FACULTY OF TECHNOLOGY

# GRANULATION AND ALKALI ACTIVATION OF MSWI BOTTOM ASH

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# ABSTRACT

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Abstract

The ever-increasing amount of municipal solid waste has become a problem around the world and in Finland, where the recycling rate of municipal solid waste has remained the same for the last decade. The disposal of municipal solid waste has instead been done mostly by incineration into energy, with 56 % of all municipal waste being incinerated by Finland in 2019. There are multiple reasons why disposing of municipal waste by incineration is the popular method. Municipal waste is mixed organic and inorganic waste, causing problems in separation for recycling and landfilling, while incineration reduces waste mass by 70 % and volume by up to 90 %, which is important with the huge amount of waste in modern society. Also, a legislation in 2016 forbade landfilling of organic waste in Finland. The resulting municipal solid waste incineration (MSWI) residues, bottom ash and fly ash contain various pollutants such as heavy metals, which means they need to be treated and stabilized before landfilling or using as a material to avoid leaching of hazardous components.

The objective of this study was to form granules by means of tumbling granulation from municipal solid waste incineration (MSWI) residues, mainly bottom ash, by using an alkali-activator as a binding liquid to geopolymerize and solidify the granule structure. The primary focus of the thesis was to study how different co-binders such as MSWI fly ash, ground-granulated blast furnace slag, coal fly ash and curing techniques affect the leaching and physical properties of granules for the use as lightweight aggregates in construction.

The first part of the study focused on the effects of different co-binders in longer and simple curing conditions such as room temperature- and oven curing for up to 28 days. The main material used was MSWI bottom ash, while 10 % of the material was substituted with co-binders, MSWI fly ash and ground-granulated blast furnace slag (GGBFS). The second part of the study used the same residues for granulation apart from substituting coal fly ash instead of GGBFS as a co-binder. The curing with sintering and microwaving was done after 24 hours of oven-curing, and possible degradation of sintered or microwaved samples over longer periods of time was not studied. The alkali-activator used in both studies was liquid sodium silicate. The residues used for samples were evaluated with thermogravimetric analysis, x-ray fluorescence, x-ray diffraction and particle size analysis along with a leaching test while the granules were tested for compressive strength, bulk density, water absorption and leaching.

The granulation was easily done by mixing MSWI bottom ash and a liquid alkali-activator in a pelletizing disk to form spherical granules. The results of the study showed that alkali-activated granules formed from MSWI residues such as bottom ash using a sodium silicate solution were classified as lightweight aggregates based on their bulk density. The compressive strength of most granules was close to a weaker commercial LECA-aggregate, but sintered samples had less strength than expected. The highest strength was obtained by substituting 10 % of GGBFS into the MSWI BA with room temperature or oven curing. Water absorption was higher in sintered samples than in other similar studies while milder curing conditions resulted in absorption properties found in other studies on alkali-activated granules. The environmental impact assessment done by leaching analysis found varying results dependent on the hazardous components and what type of curing and co-binders were used. Some hazardous components were stabilized well by milder curing conditions, while some were immobilized completely only by sintering. However, this sintering especially at 800 °C also caused some previously stabile components such as chromium to be highly leachable.

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Tiivistelmä

Kiinteän yhdyskuntajätteen jatkuvasti kasvavasta määrästä on tullut ongelma ympäri maailmaa ja Suomessa, jossa kiinteän yhdyskuntajätteen kierrätysaste on pysynyt samana viimeisen vuosikymmenen ajan. Kiinteän yhdyskuntajätteen loppusijoitus on sen sijaan tapahtunut enimmäkseen polttamalla energiaksi, ja 56 prosenttia kaikista yhdyskuntajätteistä poltettiin Suomessa vuonna 2019. On useita syitä, miksi yhdyskuntajätteet hävitetään polttamalla. Yhdyskuntajäte on sekoitettua orgaanista ja epäorgaanista jätettä, mikä aiheuttaa ongelmia kierrätyksessä ja kaatopaikalle sijoittamisessa, kun taas polttaminen vähentää jätemassaa 70 % ja määrää jopa 90 %, mikä on tärkeää nykyaikaisessa yhteiskunnassa syntyvän valtavan jätemäärän vuoksi. Lisäksi vuonna 2016 laadittu lainsäädäntö kielsi orgaanisen jätteen sijoittamisen kaatopaikalle Suomessa. Kiinteän yhdyskuntajätteen polttamisjätteet, pohjatuhka ja lentotuhka sisältävät erilaisia epäpuhtauksia, kuten raskasmetalleja, mikä tarkoittaa, että ne on käsiteltävä ja stabiloitava ennen kaatopaikalle sijoittamista tai materiaalina käyttöä haitallisten aineiden huuhtoutumisen välttämiseksi.

Tämän tutkimuksen tavoitteena oli muodostaa rakeita kiinteän yhdyskuntajätteen polttamisen tähteistä, pääasiassa pohjatuhkasta, käyttämällä alkaliaktivaattoria sitovana nesteenä rakeiden rakenteen geopolymeroimiseksi ja kiinteyttämiseksi. Opinnäytetyön ensisijaisena tavoitteena oli tutkia, kuinka erilaiset sideaineet, kuten lentotuhka, jauhettu rakeinen masuunikuona, kivihiilen lentotuhka ja eri kovettamistekniikat, vaikuttavat rakeiden raskasmetallien huuhtoutumiseen ja fysikaalisiin ominaisuuksiin käytettäväksi kevyinä aggregaatteina rakentamisessa.

Tutkimuksen ensimmäinen osa keskittyi sideaineiden vaikutuksiin pidemmissä ja yksinkertaisissa kovetusolosuhteissa, kuten huoneenlämmössä ja uuneissa kovettamalla jopa 28 päivän ajan. Pääasiallinen materiaali oli pohjatuhka, kun taas 10 % materiaalista korvattiin sideaineilla, lentotuhkalla ja jauhetulla masuunikuonalla. Tutkimuksen toisessa osassa käytettiin samoja tähteitä rakeistamiseen lukuun ottamatta masuunikuonan korvaamista hiilenpolton lentotuhkalla. Sintraus ja mikroaallotus tehtiin 24 tunnin uunissa kovettamisen jälkeen, eikä sintraus- ja mikroaaltonäytteiden mahdollista hajoamista pitkällä aikavälillä tutkittu. Molemmissa tutkimuksissa käytetty alkaliaktivaattori oli natriumsilikaatin vesiliuos. Rakeissa käytetyt materiaalit analysoitiin termogravimetrisellä analyysillä, röntgenfluoresenssilla, röntgendiffraktiolla ja hiukkaskokoanalyysillä sekä uuttotestillä. Rakeista testattiin puristuslujuutta, irtotiheyttä, veden imeytymistä ja uuttoa.

Rakeistus tehtiin onnistuneesti pelletointilevyssä sekoittamalla tuhkaa ja alkaliaktivaattoria kunnes saatiin pallomaisia rakeita. Tuloksena saadut rakeet luokiteltiin keveiksi aggregaateiksi niiden tiheyden perusteella. Useimpien rakeiden puristuslujuus oli lähellä testattua LECA-aggregaattia, mutta sintrattujen näytteiden lujuus oli odotettua pienempi. Suurin lujuus saatiin sekoittamalla 10 % masuunikuonaa ja kovettamalla huoneenlämmössä tai uunissa. Veden imeytyminen oli korkeampi sintratuissa näytteissä kuin muissa vastaavissa tutkimuksissa, ja lievemmät kovetusolosuhteet johtivat samankaltaisiin ominaisuuksiin kuin muiden alkaliaktivoitujen rakeiden tutkimuksissa. Raskasmetallien huuhtoutumisanalyysi osoitti, että tulokset riippuivat ainekohtaisesti riippuen käytetystä kovetusmenetelmästä ja sideaineista. Jotkin haitalliset aineet stabiloituivat jo alkaliaktivaatiolla lievemmissä olosuhteissa, ja toiset eivät huuhtoutuneet lainkaan sintrauksen jälkeen. Alkaliaktivaatio kaikissa näytteissä aiheutti kuitenkin joidenkin aineiden huuhtoutumisen lisääntymistä, ja varsinkin 800 °C sintrauksen jälkeen aiemmin stabiilit aineet kuten kromi pystyikin huuhtoutumaan todella vapaasti.

# FOREWORDS

This thesis was conducted for the department of Fibre and Particle Engineering in the University of Oulu as a part of research into the utilization of industrial side streams and waste recycling by the application as geopolymers. The purpose was to study municipal solid waste incineration ash as a material for stabile geopolymers to be used as a construction material using alkali-activation and granulation.

I want to thank my thesis supervisors Priyadharshini Perumal and Juho Yliniemi for giving me chance to write this thesis and helping me achieve my goals. I also want to give special thanks to the very helpful laboratory staff members Elisa Wirkkala, Jarno Karvonen and Jani Österlund and any others who have helped me with all my questions and problems or analysis.

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# SYMBOLS AND ABBREVIATIONS

°C             Degree in Celsius

APC            Air pollution control

BA             Bottom ash

FA             Fly ash

GBFS           Granulated blast furnace slag

ICP-OES        Inductively coupled plasma optical emission spectrometry

KOH            Potassium hydroxide

L/S            Liquid to solid ratio

LECA           Lightweight Expanded Clay Aggregate

LOI            Loss on ignition

MSWI           Municipal solid waste incineration

NaOH           Natrium hydroxide

SEM            Scanning electron microscopy

TGA            Thermogravimetric analysis

XRD            X-ray diffraction

XRF            X-ray fluorescence

# 1 GRANULATION AND ALKALI ACTIVATION OF MSWI RESIDUES

## 1.1 Introduction

The amount of municipal solid waste has been ever increasing in Finland and around the world due to increasing population and different wastes our way of life produces. The recycling level of this municipal solid waste has remained the same in Finland for the last decade, but instead the portion of all municipal waste incinerated into energy has risen to 56 % in 2019 (Suomen virallinen tilasto (SVT), 2020b). This has been caused by the legislation in 2016 forbidding organic waste to be landfilled, since municipal solid waste is a mix of inorganic and organic waste, and by the difficulty of recycling this mixed waste into any useful products except for the energy and ash produced by incineration (Bröckl, M. et al. 2021). Since this ash produced by incineration of municipal waste is so varied in composition and contains different leachable heavy metals, it can only be used in construction such as roadbeds and structural layers when the material abides by regulations (Vegas, I. et al. 2008). This leaching along with other construction material requirements such as compressive strength and water absorption has been limiting the use of waste ashes such as municipal solid waste incineration (MSWI) bottom ash in bricks or other more elaborate building materials. The purpose of this study was then to test alkali-activation as a solidification and stabilization method to form granules with proper compressive strength, water absorption and reduced heavy metal leaching to be used as an acceptable building material.

