit values over the pH range, respectively which indicates no Cd leaching harm occurs when these two samples are utilized in the actual field. Leaching behavior of As, Cu, Zn, Cr, Al and Mn represent amphoteric pattern which represents characteristic V-shaped curve in all three samples. Even though total content of As in diaper is the smallest among three samples, it shows highly leachable behavior. Leaching behavior of B is poorly influenced by pH.

According to the obtained leaching results, utilization of soil mixed with waste is possible for geotechnical purposes with pH range between neutral and slightly alkaline conditions. In terms of leaching characteristics, countermeasures for leaching of As and Se in mixed plastic and disposable diaper waste materials should be considered such as stabilizing with binder materials or using attenuation layers.

Acknowledgements

Undertaking this PhD has been a truly life-changing experience for me and it would not have been possible to do without the support and guidance that I received from many people.

I acknowledge a great debt of gratitude to my academic supervisor, Professor Mamoru Mimura, Geofront System Engineering Laboratory, Department of Urban Management, Kyoto University, for his academic and personal support, scientific advice, encouragement, patience and continuous support throughout the study.

I deeply appreciate Professor Takeshi Katsumi, Professor Ryosuke Uzuoka and Associate Professor Hiromasa Iwai for their valuable advice and recommendations to strengthen my research outcome.

My gratitude extends to former Assistant Professor of Geofront System Engineering Laboratory, Mai Sawada, for her teaching, academic guidance and support.

I would also like to give special thanks to Catalyst.co LTD members: Mr. Toru Kubota, Mr. Koji Yamakawa, Mr.Tanaka and Mr. Tokuhide.

I would like to express my gratitude to Secretary Ms. Chikako Itou for her administrative support, genuine kindness and care.

I gratefully acknowledge Professor Masaki Takaoka, Doctor Sylwia Oleszek and Nguyen Thi Thuong, technician Kenji Shiota from Environmental Engineering Laboratory for helping to conduct analytical experiments in XRD, XRF, TG, ICP-MS and ICP-AES.

I acknowledge and express my deepest gratitude to my former scientific supervisor and mentor Professor Askar Zhussupbekov from Eurasian National University, Nur-Sultan, Kazakhstan for his professional and personal advice and support.

I expresses my gratitude for my Japanese host-mother Mrs. Michiko Koyanagi for her kindness, support as a host family and help to learn and experience Japanese culture and hospitality through interesting conversations and visits to the unique places in Japan.

I would like to express my appreciation to Japanese language teacher Mrs. Tanimizu Satomi for teaching Japanese language voluntarily and helping to learn Japanese culture.

I acknowledge and expresses my special gratitude to my parents, siblings and husband for providing moral and emotional support throughout the study.

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Chapter 1 Introduction

1.1 General remarks

Urbanization and industrialization, living standard and consumption pattern of humanity has altered due to the increase in global population and economic development. In turn, it leads to the high levels of municipal solid waste and industrial waste generation that threatens environment without appropriate handling (Powrie and Dacombe, 2006; Demibras, 2011; Assamoi and Lawrysyn, 2012; Kawai et al., 2015; Kumar and Samadder, 2016; Nanda et al., 2020). In addition, all waste streams contain significant amount of plastic. Therefore, proper management and effective utilization for geotechnical purposes of plastic-related wastes are significant geoenvironmental and geotechnical challenge due to generated huge volume, developing effective treatment and leaching properties of waste materials when utilized.

Since an enormous space and an aeon is required for plastic to be fully degrade, the landfilling is inconvenient way to dispose plastic-related wastes. However, incineration causes a huge impact to the environment by releasing pollutants into the air. Therefore, in order to satisfy aforementioned purposes, such as reducing environmental impacts, decreasing waste volume in the landfills and decompose plastic forever, recycling and thermal recovering methods are considered (Syamsiro et al., 2014; Geyer et al., 2017). But, it is difficult to recycle plastic since it requires sorting and cleaning. In addition, most plastic wastes yield lower quality recycled materials which is economically inefficient. While plastic is challenging in some respects, it also offers an opportunity to generate energy and material resources by treating plastic waste with proper methods in a cost-effective manner (UNEP, 2009). Recently, significant attention is directed towards pyrolysis since it is efficient in many aspects of waste management and treatment. First of all, harmful emissions of dioxins and carbon dioxide are eliminated through pyrolysis since it is not combustion, but, thermal degradation of materials in the absence of oxygen. As the results of previous studies highlighted, pyrolysis emits half as much carbon dioxide as incineration which indicates its superiority over incineration. Secondly, volume of waste is significantly decreased by decomposing polymers into monomers. Moreover, energy is generated in the form of pyrolysis oil and gas. Pyrolysis oil is used for plastic production as a feedstock material or for the next pyrolysis treatment as an energy in order to preserve natural fuel resources. It is one of the main advantages of pyrolysis. In addition to pyrolytic oil and gas, waste plastic pyrolysis also yields solid char (from here terms “char” and “ash” are used interchangeably) as a by-product, which does not find wide applications and is generally discarded (Kumar et al., 2021). Since most studies focused on the effects of operation temperature, heating rate, and catalysts on the product yield of pyrolysis oil and gas, there is information gap on studies of pyrolysis ash and its utilization. Thus, it is very important to study pyrolysis char and its possible methods of utilization. Consequently, solid material yielding pyrolysis method on three types of plastic-related wastes and environmental behavior of pyrolyzed materials during utilization is studied in this research with the aim of reducing the amount of plastic waste going to be landfilled.

Selected three plastic-related wastes were pyrolyzed and investigated through volume reduction, basic mechanical property tests, thermogravimetric and XRF analysis in order to study effectiveness of pyrolysis technology. Volume reduction challenge is familiar for all three types of wastes (industrial mixed plastic, soil mixed with waste and disposable diaper) especially for diapers that increase in volume when it is wet after usage. Thus, volume and weight reduction tests were carried out in order to understand volume reduction of the original waste through pyrolysis thermal treatment. Moreover, understanding the behavior of research samples during pyrolysis thermal treatment and effectiveness of pyrolysis treatment conditions are important point to know. So, TG-DTA analysis was conducted to the original raw materials in the same condition of pyrolysis treatment. In addition, change in composition between original raw materials and thermally treated materials with pyrolysis of three samples were analyzed using X-ray fluorescence.

Even treated materials end up in the landfills due to dangerous composition of thermally treated wastes. Trying to find the way of utilization and confirming their environmental effects is very important to all types of waste. One of the potential applications of thermally treated waste materials is utilizing for geotechnical purposes. Materials resulted from thermal treatment commonly may contain heavy metals and hazardous elements, either passed down from the original waste or created during the treatment. As a result, potential environmental problems or issues such as groundwater and soil contamination by heavy metal leachates might occur. Therefore, it is required to characterize solid materials to assess their impact on the environment and humans (Czajczyńska et al., 2017). In order to reuse the thermally treated ash in geotechnical purposes, the hazardous metal content and leaching characteristics required to be determined and leaching results should meet the environmental quality standards for soil contamination. Any potential environmental issues ought to be predicted by considering received results (Zhang et al., 2016; Funatsuki et al., 2018). In order to utilize treated waste materials, these materials should satisfy Japanese regulatory leaching limits. Short-term leaching tests were conducted according to Japanese Leaching test method JLT-46 for soil. Even though leaching characteristics are defined with short term leaching test, it is unable to consider specific environmental conditions with pH dependency. Since external field conditions (low ionic strength rain fall, acid soil water, ground water, etc.) affect the leaching behavior of constituents in the ash, pH of the suspension is the key factor. Consequently, release of substances varies with different external pH scenarios and can be qualitatively predicted from pH dependent leaching tests conducted in the laboratory (Engelsen et al., 2012). The study focused only on inorganic substances: aluminum (Al), arsenic (As), calcium (Ca), copper (Cu), chromium (Cr), cadmium (Cd), zinc (Zn), manganese (Mn), selenium (Se) and boron (B).

The main objective of this study is to investigate volume reduction through pyrolysis and leaching behavior of pyrolyzed three plastic-related wastes. Three plastic-related wastes were chosen from three different waste streams, namely, mixed plastic from industrial waste stream, soil mixed with waste from disaster waste stream and diaper from municipal solid waste. In order to achieve this goal (1) pyrolysis technology was used in order to find solutions for volume reduction. (2) Effectiveness of pyrolysis method was evaluated with basic mechanical characteristics, TG-DTA and XRF analysis. (3) Batch leaching test and pH dependent laboratory test were carried out in order to evaluate leaching behavior of thermally treated materials with the future purpose of utilizing as a geo-material.

1.2 Organization of the dissertation

This dissertation consists of 5 chapters as illustrated in Figure 1.1. General background of the research is represented in Chapter 1. Theoretical framework and organizing principles on effectiveness of pyrolysis technology compared to other waste management methods and selected waste samples for pyrolysis treatment are presented in Chapter 2.

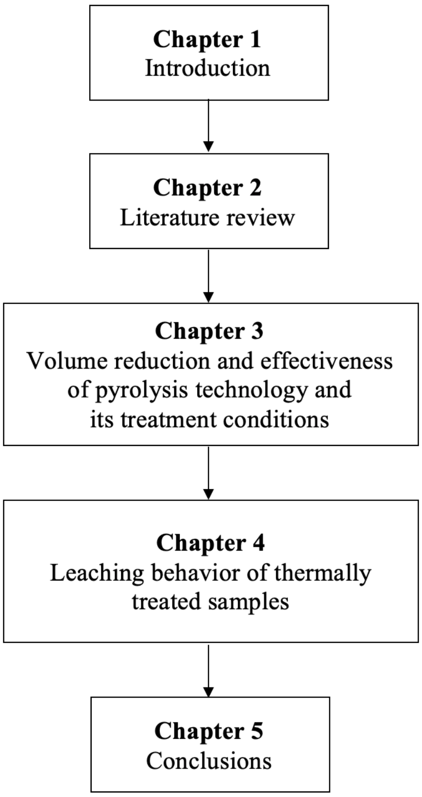

Figure 1.1: Structure and content of the dissertation

Investigations on volume reduction of three plastic-related wastes through pyrolysis technology and effectiveness of pyrolysis technology and its treatment conditions on three samples are studied in Chapter 3. Namely, basic mechanical properties, thermogravimetric and elemental composition characteristics of thermally treated research materials of interest were studied. Main objective of Chapter 3 is investigating volume reduction of three materials after pyrolysis thermal treatment. Chapter 4 presents leaching behavior of thermally treated materials by batch leaching test and pH dependent leaching test. Objective of Chapter 4 is to check environmental impacts with batch leaching test and investigate leaching behavior of pyrolysis thermally treated samples in the broad range of pH in order to understand the behavior of samples during utilization in the actual environment. Chapter 5 concludes the main findings from this research and suggestions for further research and practical implications on this topic.

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Chapter 2 Literature review

2.1 Methods of handling various waste

2.1.1 Worldwide municipal solid waste generation and management

Due to the significant increase in global population and economic development followed by rapid urbanization and industrialization, living standard and consumption pattern of humanity has altered which lead in turn to the high levels of municipal solid waste generation that threatens environment without appropriate handling (Powrie and Dacombe, 2006; Demibras, 2011; Assamoi and Lawrysyn, 2012; Kawai et al., 2015; Kumar and Samadder, 2016; Nanda et al., 2020). Worldwide municipal solid waste generation rate is increasing faster than rate of urbanization (Hoornweg, D. and Bhada-Tata, P., 2012). Global municipal waste generation by countries for year 2020 is shown in Figure 2.1. Five developing countries of China, India, Brazil, Indonesia and Mexico are leading in generating high amount of solid waste due to high density of population and thriving lifestyle in urban areas. USA, China and India stand out with the highest amount of municipal disposal from rest of the world. Japan is among the top ten countries.

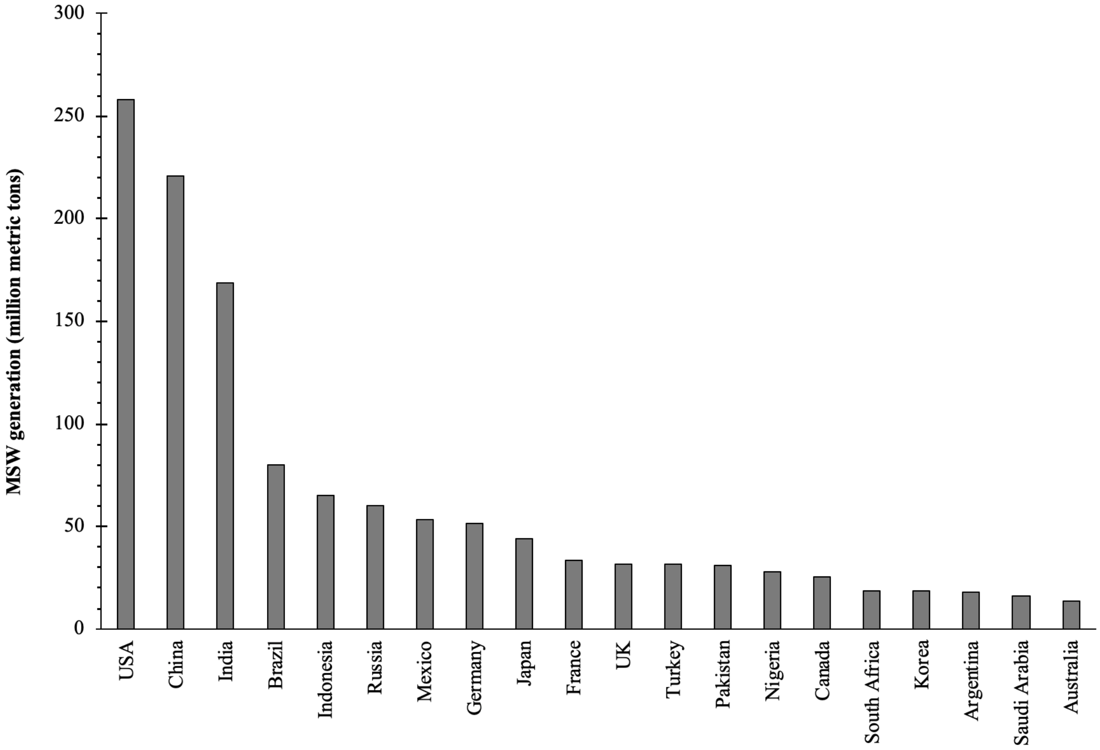

Figure 2.1: Worldwide generation of municipal solid waste (Nanda et al., 2020)

Approximately 2 billion tons of municipal solid waste is generated globally every year, which 33% remain uncollected by municipalities (Sharma et al., 2021). Moreover, according to the World Bank report results, this number is expected to be increased up to 3.4 billion by 2050 (Nanda et al., 2020; Sharma et al., 2021). Generally, municipal solid waste collected by municipalities demonstrate following management patterns: which 19% is recycled and 11% is utilized for energy recovery, whereas rest is directed to the landfills and dumpsites (Nanda et al., 2020).

As shown in Figure 2.2, current waste management system contains processes from waste generation to landfill disposal. Modern vision of waste management system is resource cycle that starts with material and energy extraction from the environment, raw material processing and mass production, followed by their consumption, and, finally, returning materials back to the environment (Powrie and Dacombe, 2006; Demibras, 2011).

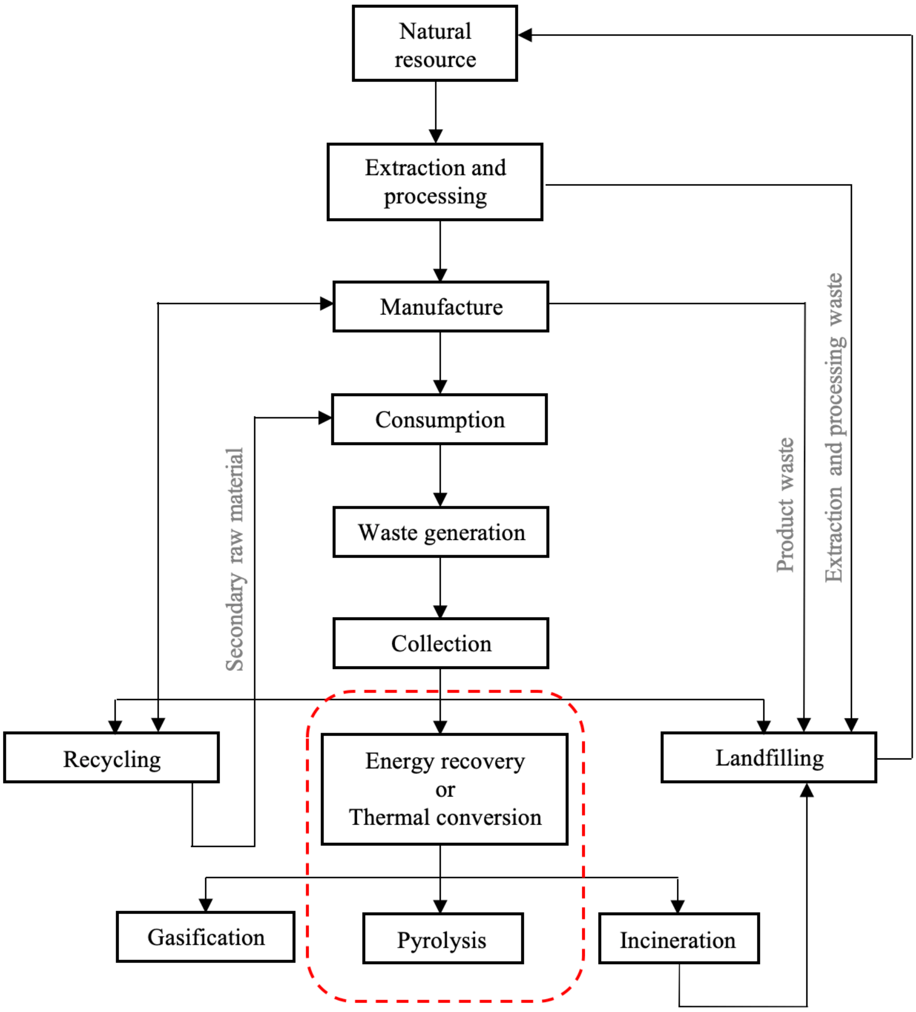

Figure 2.2: Current waste generation and management cycle system (modified from Sabbas et al., 2003; Powrie and Dacombe, 2006; Kumar and Samadder, 2016)

Practice of utilizing generated disposal from one process into the other one is the common characteristic of modern waste management. When benefits from uniformity of material and reuse process are lost, material is returned back to the environment in order material to naturally become a resource in geological timescale.

An important feature of sustainable development is economically and environmentally efficient waste management system (Cherubini, 2009; Hiratsuka-Sasaki and Kojima, 2020). Therefore, ultimate goal of any waste management system is material and energy recovery which is understood by extracting and reprocessing raw materials or converting heat content of the waste into electricity (Demibras, 2011; Kumar and Samadder, 2016). One of the key points of sustainable waste management is reusing and recycling. However, when reusing or recycling is not the best option in terms of sustainability, concept of Waste to Energy which converts waste into valuable energy and reduces amount of waste going to landfill is considered (Moharir, 2019). If none of the previous methods work then landfilling is the only option.

2.1.2 Landfilling and recycling

Landfilling is least preferred yet the most widely used method of waste management. Sanitary landfilling dominates with 37% among the organized methods of non-recyclable solid waste disposal in developed countries, however, landfilling is uncommon practice in developing countries with limited space due to dense population (Nanda et al., 2020; Anshassi et al., 2021).