## 1.2 Industrial side streams

### 1.2.1 MSWI residues

Municipal solid waste incineration (MSWI) residues come from the incineration of municipal waste. Incineration of waste has become a popular way to manage the increasing amount of waste in modern societies, since it reduces the volume of waste up

to 90 percent when comparing ash landfills to regular refuse. Incineration also provides energy in the form of heat or electricity (Kirby, C. S. & Rimstidt, J. D. 1993).

Generally, two different types of ash are generated from incineration of solid waste. These are bottom ash (BA) and fly ash (FA), from which fly ash comes from air pollution control (APC) residues and is hazardous waste, while bottom ash is usually non-hazardous and mainly consists of calcium oxide and silica. The APC residues containing fly ash need to be treated and stabilized before landfilling or possible use as a material because of their high heavy metal content which can leach into the environment. (del Valle-Zermeño et al. 2013)

### 1.2.2   Ground granulated blast furnace slag

Granulated blast furnace slag (GBFS) is a side stream from steel industry, where molten slag is produced when iron ore, limestone and coke is melted in a blast furnace. This blast furnace slag has pozzolanic properties since it is high in calcium oxide, silica, and alumina content. The granulated form is caused by the quenching process of molten iron slag, where it is blasted with high pressure water. For use as a cementitious material, this granulated slag is ground to a fine powder. (Chindaprasirt, P. & Cao, T. 2015)

### 1.2.3   Coal fly ash

Burning coal in an electric power plant produces exhaust gases, which have suspended and fused minerals such as clay, feldspar, quartz, and shale escaping the combustion chamber. These fused particles cool down and form spherical particles which are gathered by filters or electrostatic precipitators and is called fly ash. The type of coal used in combustion determines the chemical composition of fly ash but is usually high in silicon dioxide (both amorphous and crystalline), aluminium oxide and calcium oxide. The original particle size of fly ash varies based on the collection equipment used. (Chindaprasirt, P. & Cao, T. 2015)

## 1.3 MSWI residues as construction materials

### 1.3.1 Cement

For use as cement, both BA and FA have usually been solidified with hydraulic binders such as Portland cement due to its availability and properties. Chemical immobilization of heavy metals and good mechanical properties such as compressive strength has been observed with high ash content in cement and concrete mixtures. (del Valle-Zermeño et al. 2013)

### 1.3.2 Aggregates and granulation

Aggregates can be artificially formed from MSWI residues by cement-based granulation or high temperature sintering. Sintering is more widely known and applied method for creating aggregates from different residues, but granulation is seen as a possibly better way to create aggregates from hazardous waste material, where solidification/stabilization allows for safer disposal or recovery of materials. Cement-based granulation is also more ecological, since it does not require as much energy as high temperature sintering when it happens in room-temperature, and it also does not release harmful gas emissions. (Cioffi et al. 2011)

Granulation can be done with shearing forces in a granulating mixer, or with other techniques such as granulating drums, pans, or a rotary plate. The general mechanism of granulation is a rolling motion of the material with addition of some liquid which forms adhesive forces through liquid bridges or other interactions. This rolling motion and mixing with liquid bonding then produces spherical agglomerates of some size distribution depending on the system. Granulation can also be done using a press, where the material is forced through holes and cut into granules by a knife. (Sommer, K. 1991) (Cioffi et al. 2011)

## 1.4 Alkali activation

The reaction kinetics and reaction products along with the resulting mechanical properties in alkali activation depend largely on the raw materials and alkali activator used. In the case of fly ash and other silica- and alumina-rich materials, the alkali activation reaction produces an amorphous alkali aluminosilicate hydrate, also known as N-A-S-H gel. This gel along with secondary reaction products such as zeolites are responsible for the mechanical properties of alkali activated materials. The characteristics and concentrations of these reaction products vary with curing time and temperature which affect the degree of reaction. Longer curing times with higher temperatures tend to give better strength properties. (Garcia-Lodeiro et al. 2015)

### 1.4.1 One-part and two-part alkali activated materials

Two-part alkali activated materials or geopolymers are composed of a solid aluminosilicate material and liquid activator, typically alkali hydroxide, silicate, carbonate, or sulphate. The liquid activator first (partly) dissolves the solid precursor. The dissolved chemical species will form cementitious binder gels in a composition depending on the chemical and physical properties of the solid and the liquid. (Luukkonen et al. 2018)

One-part alkali activated materials have been in development due to the need for an easy-to-use and low-carbon replacement for Portland cement-based material. This means that the materials should be ready to use with just the addition of water like ordinary Portland cement. These one-part alkali activated materials could be prepared as a dry mix by combining the aluminosilicate material, solid alkali activator and possible aggregates or additives and calcinating if necessary. (Luukkonen et al. 2018)

### 1.4.2 Alkali activators

The different alkali activators used in alkali-activated cements have been divided into six groups: alkalis, weak acid salts, silicates, aluminates, aluminosilicates, and strong acid salts. The most used alkali activators are sodium silicates such as sodium waterglass

(nSiO$_2$·Na$_2$O) or its potassium counterpart and sodium/potassium hydroxide (NaOH, KOH). These alkali activators can be in solid or liquid form. (Pachego-Torgal et al. 2014)

## 1.5 Curing and post-processing

### 1.5.1 Curing conditions

The curing conditions of a geopolymer greatly affect the reactions happening in the system and therefore also the resulting mechanical properties. Especially the curing temperature has a big effect on the alkali-activation reaction kinetics in cements made from aluminosilicate materials such as fly ash. The speed of these reactions also affects the setting time of these geopolymers. Generally, a lower curing temperature results in slower setting, which can be over 24 hours for alkali-activated cements. Therefore, most geopolymers such as those made from fly ash are cured in a high temperature of 40 – 90 °C. In cases where the setting time is too quick or slow, it is possible to mix other co-binders, activators, or other admixtures to accelerate or delay the hardening. A longer curing time and higher temperature also results in higher compressive strength for most geopolymers. (Chindaprasirt, P. & Cao, T. 2015)

### 1.5.2 Cold bonding

Cold bonding, also known as room temperature curing, is the process of materials bonding without added heat. Compared to sintering and other energy intensive methods, it has the lowest energy consumption and therefore is the most environmentally friendly bonding method (Their, J. M. & Özakça, M. 2018). In addition to less energy consumption, cold bonding also does not emit gaseous pollutants, which happens during sintering. The main disadvantage of cold-bonded aggregates is their high density compared to their sintered counterparts (Tajra, F. et al. 2018). Cold bonding is in most cases made possible by the pozzolanic reaction ability of materials such as ashes at ambient temperatures (Terzić, A. et al. 2015).

### 1.5.3 Sintering

Sintering is a high temperature thermal treatment which is used to bond particles together and improve their properties such as mechanical strength, density, and water absorption. The changes caused by high temperatures are usually caused by crystallization and phase transformation reactions. Geopolymers are mostly sintered without added external pressure in the same way ceramics are sintered by placing them in an oven or furnace (Liew et al. 2017). Sintering temperatures used in geopolymer research have been as high as $600 - 1200$ °C. Sintering has been shown to both increase and decrease compressive strength properties of fly ash-based geopolymers depending on their $Na_2SiO_3/NaOH$ ratio and sintering temperature (Abdullah et al. 2012).

In another study on pelletized geopolymer aggregates made from volcano ash and alkali activator, the sintering in 600, 800 and 1000 °C caused more pores to appear in the geopolymer structure with increasing temperature, as water was removed by heat. However, sintering is usually capable of decreasing pores by melting and crystallizing the structure further. (Rafiza et al. 2013)

### 1.5.4 Microwaving

Microwaving as a curing method for geopolymers has not been studied as much as more conventional methods such as furnace sintering. The main advantages for using microwave heating as opposed to conventional heating is the way heating is applied along with energy usage. In microwave heating, the targeted material absorbs energy directly and transforms it to heat, which can open new opportunities for curing reactions. The conventional indirect heating in furnaces affects the whole material through conduction, radiation and convection which can lead to unnecessary use of energy. The proposed other advantages of microwave sintering include reduced processing time, rapid heating with lower required heat which leads to lower energy consumption, along with possible unique properties gained with direct heating. (Oghbaei, M., & Mirzaee, O. 2010)

## 1.6   Properties of granulated aggregate

### 1.6.1   Compressive strength

Compressive strength is one of the most important properties to evaluate when planning to use a material for construction. In some cases, the compressive strength of a material can also be too low to even survive transportation or to be used for other uses such as roadbeds or landfilling. For example, the U.S Environmental Protection Agency requires a minimum compressive strength of 0,35 MPa for materials disposed of at landfills, since it has been determined the minimum strength to support heavy machinery working at the landfill. (Azim, M A M et al. 2017)

The compressive strength of geopolymers is dependent on many parameters in addition to the mix design and the properties of the material particles it is mainly composed of. These parameters include the water to binder ratio, fine aggregate ratio, water content, porosity, curing time and conditions and ultimately the different reactions caused by various binders and additives interacting with the main material during geopolymerization and curing. (Nazari, A. & Sanjayan, J. G. 2015)

### 1.6.2   Bulk density

Bulk density is an important property in structural materials. In the case of aggregates such as granules, it is usually defined as loose bulk density by dividing a mass with the volume it occupies and expressed as either $g/cm^3$ or $kg/m^3$. Because this kind of measurement is done by filling a container loosely to a given volume, the bulk density can change depending on the amount of air or free space between aggregates.

For geopolymer aggregates such as granules to be considered lightweight aggregates (LWA), the loose bulk density has to be less than 1.20 $g/cm^3$ or a dry density of less than 2.0 $g/cm^3$ according to SFS EN 13055-1 (2002). Different kinds of fly ash -based granules mixed with co-binders such as metakaolin or slag and alkali-activated by either potassium silicate or natrium silicate have been studied to be within these limits, though higher in density than commercial LECA-aggregates. (Yliniemi, J. 2017)

### 1.6.3   Water absorption

Water absorption measurement of a geopolymer gives a good representation of its porosity. For a geopolymer mortar and concrete based on fly ash, the water absorption has been studied to vary from 3 to 5 percent. It has also been determined, that increasing the alkali activator content of a geopolymer clearly increases its water absorption ability, since the activator such as sodium silicate causes high porosity in increasing amounts. (Abdullah et al. 2012)

In the case of geopolymer lightweight aggregates such as granules however, the water absorption can vary between 18 to 36 percent as shown in a thesis by Juho Yliniemi on the granulation of alkali-activated fly ash mixed with different binders and activators. The water absorption in granules seems to be affected by more variables than mortar and concrete, such as the granulation technique affecting the aggregate density and how the particles stick together. This is in addition to the effect of used materials, their specific gravity and the amount and type of alkali-activator used in granulation. (Yliniemi, J. 2017)

### 1.6.4   Leaching

Leaching of heavy metals and other substances from any construction material is an important property to analyse, since it is a part of the environmental assessment of the material and leaching concentrations must comply with any limits set by government decrees to be used for construction. The leaching limits for different harmful substances are usually set based on a commonly used leaching test standard and limits set by Environmental Protection Act and Waste Act (1072/1993) separately for covered and paved structures in addition to waste disposal (FINLEX® 591. Government Decree 591/2006).

Solidification and stabilization methods, thermal treatments and other special treatments are used for MSWI and APC residues such as bottom- and fly ash in order to reduce the leaching of toxic heavy metals before use in landfilling, construction, disposal or agriculture (del Valle-Zermeño et al. 2013).

# 2 MATERIALS AND METHODS

## 2.1 Materials

### 2.1.1 MSWI residues, coal ash and blast furnace slag

The MSWI bottom ash used in granulation was sieved through a 2 mm sieve to remove unwanted debris such as pieces of glass, metal and burned fibers and to get a specific particle size distribution. In the case of MSWI fly ash, the original size fraction mostly had black flakes of carbon to be filtered along with getting the determined under 1 mm size. The dry mixes for the granulation consisted of 2 mm sieved municipal solid waste incineration (MSWI) bottom ash (BA), 1 mm sieved MSWI fly ash (FA) and ground granulated blast furnace slag (GBFS) along with coal fly ash. The source for the MSWI BA was Suomen Erityisjäte Oy, while the MSWI FA came from Oulun Energia and GGBFS from Finnsementti, Finland. The coal fly ash came from a power plant in Finland. The chemical composition of different materials obtained by X-ray fluorescence (XRF) and used in these trials are shown in table 2. MSWI bottom ash was the main component in the experiments. MSWI fly ash, ground granulated blast furnace slag, and coal fly ash were used as co-binders. These final MSWI powders along with slag and coal fly ash can be seen in figure 1.

**Figure 1. Materials used in experiments.**

### 2.1.2 Activator

The only liquid used as a binder and activator in these trials was liquid sodium silicate solution (30% w/v water dilution), since pure deionised water tested in preliminary solid activator trials was not producing successful granulation results. The sodium silicate solution was commercial.

## 2.2 Methods

### 2.2.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was done to determine the characteristics of materials during heating such as possible organic material percentage in MSWI and coal ashes with loss on ignition (LOI). The TGA was done using a Precisa Gravimetrics AG prepASH automatic drying and ashing system (Precisa Gravimetrics AG, Dietikon, Switzerland). The samples were heated from 23 °C to 950 - 1000 °C over 13 hours of runtime and mass changes were observed.

### 2.2.2 X-ray fluorescence (XRF)

X-ray fluorescence (XRF)-analysis was made to determine the elemental composition of the mix materials used for the study. The device used for this was an Omnian Panalytical

AXIOS X-ray fluorescence (XRF) spectrometer (Malvern Panalytical, Malvern, UK) and the analysis was done on a fine ground melt-fused tablet formed by melting 1.5g of LOI treated clinker from TGA with 7.5g of X-ray flux type 66:34 (66% LiB4O7 and 34% LiBO2) using a Pananalytics Eagon 2 fluxer at 1200 °C.

### 2.2.3    X-ray diffraction (XRD)

X-ray diffraction (XRD) was done to analyse the crystalline composition of materials used in this study (MSWI BA, MSWI FA, GBFS, coal FA). The machine used in XRD-analysis was a Rigaku SmartLab 9 kW (Applied Rigaku Technologies, Austin, TX, USA) using 40 kV and 135 mA radiations. The step interval used was 0.02°/step and scan rate was 4°/min for a scan range of 5 ° to 120 ° ($2\theta$). Titanium oxide powder (10 wt%) was added to each sample to act as a standard for quantification while comparing the diffraction data with International Center for Diffraction Data (ICDD) database. The final analysis was done with Rigaku PDXL2 software and using WPPF (Whole Powder Pattern Fit) analysis with internal standard methods.

### 2.2.4    Granulation

The device used for granulation was a pelletizing disk, which was basically just a rotating disk attached to a motor and a frequency converter made by ABB Oy (Figure 2). The operation parameters which could be configured in the device were only the angle and speed, from which the speed was only set as a frequency from 0 to 50 Hz. The speeds used in these trials are thus expressed mainly with the frequency, but the speed in rounds per minute (rpm) could be calculated with a stopwatch while observing the rotations, giving 30 Hz a speed of roughly 45 rpm. This was a bit unreliable however, since outside forces such as the weight of the material or friction from the scrapers and material affected the speed while the frequency in the device did not change.

In the granulation using liquid sodium silicate, the total amount of dry mix used was 200 grams, and the liquid dose was measured by weighing a dropper bottle after enough liquid was used and a suitable number of granules were formed. The angle inclination of the disk was kept at 40 degrees for all the trials, which is the same position as seen in figure 2.



**Figure 2. Tumbling granulation device.**

The granulation began by first adding the weighed 200 grams of dry material onto the granulation disk and letting it mix while running at 30 Hz, though the dry ash and binder materials were also hand mixed before adding onto the disk.

Liquid sodium silicate solution was added with a dropper bottle as a steady stream of droplets until enough granules were formed but also while keeping the granules dry enough on the surface to avoid granules sticking and so the result would not be a wet mass. The speed of the granulator was kept mostly at 30 Hz, which is roughly 45 rpm when calculated using a stopwatch. Sometimes the material would stick on the disk due to either too high speed or liquid-to-solid ratio, in which case it required manual scraping or changing the speed momentarily.

Since the tumbling granulation was a batch process, it was continued until a sufficient amount and size of granules were formed, after which they were put on a tray inside a sealed plastic bag for a determined curing process and time.

### 2.2.5   Curing conditions

The curing methods for granules in the co-binder experiments were room temperature curing and 60 °C oven curing for 1, 7 and 28 days. For the second curing method experiments there was a preceding curing of 60 °C oven for 4 hours before curing the granules further in either 400 – 800 °C sintering for 30 minutes or 4 kW, 60 °C microwave treatment for 5 – 15 minutes.

## 2.3   Properties of granules

### 2.3.1   Particle size distribution

The particle size of dry mix materials was analysed with a Beckman Coulter LS 13 320 Particle Size Analyzer using a wet dispersion method with isopropyl alcohol (IPA) as the dispersion medium.

Particle size distribution for granules was determined by sieving them through 2-, 4-, 6- and 8-mm sieves in series as seen in figure 3 and calculating the percentage of each particle size retained of the total granulated mass.



**Figure 3. Sieves in series.**

### 2.3.2   Leaching tests

The leaching tests were done as per European standard SFS-EN 12457-3 (Characterisation of waste. Leaching. 2002). Samples were poured onto a 4 mm sieve and granules bigger than sieve size were crushed by hand in a metal mortar until 45 grams of sample under 4 mm was available. This crushed sample was mixed with 0.5 L deionised water over 24 hours according to the standard with a liquid/solid ratio of 10. Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to analyse leached concentrations of elements.

### 2.3.3   Bulk density

The bulk density of cured samples was determined by filling a beaker to 50 ml with granules, so they were loosely packed without outside force crushing them to pack more tightly. The loose bulk density was then calculated by weighing the mass of granules occupying the volume of 50 ml and dividing mass with volume to get the bulk density in g/ml or $g/cm^3$.

### 2.3.4   Water absorption

The water absorption of samples was determined by immersing a variety of 4 – 10 mm granules under water for 24 hours. These wet granules were then dried from the surface by paper towels and weighed to get the water saturated wet weight. Finally, the wet granules were put into a 100 °C oven for 24 hours to get the dry weight of granules. Using the equation (1) the water absorption was then calculated as the difference of wet and dry weights divided by dry weight.

$$Water\ absorption = \frac{W_s - W_d}{W_d} \times 100\ \%  \hspace{2cm} (1)$$

In this equation (1), $W_s$ represents the water saturated weight and $W_d$ the dry weight of granules (Liew et al. 2017).

### 2.3.5  Compressive strength

The compressive strength of granules was measured with a Zwick Z100 testing machine which had a load cell of maximum 10 kN force. The compression was set to a speed of 1 mm/min with maximum deformation of 50%. The compressive strength analysis was done by choosing 10 granules that were as round as possible for best results and easier determination of average diameter. In addition to shape, the granules were also chosen to be from a specific diameter range to get a better average result for comparison.