Some of the previous studies indicated that environmental impacts from landfilling practice is significant compared to material or energy-recovery methods (Kumar and Samadder, 2016). One of them is land space utilization, if landfilling is compared with thermal treatment in terms of desired space, 30 million tons of waste is sealed in 300 000 m^2 landfill, while the same amount of waste is treated in thermal treatment facilities with 100 000 m^2 land (Kumar and Samadder, 2016). Core concept of landfilling is preventing decomposition in order to protect environment from harmful contamination, thus, its design represents a tightly concealed storage container (Demibras, 2011; Nanda et al., 2020). Figure 2.3 represents desired time for different municipal solid waste components to be fully decomposed. For instance, plastic wastes such as disposable diaper and plastic bottle take 500 years while mixed plastic waste requires 1000 years in order to be fully decomposed. Moreover, indicated desired time can be extended due to conservation properties of landfill. Consequently, landfilling requires not only larger space but longer time is needed for mixed waste to be decomposed and perceived into the environment.

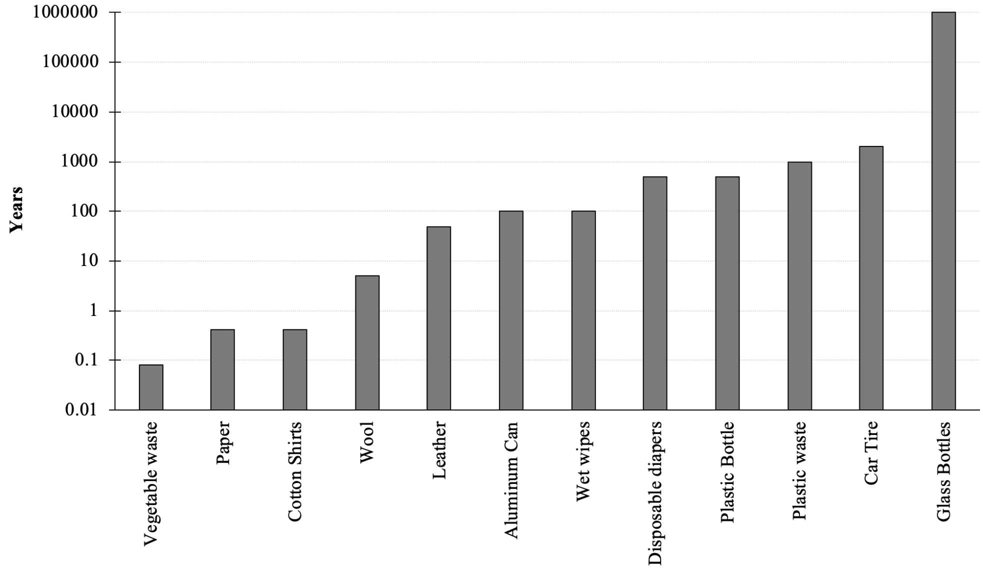

Figure 2.3: Time required for decomposition of different waste components (Stewart, 2019)

Input waste content which is key for sustainable landfilling system is very important in order waste to be biologically assimilated to natural soil in 20-30 years. For this purpose, waste should fulfill following characteristics:

1. a minimum amount of recyclables
2. least amount of plastics
3. several percentage of organic matters to maintain biological degradation
4. a minimum amount of hazardous chemicals, such as heavy metals (Tanaka, 2005).

Even though 50% of landfill gas is collected and combusted to generate energy, it is equal to part of potential resource generated through recycling or incineration of the same amount of waste, which is the weakness of landfilling (Moberg, 2005). As life cycle assessment results of Cherubini (2009) shows, the landfilling is least efficient method of waste management.

Recent increasing environmental consciousness on serious environmental impacts and rising raw material price trigger policymakers, environmentalists and citizens to be interested in recycling methods than other existing options (Pajunen, 2015; Kumar and Samadder, 2016; Wang et al., 2019; Honma and Hu, 2020). Recycling has its many benefits such as preserving natural resources, reducing environmental contamination and landfill sites (Honma and Hu, 2020). Antoni and Marzetti (2019) indicated that 10% increase in recycling rate is equal to 1.5-2% decrease in municipal solid waste.

Environmental impacts are captured within the early stages of product design process indicating that early decisions are essential at the end of life cycle. Number of complex modern materials (composite and hybrid) are increasing day by day as a product of any conceivable material mixture with the purpose of inventing better alternative lightweight material to existing ones in order to reduce carbon footprint and energy consumption (Pajunen et al., 2015).

Consequently, attempts of finding new energy solutions lead to producing poorly recyclable materials that makes having unique recycling system impossible. Most of the time, poor recyclability is typical for plastics because of unique chemical structures and complex processing while glass and metals, such as steel, aluminum and titanium, are able to be recycled into high-value products (Yedinak, 2022). Even though polymer recycling is complicated, long-term goals set by oil and gas manufacturers to develop plastic production demonstrate energy saving and economic profit potentials of plastic waste recycling in the future (Yedinak, 2022).

The other issue in case of material recycling is separation. For instance, extracting monomers from plastic waste in order to produce new product is the best sustainable option. However, in this case, thoroughly separated mixed plastic waste is critical, otherwise many polymers yield low properties compared to original product (Hodzic, 2004). It is not typical only for plastics but for other waste materials as well. It is difficult to separate all the recyclable materials from mixed waste stream sorted with present system (Yedinak, 2022). Furthermore, water contamination due to various material recycling is another issue. Suzuki et al. (2022) reported that mechanical plastic recycling is likely the reason for surface water pollution with microplastics. According to Birjandi et al. (2016), during paper manufacturing about 250 chemicals are produced, while during recycling, every ton of paper pulp production generates 80m^3 of wastewater and this wastewater is possibly contaminated with aforementioned various chemicals. Therefore existing specific material stream recycling methods have to be shifted towards product-centered approach (Pajunen et al., 2015). Both short-term adjustments and long-term recycling solutions need to be considered, since present recycling models are not environmentally sustainable enough (Yedinak, 2022).

Consequently, even the best sustainable option, recycling, is also not able to solve waste management issues. While some researchers indicate that incineration is more beneficial compared to landfilling, other scientists suggest focusing on energy and material recovery through thermal treatments instead of recycling (Pan et al., 2015; Moharir, 2019; Anshassi et al., 2021).

2.1.3 Incineration

Nowadays after landfilling, incineration is widely used as a thermal treatment for different types of waste, including municipal solid waste. General diagram of the incineration process is shown in following Figure 2.4.

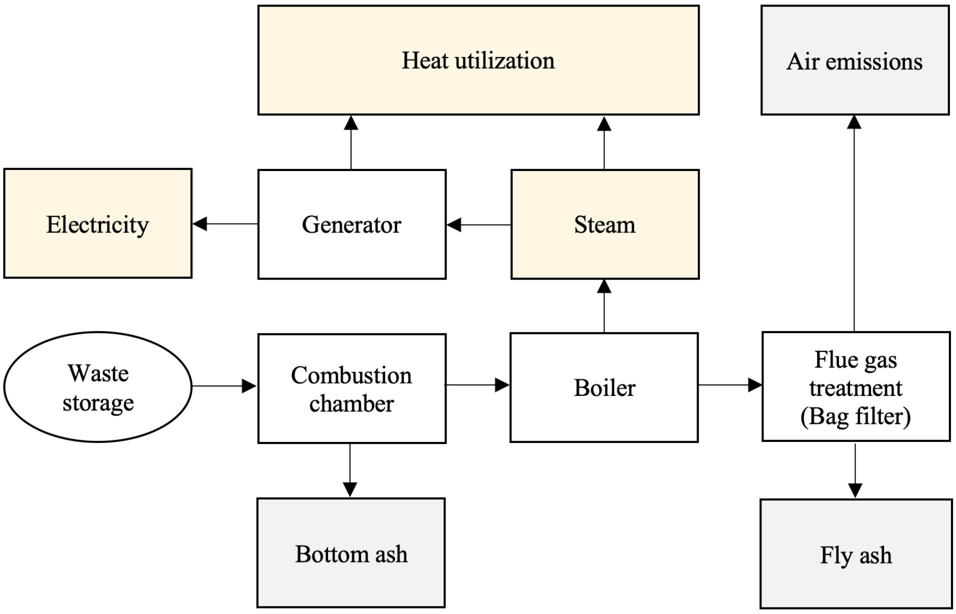

Figure 2.4: General schematic diagram of the incineration process with energy recovery (Liu et al., 2020)

Incineration is a controlled waste combustion at 850-1200℃ temperature in order to destroy hazardous wastes and decrease amount of waste with energy recovery through steam production as a secondary benefit (Powrie and Dacombe, 2006; Demibras, 2011; Kumar and Samadder, 2016; Nanda, et al., 2020). Thus, incineration usage is directly associated with the amount of trash generated. Incineration solves following targeted issues by reducing the amount of waste to be landfilled while considering the waste sanitization:

1. Reducing the organic matter present
2. Destroying organic contaminants
3. Concentrating the inorganic contaminants
4. Reducing the mass and volume of the waste
5. Recovering the energy content of the waste as a heat energy
6. Preserving raw materials and resources (Sabbas et al., 2003; Kumar and Samadder, 2016).

More specifically, incinerating wastes decreases weight and volume of waste by 70% and 90%, respectively (Powrie and Dacombe, 2006; Golke and Martin, 2007; Cheng and Hu, 2010; Nixon et al., 2013; Lombardi et al., 2015; Kumar and Samadder, 2016).

As mentioned before, during combustion organic content of waste is converted into energy through heat production. The energy recovering is most beneficial in terms of sustainability and environmental impact, on the other hand, inorganic content contributes to the ash production (Moharir, 2019). There are two types of ash produced after incineration as shown in the Figure 2.4: fly ash and bottom ash. Pieces of metal exist in the bottom ash inherited from waste. Although several treatment methods for bottom ash exist, these recycling methods have limits. On the other hand, fly ash is collected with bag filters and contains salt compounds with an acidic gas, sulfur dioxide and hydrogen chloride, dust with heavy metals and dioxins (Liu et al., 2020). Fly ash is more complicated than bottom ash in order to be treated. Thus, incineration is not able to avoid landfilling (Cherubini, 2009).

According to Powrie and Dacombe (2006), significant amount of air is used for each ton of waste combustion which generates up to 2.8 tons of carbon dioxide, sulphur and nitrous oxides (SO_x and NO_x), dioxin, furan and ash. This shows mass combustion of unsorted municipal solid waste is not the best option to rely on concerning sustainability (Powrie and Dacombe, 2006).

Since incineration requires high operational and maintenance cost, it is not economically beneficial all the time. Consequently, combustion demolishes the material irresistibly polluting air and land through poor combustion and end products of gas, liquid and solid (Hodzic, 2004).

As a result, incineration is pricey, unable to eliminate landfilling, unsustainable in terms of toxic gas emissions (Oliveira and Rosa, 2003; Troschinetz and Mihelcic, 2009; Butler et al., 2011; Kumar and Samadder, 2016).

2.1.4 Pyrolysis

Today, incineration is the most common worldwide thermal treatment technology utilized for plastic waste disposal even though it is not safe due to health and environmental impacts. Because, other thermal conversion technologies for energy recovering are still in research phase (Hodzic, 2014; Moses, 2014). One of them is pyrolysis which is promising thermal technology due to its effectiveness and environmental advantages among all technologies for municipal solid waste management (Yansaneh and Zein, 2022). Waste converted into raw materials, fuels and valuable chemicals through disintegration of chemical bonds at lower-temperature range of 400-800°C heating without oxygen is defined as pyrolysis method (Powrie and Dacombe, 2006; Kumar and Samadder, 2016; Moharir et al., 2019; Kumagai et al., 2020). Therefore, there is increasing global demand for feedstock recycling recently since pyrolysis is preferred to incineration due to aforementioned advantages of pyrolysis (Chen et al., 2014; Kumar and Samadder, 2016; Kumagai et al., 2020). Most of the time, pyrolysis is associated with plastic waste and the main goal is recovering pyrolysis oil from polymers to the fullest extend (Al-Salem et al., 2010, Chen et al., 2014; Kumagai et al., 2020). Also, it has an advantage of recycling composite and relatively contaminated plastic waste containing different polymers and additives that have difficulty in mechanical recycling methods (Butler et al., 2011; Saruddin et al., 2016; Kumagai et al., 2020; Iwanek and Kirk, 2022). Therefore, pyrolysis should be the priority in management of materials which are very expensive to sort and treat (Al-Salem et al., 2017).

Pyrolysis is favored as a prosperous method for avoiding sorting of waste components and demolishing pathogens at the same time (Iwanek and Kirk, 2022). Recently, small towns are interested in using pyrolysis facilities in order to avoid distant transportation expenses, while in megapolises it is favored for finding solution for required enormous space for incineration and landfills (Chen et al., 2014). Waste volume reduction can be reached up to 95-98% through pyrolysis which is little higher than incineration.

The main different parameters between incineration and pyrolysis, atmospheric condition (presence of oxygen) and operating temperature are represented in the Table 2.1.

Table 2.1: Typical reaction conditions and products of thermal process (incineration, pyrolysis)

Parameters	Incineration	Pyrolysis
Principle	Full oxidative combustion	Thermal degradation of organic material in the absence of oxygen
Operating temperature (°C)	850-1200	400-800
Atmosphere	Presence of sufficient oxygen	Absence of oxygen
Solid	Bottom ash, fly ash, slag, other non-combustible substances like metals and glass	Ash, char (combination of non-combustible and carbon)
Liquid	none	Condensate of pyrolysis gas (pyrolysis oil, wax, tar)
Gas	CO_2, H_2O, O_2, N_2	Pyrolysis gas (H_2, CO, hydrocarbons, H_2O, N_2)
Pre-treatment	Not necessary	Required
Raw MSW	Usually preferred	Usually not preferred

Source: Kumar and Samadder (2016)

One of the biggest disadvantages of incineration compared to pyrolysis is emitting hazardous gases and dioxins. Generally, one of the reasons of dioxins generation as a result of incineration is due to incomplete combustion of organic wastes (McKay, 2002). However, according to Yansaneh and Zein (2022), pyrolysis is a thermal decomposition of organic molecules occurring in the absence of oxygen, so oxidation does not occur. Therefore, dioxins are not formed in the reaction process which is big advantage of pyrolysis in terms of environmental impact. Moreover, limited amount of nitrogen oxides (NO_x) and sulfur oxide (SO_2) are generated compared to incineration.

Krüger (2020) studied the difference of carbon dioxide emission resulted from three different methods. 1 ton of mixed plastic is treated via pyrolysis, recycling and incineration separately (Figure 2.5). Production and end-of-life treatment of 1t of plastics via pyrolysis emits 2,100 kg CO_2e, whereas mechanical recycling emits 1,973kg CO_2e. Incineration of 1t of mixed plastics emits 3,700 kg CO_2e. It can be easily seen that pyrolysis of mixed plastic waste emits 50 percent less CO_2 than incineration of mixed plastic waste (Krüger, 2020).

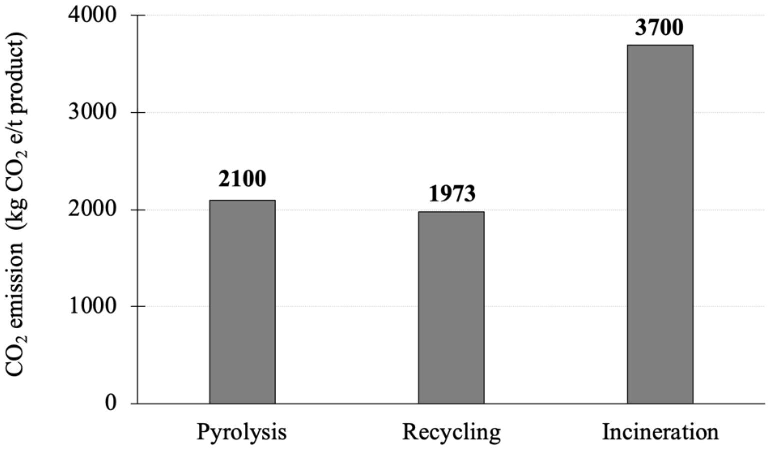

Figure 2.5: Comparison of carbon dioxide emission via three methods: pyrolysis, recycling and incineration (Krüger, 2020)

Furthermore, pyrolysis has other advantages such as operational advantages of utilizing resulted materials as an energy and environmental advantages of finding alternative solution to landfilling. Pyrolysis reactor functions as an effective waste-to-energy convertor through melting and cracking that produces gas, liquid and condensation that forms ash (Moharir et al., 2019). As previous studies indicated, properties and proportions of these products are highly influenced by process parameters, such as temperature, type of reactor, pressure, heating rate (HR), residence time, waste component, etc.(Chen et al., 2014; Lombardi et al., 2015; Kumar and Samadder, 2016; Saruddin et al., 2016).

Decomposition behavior of the plastic waste material is governed primarily by temperature. In addition, cracking reaction which disintegration in carbon chain is controlled by temperature as well. Westerhout et al., 1998 studied the comparison of process parameters at high temperature pyrolysis and indicated insignificant influence of plastic type and residence time on product distribution compared to temperature effect. Residence time is average amount of time that particle spends in the reactor. According to Yansaneh and Zein (2022), reaction temperature and residence time are strongly related to each-other. As a result of numerous experiments conducted, it was concluded that residence time is temperature dependent parameter and only has potential influence on end product during low temperature pyrolysis (Sharuddin et al., 2016). As a result, it was found out that priority of char production can be obtained by longer exposure (minutes to hours) combined with lower temperature range of 400-500°C, while maximum gas or liquid production is achieved through short exposure (few seconds or less) at high temperature range of 500-1000°C (Moharir et al., 2019). Thus, previous studies mainly concentrated on the process itself by improving reactor design, heat transfer rate in order to advance liquid fuel properties since liquid energy is easily stored and has higher economic value than electricity generated through combustion steaming (Butler et al., 2011; Kumar and Samadder, 2016; Kumagai et al., 2020). Therefore, pyrolysis char was neglected due to the higher value of pyrolysis oil. Despite the superiority of pyrolysis, it encounters obstacles of handling pyrolysis char produced because pyrolysis ash is obtained from all types of pyrolysis (Al-Salem et al., 2009). Even though pyrolyzing contaminated plastics is one of its main advantages, it turns out disadvantage: char production increases when plastic waste is contaminated and various plastic materials are mixed (Yansaneh and Zein, 2022). Therefore, in order to solve mixed plastic waste and contaminated plastic waste issues, pyrolysis ash should be studied. Moreover, many studies were conducted on individual plastics or very simple plastic mixtures which do not represent real plastic waste (Lopez et al, 2011).

Pyrolysis of waste has attracted the attention of scientists for several decades and benefits of pyrolysis are technically proven, yet this method could not find its applications nowadays due to economic challenges. One of the examples that emphasizes this fact is that when Container and Packaging Recycling Law was implemented in 1997 about 25 Japanese companies have been working on pyrolysis, however after decade it was reduced to 2 (Butler et al., 2011). Aforementioned information indicates the importance of studying pyrolysis ash in order to reduce the volume of solid waste since solid pyrolysis char is generated as a result of any pyrolysis treatment and importance of complexity of materials being treated.