Since the machine originally reported the values as a crushing value in newtons (N), the following equation (2) was used to convert the values to megapascals (MPa) of compressive strength as newtons per square millimetre (N/mm$^2$) by assuming the shape of granule surface as a circle with the measured average diameter:

$$Force\ (MPa) = \frac{N}{\frac{1}{4}\pi d^2} \qquad\qquad (2)$$

In some cases, the produced granules from a sample did not have enough granules of a specific size and round shape or the majority of granule size range was smaller than in other samples, in which case smaller granules had to be used in strength testing. Generally, the granule size varied from 5 to 9 mm.

Compressive strength could not be tested from 4-hour room temperature samples, since they were so wet and weak that they would either break when measuring the height and average diameter or give no registered force value in the testing machine.

# 3    RESULTS AND DISCUSSION

## 3.1    Properties of raw materials

### 3.1.1    Loss on ignition

The materials used for granulation were characterized by thermogravimetric analysis before X-ray fluorescence to obtain mass loss on ignition at 525°C and 950°C. As can be seen in table 1, the mass losses for all four materials were quite insignificant due to prior burning to ash, especially coal fly ash and blast furnace slag. Both MSWI residues had more mass loss especially at 950°C since they are clearly more impure and diverse materials coming from municipal solid waste incineration.

**Table 1. Loss on ignition**

|         | LOI 525°C % | LOI 950°C % |
|---------|-------------|-------------|
| COAL FA | 1,3         | 1,4         |
| MSWI FA | 0,8         | 6,2         |
| MSWI BA | 4,7         | 6,6         |
| GGBFS   | 0,4         | -2,1        |

### 3.1.2    Chemical composition

The results for XRF-analysis can be seen in table 2. The analysis shows that the major components of all materials are calcium oxide and aluminium oxide with smaller amounts of magnesium oxide, ferric oxide and sulphur trioxide, with the exception of MSWI BA having as much ferric as aluminium oxide and coal fly ash having a very small amount of calcium oxide compared to the other three materials. The chemical compositions are typical for each material, with coal ash having almost no calcium oxide since it is not a lime-based material, and silica being the major constituent in all materials. The higher concentration of calcium oxide in MSWI fly ash compared to bottom ash is possibly caused by reaction products during the gas cleaning in air pollution control and the use of lime-slurry (del Valle-Zermeño et al. 2013).

**Table 2. Chemical compositions of main materials as oxides according to XRF.**

| Material | Element / oxides (% w/w) | | | | | |
|---|---|---|---|---|---|---|
| | $Al_2O_3$ | CaO | $SiO_2$ | MgO | $Fe_2O_3$ | $SO_3$ |
| MSWI BA | 10,6 | 18,2 | 38,5 | 2,1 | 11,9 | 2,7 |
| MSWI FA | 9,1 | 26,7 | 26,6 | 3,1 | 2,9 | 7,5 |
| GGBFS | 9,2 | 37,9 | 33,1 | 9,9 | 0,6 | 3,2 |
| Coal FA | 21,1 | 4,2 | 56,6 | 2,2 | 6,4 | 0,4 |

### 3.1.3   Mineralogical composition

The results of XRD-analysis for MSWI BA can be seen in figure 4. The most intense signals are for quartz, as supported by the high $SiO_2$ content based on XRF-analysis, alongside with signals for calcite, dellaite, muscovite and iron oxides. There was also a signal for rutile which was only used for the internal standard method.
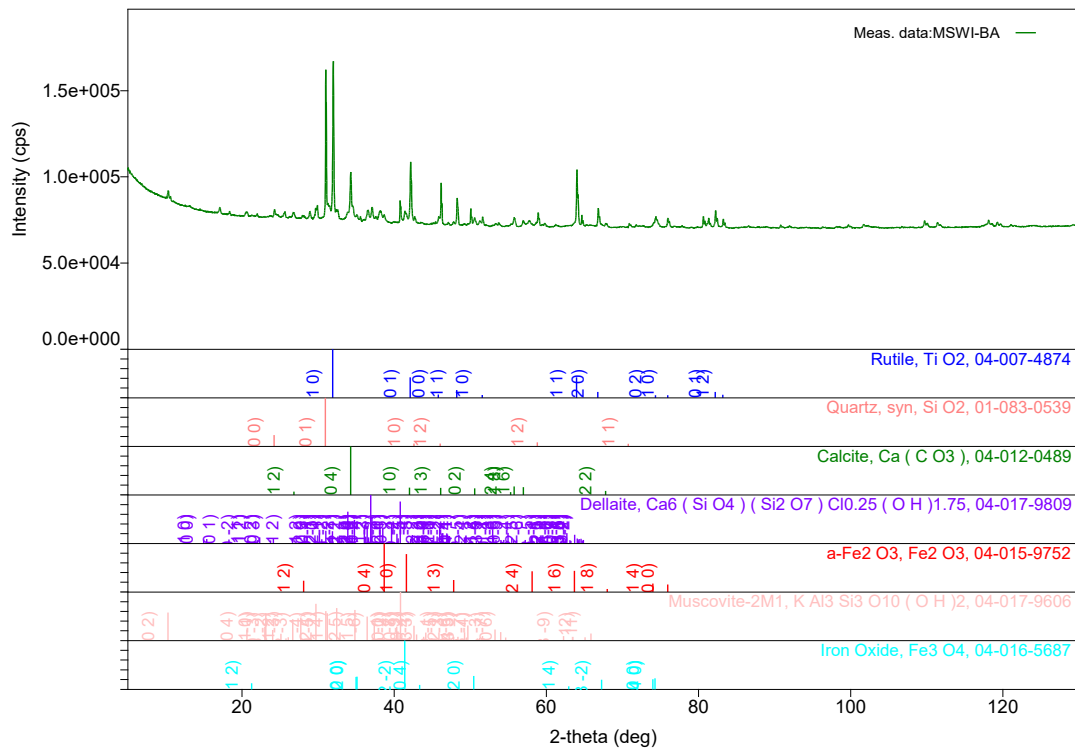


**Figure 4. X-ray diffraction pattern of MSWI BA.**

The XRD-analysis of MSWI FA (figure 5) determined that it also had a major presence of quartz and calcite, but otherwise the crystalline phases were different compared to bottom ash. Smaller constituents of the mineral composition were anhydrite ($CaSO_4$), albite, oldhamite and sylvite. Similar presence of anhydrite has been shown in other fly ash XRD measurements (Liu et al. 2009), but the composition of fly ash seems to vary otherwise depending on the source of ash and how it is collected.
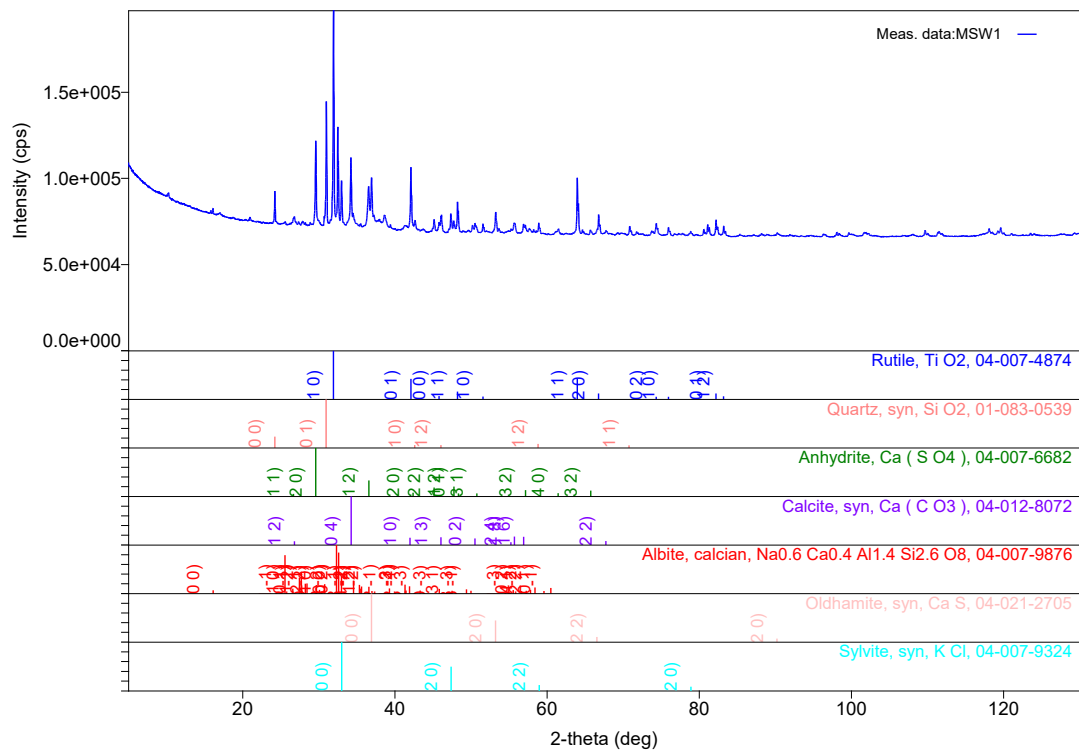


**Figure 5. XRD diffraction pattern of MSWI FA.**

XRD-measurements of blast furnace slag are presented in figure 6. It shows that the blast furnace slag is mostly an amorphous material. The only crystalline spikes reported by the XRD-analysis were altisite and gypsum along with the rutile which was only used for the internal standard method.