2.1.5 Current waste management situation in Japan

The Japanese government promotes 3R policies that focus on creating a sound material-cycle society through "Reduce," "Reuse" and "Recycle” in the country in order to provide highly fulfilled life for citizens (Kodera, 2012; Ministry of Environment of Japan, 2020; Honma and Hu 2020). However, Japan ranks second among developed countries in terms of the volume of disposable containers and waste packaging per person (OPRI, 2019). Generally, waste consists of municipal waste (discarded from homes, small stores and offices) and industrial waste (discarded from industrial activities) in Japan (Amemiya, 2018). According to Ministry of Environment, Government of Japan, in 2020 amount of generated total municipal waste was equal to 41.67 Mt, of which 29.7 Mt was reduced by incineration, 8.33 Mt was recycled, 3.64 Mt was disposed in landfill. Decision-making process of waste burying or burning depends on the resource reserves, legislation and environmental impacts (Anshassi et al., 2021). Incineration is the leading waste management method for municipal solid waste in Japan (Castaldi and Themelis, 2010; Moharir, 2019). Not only this, Japan relies heavily on incineration compared with other countries in the world and it can be observed in Figure 2.6 (Hiratsuka-Sasaki and Kojima, 2020).

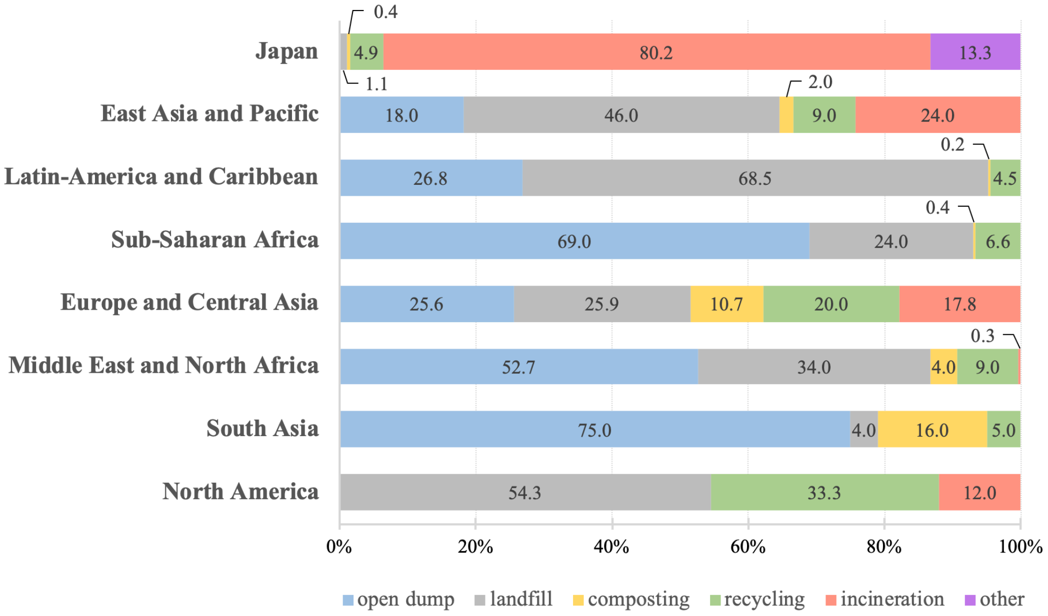

Figure 2.6: Waste Disposal Methods by Regions (Hiratsuka-Sasaki and Kojima, 2020)

Japan is compelled to actively utilize incineration technology in waste management by strict environmental rules, high density of population, and landfill area limitation (Gohlke and Martin, 2007; Kumar and Samadder, 2016). In current situation of Japan, incineration is the most appropriate solution with opportunity of reducing volume and generating energy in waste management (Sakai, 1996; Hiratsuka-Sasaki and Kojima, 2020). However, regarding to data from Ministry of Environment, Government of Japan, only 36.6% of total incineration plants were equipped with power generation facilities which indicates incomplete recovery of potential energy from municipal solid waste. Because, the smaller the size of incinerator, the less efficient steam turbine performance (Lombardi et al., 2015). Moreover, the energy generated by burning is used only for heating swimming pools, hot water supply of public facilities in nearby areas due to low heat production (Tabata, 2013). Landfill reduction is a priority for the Japanese government and Tanigaki et al. (2013) pointed out this as a reason for active utilization of waste incineration even without energy recovery. Besides incomplete energy recovery, air contamination is of great concern, especially, dioxin emission resulted from combustion (Honma and Hu, 2020). Therefore, larger incineration facilities that enables dioxin reduction through stable combustion are recommended by Japanese government. However, there exist difficulties of having high-performance facilities for several neighboring municipalities (Ministry of Health and Welfare, 1999; Hiratsuka-Sasaki and Kojima, 2020).

2.2 Materials of interest

The composition of waste is getting more complex due to technology development on modern materials and consumption pattern of modern lifestyle. Consequently, various plastics are in every section of waste stream. This is not the only issue, volume of these types of plastic-related wastes is increasing day by day. In fact, approximately 4% of manufactured total crude oil is directly utilized for plastic production. According to Butler et al. (2011), generally average lifespan of all plastic is about 8 years, of which 40% becomes waste after one month. It indicates huge amount of plastic waste is generated every year.

However, nowadays it is difficult to imagine the world without plastics or synthetic organic polymers. The superior properties of plastic, such as relatively low-cost, ease of manufacture, light weight and being non-corrosive, greatly contributed in substitution for wood and metal usage (Hodzic, 2004; Syamsiro et al., 2014; PWMI, 2019; Kumagai et al., 2020). When single-use containers started being preferred to reusable, plastic packaging production in order to meet the increased demand exceeded other man-made materials production except steel and cement for construction purposes (Syamsiro et al., 2014; Geyer et al., 2017). As a result, it can be witnessed that packaging category occupied more than 30% of overall manufactured plastic polymers in 2015 and it generated one of the major constituent in solid waste (Geyer et al., 2017). Plastic waste is in third place after food and paper waste in urban areas (UNEP, 2009).

Majority of plastics that are the result of polymer synthesis made of carbon and hydrogen, derived from finite resources, such as petroleum and natural gas, are not eco-friendly (Geyer et al., 2017; PWMI, 2019). Therefore, in order to satisfy environmental requirements plastic waste should be handled in a proper way. Moreover, aeon is required for plastic to be fully degrade. Consequently, following three types of plastic-related wastes were selected due to generated significant volume, complexity of the waste and required long time for full decomposition: industrial mixed plastic waste, soil mixed with waste and disposable diapers.

2.2.1 Industrial mixed plastic

Plastic waste is not only generated as a results of daily activities, but huge amount of various plastic waste is generated as a results of industrial activities. In order to fulfill required qualities of plastic materials for specific purposes manufacturers utilize significant types of polymers and additives. This gives an opportunity to achieve targeted utilization of plastic materials for specified fields, on the other hand it makes complicated industrial waste composition. As a matter of fact, global plastic waste generation according to polymer type shown in Figure 2.7 represents diversity of plastic materials and their rapid increase in generated amount since 1950.

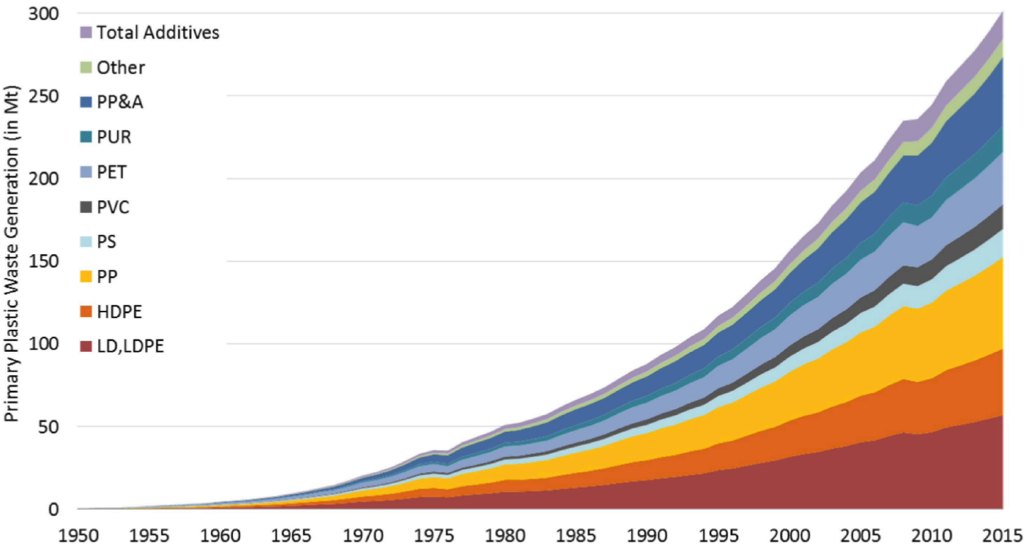

Figure 2.7: Global primary plastic waste generation according to polymer type (Kumagai et al., 2020)

Before Japan had been exporting its significant amount of industrial plastic waste overseas, particularly, to China. However, Japan had to alter its plastic waste disposal methods since Chinese government banned importing plastic waste in 2017. For instance, total amount of generated plastic waste in Japan was equal to 863 Mt, of which 54% was industrial mixed plastic. In 2018, 1.37 Mt of industrial plastic waste were mechanically recycled due to suitable quality for mechanical recycling. However, when industrial plastic waste from different sections is mixed due to difficulty of separation and identification of plastic type after usage, it is difficult to recycle kind of plastic waste. Currently, treatment methods and utilization of industrial mixed plastic waste is not studied enough. Thus, there is an information gap on industrial mixed plastic waste in Japan and worldwide.

2.2.2 Soil mixed with waste

Since 2011, challenges related to the waste management of natural disasters became one of the biggest challenges in Japan. Disaster waste causes huge geotechnical and geoenvironmental problems related to significant amount. For instance, the amount of disaster debris and tsunami deposit, generated as a result of 2011 earthquake of the Pacific coast of Tohoku and subsequent tsunami, were approximately 20,000 Gg (20 million ton) and 10,000 Gg (10 million ton), respectively (Inui et al., 2012; Katsumi et al., 2015; Katsumi et al., 2017). As a result of tsunami, specific waste is generated as mixture of tsunami deposit, once seabed soil transported by tsunami, tsunami debris and miscellaneous things. Disaster debris consists of various materials, such as wood, plastics, soil, paper, textiles, concrete, metal, tatami, etc., and is formed as a result of the destruction of buildings by tsunami hit (Figure 2.8). Therefore, large quantity of generated mixed waste requires appropriate treatment and utilization (Takai et al., 2013).

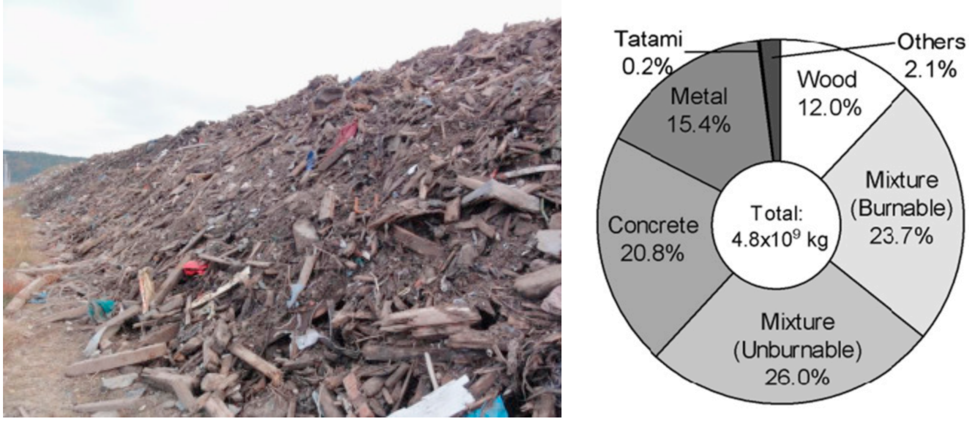

Figure 2.8: Disaster debris placed in a stockyard and composition of disaster debris in Iwate Prefecture (November 2011) (Inui et al., 2012)

Basic concept of this type of waste management is separating reusable materials of concrete debris, wood fractions, electric appliances from mixed tsunami waste followed by proper treatment with reuse and, finally, minimizing endpoint waste to the landfill and economical expenses (Inui et al., 2012). According to Katsumi et al. (2017), primary and secondary storage sites, two or more separation steps using operation vehicles and manual separation were needed in order to subject the post-disaster wastes to the treatment and only after that waste materials will be utilized as a construction material or sent to the landfill. In Japan, reduction in landfilling practice of unusable soils is encouraged due to lack of landfill sites as mentioned before. Therefore, mixture of soil with waste, such as PET bottle, plastic bag and wood, is chosen as a representative of natural disaster waste mixture.

2.2.3 Disposable diaper

Two main generations use disposable diapers: infants and adults. Since 1960s disposable diapers, particularly for infants, gained popularity among parents and nursing houses due to single usage without laundering and super-absorbent ability (Itsubo et al., 2020; Khanyile et al., 2020; Zuraida et al., 2021). Consequently, nowadays, adult disposable diapers become irreplaceable due to average life expectancy increase in Japan. According to Sheila (2016), a child uses approximately 5500 diapers from birth to elimination communication (potty training) which is significant amount to consider. For last decade from 2010 to 2020, waste volume production of adult diapers and infant diapers were increased by 1.7 and 1.9 times, respectively. Moreover, number of demanded disposable diapers for adults are expected to increase (Itsubo et al., 2020).

Currently disposable diaper waste is mainly managed through incineration and landfilling than recycling (Khanyile et al., 2020). For instance, Japanese kinder gardens in many prefectures, such as Shiga (89%), Nagano (85%), Kagawa (75%), Kyoto (73%), Shimane (67%), Yamaguchi (67%), Fukui (65%), Okayama (60%), Miyazaki (60%), and Tokushima (59%), practice "take home" policy in terms of used diapers which means parents bring used diapers back home and dispose them as a burnable waste (Fujisawa, 2022). Diapers take place 6-7% of household combustible waste (Itsubo et al., 2020). But, Itsubo et al. (2020) and Khanyile et al. (2020) indicated that incineration is not suitable due to low calorific value suppressing efficiency of incineration heat recovery because used diapers have high moisture content. Moreover, according to Khanyile et al. (2020) and Zuraida et al. (2021), incinerating diapers generate dioxins which is great impact to the environment.

Even though disposable diapers are managed by incineration in Japan, some Japanese researchers were focused its energy recovery and recycling. Fujiyama et al. (2012) conducted an analysis and a comparison between incineration and thermal recycling of used diapers. While Itsubo et al. (2020) studied life cycle assessment of recycled disposable diapers and illustrated life cycle flow and treatment scenarios between landfilling, incineration and recycling methods. However, disposable diaper recycling is not common practice worldwide. Nevertheless, several studies have been carried out on the recycling of disposable diapers overseas. Khanyile et al. (2020) analyzed the thermal performance of a diaper during pyrolysis, concluding that a diaper material recovery method is possible. Zuraida et al. (2021) studied utilization of recycled disposable diaper as concrete component for road pavement and indicated that disposable diaper concrete does not differ significantly from conventional concrete in terms of mechanical properties and microbial content. However, results on thermally treated disposable diaper utilization are not sufficient currently.

Generally, disposable diaper contains superabsorbent polymer (SAP) to absorb moisture in the interior layer, plastic materials such as polyethylene or polypropylene in the exterior layer (Itsubo et al., 2020; Rocío and Alejandra, 2021). As represented in Figure 2.3, polyethylene and polypropylene contribute to the slow degradability of disposable diapers which requires 500 years to fully degrade indicating landfilling is not the best option for diaper disposal (Khanyile et al., 2020; Zuraida et al., 2021; Rocío and Alejandra, 2021).

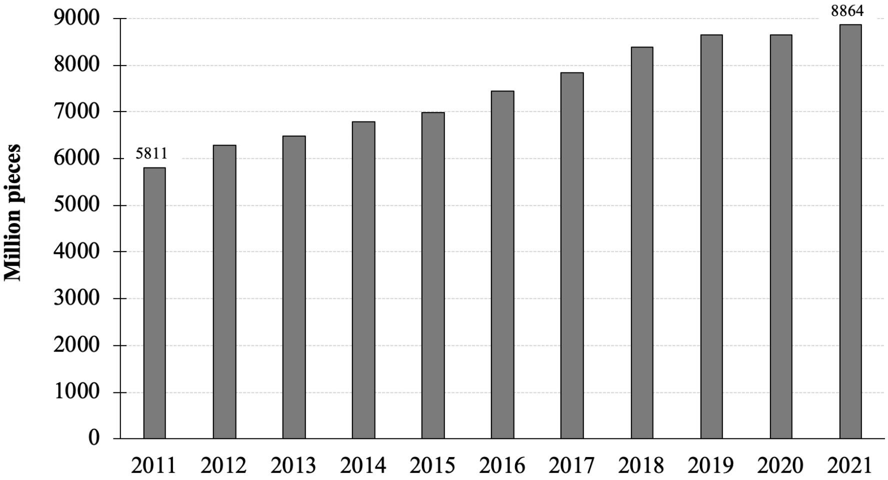

Figure 2.9: Production of adult disposable diaper in Japan (JHPI, 2021)

According to the data from Japan Hygiene Products Industry Association (Figure 2.9), production of adult diaper is increasing year by year for the last decade which indicates that it is very important to find disposable diaper waste treatment other than incineration followed by landfilling.

2.3 Leaching characteristics of thermally treated waste materials

When recycled thermally treated ash is utilized, potential environmental impact to the soil, ground and surface water is very important. Proper way of judging such impact is evaluating the potential leaching of chemical constituents from the material in order to identify the most important release mechanisms. Previous studies mainly investigated leaching behavior of MSWI ash (bottom ash and fly ash) characteristics (Luo et al., 2019). Specific waste materials represent systematic leaching behavior which is difficult to obtain from single point leaching test results Waste materials in order to be recycled and utilized as a construction material should be investigated with detailed characterization tests. Understanding the leaching properties of major constituents that significantly affect the trace contaminants is essential in order to understand leaching behavior of any waste material (van der Sloot et al., 2006).

Characteristics of thermally treated ash is controlled by various features that fall into two groups: treatment conditions and waste composition. Contamination of soil, ground and surface water with leaching of toxic substances are essential when treated ash utilized as recycled material (Chen et al., 2022). Different factors such as pH, liquid-to-solid ratio, ash composition, weathering and aging, leaching methods and contact time are the main factors affecting leaching behavior of recycled ash material (Luo et al., 2019). There are diversity of laboratory leaching tests exist worldwide. In order to select an appropriate test, it is crucial to decide which parameters should be detected by the test in order to get desired information such as effect of pH, maximum release, equilibrium concentrations and diffusion controlled release. In addition, understanding fundamental leaching processes influenced by element speciation in the solution and the solid phase is necessary. Generally, many studies are often confined within the pH range of neutral to acidic region established by tested material. Partitioning of chemical species occur as a result of different surface processes characterized by ion exchange/sorption, complexation, precipitation/dissolution and incorporation into mineral phase within the pH domain (1-14) (Elgensen et al., 2009; Elgensen et al., 2010). Therefore, one of the main controlling factors is the pH, as recognized in many previous studies and testing pH dependence leaching behavior of constituents is essential in order to study scenario-based risk assessment (Engelsen et al., 2010).

In order to identify and describe the various processes occurring at different pH values, characterizing the leaching pattern in an extensive way is necessary which is important due to the strong alkaline nature of the material (primarily thermally treated materials are alkaline) and the differing external pH experienced in the actual field.

Heavy metal speciation in solution and their attraction to bind to reactive surfaces and pore water influence leaching of heavy metal cations and their transportation (Engelsen et al., 2010). Therefore, aspects of chemical speciation are observed with pH dependent leaching test. When single point leaching test data is combined with pH dependent leaching test results, it gains more value in perspective. pH dependent leaching test data enables to obtain “geochemical fingerprints” of the material of interest and make predictions for utilizing waste material in the actual environment (van der Sloot et al., 2006; Engelsen et al., 2010).

2.4 Conclusions for Chapter 2

Nowadays, every waste stream contains plastic materials which is significant threat to the environment. Some waste streams not only contain plastic but generated volume is huge. Therefore, three waste types were chosen as materials of interest according to the current challenges of generated significant volume of waste and complexity of the material or waste mixture in Japan. First of all, industrial mixed plastic waste is a worldwide challenge, particularly in Japan. Since China stopped importing plastic waste, Japan started looking for alternative methods of handling industrial mixed plastic waste. Secondly, as a result of natural disasters, generated volume of contaminated soil with miscellaneous materials is significant and it requires several steps of separation and treatment. Lastly, generated disposable diaper waste volume is a big problem in Japan due to increase of older generation and its environmental impact triggered by combustion of used diapers with municipal solid waste due to “take home” policy.

According to the previous studies, landfilling is the least preferred method of plastic-related waste disposal due to space limitation in developing and developed countries and long time that plastic materials require to be fully decomposed. In order to recycle, plastic material should be cleaned and sorted which indicates inapplicability of recycling to all plastic-related wastes. Incineration is the best method for reducing volume of any plastic-related waste, however its environmental impact through dioxin and carbon dioxide emission is significant. Moreover, incineration is not able to displace landfilling due to toxicity and complexity of incineration ash. Therefore, scientists are interested in pyrolysis technology due to its volume reduction capability, energy and material recovery and environmental friendliness. As a result of pyrolysis process, pyrolysis oil, gas and solid char is obtained. However, previous studies were focused only on characteristics and yielding properties of pyrolysis oil due to its economic values and pyrolysis solid char is simply ignored. The challenge is all types of pyrolysis generate pyrolysis char in various quantities. Moreover, char production increases, especially, when plastic waste is contaminated and various plastic materials are mixed. Since pyrolysis ash is not considered in previous researches, there is information gap on studies of pyrolysis ash and its utilization. Therefore it is very important to study pyrolysis char and its possibilities of utilization. Studying pyrolysis ash is focused in this research with the purpose of reducing the waste volume going to landfill and investigating properties of pyrolysis ash for the future utilization.

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Chapter 3 Volume reduction and effectiveness of pyrolysis technology and its treatment conditions

3.1 General remarks

In general, waste materials are generated as a result of industry and daily life processes (Demibras, 2011). Since plastic is used in different aspects of life there are many types of plastic relates wastes. However, due to time restrictions related to research it is impossible to consider all types of wastes. Therefore, in this research only three types of polymer-related wastes were elected from different three waste streams due to generated significant amount, impracticality of landfilling in terms of required huge space, environmental impacts of incineration and difficulty of recycling: mixed plastic waste from industrial waste stream, soil mixed with waste (wood, PET bottle, plastic bag) from disaster waste steam and lastly, disposable diaper from municipal waste stream.

Selected three samples were thermally treated by high temperature steaming alternative to mechanical crushing (for mixed plastic) as a pretreatment and pyrolysis treatment, then effectiveness of pyrolysis treatment and its treatment conditions were determined through volume reduction, mechanical properties of pyrolyzed waste samples, thermogravimetric and XRF analysis. Generally, sorting of plastic waste is conducted through a sequence of sorting steps. It includes sorting by size, either manually or by means of sieves, by types of plastic materials, elimination of foreign materials (e.g., metal and glass) and so on (Lange, 2021). Detach metal parts from the bulk plastic is the difficult task to handle and mechanical crushing of metal-bonded waste tends to cause damage to the crushing blades, which does not allow the pyrolysis process to run smoothly. In order to reduce all these difficulties, high-temperature steaming of plastic as pretreatment is used in order to crush waste materials to facilitate chemical reactions and this technique was adopted as an alternative method for mechanically crushing materials, particularly for industrial mixed plastic waste from different sources.

Volume and weight reduction of elected three wastes with pyrolysis technology was observed. Since samples experience chemical and physical changes after thermal treatment, effectiveness of pyrolysis technology and its treatment conditions on waste materials were studied by basic mechanical properties, thermogravimetric analysis and X-ray analysis.

3.2 Materials of interest

Following plastic-related waste materials were chosen and applied to pyrolysis thermal treatment:

(a) Mixed plastic: Production of home appliances, vehicles, furniture and other specific goods uses various types of polymers, additives, metals and fillers in order to produce plastics with desired properties, of which Japanese production of polymers and additives surpasses 150 and 200 types, respectively (Kumagai and Yoshioka, 2016). As a result, amount of generated complex mixed plastic waste is enormous. As mentioned before, landfilling these plastic wastes is impractical since it requires significant amount of land space. These plastics have their specific characteristics that fulfilled beforementioned applications which makes them difficult to recycle since recycling requires polymer type separation. Therefore, significant amount of these plastics end up in the incineration and landfills without energy recovering. Moreover, recovered plastic material is often produces lower quality. Especially, home appliances, electronics and car production companies suffer from this problem. Consequently, mixture of numerous types of plastics collected from different sources was received from industrial waste disposal company and crushed into smaller pieces with 5-15 mm diameter. General representation of mixed plastic waste material is shown in the Figure 3.1.

(b) Soil mixed with waste: Since 2011, challenges related to the waste management of post-natural disasters became one of the biggest considerations in Japan. Each time, generated volume of disaster debris is huge because natural disaster affects many places in a very short time. Disaster debris contains miscellaneous materials such as wood, paper, textiles, plastics, concrete, metal, tatami, soil, etc. Large quantity of generated disaster waste requires appropriate treatment and utilization (Takai et al., 2013). Basic concept of this type of waste management is separation based on the material type, reuse them and minimize endpoint waste to the landfill. According to Katsumi et al. (2017), primary and secondary storage sites, two or more separation steps using operation vehicles and manual separation were needed in order to subject the disaster wastes to the treatment and only after that waste materials will be utilized as a construction material or sent to the landfill. So, even though waste material is treated, it might end up in landfill. As it can be noticed, it is labor, storage site and time consuming; therefore, it is decided for attempting to use pyrolysis thermal treatment since it does not require such separations and storage sites.

Table 3.1: Information on constituents of soil mixed with waste sample

Material type of constituents	Size of each chip	Volume (out of 100%)
Soil	Sand with fine fraction	25% (11000 cm^3)
Wood chips	5 mm	25% (11000 cm^3)
PET bottle (cut into square)	5-7 mm (each side)	25% (11000 cm^3)
Plastic bag (cut into square)	5-7 mm (each side)	25% (11000 cm^3)

Therefore, soil mixed with waste was prepared in the following way: store bought wood chips in the form of square with the side of 5 mm were used. Clean PET bottle and plastic bag were cut into side of 5-7 mm squares. Soil was taken near the pyrolysis plant in Okinawa and basic mechanical characteristics of soil are shown in Figure 3.9. Particle size distribution of soil was determined according to the Japanese Geotechnical Standard JGS 0131 and it was classified as sand with fine fraction (S-F) based on JGS 0051. Finally, soil, wood, PET bottle and plastic bag in the same volume ratio (11000 cm^3 each) were mixed. Overall information on each constituents were represented in the Table 3.1 and visual overview of soil mixed with waste mixture is shown in the Figure 3.1 as well.

(c) Disposable diapers: As it was mentioned before in sub-chapter 2.2.3, waste volume production of adult and infant diapers were increased. Moreover, disposable diapers for adults, in particular, are expected to increase in the future due to the rise of elderly population in Japan. Disposable diaper contains superabsorbent polymer (SAP) to absorb moisture in the interior layer, plastic materials such as polyethylene or polypropylene in the exterior layer (Itsubo et al., 2020; Rocío and Alejandra, 2021). Therefore, it takes about 500 years for diaper to be fully decomposed in landfill conditions. Used diapers are usually discarded as municipal solid waste and take place 6-7% of household combustible waste (Itsubo et al., 2020). But, Itsubo et al. (2020) and Khanyile et al. (2020) indicated that incineration is not suitable due to low calorific value suppressing efficiency of incineration heat recovery since used diapers have high moisture content. Moreover, according to Khanyile et al. (2020) and Zuraida et al. (2021), incinerating diapers generate dioxins which is great impact to the environment.

(a) industrial mixed plastic (b) soil mixed with waste (c) disposable diaper

Figure 3.1: Waste samples of interest

3.3 Methods and procedures

3.3.1 Pretreatment through high-temperature steaming

High-temperature steaming is the degradation of a polymeric material through contact with water, specifically the hydrogen cations (H^+) or hydroxyl anions (OH^-). Hydrolytic degradation can occur within plastic material as a result of exposure to steam. Like other types of molecular degradation, hydrolytic degradation represents a chemical reaction that results in a permanent change within the molecular structure of the polymer (Jansen, 2015).

High-temperature steaming disassembly was carried out as a pretreatment for pyrolysis thermal treatment in order to crush waste materials to facilitate chemical reactions and this technique was adopted as an alternative method for mechanically crushing materials. Since mechanical crushing of hardened plastic and metal-bonded waste, such as waste plastic discharged from home appliances, tends to cause wear and damage to the crushing blades, which hinders the smooth decomposing process. Therefore, a high-temperature steam cracking unit was introduced as a substitute.

The temperature of the steam is set at 500°C. Organic substances, except minerals and metals, are melted and decomposed by the high-temperature steam, leaving behind as carbides other than those discharged as H_2O and CO_2.

Mixed plastic sample containing metal parts, such as screws, wires and aluminum foils, was subjected to the specific high-temperature steaming pretreatment. Since this method is still in the laboratory scale, only plastic with small metal parts were able to be treated. After high-temperature steaming pretreatment, the metal parts and plastic is separated and it is very easy to pick up metals with specific electronic magnet or sieving systems. The resulted outcomes of high-temperature steaming pretreatment utilized for separating metals from the plastic is shown in the Figure 3.2.

Figure 3.2: Separation of plastic and metal parts through high-temperature steaming: left –plastic, right – separated metal parts

3.3.2 Main treatment through pyrolysis technology thermal treatment

Pyrolysis thermal treatment is an endothermic process that transfers large amount of heat to waste materials in the absence of oxygen in order to thermochemically decompose long chain organic polymers into smaller hydrocarbons (Haruon, 2013; Pandey et al., 2020). Pyrolysis technology thermal treatment promises that many waste materials can be handled without any effort to separate for chemical value. Specific ceramics that generates far-infrared rays during pyrolysis thermal treatment were used in low-oxygen conditions to decompose and reduce volume through chemical reactions. Pyrolysis technology thermal treatment conditions can be altered depending on the place of installation and the waste to be treated. The main advantages of pyrolysis technology compared to incineration are listed below:

1. Reduces volume of all combustible waste
2. It is also possible to render hazardous substances into harmless
3. Reduced operating costs and compact equipment
4. Decomposition by chemical reaction instead of incineration
5. Reduction of CO_2 emission
6. No sorting of combustibles
7. Compatible with PVC and mixed resins.

Previous studies mainly concentrated on the process itself by improving reactor design, heat transfer rate in order to advance liquid fuel properties since liquid energy is easily stored and has higher economic value than electricity generated through combustion steaming (Butler et al., 2011; Kumar and Samadder, 2016; Kumagai et al., 2020). Since purpose of this study is volume reduction and characteristics of generated solid residue (ash), not energy recovery, only production of ash was considered. Priority of ash production can be obtained by longer exposure (minutes to hours) combined with lower temperature range of 400-600℃ (Moharir et al., 2019). However, according to the previous studies, time was not indicated exactly. Therefore, pyrolysis treatment conditions set as follows: temperature – 600℃ and time – 3 hours. All three samples were treated with pyrolysis technology at 600℃ for 3 hours in the absence of oxygen in order to get pyrolysis char. Utilized pyrolysis technology chamber and far-infrared ray generator ceramics inside the chamber are shown in Figure 3.3.

Figure 3.3: Demonstration of pyrolysis technology chamber and ceramic wall inside the chamber

In addition, before pyrolysis thermal treatment, sulfur (3% of waste weight) was mixed with the waste materials by Catalyst Co., Ltd with the purpose of stabilizing heavy metals in the further leaching since the most stable inorganic compounds are sulfates. The pyrolyzed samples were received from Catalyst Co., Ltd.

3.3.3 Thermogravimetry/Differential thermal analysis

The same thermal treatment condition as in pyrolysis technology was created in the TG-DTA thermal analysis in order to understand the effectiveness of pyrolysis thermal treatment conditions (temperature and residence time) and how materials behave during the treatment. Since pyrolysis thermal treatment conditions were fixed according to previous studies, it is very important to check if treatment conditions are effective. Rigaku Thermo Plus TG 8120 (Japan) analyzer was used to assess the thermal behaviors of selected samples. Approximately, 10 mg of each sample was placed into an open alumina pan and heated from room temperature to maximum temperature of 600°C at a constant heating rate of 15.0°C/min in the presence of inert gas N_2 (absence of air). The apparatus and analyzed samples were shown in the Figure 3.4. Repeatability experiment check for all the samples was performed in triplicates. Obtained TG, DTG and DTA curves were almost identical.

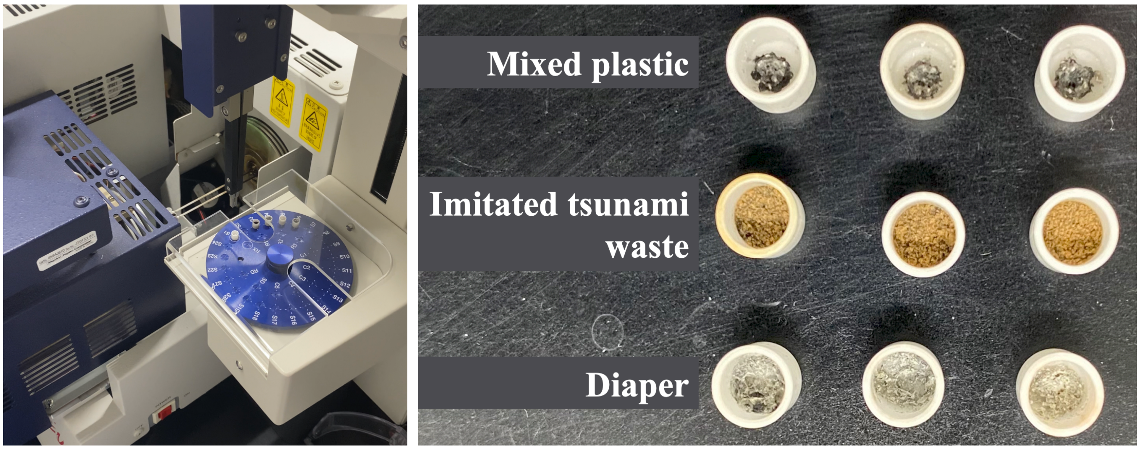

Figure 3.4: TG-DTA instrument and analyzed samples

3.3.4 X-ray Fluorescence analysis

In order to understand the effect of treatment on the concentration of elements in materials X-ray studies were conducted for original raw and thermally treated samples. Original raw and treated samples quite differ from each other, therefore, two types of sample preparation were applied. Since all the samples contain different types of plastics (polymers) whose composition or structure is altered by the heat generated by conventional grinding, raw mixed plastic, soil mixed with waste and disposable diapers were crushed using Freezer Mill SPEX Sample Prep 6770 Freezer/Mill. Liquid nitrogen was used in order to maintain cryogenic temperature of the sample during grinding and its key properties, and compositions were preserved. 10 minutes of precool followed with 2 cycles of 3 minute grinding in order to homogenize the sample particle size and composition. After crushing, samples were prepared for the XRF. However, thermally treated materials were crushed using conventional milling machine CMT CO. TI-100 Vibrating Sample Mill by grinding the samples for 2 minutes. After grinding all the samples, approximately five-grams of each sample in a briquette form was pressed under 30 tons for 10s and it was applied to XRF analysis.

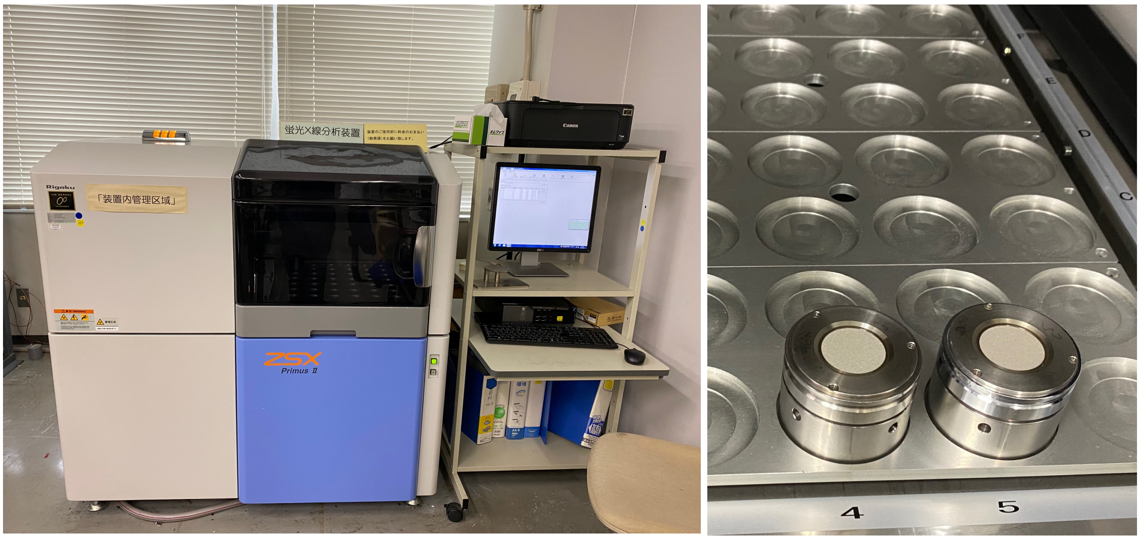

Figure 3.5: XRF instrument and analyzed samples

Chemical compositions of raw and thermally treated all three samples were determined by XRF-1700 Shimadzu spectroscopy (Figure 3.5) at the laboratory of Environmental Engineering Department in Kyoto University and Kyoto Research Park.

The advantage of this method is being nondestructive. XRF technique is a non-destructive method for the elemental analysis, which is fast and fully suitable for simultaneous quantitative determinations.

3.4 Results and discussions

3.4.1 Results of weight and volume reduction test

Before and after pyrolysis thermal treatment (Figure 3.6), volume and weight of samples were measured and calculated for volume and weight reduction.

Figure 3.6: Before and after pyrolysis thermal treatment of industrial mixed plastic, soil mixed with waste and disposable diapers

After pyrolysis thermal treatment different volume reductions occurred depending on the waste material type. Volume and weight reduction results of three samples are represented in the Table 3.2.