**Figure 6. X-ray diffraction pattern of granulated blast furnace slag.**

The coal fly ash XRD-analysis in figure 7 shows an amorphous hump between 20 and 30 degrees 2-theta typical to a less crystalline type of ash. In addition to this, the crystalline composition shows a high presence of quartz, mullite, franklinite and magnetite. Especially mullite has been shown to appear in other studies of coal fly ash as well (Tang, P. & Brouwers, H. 2017).
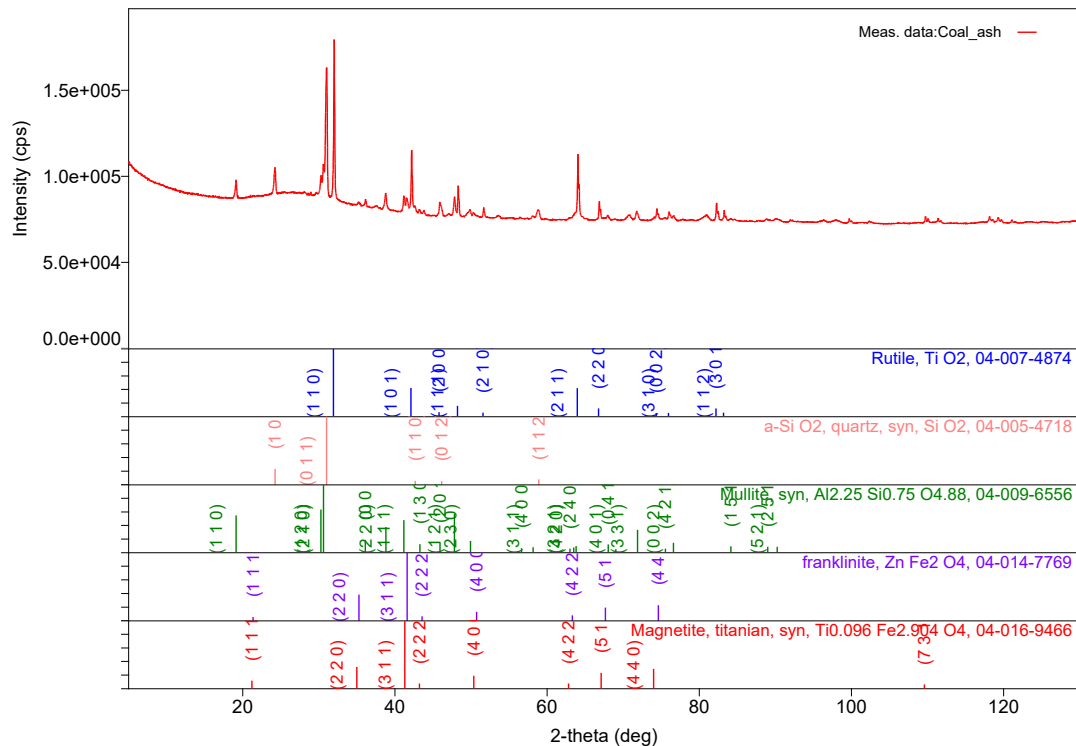


**Figure 7. XRD results for coal fly ash.**

### 3.1.4   Particle size distribution

The particle size distribution of materials is presented in figure 8. From the particle distribution it is clear, that the 2 mm sieved MSWI bottom ash is the coarsest material with largest variety and distribution of material size, with a mean diameter of 116,9 μm and median of 32,93 μm. This was also very apparent from figure 1, where a picture of all the materials can be seen. The finer materials are the ones used as a substituting co-

binder with MSWI BA. From these co-binders, granulated blast furnace slag (GBFS) is the finest with a mean particle diameter of 14,01 μm and median of 11,13 μm. The coal fly ash had mean and median diameters of 24,17 and 11,37 μm respectively while the 1 mm sieved MSWI fly ash was much coarser with a mean diameter of 62,07 μm and median of 29,68 μm.
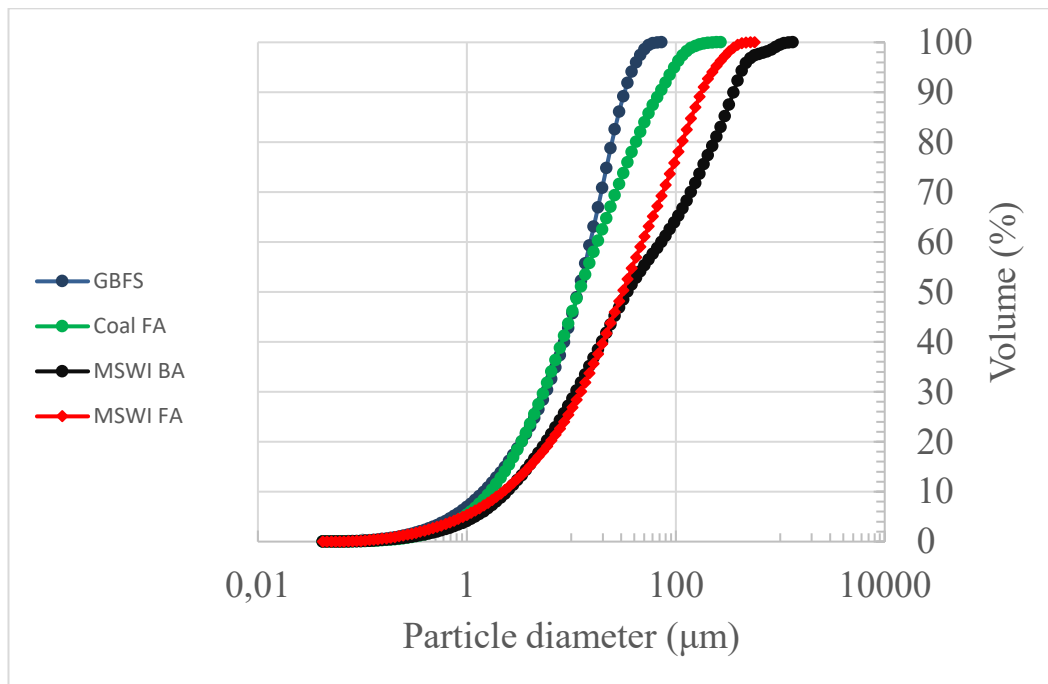


**Figure 8. Particle size distribution of materials**

## 3.2 Properties of granulated and alkali-activated MSWI bottom ash

### 3.2.1 Compressive strength

The compressive strength of granules in the co-binder and curing effect trial was analysed from 1, 7 and 28 days of curing at either room temperature (RT) or 60 °C. The compressive strength results of each different sample mix at different curing times and methods can be seen in figure 9.
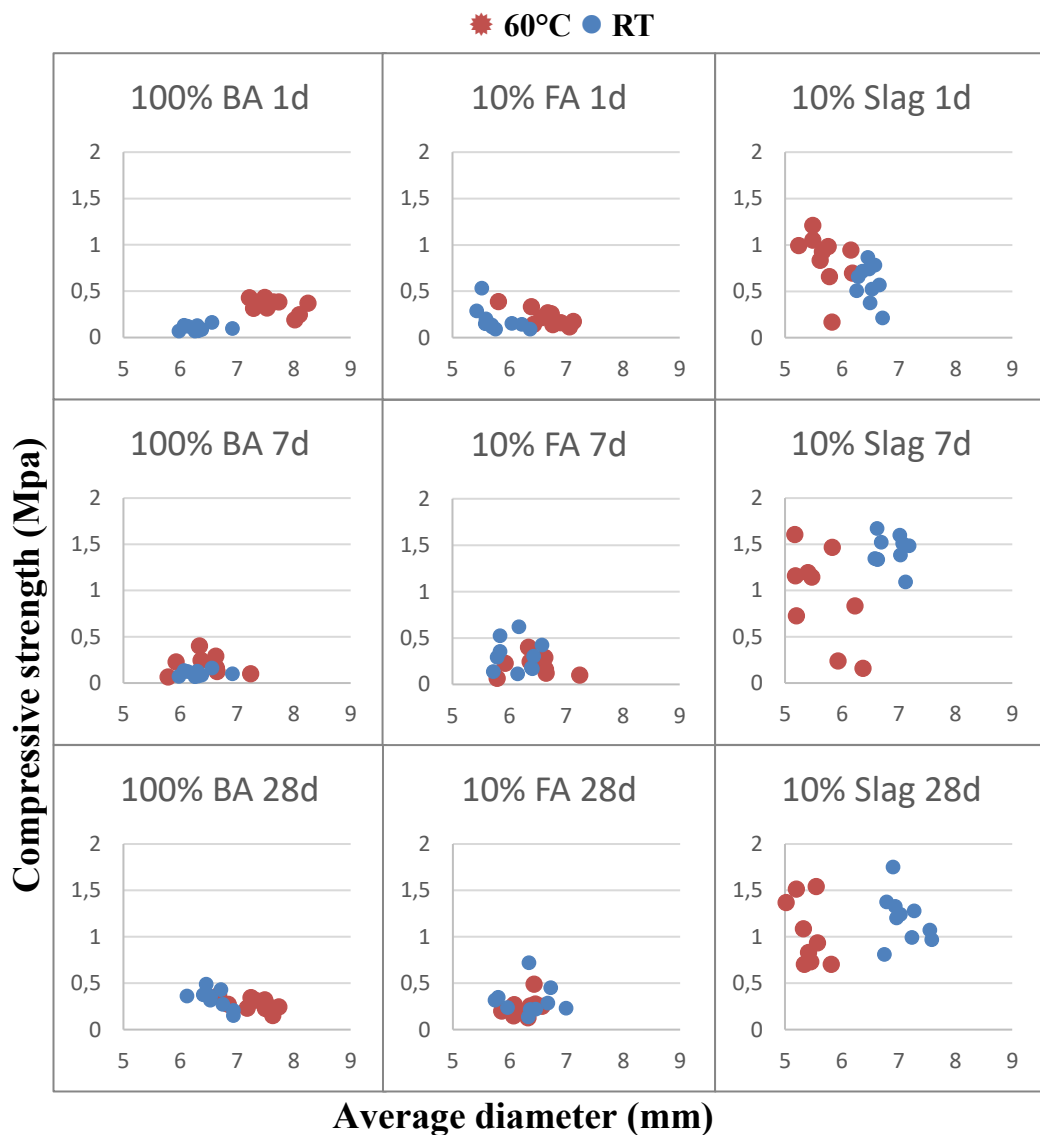


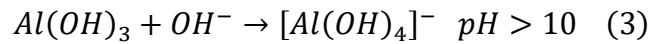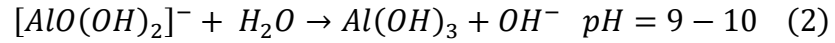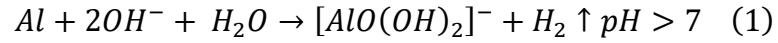Figure 9. Compressive strengths for co-binder and curing effect trial.

The first thing that can be seen from figure 9 is that while other mixes have similar strength between 0 and 0,5 MPa at all curing times, the 10% slag mix almost doubled the compressive strength even by room temperature curing. There is some variance in granule average diameter between the samples, since they were different batches for 60°C oven and room temperature curing, but in the case of these tests, larger granule size was not observed to yield better strength compared to smaller granules.

Based on the results it seems that oven curing for these mixes is only beneficial for 1 to 7 days, but after a longer curing period the higher curing temperature affects negatively on the strength performance of granules except for samples containing 10 % slag, which also achieves similar strength in room temperature after 28 days. While the 100 % bottom ash and 10 % slag samples seem to gain strength after the first day of oven curing, the 10 % fly ash samples stay mostly the same in strength during 1 to 28 days. Overall, the best strength performance was measured from the 10 % slag samples held in 7 days of room temperature, with most samples having a strength of around 1,5 MPa or over.

The overall strength performance of the granules is not great compared to other lightweight aggregates that have been studied or are commercially available, such as Lytag, which can have a strength of 7 MPa (Cheeseman, C. et al. 2005), but it was similar to a self-tested 7 – 8 mm LECA-aggregate (Lightweight Expanded Clay Aggregate), which had an average compressive strength of around 0,5 MPa.

A possible explanation for the reducing strength with increased time in the oven in MSWI fly ash-based granules and overall weak compressive strength compared to BFS-based granules can be the metallic aluminium content of MSWI fly ash used in this study, which causes a reaction by alkali-activation with sodium silicate, producing hydrogen gas and thus creating a porous structure inside the granules. This makes them lightweight in nature, but also decreases strength. This same reaction has been observed in other studies using MSWI ashes of high aluminium content (Müller, U. & Rübner, K. 2006).

The aluminium reaction forms aluminate in alkaline conditions (pH > 10) and produces hydrogen gas according to the following equations 1 – 3. (Müller, U. & Rübner, K. 2006)

$$Al + 2OH^- + H_2O \rightarrow [AlO(OH)_2]^- + H_2 \uparrow pH > 7 \quad (1)$$

$$[AlO(OH)_2]^- + H_2O \rightarrow Al(OH)_3 + OH^- \quad pH = 9 - 10 \quad (2)$$

$$Al(OH)_3 + OH^- \rightarrow [Al(OH)_4]^- \quad pH > 10 \quad (3)$$

Because metallic aluminium could only be found in MSWI fly ash and not the other binders, most of the strength reduction during longer curing times could be attributed to other reactions or cracking along with bad granule formation during the tumbling granulation.

**Effect of curing conditions**

In the second set of trials, the effect of curing conditions was studied between regular 60 °C oven curing for 24 hours, sintering at 400, 600, and 800 °C for 30 minutes after the initial oven curing, and finally microwaving at 60°C with 4 kW power for 5 to 15 minutes after initial oven curing. In figures 10, 11 and 12 it can be observed that the average diameter of coal fly ash granules is a bit larger than other mixes since it was forming round aggregates much easier, but the difference of only 1 to 2 millimetres did not affect their strength significantly.
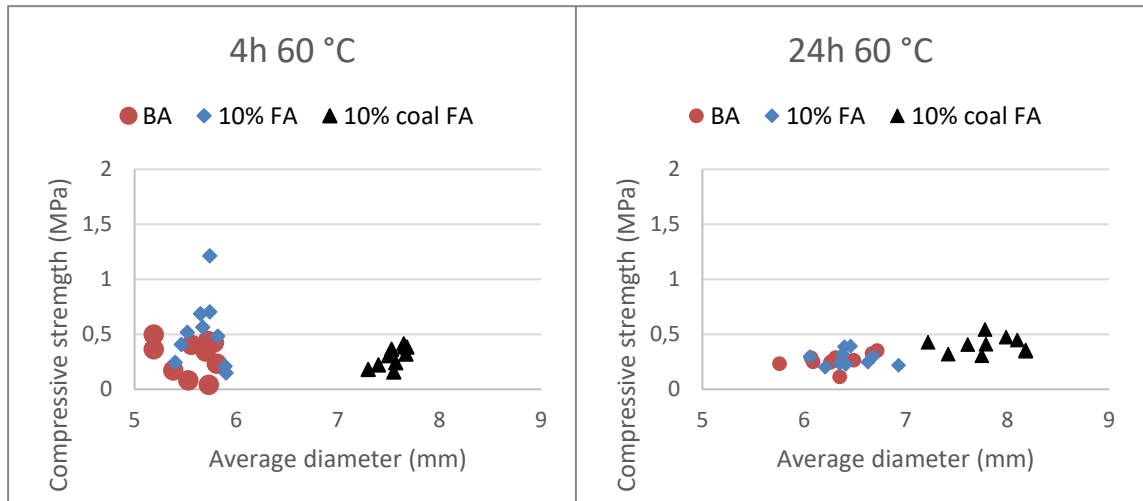


**Figure 10. Effect of oven curing on compressive strength.**

The most significant change in compressive strength was observed for the 10 % MSWI fly ash sample after 800 °C sintering (Figure 11) compared to other mixes at any of the three sintering temperatures. In a sintered MSWI fly ash study by Liu et al. (2009), it was observed that more complex aluminosilicates form in higher sintering temperatures. In addition to simple minerals turning into more complex ones, they noticed the element Mg being used to form glaucophane ($Na_2Mg_3Al_2Si_8O_{22}(OH)_2$) and cordierite ($Mg_2Al_4Si_5O_{18}$) when the sintering temperature reached 800 °C. These reactions along with glass formation reactions in fly ash after 700 °C could be the explanation for the increased strength in 10 % MSWI fly ash aggregates along with their change of shape during sintering. (Liu et al. 2009)

**Figure 11. Effect of sintering on compressive strength.**
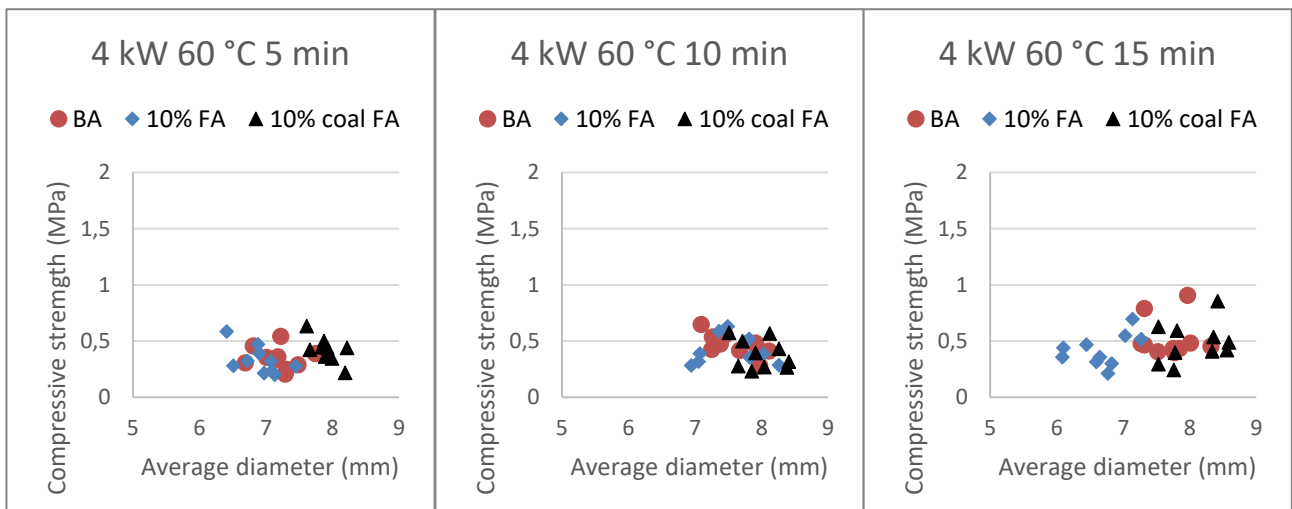


**Figure 12. Effect of microwaving on compressive strength.**

Initial observations of sintered samples showed decolorization to a shade of brown in 600 °C and 800 °C samples, but not as much in 400 °C sintering. No visible cracks were seen without microscopy, but in the 800 °C samples a dimensional change was observed as a more elongated and flat shape in all three types of samples as can be seen in figure 13, where both flatter and pointier 800 °C sintered samples were chosen for observation.