Table 3.2 Volume and weight reduction

Plastic type	Before Treatment		After Treatment		Weight reduction	Volume reduction	Density	
	Weight (g)	Volume (cm^3)	Weight (g)	Volume (cm^3)			Before (g/ cm^3)	After (g/ cm^3)
Mixed plastic	4900	8750	800	1475	1/6	1/6	0.560	0.542
Soil mixed with waste	20750	44000	12500	12800	3/5	3/10	0.472	0.977
Diapers	5000	11000	75	75	3/200	7/1000	0.455	1

Volume and weight of mixed plastic were reduced by 6 times after pyrolysis treatment. Volume of soil mixed with waste was reduced by 3/10 while weight was reduced by 3/7. In general, the least volume reduction occurred in soil mixed with waste and it is the minimum volume reduction because it contains soil. In addition, Basransyah et al. (2019) reported that homogenized waste is treated very well through pyrolysis in terms of volume reduction because different plastic materials decompose differently. When waste is mixed, such as in industrial mixed plastic and soil mixed with waste, less volume reduction occurs compared to homogenized wastes like disposable diaper.

The highest reduction ratio occurred in diaper both in volume and weight which are 7/1000 and 3/200, respectively. Moreover, recently, attempts on weight and volume reduction of adult disposable diapers through thermal treatment were done by company LIXIL Co. (Tonozaki, A., 2022). Volume and weight reduction comparison between pyrolysis and LIXIL method is shown in Figure 3.7. According to the data from article published on online Sankei newspaper, the weight and volume of adult diaper were reduced by 1/2 and 1/6 times with LIXIL method. Pyrolysis method weight and volume reduction are 33 and 24 times higher than LIXIL method reduction, respectively. From this, it is obvious that pyrolysis method is more practical in terms of weight and volume reduction for disposable diaper without environmental impacts.

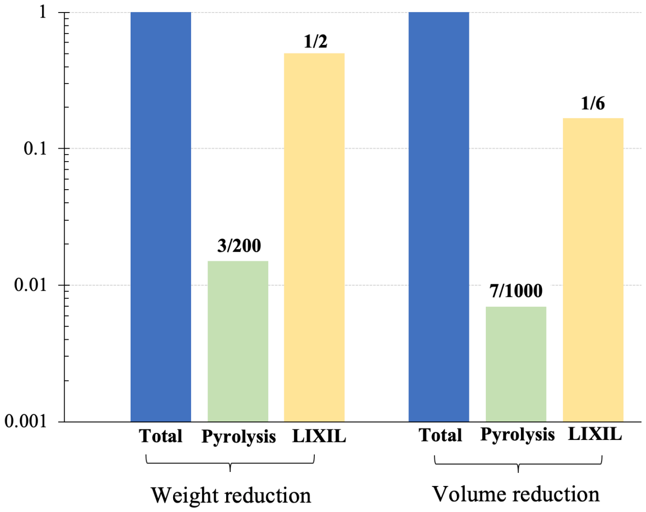

Figure 3.7: Comparison of pyrolysis method volume and weight reduction with LIXIL method

According to the obtained results of density change before and after pyrolysis technology, increase of density after pyrolysis in soil mixed with waste and disposable diapers was observed. However, in case of the mixed plastic density is decreased after pyrolysis.

3.4.2 Basic mechanical characteristics

3.4.2.1 Mixed Plastic

Pyrolysis technology thermally treated industrial mixed plastic (from here mixed plastic) has a particle density (ρ_s) of 2.943 g/cm^3. Particle size distribution of treated mixed plastic was determined according to the Japanese Geotechnical Standard JGS 0131 and it was classified as sand with fine fraction (S-F) based on JGS 0051. Maximum and minimum densities of mixed plastic were determined using Japanese testing method JGS 0161 and are equal to 0.796 g/cm^3 and 0.574 g/cm^3, respectively. Particle size distribution and compaction curve of the mixed plastic sample are shown in the Figure 3.8. All three samples were measured with the abovementioned methods according to Japanese Geotechnical Standards.

The grain size distribution curves of mixed plastic shows that finer particle fraction (less than 75 μm) is equal to 41.7%. According to the previous studies ash materials having particle range of sand with higher silt fraction were used as a fill material in road construction (Noaman et al., 2022). Thus, attempts to use industrial mixed plastics for road construction can be considered in the future. Compaction characteristics of pyrolyzed mixed plastic are similar to fly ash, bottom ash materials previously utilized for road construction (Reddy et al., 2018).

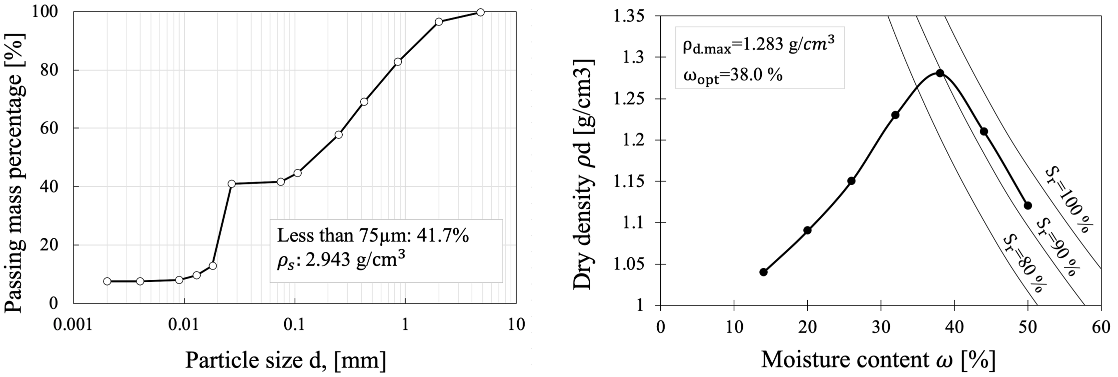

Figure 3.8: Characteristics of thermally treated mixed plastic sample in (a) particle size distribution and (b) compaction properties

3.4.2.2 Soil mixed with waste

Measured particle density, maximum and minimum densities of soil mixed with waste are 2.539 g/cm^3, 1.002 g/cm^3 and 1.357 g/cm^3, respectively. Particle size distribution of original soil and pyrolyzed soil mixed with waste were determined and they were classified as sand with fine fraction (S-F) based on JGS 0051. Figure 3.9 represents the particle size distribution curve of these two samples.

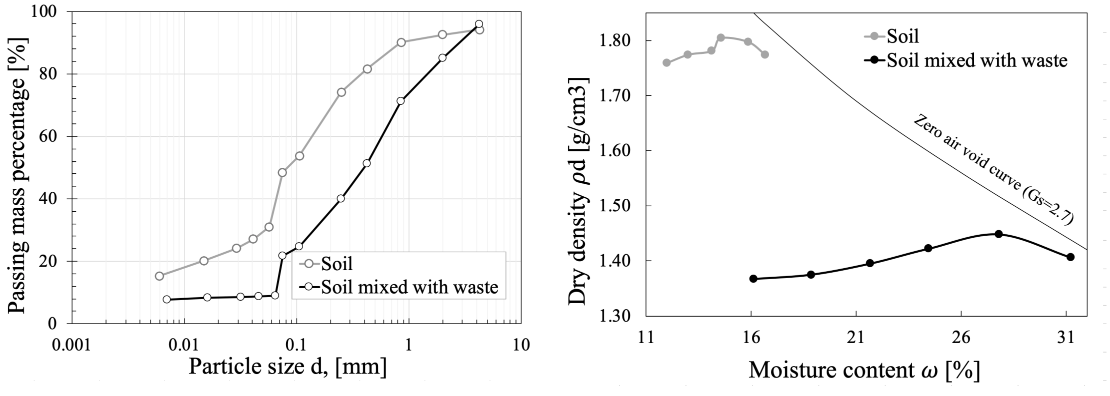

Figure 3.9: Characteristics of soil and thermally treated soil mixed with waste in (a) particle size distribution and (b) compaction properties

Fine particle fraction of pyrolyzed soil mixed with waste (21.8%) is less compared to the original soil and it represents gap graded grain-size distribution curve. This is due to the fact that smaller soil particles stuck together, then turned into lumps and as a result of heat treatment, these lumps turned into ceramic like hard bigger particles. However, even after thermal treatment, sample contains particles of wood chips. Decrease in density of particles is also can be explained by the contained wood chip particles. Moreover, maximum dry density of soil mixed with waste is decreased from 1.804 g/cm^3 (original soil) to 1.448 g/cm^3 (pyrolyzed soil mixed with waste) while optimum moisture content is increased.

Furthermore, if characteristics of industrial mixed plastic and soil mixed with waste are compared it can be noticed that industrial mixed plastic is finer. Maximum dry density of mixed plastic is less while optimum moisture content is quite higher compared to soil mixed with waste. Therefore, according to the previous studies, thermally treated ash materials having grain size distribution and compaction characteristics similar to soil mixed with waste can be used as a back fill material in retaining structures, embankment fills and fill material in low laying areas (Reddy et al., 2018). However, in order to attempt for utilization of soil mixed with waste sample, reducing wood chips in the sample should be considered. In addition, even though samples have fine fractions, none of the pyrolyzed samples show plasticity behavior. Following Table 3.3 summarizes beforementioned results of soil, soil mixed with waste and industrial mixed plastic.

Both untreated mixed plastic and soil mixed with waste samples were unable to compact, however after pyrolysis it was possible to compact both pyrolyzed samples which is big advantage in terms of utilizing these pyrolyzed samples.

Table 3.3 Basic mechanical characteristics of original soil and pyrolyzed soil mixed with waste and industrial mixed plastic

Properties/ samples	Soil	Pyrolyzed soil mixed with waste	Industrial mixed plastic
Density of soil particles (g/cm^3)	2.713	2.539	2.943
Particle size distribution (%)			
Sand fraction (0.075-2 mm)	44.0	63.4	54.9
Silt fraction (0.005-0.075 mm)	33.2	14.1	34.1
Clay fraction (<0.005 mm)	15.3	7.7	7.6
Maximum dry density (g/cm^3)	1.804	1.448	1.283
Optimum moisture content (%)	14.6	24.5	38.0

3.4.2.3 Disposable diaper

Particle density of pyrolyzed disposable diaper is 3.287 g/cm^3. Regarding with the sieve analysis results, fine particle fraction is significantly high in pyrolyzed disposable diaper sample, which is equal to 90.4%. Maximum and minimum densities are 0.438 g/cm^3 and 0.662 g/cm^3, respectively. As observed in section 2.3.1, when disposable diaper is thermally treated its volume reduction ratio is equal to 7/1000, it is difficult to get enough treated diaper sample for compaction test. Therefore it was impossible to conduct compaction test for disposable diaper sample. In the Figure 3.10 particle size distribution curve of treated disposable diaper waste is represented.

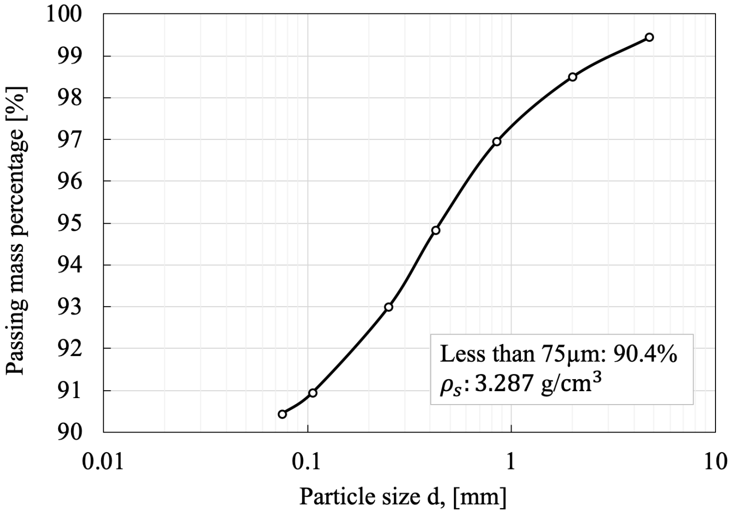

Figure 3.10: Sieve analysis of disposable diaper

3.4.3 TG-DTA analysis

3.4.3.1 Mixed plastic

Thermogravimetric analysis was performed by determining the mass loss as temperature increases. Three types of curves obtained from thermogravimetric analysis: thermogravimetric analysis (TGA) curve, derivative thermogravimetric (DTG) curve and differential thermal analysis (DTA) curve. TG curve is plotted between weight loss percentage and temperature, while DTG curve represents the first derivative of TGA curve. Sudden DTG peaks indicate thermal decomposition of sample fraction at corresponding temperature points. DTA measures the difference in temperature between the sample and the reference as the temperature rises, which allows to identify exothermic and endothermic reactions that may occur in the sample.

TGA, DTG and DTA results are represented in Figure 3.11. TGA experiments show that plastic degradation ranges between 285°C and 500°C. DTG curve of mixed plastic has two peaks at 358°C and 457°C. According to Sørum et al. (2001), the first peak at 358°C is related to the release of chlorine in PVC which indicates that mixed plastic sample contains PVC in it whose weight loss is about 20.7%. Second stage shows the thermal degradation of other plastics such as polystyrene (PS), polypropylene (PP), low-density polyethylene (LDPE) and high-density polyethylene (HDPE) between 350-500°C and which are main constituents of the sample. Its weight loss is equal to 55.9%. Values of residual weight fractions were calculated to be about

20%. According to DTA curve, at temperature of 164°C melting process of polypropylene (PP) occurs (Guzdemir and Ogale, 2019). The latter two peaks indicate decomposition of other polymers. After 33 minutes, at around 500°C almost all degradation processes were completed and mass loss stabilized.

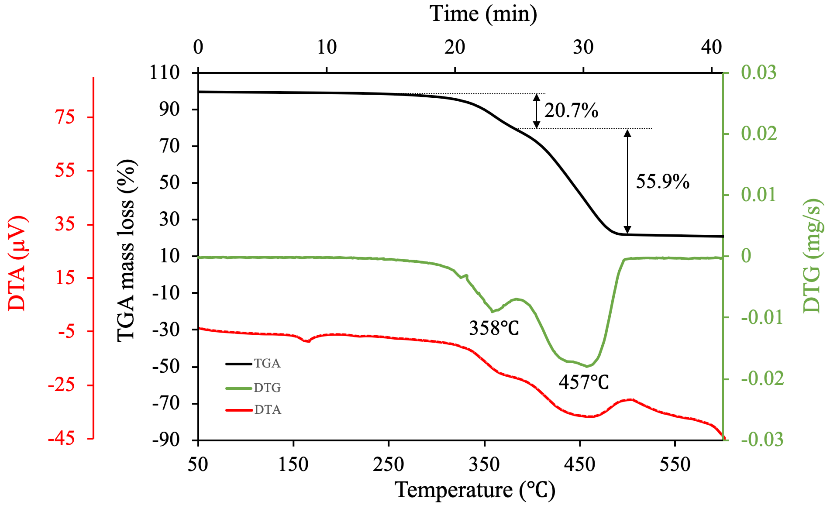

Figure 3.11: Result of TG-DTA analysis of industrial mixed plastic

3.4.3.2 Soil mixed with waste

TG-DTA analysis results for soil mixed with waste is shown in Figure 3.12. Degradation of soil mixed with waste ranges between 30°C and 500°C can be seen from TGA curve. Overall 3 peaks are observed from the DTG curve. The first peak at 56°C indicates moisture evaporation of the sample which is 2.7% and it is also indicated in DTA curve.

Wood materials are known to exhibit different degradation profiles depending on the composition of the wood. Wood consists of major chemical components such as cellulose, hemicellulose and lignin. Cellulose has higher thermal stability compared to other two components (Sebio-Punal, 2012). It can be noticed that the second peak has shoulder between 224°C and 315°C that shows decomposition of lignin, while main peak corresponds to the cellulose decomposition from 315°C to 385°C (Sørum et al., 2001; Na et al., 2008). The total degradation of both cellulose (4.4%) and lignin (7.1%), which are wood composites, constitutes over 11%. Weight loss between 385-500°C demonstrates the PET bottle and plastic bag degradation. Since sample contains soil particles (SiO_2) about 75% of the total sample remains even after 600°C pyrolysis. When temperature reached approximately 510°C, weight loss in the sample is slightly stabilized after 35 minutes.

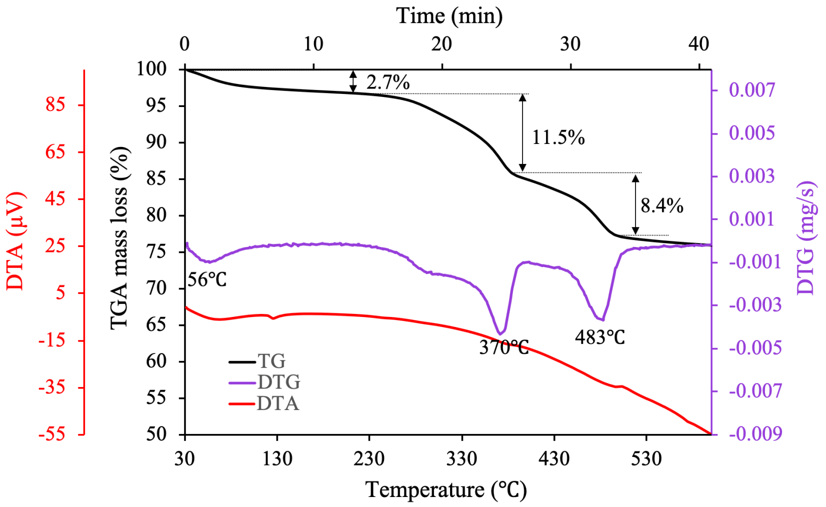

Figure 3.12: Result of TG-DTA analysis of soil mixed with waste

3.4.3.3 Disposable diaper

Khanyile et al. (2020) indicated that, generally, disposable diapers consists of 70% wood pulp and 30% petroleum, of which the latter is regarded as a finite resource. TGA results of disposable diaper is shown in Figure 3.13. Three peaks can be observed from the DTG curve. 3.9% of moisture evaporation took place at 62°C. At 350°C degradation of cellulosic matter as known as a wood pulp in the diaper was observed.

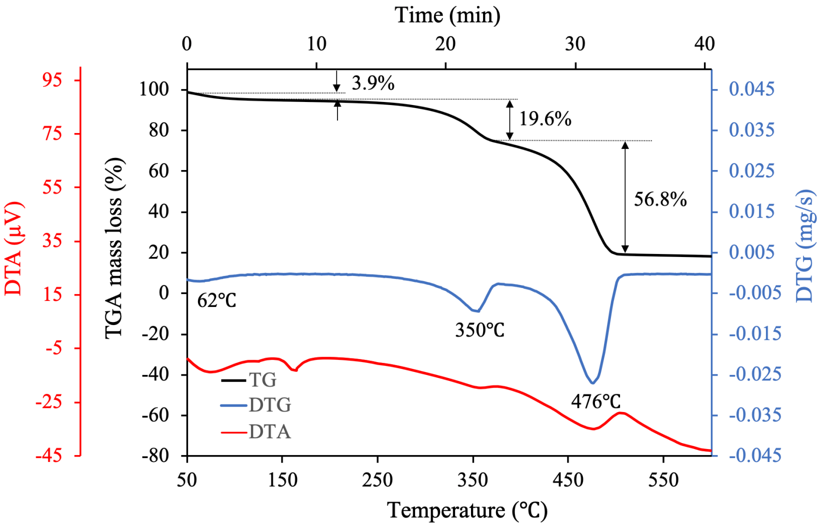

Figure 3.13: Result of TG-DTA analysis of disposable diaper

Exterior layers of disposable diaper is lighter in weight and are mostly polymer materials. Main part of the weight loss at 476°C is due to the degradation of plastic matter that are superabsorbent polymer and exterior fractions of diaper (mainly fossil-based plastics and rubbery materials) and is equal to 56.8%. According to Wolston (2015) and Khanyile et al. (2020), inner materials of the diaper are highly volatile, therefore ash content is very low. DTA curve indicates there is a plastic melting at 185℃ probably the exterior part of disposable diaper, while other two peaks represent decomposition. After 33 minutes at 500℃ sample mass loss is stopped.

As a results of thermogravimetric analysis results, it was observed that in all three samples, after 35 minutes no more weight loss at around 510℃ is observed. This indicates that almost the same result from pyrolysis thermal treatment can be reached at this condition. Instead of treating all three samples at 600℃ for 3 hours in pyrolysis technology, thermal treatment condition can be altered from 600℃ for 3 hours to 510℃ for maximum 1 hour. So, total energy can be saved through temperature and time reduction.

3.4.4 XRF analysis

3.4.4.1 Original raw and thermally treated mixed plastic

Results of elemental concentration of mixed plastic is represented in Figure 3.14. Silica, antimony, calcium, aluminum, magnesium, and titanium are the main components of mixed plastic. Silica (Si) is used to improve yield stress of plastic (Murphy, 2001).

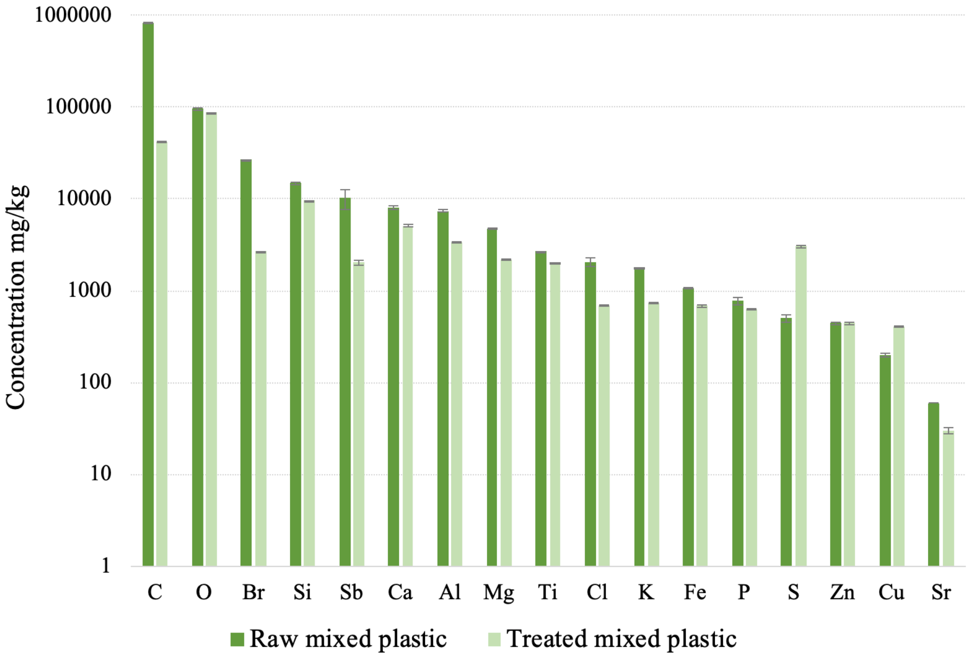

Figure 3.14: Result of XRF analysis of industrial mixed plastic

While calcium carbonate is the main component of various plastics in weight ratio and used to advance mechanical properties (Martín-Lara, 2021). The term calcium carbonate in plastic industry covers chalk, limestone, marble and precipitated calcium carbonate etc. Bromine (Br), antimony (Sb), aluminum (Al), chlorine (Cl) and phosphorous (P) are mainly used as flame retardant additives.

Another important property of polymers is thermo-oxidative stability which is achieved due to trace amounts of iron, magnesium and copper in carbonates and silicates. These also provides UV resistance for outdoor applications. Following specific metal oxides such as antimony, titanium, aluminum, zinc, iron and copper are required in order to obtain desired color of plastics. For instance, titanium is used as a white pigment (Murphy, 2001; Martín-Lara, 2021). In case of the mixed plastic, chemical composition of almost all elements has decreased after thermal treatment, except sulfur and cupper. High decrease in carbon (C), bromine (Br) and antimony (Sb) has occurred.

3.4.4.2 Original raw and thermally treated soil mixed with waste

Elemental composition results of soil mixed with waste from XRF is shown in Figure 3.15. Elemental composition of soil mixed with waste is complex and influenced with various factors and components of 4 types of materials such as soil, wood chips and polymers (PET bottle and plastic bag).

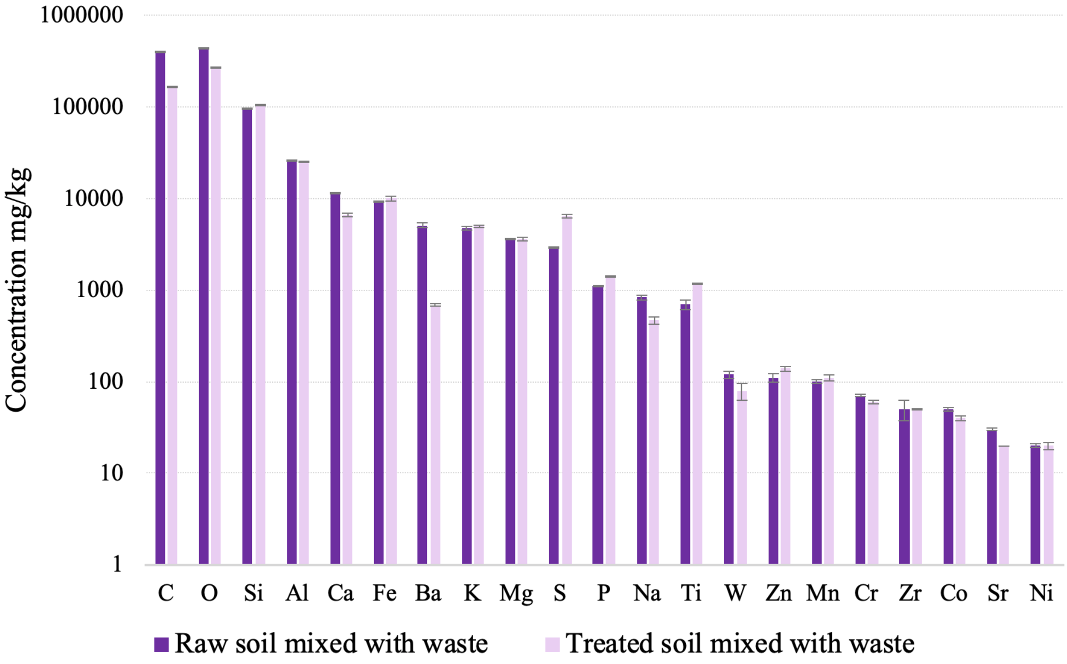

Figure 3.15: Result of XRF analysis of soil mixed with waste

All four materials contain aluminum (Al), calcium (Ca) and iron (Fe) as a major elements. For instance, aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na) and manganese (Mn) are major ash-forming elements in wood chips, while chromium (Cr), zinc (Zn), and nickel (Ni) are minor ash-forming elements. Sometimes, wood cells contain some heavy metals taken up by plant roots (Telmo, 2010; Chandrasekaran, 2012).

In case of the soil mixed with waste, Si content is higher than other two samples and has no change. It is because sample contains soil particles. The results of original and treated soil mixed with waste show stable and decreased concentration of elements mostly. Concentration of some elements such as Al, Fe, K, Mg, Mn, Zr and Ni has not been changed after thermal treatment. These elements are probably captured inside the soil particles. Phosphor, titan and zinc were increased a little after treatment.

3.4.4.3 Original raw and thermally treated diapers

XRF results of disposable diaper is represented in Figure 3.16. The first thing to notice that elements contained in the disposable diaper is limited compared to previous two samples. Sodium is the major constituent in the disposable diaper sample due to sodium polyacrylate (SAP) located in the core of the diaper with the function of liquid absorption and retention (Castrillon, 2019; Nailah, 2021). Calcium carbonate is used in diaper production in order to make diaper breathable. Therefore, sodium and calcium are the main components.

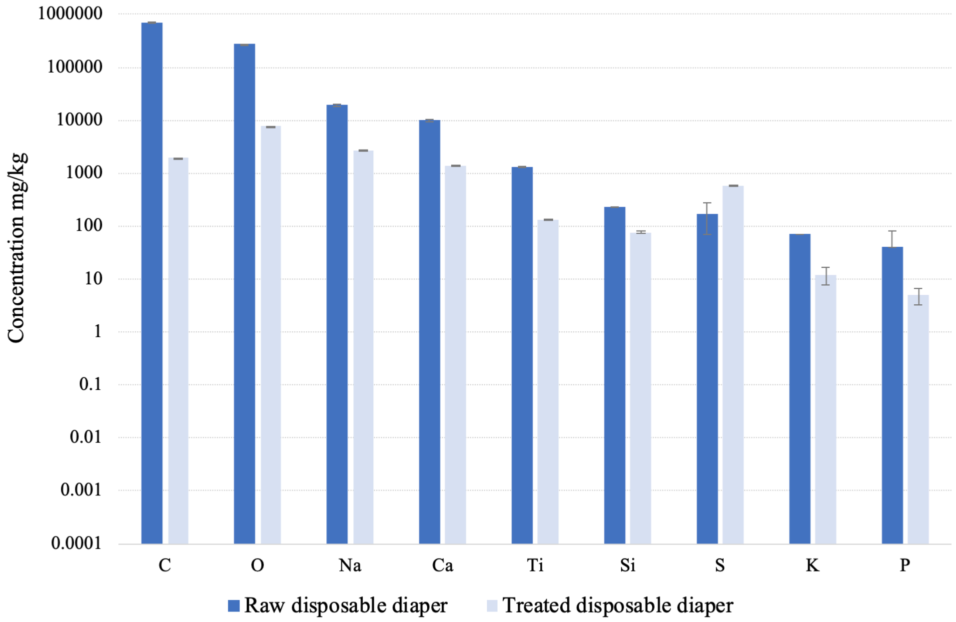

Figure 3.16: Result of XRF analysis of disposable diaper

Concentration of all elements from original diaper sample were decreased except sulfur. Also, the highest carbon decrease is observed in disposable diaper. As mentioned before, sulfur was added before the treatment in order to make other components stable, therefore sulfur concentration increase occurred in all samples. Even though high decrease of carbon in all three samples is observed, carbon content in the end products is quite high compared to other elements. Moreover, low carbon content is required for ash utilization for geotechnical purposes, it is suggested to consider additional treatments for reducing carbon content in pyrolyzed samples.

3.5 Conclusions for Chapter 3

In this chapter, volume reduction of three types of waste materials, namely, industrial mixed plastic, soil mixed with waste and disposable diaper through pyrolysis thermal treatment was considered. Moreover, effect of pyrolysis thermal treatment and its treatment conditions on three samples were considered by studying basic mechanical properties, thermogravimetry/differential thermal analysis and X-ray fluorescence analysis of samples. It was found out:

After treatment, volume and weight of industrial mixed plastic were reduced by 6 times. Volume of soil mixed with waste was reduced by 3/10 while weight was reduced by 3/7 which were the least reduction ratios among the samples. It is because of the soil contained in the soil mixed with waste. The highest reduction ratio was occurred in diaper both in volume and weight which are 7/1000 and 3/200, respectively. Consequently, it is obvious that pyrolysis method is more practical in terms of weight and volume reduction for disposable diaper without environmental impacts.

Regarding with the sieve analysis results, waste materials, industrial mixed plastic and soil mixed with waste, were classified as sandy soil with fine fractions and represent gap graded grain size distribution curve. However, fine particle fraction of disposable diaper is significantly high in thermally treated disposable diaper sample, which is equal to 90.4%. This is probably due to the sodium polyacrylate (sodium salt of polyacrylic acid) or gel like substance, super absorbent polymer (SAP). Even though samples have fine fractions, none of the pyrolyzed samples show plastic behavior. In addition, compaction characteristics of soil and soil mixed with waste were compared. It was observed that dry density in soil mixed with waste is less than original soil while optimum moisture content is increased. One of the reasons is explained by increase in grain size after pyrolysis thermal treatment and its gap-graded distribution curve characteristics. Also, industrial mixed plastic represents lower compaction characteristics. Compaction characteristics of samples are similar to previously utilized fly ash and bottom ash resulted from coal and municipal solid waste incineration by other scientists.

According to the TG-DTA curves it was determined that mixed plastic contains PVC. Values of residual weight fractions for mixed plastic and disposable diaper were calculated to be about 20% in TG-DTA analysis, however in actual thermal treatment residual sample weight is about 30% for mixed plastic. It is probably because thermal heat is not evenly distributed throughout the sample. In case of the soil mixed with waste, about 75% of the total sample remains even after 600℃ pyrolysis due to sample containment of soil particles (SiO_2). According to the thermogravimetric results, actual pyrolysis treatment condition is suggested to be reduced: temperature from 600℃ to 510℃ and time from 3 hours to maximum 1 hour since waste material decomposition finishes before this time. Thus, total energy consumption can be saved by reducing conditions.

From XRF data, in all three samples high decrease of carbon is observed after thermal treatment due to decomposition of polymer molecules. However, carbon is the highest among other elements and other methods of decreasing carbon content in the samples should be considered since ash with less carbon content is required for geotechnical purposes.

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Chapter 4 Leaching behavior of pyrolysis thermally treated samples

4.1 General remarks

Thermally treated waste material utilization leads to leaching of potentially toxic substances into soils, surface water and groundwater which is great concern of environmental countermeasures. When water percolates through soil, the leachate liquid that contains either dissolved or suspended toxic materials is produced. Therefore samples are subjected to batch leaching test, the Japanese regulatory leaching test method (JLT-46), in order to evaluate the leaching potential and compared with the limit values.

Single point short term leaching test is suitable for identifying whether or not waste material is safe to utilize. However, many scientists argue that it is insufficient for assessing material leaching under varying environmental conditions (van der Sloot et al., 2006; Engelson et al., 2010; Kosson et al., 2014). Therefore, leaching behavior of samples were investigated further with different pH conditions. In order to evaluate materials for utilization, pH dependent leaching values can be used as a reference for environmental decision-making to estimate potential risks and utilize waste material successfully in actual environmental conditions.

4.2 Methods and procedures

4.2.1 Batch leaching test

Leaching characteristics of pyrolysis ash was determined by following Japanese standard leaching test (JLT-46). In 500 ml of polyethylene bottle, 20 g of treated sample was mixed with 200 ml of distilled water by 1/10 solid-liquid ratio. The mixture was shaken for 6 hours with 200 rpm at room temperature and atmospheric pressure using a reciprocating horizontal shaker. After shaking, centrifuge separation with 3000 rpm for 20 minute was conducted. Later, liquid was filtered through a 0.45 μm membrane filter. Separated extract was diluted as needed. Concentrations of aforementioned elements (As, Cd, Cr, Cu, B, Pb, Se, Zn) were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Visual batch leaching test steps are shown in Figure 4.1. Leaching values were determined by the leaching test prescribed Japan Leaching Test Method #46 (JLT-46) and shown in Table 4.1. The results were compared with the limit leaching values according to the JLT-46 Soil elution standard.

For analytical measurements, single element calibration solutions were prepared from 1000 mg/L stock solutions of Cd, Cr, Se, Pb, As, B, Cu and Zn with 1M HNO_3. The same procedure was followed for the preparation of internal standard of Yttrium.

Figure 4.1: Batch leaching test steps: shaking, separating with centrifuge and ICP- AES and ICP-MS analysis

4.2.2 Total concentration analysis

Even though total elemental content of the pyrolyzed samples were determined by XRF analysis, some elements of interest are in a very small concentration cannot be detected because of the XRF detection limits. Therefore, concentration of elected elements were determined by ICP-AES and ICP-MS methods. Samples subjected to the ICP-AES and ICP-MS analysis should be dissolved into liquid form. Thus, microwave digestive system was used to efficiently decompose the sample matrix in order to completely release and solubilize analytes of interest of the thermally treated samples (Lamble and Hill, 1998).

In this study, total content of aforementioned 10 elements in the treated samples were identified using a microwave-assisted digestion procedure. Choosing the right acids by taking metals contained in the ash into account and combining them correctly in order to fully dissolve the sample is very important for microwave digestion (Das and Ting, 2017). Theoretically, hydrochloric acid (HCl) is used in order to extract metals from carbonates, phosphates, borates, and some oxides and sulfides while nitric acid (HNO_3) is used for releasing metals from metal salts. In case of the siliceous ashes, hydrofluoric acid (HF) is applied to extract metals bound to silicate fractions (Das and Ting, 2017). However, when HF acid is used for dissolution, afterwards dissolved sample should be buffered with boric acid. Since boron is one of the elements of interest of this study, using HF and buffering it with H_3BO_3 gives incorrect results of boron concentration. Consequently, it was decided that two methods of the sample dissolution are going to be used: (a) dissolving samples with HNO_3 and HCl acids for boron detection, while using (b) combination of HNO_3, HCl and HF acids followed by buffering with H_3BO_3 was chosen in order to determine the total elemental concentrations of rest analytes. In addition, in order to avoid excess pressure during the digestion of samples with a high organic content it was concluded to use pre-digestion (Lamble and Hill, 1998).

High Performance Microwave Digestion System ETHOS One, Milestone was used for dissolving thermally treated mixed plastic, soil mixed with waste and disposable diaper samples. The apparatus used is shown in the following Figure 4.2.

Figure 4.2: High Performance Microwave Digestion System ETHOS One, Milestone and samples

The acids used to digest treated samples were high-purity concentrated HNO_3, HF and HCl.

(1) For B analysis

Samples were prepared as following: about 0.3 grams of sample was weighed and transferred into the Teflon vessel followed by adding 4 ml of nitric acid (69%) and left overnight to pre-digest. Following morning, rest 5ml of nitric acid (69%), 3ml of hydrochloric acid (46-48%) were added. Then samples were digested at microwave power of 800W at 220℃ temperature for 20 minutes. Digested samples were cooled to the room temperature and filtered with 0.2 µm filter and diluted for the analytical examinations.

(2) For the rest elements (Ca, Cd, Al, As, Cu, Cr, Zn, Mn and Se) analysis

Up to pre-digestion method of samples and including pre-digestion were conducted same as in the previous method. Then, following morning, 5ml of nitric acid (69%), 3ml of hydrochloric acid (46-48%) and 3ml of hydrofluoric acid (48%) were added. Then samples were digested at microwave power of 800W at 220℃ temperature for 20 minutes. Digested samples were cooled to the room temperature and 10 ml of boric acid was added and heated at 180℃ in the microwave for another 20 minutes. Samples were cooled to the room temperature and filtered with 0.2 µm filter and diluted for further analysis. Then content of solution was measured using ICP-MS and ICP- AES. Ten elements, namely: Ca, Cd, Al, As, Cu, Cr, Zn, Mn, Se and B have been quantified using ICP-MS and ICP-AES.