**Figure 13. Elongated shapes in 800 °C sintered samples.**

The most significant change in compressive strength was observed in the 10 % MSWI fly ash samples after 800 °C sintering (figure 11) compared to other mixes at any of the three sintering temperatures. In a sintered MSWI fly ash study by Liu et al. (2009) it was observed that more complex aluminosilicates form in higher sintering temperatures. In addition to simple minerals turning into more complex ones, they noticed the element Mg being used to form glaucophane ($Na_2Mg_3Al_2Si_8O_{22}(OH)_2$) and cordierite ($Mg_2Al_4Si_5O_{18}$) when the sintering temperature reached 800 °C. These reactions along with glass formation reactions in fly ash after 700 °C could be the explanation for the increased strength in 10 % MSWI fly ash aggregates along with their change of shape during sintering. (Liu et al. 2009)
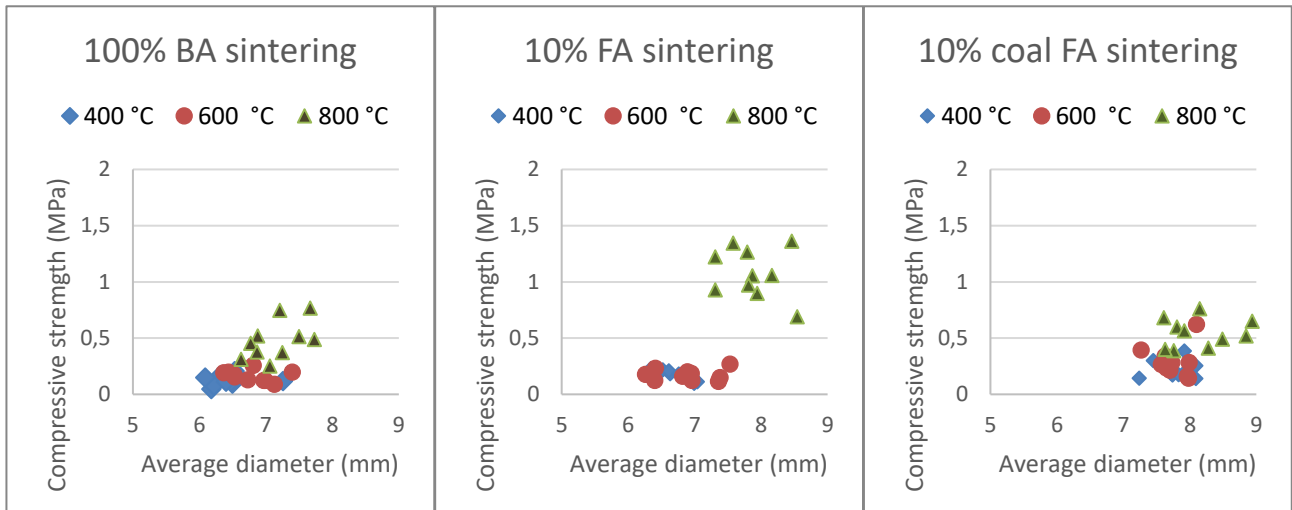
The microwave-cured samples shown in figure 12 did not show any significant change in compressive strength compared to regular oven-cured samples, even though they were subjected to the same 24-hour curing in 60 **°C** before the microwave. The compressive strength had more significant change between the first 4 and 24 hours of oven-curing, shown in figure 10, than between the oven-cured and any of the three 5-to-15-minute samples radiated by the 4 kW in 60 °C microwave. However, there was still a small

improvement observed in the 15 minutes of microwave curing compared to the shorter 5 and 10 minutes of radiation time. From these three samples, the 10 % fly ash was again the weakest, probably caused by the porosity. Similar results have been observed in other studies (Franus, M. et al. 2019) with a lower 1,1 kW radiation and shorter times of 1 – 5 minutes, where also the compressive strength was increasing with longer microwave-heating time and the porosity of fly ash was causing a low compressive strength. They also noticed that the changes in the chemical composition of microwaved samples was related to their carbon content, which was decreasing with increased time in the microwave.

### 3.2.1 Bulk density

The bulk density of all different mixes in various curing methods are presented in table 3. The values are all lower than 1200 kg/m$^3$ or 1,2 g/cm$^3$, which makes all produced granules lightweight aggregates according to SFS EN 13055-1 (2002). The bulk densities observed in this study are similar to other studies using a majority of bottom ash fines in this particle size range along with additional binders, ranging from 0,626 g/cm$^3$ to 0,944 g/cm$^3$. (Tang, P. & Brouwers, H. 2017)

The bulk density was expected to decrease over time as the metallic aluminium in the MSWI ashes was observed to cause a reaction producing hydrogen gas and create voids inside the aggregate structure. This happened to some degree in other curing samples especially room temperature MSWI BA compared to 60 °C oven, but 10 % BFS became much denser with 28 days in room temperature compared to oven. In the sintering and microwave samples the bulk density change can be more likely to be attributed to the effect of high heat, especially with up to 800 °C sintering.

**Table 3. Bulk densities in g/cm3**

| Curing method | | Composition | | | |
|---|---|---|---|---|---|
| | | **100% BA** | **10%BFS** | **10%FA** | **10%CFA** |
| **Oven at 60°C** | **4h** | 0,746 | | 0,668 | 0,944 |
| | **24h** | 0,812 | | 0,820 | 0,918 |
| | **28 d** | 0,826 | 0,769 | 0,706 | |
| **Room temperature** | **28 d** | 0,728 | 0,912 | 0,694 | |
| **Sintering 30 min** | **400 °C** | 0,704 | | 0,644 | 0,698 |
| | **600 °C** | 0,655 | | 0,628 | 0,697 |
| | **800 °C** | 0,664 | | 0,626 | 0,686 |
| **Microwave 4kW 60°C** | **5 min** | 0,762 | | 0,796 | 0,892 |
| | **10 min** | 0,702 | | 0,764 | 0,838 |
| | **15 min** | 0,760 | | 0,726 | 0,742 |

**3.2.2 Water absorption**

The results for water absorption of the granules in different curing conditions are presented in table 4. In the case of the first study on co-binder effect, the water absorption was taken only from 28-day samples while in the curing condition trial there were absorption tests at 4 and 24 hours and directly after sintering or microwaving.

**Table 4. Water absorption percentages (%)**

| Curing method | | Composition | | | |
|---|---|---|---|---|---|
| | | **100% BA** | **10%BFS** | **10%FA** | **10%CFA** |
| **Oven at 60°C** | **4h** | 39,60 | | 44,60 | 35,50 |
| | **24h** | 35,50 | | 40,20 | 33,50 |
| | **28 d** | 29,40 | 20,90 | 29,80 | |
| **Room temperature** | **28 d** | 38,70 | 31,60 | 38,20 | |
| **Sintering 30 min** | **400 °C** | 34,30 | | 36,10 | 31,90 |
| | **600 °C** | 29,70 | | 37,40 | 29,90 |
| | **800 °C** | 38,50 | | 35,60 | 33,60 |
| **Microwave 4kW 60°C** | **5 min** | 40,30 | | 40,10 | 33,90 |
| | **10 min** | 38,50 | | 40,10 | 31,50 |
| | **15 min** | 38,30 | | 41,90 | 32,40 |

There are results that have been reported in other studies on ash based lightweight aggregates, where water absorption and porosity were lowered after sintering. This effect was attributed to the microstructure of aggregates becoming more compact after subsequent activation and sintering. Meanwhile the aggregates with higher water absorption had large, interconnected pores on the outer shell (Terzić, A. et al. 2015). The same kind of significant reduction in water absorption after sintering was not observed in the samples from this study and was surprisingly close to the water absorption of regular oven-cured samples or even cold bonded samples. This is an unexpected result since other studies have shown far lower water absorption in the 10 – 20% range especially after sintering (Ren, P. et al. 2021). The water absorption percentage of the non-sintered granules are closer to results published in another study on alkali-activated fly ash granules (Yliniemi, J. 2017), where the absorption varied between 18 – 36 % in different sample mixes while the absorption of commercial LECA-aggregate was found to be 29,9 – 32,6 %. This shows that most of the granules, especially the samples of 10% coal fly ash were close to the absorption properties of LECA, while microwaved 100 % BA and 10 % MSWI FA granules had around 10 % more water absorption. The lowest water

absorption percentage of 20,90 % was achieved by oven curing 10 % BFS samples at 60°C for 28 days. This was nearly 10 % lower than the water absorption of same 10 % BFS samples cured 28 days in room temperature.

If the porosity and therefore water absorption is not increasing from aluminium reaction (in MSWI FA) then a possible explanation is the void areas in structure caused by irregular formation in granulation or cracks formed during curing, especially by high heat in sintering. However, the sintering was done by gradually heating to avoid cracking and exploding of the granules so perhaps it was not slow enough to avoid it. A change in composition by reactions can also affect water absorption. Generally, a lower density should lead to higher water absorption which was not always the case in these results. Ultimately the reason in lower density and higher water absorption in majority of the granules can be mostly attributed to a lower amount of geopolymer matrix caused by the choice in granulation technique or the material mix design and amount of alkali-activator. (Yliniemi, J. 2017)

### 3.2.2 Environmental impact assessment

### 3.2.3 Leaching

The results of the leaching test for materials are presented in table 5. The heavy metals leached from the different ashes and slag were arsenic, barium, chromium, copper, molybdenum, lead, antimony, selenium, vanadium, and zinc. From these elements, arsenic, copper, and antimony had negligible leached concentrations in majority of the materials. The most important material to observe is MSWI BA, since the granules formed in this study are 90 % MSWI bottom ash.

**Table 5. Leaching of heavy metals from materials (mg/kg), LS = 10 according to SFS-EN 12457-3.**

| Component | MSWI BA | MSWI FA | Coal FA | GBFS |
|:---:|:---:|:---:|:---:|:---:|
| As | 0 | 0,011 | 0,14 | 0 |
| Ba | 0,62 | 4 | 14 | 0,71 |
| Cr | 3,9 | 0,021 | 1,7 | 0,14 |
| Cu | 0,56 | 0,026 | 0 | 0 |
| Mo | 1,3 | 7,3 | 6,6 | 0,053 |
| Pb | 0,057 | 11 | 0,0099 | 0 |
| Sb | 0,047 | 0 | 0,016 | 0 |
| Se | 0,04 | 0,093 | 0,51 | 0 |
| V | 0,055 | 0,018 | 0,41 | 0,98 |
| Zn | 1 | 25 | 0,48 | 0,095 |

As can be seen from table 5, each material is very different from each other. For example, 25 times more zinc is leached from MSWI FA compared to MSWI BA. Also, significant amounts of lead was leached from MSWI FA, while only minor lead leaching was detected from other raw materials. Both MSWI and coal fly ashes leach a lot of molybdenum, whereas low leaching of these metals is observed for slag. Barium has a very high leached concentration in coal fly ash and much smaller from MSWI FA, but barely any is leached from BA and slag. Copper was basically only present in MSWI BA, which is not surprising given how the material is only 2 mm sieved incinerated waste. FINLEX® 591. Government Decree 591/2006.