4.2.3 pH dependent leaching test

Solubility of many elements in the thermally treated samples is mainly controlled by the pH of the leaching environment. Evaluating the leaching behavior of inorganic species with regard of equilibrium concentrations at various pH values is the principle of this method (Engelsen et al., 2010). pH dependent leaching behavior of selected elements were determined using Method 1313 (Liquid-solid partitioning as a function of extract pH using a parallel batch extraction). In order to obtain liquid-solid equilibrium, sample is homogenized by reducing particle size. According to the reduced particle size leaching time is determined. Particle size of the samples were reduced to 85% less than 0.3 mm by grinding. Considering the reduced particle size (less than 0.3 mm) extraction time is determined to be 24 hours.

Acid/base titration and buffering capacity of the tested material at an L/S of 10mL extractant/g-dry sample was determined and pre-test titration curve was prepared. A schedule of nitric acid and sodium hydroxide additions is defined from a pre-test titration curve presented in Figure 4.3 in order to obtain eluates of aforementioned specified pH values.

Leaching tests were conducted to investigate the release of major and trace elements between pH 2 and 13. These pH range indicates exposure conditions for utilization of thermally treated waste, similar to acidic rain (slightly acidic to neutral), natural soils (natural to slightly alkaline) and thermally treated ash (alkaline to highly alkaline). Therefore, nine parallel batch extractions of a particle-size reduced solid materials at L/S 10 mL/g-dry in dilute nitric acid (HNO_3) or base, sodium hydroxide (NaOH), including reagent water as a “natural pH” at a targeted end-point pH values were prepared. Besides 9 test extractions, three method blanks with no solid samples were carried out to confirm no reagent impurities or equipment contaminations are not happened. All samples were rotated end-over-end at 28±2 rpm for 24 hours. After, centrifuge separation with 3000 rpm for 20 minute was conducted and followed with liquid filtration through a 0.2 μm membrane filter. Ultrapure water (Milli-Q gradient, Merck, Germany) was used throughout analysis.

4.3 Results and discussions

4.3.1 Batch leaching test

Results of batch leaching test for three samples are presented in table 4.1. Leaching concentrations of elements except As and Se are less than JLT-46 limit values. Cd, Cr and Pb leached concentrations are very low. Cd was not detected in disposable diaper, while Cr and Pb were not detected in mixed plastic and soil mixed with waste samples due to the detection limits of ICP-MS. However, As and Se leaching behavior in mixed plastic and disposable diaper are over the limit concentrations.

Table 4.1 Batch leaching test results for mixed plastic, soil mixed with waste and disposable diaper

Elements	Sort term leaching test result (mg/L)			JLT-46 (mg/L)	Analytical method
	Mixed plastic	Soil mixed with waste	Disposable diapers		
Cd	$0.5*10^{-3}$	$0.1*10^{-3}$	ND	0.01	ICP-MS
Cr	ND	ND	0.01	0.05	ICP-MS
Se	0.55	0.01	0.04	0.01	ICP-AES
Pb	ND	ND	$1*10^{-3}$	0.01	ICP-MS
As	0.04	$2*10^{-3}$	0.02	0.01	ICP-MS
B	0.77	0.14	0.76	1.00	ICP-AES
Cu	0.02	$0.2*10^{-3}$	0.25		ICP-MS
Zn	0.46	0.14	0.17		ICP-MS

*ND – not detected

4.3.2 Acid-base neutralizing capacity

Acid neutralization capacity (ANC) curves for all three samples were obtained. Mixed plastic and soil mixed with waste have a similar neutralization behavior, which pH decreases by acid addition.

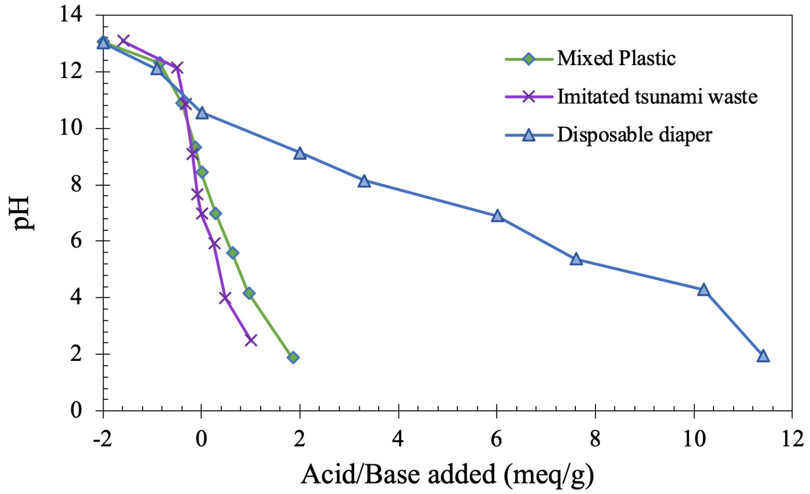

Figure 4.3: Acid neutralizing capacity of three samples

Diaper has high neutralization capacities due to the higher concentrations of alkali metals and alkaline earth metal contents. According to the XRF results from Figure 3.17, Na, K (alkali metals) and Ca (alkaline earth metal) are major constituents of disposable diaper sample. Neutral pH of mixed plastic and soil mixed with waste were 8 and 7, respectively, while disposable diaper had neutral pH of 10.5.

4.3.3 pH dependent leaching test

The four broad pH leaching behavior were observed from the thermally treated mixed plastic sample: (1) leaching of Ca and Cd shows cationic pattern where the concentration decreases slowly as pH increases; (2) Al, As, Cu, Cr, Zn and Mn leaching follows amphoteric pattern where solubility of these metals increases at both low and high pH values; (3) leaching of Se interprets oxyanionic pattern where solubility slightly increases at acidic and alkaline pH; (4) lastly leaching of B is not influenced by pH value.

ICP-AES and ICP-MS were used to determine major elements (Al and Ca), minor and trace metal cations (Cd, Cu, Mn and Zn) and elements that under certain conditions form oxyanions (As, B, Cr and Se). In Figures 4.4, 4.5, 4.6 and 4.7, the pH dependent release of aforementioned elements is shown. Leaching results over a range of pH values are graphically compared with the regulatory limit (JLT-46) and total content of the constituent in the material since it is very important to understand what portion of the element is leached out.

4.3.3.1 Leaching behavior of Ca and Cd

Ca and Cd leaching behavior as a function of pH represents a cationic pattern where the solubility gradually decreases as pH increases. Cationic pattern represents increasing release of absorbed elements from metal-bearing minerals as pH decreases, however when pH increases reduced leaching occurs due to precipitation and increasing sorption (Wang, 2004; Cetin, 2013; Komonweeraket et al., 2014). Therefore, high solubility of cationic metals at low pH values occur as a result of increase in dissolved mineral phases and decrease in adsorption of dissolved cationic ions.

In all three samples, released Ca concentration represents continuous negative correlation with pH by representing cationic pattern (Gitari et al., 2009; Cui et al., 2019). The influence of pH on leaching behavior of Ca is indicated by respective Ca concentration in relation to the volume of acid added. High Ca release is resulted not only by dissolution of its soluble salts on the surface of thermally treated sample particles but also by strong acid attack on Ca-bearing minerals (Gitari et al., 2009; Cui et al., 2019).

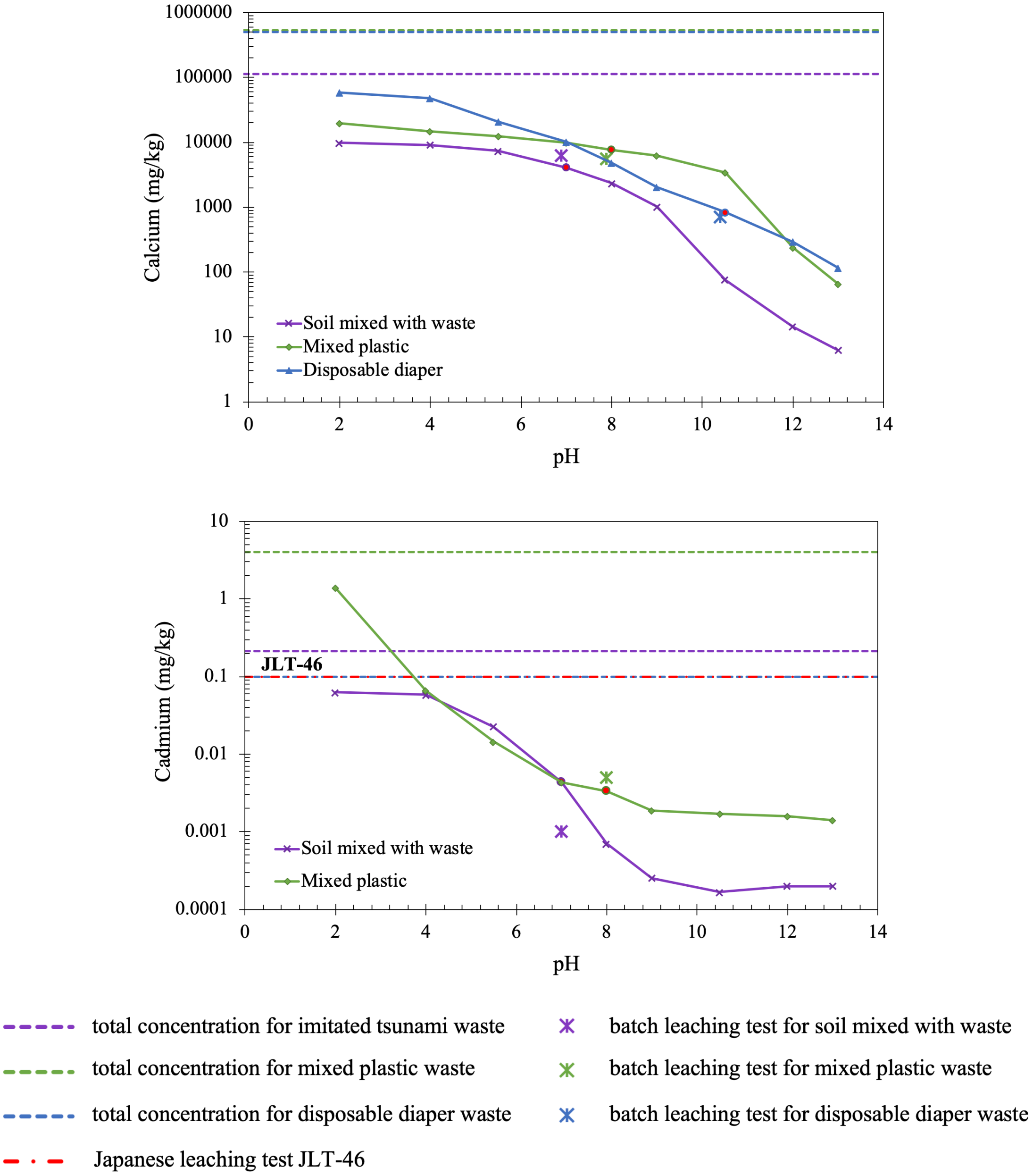

Figure 4.4: Concentrations of Ca and Cd metals as a function of pH

According to the total content of Cd (0.099 mg/kg) in disposable diaper is little less than JLT-46 limit value therefore, pH dependence characteristics of cadmium had not been checked in this sample.

Two main minerals such as sulfate and carbonate precipitation occurs with leached Ca and Cd elements and these minerals govern their leaching behavior as a function of pH (Stum and Morgan, 1996). According to van der Sloot et al. (1996) and Apul et al. (2005), carbonate minerals such as calcite [$CaCO_3$] or aragonite [$CaCO_3$] and otavite [$CdCO_{3(s)}$] control leaching behavior of

Ca and Cd, respectively, at high pH values. However, Comans and Middelburg (1993) suggested that when considering decrease of Cd concentrations to lower levels, co-precipitation or solid-solution formation with calcite should take precedence over predicting the solubility of ottavite. Maximum release of cadmium at pH 2 in soil mixed with waste is still less than JLT-46 limit value. Moreover, release in the pH of 2 reflects the availability of Cd in both samples which is almost the total content.

4.3.3.2 Leaching behavior of As, Cu, Zn, Cr, Al and Mn

Leaching behavior of As, Cu, Zn, Cr, Al and Mn followed amphoteric pattern which represents characteristic V-shaped curve. Generally, sorption of cations to differently charged surfaces is weaker at acidic condition compared to neutral pH values due to competition for surface sites by protons and repulsive charge effects. Increased heavy metal sorption occurs between neutral and slight alkaline pH values because of surface deprotonation, supportive hydroxide mineral surface charge which leads to decreased release. Since cations are involved into complex inorganic and organic reactions in alkaline conditions, sorption of cations to the particle surface decreased (Dijkstra et al., 2004).

(1) Major elements: Al

Al leaching is strongly pH-dependent and results in similar shape as cationic species in acidic condition followed by minimum in the alkaline pH range and increase in highly alkaline which is typical for Al-hydroxide solubility. The formation of aluminosilicates controls the solubility of Al in the high pH ranges. However, Gitari et al. (2009) indicates that boehmite and gibbsite are more stable under acid attack compared to aluminosilicate phases. Therefore, Al release at high pH values may be controlled by formation of aluminosilicates. Overall, the trend of leaching of Al could be controlled by Al bearing amorphous and crystalline phases. Several modelling studies represented the release of Al is governed by amorphous $Al(OH)_3$ at pH between 6 and 9 and by gibbsite (crystalline $Al(OH)_3$) at pH value of higher than 9 (Chandler et al., 1997; Gitari et al., 2009).

(2) Minor elements: As, Cr, Cu, Zn, and Mn

Total concentration of Pb in all three samples were too small and had not been investigated. Leaching behavior of As in soil mixed with waste is quite different from two samples showing amphoteric pattern. As(III) shows amphoteric pattern while As(V) represents oxyanionic pattern which might be the reason for different leaching patterns of arsenic in samples. Therefore, it is predicted that As (III) and As (V) exist in the soil mixed with waste sample, since its concentration is quite high at alkaline pH.

At pH between 5.5 and 6.5 relatively lower concentration of amphoteric elements is released due to formation of relative insoluble hydroxides.

Both alkaline and acidic pH conditions As and Cr form soluble oxyanions (AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$, H_3AsO_4, CrO_4^{2-}) or cation (Cr^{3+}) that leads to high concentrations (Cui et al., 2019). Calcium plays an critical role on the leaching of arsenic. Sharpened increase in arsenic release in alkaline pH is explained by decreased precipitation of calcium arsenate particularly when calcium concentrations decreased below approximately 1000 mg/kg.

Since total concentration of Cr in mixed plastic is less than JLT-46 limit value, pH dependent release had not been considered. Chromium leaching behavior of both soil mixed with waste and disposable diaper waste samples follow amphoteric pattern. Cr(III) is less leachable than Cr(V) at neutral pH. Moreover, Cr(III) is leachable only at relatively low pH values (pH<4). According to the previous studies of geochemical modelling, V shape of Cr leaching curve as a function of pH is explained by binding of Cr to sulphoaluminates (ettringite).

The leaching behavior of Cu has been studied in detail by van der Sloot et al. (1992). A relation between Cu solubility and the presence of organic matter exist. However, organic matter was not considered in this research. Previous studies indicated that thermally treated waste particle surface is negatively charged at alkaline pH which leads to adsorption of Cu from the solution. Sorption is highly dependent on pH and the sorption of Cu, Pb and Zn is much stronger than base cations such as Ca. In addition to sorption at metal hydroxides surface, copper is also able to bind within the metal hydroxide due to co-precipitation, especially for iron hydroxides.

Similar to the aforementioned other heavy metals, increased leaching concentrations of Zn occur at low pH and strongly decreases (four orders of magnitude) up to pH 10. Complex solution hydroxide induces increase of dissolved Zn at strongly alkaline pH. Generally, zincite (at intermediate pH) and $ZnSiO_3$ (pH 4-6 and pH > 12) govern Zn leaching from thermally treated ash samples.

Dissolved Mn is also decreases strongly with pH, and reaches minimum values at approximately pH 10 followed by slight increased release at higher pH values. Although the solutions are not in equilibrium with pyrocroite ($Mn(OH)_2$), the shape of the curves may suggest another less soluble Mn hydroxide to control Mn leaching. Recent work suggests manganite ($MnO(OH)$) as the solubility controlling phase. Mn hyrdroxide appears to control the solubility at pH >12.

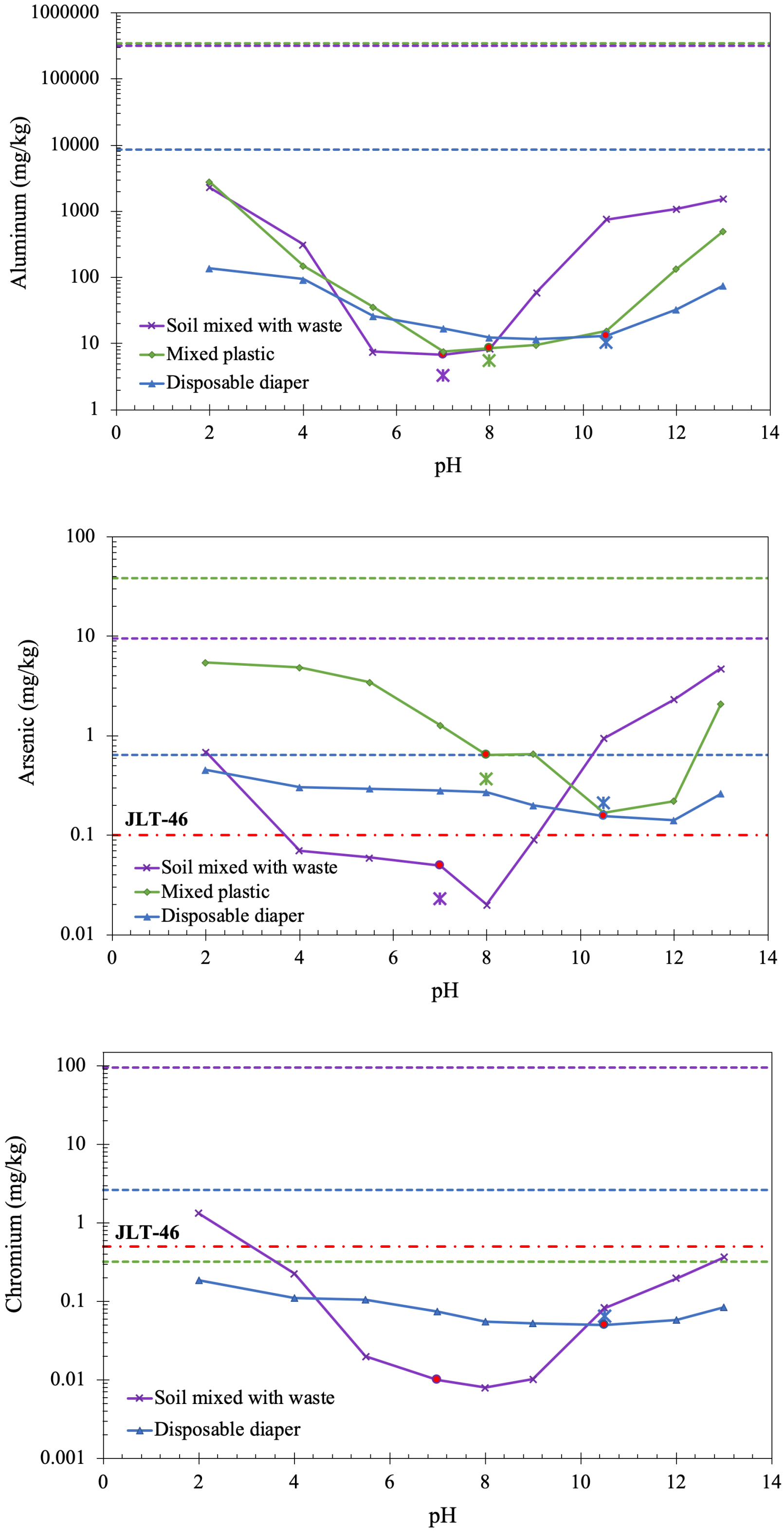

Figure 4.5: Concentrations of Al, As and Cr metals as a function of pH

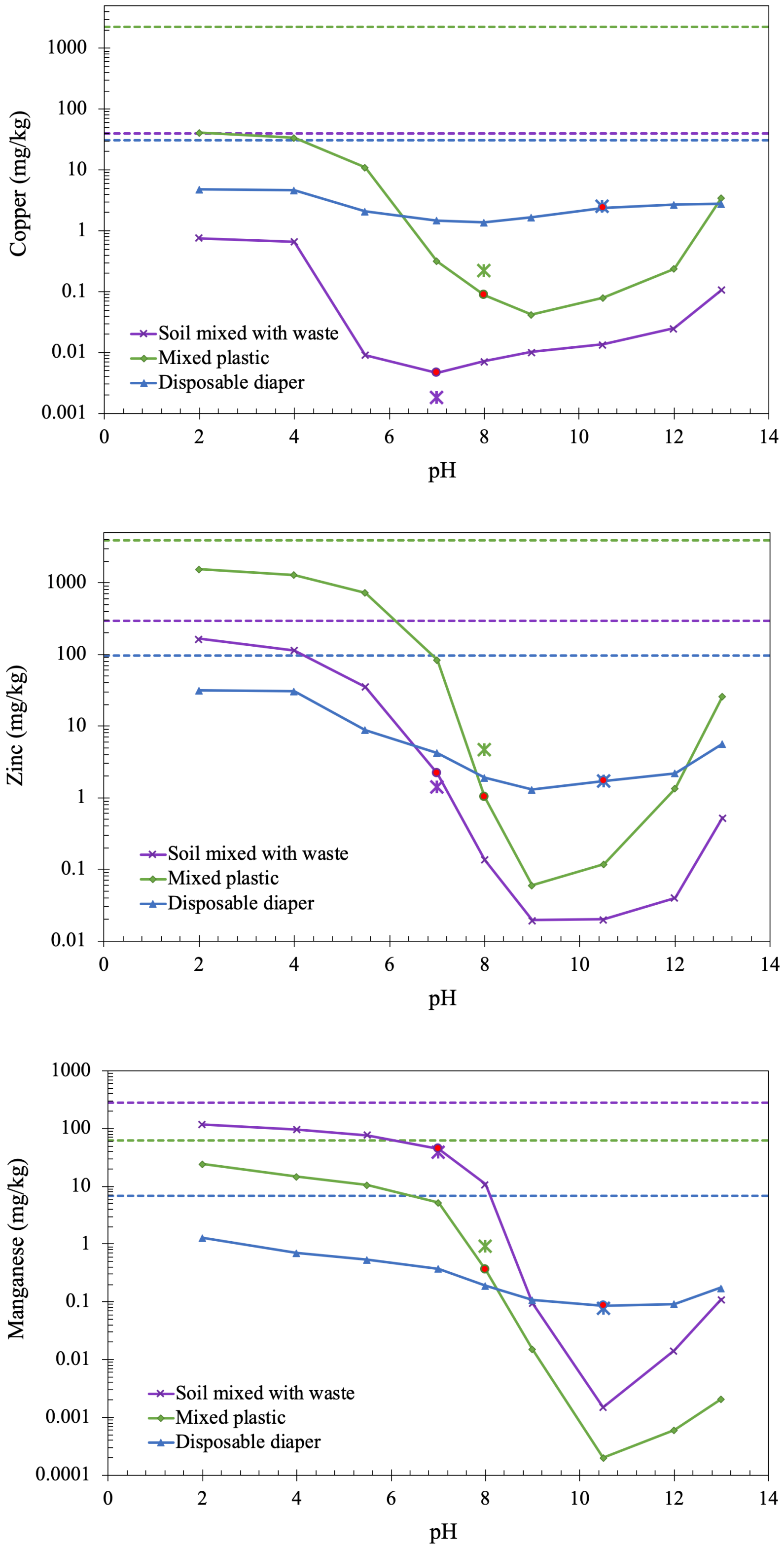

Figure 4.6: Concentrations of Cu, Zn and Mn metals as a function of pH

4.3.3.3 Leaching behavior of Se

Too much attention has been paid to heavy metals (e.g., Pb, Cu, Cd, Zn, Hg) and too little to oxyanions (e.g., Se, Sb, Mo, V, W), which are quite mobile under neutral pH conditions. Because of the negative charge leaching pattern of oxyanions differ from leaching behavior of cations. In case of the oxyanions, metal and oxygen forms covalent chemical bonding. Oxyanionic pattern follows increase of element solubility at alkaline pH and decreased leaching as pH lowers due to sorption of anions on mineral surface.

Leaching concentration of Se alters as pH changes due to in leachate species and pH dependent surface charge of thermally treated samples (ash). High concentration of leached Se at alkaline pH is due to repulsive effect between negatively charged oxyanionic Se (SeO_3^{2-} or SeO_4^{2-}) and negatively charged surface of particles. According to results of chemical modelling done by Cornelis (2008), Se mainly exist as SeO_3^{2-} at pH value higher than 7.5. At the same range of pH (7.5<pH<13) ash particles are negatively charged (Komonweeraket et al., 2014).

Low affinity of Se species for surface sorption at pH<5 is due to increased protonation of negatively charged Se which leads to high concentration of leached Se at low pH value (Dijkstra, 2020; Komonweeraket, 2014). Decreased leaching concentration of Se at slightly acidic pH is explained by significant adsorption of Se onto the neutral or slight positive particle surface.

However, Se leaching behavior in disposable diaper does not follow the oxyanionic pattern. This is probably due to different factors and controlling mechanism, various dominant Se species existing in the leachates in different pH and effects from the presence of other dissolved ions in the leachates. The possibility of one reaction proceeding over the other depends on the type of Se species with different affinities for adsorption and ion incorporation to form solid. For instance, from geochemical modelling results of Komonweeraket (2015) species of Se between pH 1.5 and 12 were defined as $HSeO_3^-$, $CaSeO_3$ and $SeO_3^{2-}$for selenite (Se(IV)); SeO_4^{2-}, $CaSeO_4$ and $MgSeO_4$ for selenate (Se(VI)). Moreover, adsorption and solid forming ability of selenium in trace amount is reduced by existence of other leachate omnipresent anions (SO_4^{2-}, CO_3^{2-}, NO_3^-, Cl^-) that competes for surface sorption. Leaching behavior of Se in disposable diaper waste sample represents different pattern. Some studies confirmed that selenite is highly adsorbed in the pH range of slightly acidic to slightly alkaline which leads to decrease in Se release (Hyun et al., 2006).

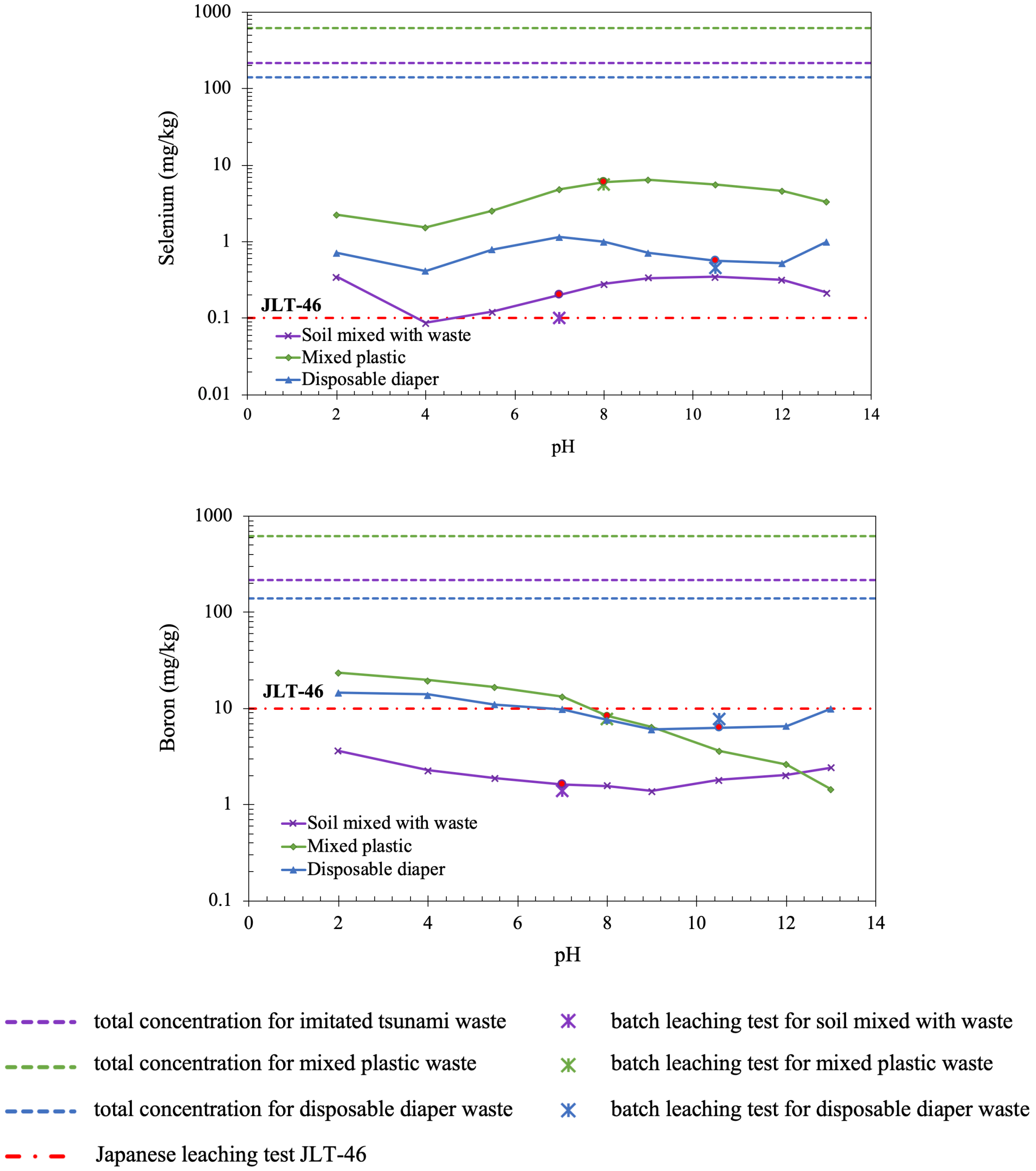

Figure 4.7: Concentrations of Se and B metals as a function of pH

4.3.3.4 Leaching behavior of B

Boron is one of the highly soluble species and leaching pattern of boron represents a weak function of pH. Gradually increase of released B concentration with pH decrease indicates the existence of B as a soluble salt both on the surface and within the matrix of particle (Gitari et al., 2009). Boron is immediately solubilized when the sample is mixed with solution by showing high solubility in both acidic and alkaline pH values. From the previous studies, it was observed that lower concentrations of B occurs at pH >11 due to co-precipitation with $CaCO_3$ (Hollis et al., 1988). Ettringite is easily formed when its components are available in very alkaline solutions that leads to entrapment of boron existing as oxyanion in this pH range (Gitari et al., 2009). Since ettringite and calcium carbonate cannot be formed in acidic condition, high release of boron occurs in low pH values.

4.4 Conclusions for Chapter 4

This chapter focused on the characterization of leaching behaviors of thermally treated samples with the aim of identifying environmental effects of elements with regards of Japanese leaching test for soil elution (JLT-46), better understanding and recognizing the limitations of further utilization of these samples. Batch leaching test and pH dependent test were conducted. According to the batch leaching test results, Cd, Cr and Pb leached concentrations were very low. Particularly, leaching amount and total content of cadmium in soil mixed with waste and disposable diaper waste are smaller than the JLT-46 limit values over the pH range, respectively which indicates no Cd leaching harm occurs when these two samples are utilized in the actual field. While Cr and Pb were not detected in mixed plastic and soil mixed with waste samples due to the detection limits of ICP-MS. However, As and Se leaching amounts in mixed plastic and disposable diaper waste materials are higher than JLT-46 limit values.

Acid neutralizing capacity of diaper higher compared to other two samples. Leaching characteristics are not influenced by independent factors, but mostly release of constituents is occurred as a result of multiple factors. Ca and Cd leaching behavior as a function of pH represents a cationic pattern where the solubility gradually decreases as pH increases. Leaching behavior of As, Cu, Zn, Cr, Al and Mn represent amphoteric pattern which represents characteristic V-shaped curve in all three samples. Even though total content of As in diaper is the smallest among three samples, its batch leaching value is higher than JLT-46 limit values. Furthermore, it was hypothesized that the excess selenium leaching in mixed plastic and disposable diaper samples from batch leaching tests were due to the oxyanionic pattern of selenium, which exhibits higher leaching characteristics at neutral pH. However, from pH dependent test results, it was found out that Se leaching values were higher than JLT-46 leaching limit values over the entire pH range which indicates it is not the case. Leaching behavior of B is poorly influenced by pH and even though total concentration of boron is quite high leaching values were less than limit values.

Higher concentrations of As and Se require countermeasures to As and Se leaching during utilization.

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Chapter 5 Conclusions and future research

5.1 Conclusions

Pyrolysis technology is recognized as the promising method of handling modern complex plastic-related wastes among other existing treatment technologies. As a waste material industrial mixed plastic waste, soil mixed with waste and disposable diaper waste were considered according to their importance in Japan and worldwide. Key issue related to plastic-waste management is generated significant amount of waste and leaching behavior of thermally treated waste materials during utilization.

Main objective of this study was to investigate volume reduction of beforementioned waste materials through pyrolysis technology and leaching behavior of these materials with the future purpose of utilizing for geotechnical purposes. To achieve this goal (1) volume reduction through pyrolysis technology was considered. (2) Effect of pyrolysis method was evaluated with basic mechanical characteristics of pyrolyzed waste materials, TG-DTA and XRF analysis. (3) Batch leaching tests and pH dependent laboratory tests were carried out in order to evaluate leaching behavior of thermally treated materials.

From Chapter 3 it was found out that pyrolysis technology operates well for disposable diapers in terms of volume and weight reduction, which represents volume and weight reduction of 7/1000 and 3/200, respectively. According to the TG-DTA analysis it was concluded that it is better to reduce pyrolysis temperature and residence time conditions from 600℃ for 3 hours to 510℃ for maximum 1 hour. From XRF data, even though high decrease of carbon in all three samples is observed after pyrolysis thermal treatment, carbon concentration is the highest among other elements. Since less carbon content is preferred for utilizing in geotechnical fields, it is suggested to find a method for reducing carbon concentration. Moreover, fine particle fraction of disposable diaper is significantly high in thermally treated disposable diaper sample which is equal to 90.4% indicates difficulty of utilizing this material as geo-material per se. This issue can be handled by mixing this material in order to improve geotechnical properties of poorly graded sand materials.

From Chapter 4 it was found out that leaching behavior of heavy metals are under JLT-46 leaching limit values, except As and Se in mixed plastic and disposable diaper waste materials. It was also found out that disposable diaper sample represents higher acid neutralizing capacity compared to other two samples. As a result of pH dependent test results, leaching amount and total content of cadmium in soil mixed with waste and disposable diaper waste are smaller than the JLT-46 limit values over the pH range, respectively. It indicates that these two samples poses no Cd leaching threat when utilized in the actual field.

According to the previous studies, in order to reduce landfill space limitation problems, conventionally incinerated coal and waste materials have been utilized in geotechnical applications of filling low laying areas, using as backfill material for retaining structures, fill material for embankment construction, added materials for stabilizing problematic soft soils, etc. Well-compacted incinerated ash materials show good shear strength comparable to normal soils used in earth-fill operations. However, leaching issues are the main concern since incinerated ash materials contain high concentrations of heavy metals. In this case, pyrolysis ash is safer compared to incinerated ash materials except As and Se leaching. Presence of heavy metals like As and Se poses a threat to soil and underground water, therefore pretreatment and use of additives can play a crucial role in order to avoid this problem. There are several techniques such as a site grading, compaction, attenuation layer, surface water control that can be used to prevent leachate from happening.

Utilization of thermally treated pyrolysis ash in road and embankment construction has many advantages. It avoids creation of low-lying areas resulted from excavation and saves natural soil resources which otherwise used as fill material. The construction of roads requires various materials, one of which is sand or cement bases. Pyrolysis ash is technically can be used for this purpose, particularly, soil mixed with waste can be utilized as an alternative to sand material.

Using lime and cement to stabilize soil is a common practice in order to achieve geotechnical properties. This stabilization increases the shear strength and reduces soil compressibility. Therefore in order to use pyrolysis ash for this purpose, pozzolanic characteristics of pyrolysis ash should be checked for further research, especially industrial mixed plastic and disposable diaper samples since these samples are very fine like cement material. Easily available pyrolysis ash with positive physical properties generates an opportunity of cost effective pyrolysis ash soil stabilization. Therefore, required amount of pyrolysis ash depending on specific geotechnical building works and the availability of different pyrolysis ash types should be considered in terms of pyrolysis technology practicality.

The results and limitations of this research can be used for the future investigations of other plastic-related waste materials such as anti-COVID plastic dividers, complex construction wastes, food containers, etc.

5.2 Recommendation for future research and Practical implications

In this research batch and pH dependent leaching behavior of samples were investigated. However, this approach does not fully represent actual field conditions with respect of flow conditions through materials. Moreover, even though basic mechanical characteristics were studied, these are not enough for future utilization as a geo-materials. Utilizing pyrolysis ash in the field of geotechnical engineering requires determination of its physical, chemical, morphological and engineering properties. Therefore following future research and practicality of pyrolysis technology on utilization of these pyrolyzed materials with the purpose of developing geotechnical properties of the soils are considered. Therefore, it is crucial to consider following aspects in future research:

1. Performing scanning electron microscope (SEM) in order to study morphology of waste materials
2. Finding other methods of decreasing carbon content in the pyrolyzed waste samples before utilization
3. Conducting loss on ignition test for pyrolyzed waste samples
4. Determining permeability characteristics of these waste materials
5. Checking pozzolanic characteristics of pyrolysis ash in order to utilize for soil stabilization
6. Determining bearing capacities of pyrolyzed ashes when utilized as geo-material for retaining structures, embankment and road pavement
7. Studying countermeasures for As and Se leaching by utilizing attenuation layers and mixing with binders
8. Studying liquefaction behavior of these samples when utilization as a fill material is considered, since research samples are cohesionless and non-plastic

According to the analysis of previous researches, following potential utilization options are suggested for future practical:

1. Decreasing the swelling, plasticity index (PI) and the clay amount percentage by adding these pyrolyzed waste materials in order to stabilize clay soils
2. Utilizing pyrolyzed ash for poorly graded sands in order to improve its compaction characteristics
3. Utilizing for solidifying sludge, decreasing its water content and improving its shear strength
4. Applying pyrolysis technology for other plastic wastes such as food packaging, vehicle tire, etc.
5. Applying pyrolysis technology for construction waste (mixture of glass, plastics, wood, surplus mortar, surplus concrete, broken bricks and excavated soil).