The leaching values of zinc, lead, and molybdenum in MSWI FA is too high for both covered and paved structures according to the Finnish government limits (table 6), so unless stabilization by the alkali-activation and granulation is not achieved, it is not to be considered a material for construction. As a co-binder or filler, it might be applicable like in this study, but not as the main ingredient in a construction material.

**Table 6. Leaching limits for Finnish earth construction with fly- and bottom ashes according to Government Decree 591/2006**

| Component | Covered structure mg/kg dry substance, L/S = 10 l/kg | Paved structure mg/kg dry substance, L/S = 10 l/kg |
|---|---|---|
| As | 0,5 | 1,5 |
| Ba | 20 | 60 |
| Cr | 0,5 | 3,0 |
| Cu | 2,0 | 6,0 |
| Mo | 0,5 | 6,0 |
| Pb | 0,5 | 1,5 |
| Sb | 0,05 | 0,18 |
| Se | 0,1 | 0,5 |
| V | 2,0 | 3,0 |
| Zn | 4,0 | 12 |

Since 90 – 100 % of the material used in this study is MSWI BA, it is the most important point of observation in leaching. All the other leaching values of heavy metals are within limits of the Finnish earth construction decree except for chromium and molybdenum, from which chromium exceeds the limit for both covered and paved structure while molybdenum was only within limit for paved structures, as can be seen from table 6.

The environmental impact assessment for granules produced in this study was reviewed by analysing the results of leaching tests done for the most interesting samples that were chosen based on other results. The granules chosen for leaching were 28-day room temperature and 24-hour 60 °C oven samples from the co-binder study, along with 800 °C sintered samples from the curing effect study. The results of the leaching analysis for these samples are shown in table 7. Compared to the leaching results for the original materials shown in table 5, there were some new heavy metals appearing in the results for granules in the form of cobalt, iron, and titanium along with metallic aluminium released in leaching.

**Table 7. Leachable components from granules (mg/kg) with a liquid-solid ratio L/S=10 l/kg according to the standard SFS-EN 12457-3**

| Element (mg/kg) | 100% BA 28d RT | 10% GBFS 28d RT | 10% FA 28d RT | 100% BA 800°C | 10% coal FA 800°C | 10% FA 800°C | 100% BA 24h oven | 10% GBFS 24h oven | 10% FA 24h oven |
|---|---|---|---|---|---|---|---|---|---|
| Al | 7,3 | 9,3 | 2,8 | 98 | 110 | 330 | 3,7 | 4,1 | 3 |
| As | 1,2 | 0,84 | 2,2 | 0,049 | 0,044 | 0,11 | 0,7 | 0,73 | 1,9 |
| Ba | 0,12 | 0,088 | 0,09 | 1,5 | 1,2 | 0,98 | 0,083 | 0,075 | 0,085 |
| Cd | 0,002 | 0,002 | 0,0053 | 0,002 | 0,002 | 0,002 | 0,002 | 0,002 | 0,0024 |
| Co | 0,025 | 0,025 | 0,022 | 0,004 | 0,004 | 0,004 | 0,02 | 0,017 | 0,019 |
| Cr | 1,2 | 0,36 | 3,1 | 79 | 62 | 89 | 0,94 | 0,42 | 3,2 |
| Cu | 4,3 | 4 | 3,9 | 0,01 | 0,01 | 0,01 | 5,4 | 3,8 | 4 |
| Fe | 1,2 | 0,55 | 0,63 | 0,5 | 0,5 | 0,5 | 0,51 | 0,83 | 0,5 |
| Mo | 1,8 | 1,9 | 2,7 | 5,6 | 5,4 | 6,8 | 2,3 | 1,5 | 3,1 |
| Ni | 0,073 | 0,066 | 0,078 | 0,01 | 0,01 | 0,01 | 0,081 | 0,073 | 0,068 |
| Pb | 0,18 | 0,02 | 0,12 | 0,004 | 0,004 | 0,0044 | 0,062 | 0,048 | 0,083 |
| Sb | 4 | 1,6 | 5 | 0,044 | 0,045 | 0,074 | 2,6 | 2,3 | 5,2 |
| Se | 0,2 | 0,24 | 0,28 | 0,24 | 0,15 | 0,47 | 0,18 | 0,19 | 0,27 |
| Ti | 0,15 | 0,15 | 0,15 | 0,15 | 0,15 | 0,15 | 0,15 | 0,2 | 0,15 |
| V | 1,5 | 11 | 2,2 | 1,2 | 1,1 | 1,6 | 1,2 | 4,6 | 2,2 |
| Zn | 1,1 | 0,12 | 0,39 | 0,11 | 0,1 | 0,2 | 0,37 | 0,55 | 0,4 |
| Hg | 0,004 | 0,004 | 0,004 | 0,0067 | 0,004 | 0,004 | 0,004 | 0,004 | 0,004 |

The metallic aluminium released by all the granules is due to the high amount of bottom ash which the granules were mostly based on (90 – 100 %) since it is typical for all municipal solid waste to contain aluminium. The very high amount of aluminium released from the 800 °C sintered samples is most likely due to the liberation of aluminium by high temperatures from crystalline phases such as mullite to be readily available for leaching (Matjie, R.H et al. 2005). Since aluminium is not a heavy metal or toxic, it can be considered a non-issue and it is not a part of any government decree for leaching limits.

In order to analyse how well the granulation, alkali-activation and different curing methods solidified and stabilized the toxic heavy metals, the leaching concentrations of the most interesting granule samples were compared to the leaching of original MSWI BA, since 90 – 100 % of the granules were made from this bottom ash. The reductions in leaching concentration of different heavy metals can be seen in figure 14, In the case of

environmental assessment, a large enough reduction of leaching is seen as beneficial and means the heavy metal was successfully stabilized by the granulation process, and the increase of heavy metals means the process is detrimental in making of acceptable construction material.
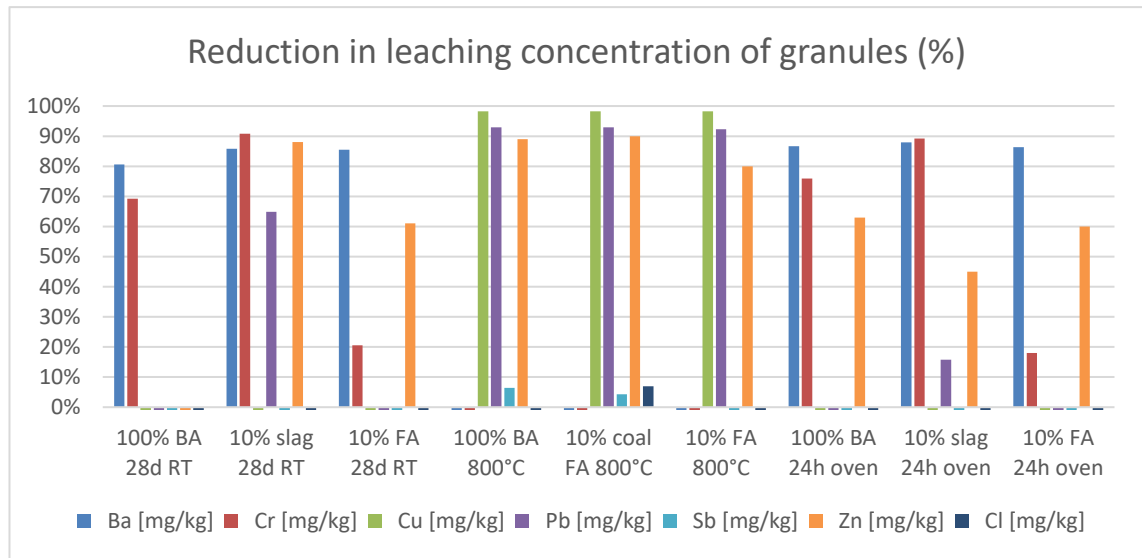


**Figure 14. Reduction in leaching concentration of granules compared to original MSWI BA.**

Arsenic was found to be leaching from all types of granules, with 10 % FA samples leaching the most arsenic except when it was sintered at 800 °C. However, the sintered granules leached more arsenic than pure MSWI FA as seen from table 5, even when MSWI BA had no arsenic leaching. Because 90 % of the ash mix was bottom ash, this would lead to the conclusion that all of the curing types increased arsenic leaching instead of stabilizing it. The leaching limit for arsenic is 1,5 mg/kg in paved structures and 0,5 mg/kg in covered structures for Finnish earth construction according to table 6, which means the 10 % FA 28-day room temperature and 10 % FA 24-hour oven sample are the only ones exceeding both limits and only the 800 °C sintered samples are within limits for covered structures.

Barium was originally found in all materials, with coal fly ash having significantly more barium than the other materials. Therefore, it is not surprising to see leachable barium in all granules. From figure 14 and table 7 it can be observed that the leachable barium was

reduced by stabilization-solidification in all 28-day room temperature curing and 24-hour oven samples. The addition of any co-binder was found to be reducing leachable barium a bit further. However, when sintering in 800 °C, the leachable barium concentration increased dramatically. This could be due to either the changes in granule surface due to very high heat, or the crystallization of the whole inner structure affecting the leachability of different metals. Since the construction limits of barium for both covered and paved structures are very high, 20 and 60 mg/kg respectively, all granules are within both limits.

The leaching of cadmium was found to be below the determination limit of 0,02 mg/kg (Table 7) in all granules except for the 10 % FA room temperature and oven samples, which were still very low (0,0053 mg/kg and 0,0024 mg/kg, respectively). Since the presence of leachable cadmium was not determined for the original materials, it can be deduced that at least the original MSWI FA had cadmium, which was only slightly soluble in high pH after alkali-activation. This similar kind of observation was found in a thesis on granulated fly ashes by Juho Yliniemi (Yliniemi, J. 2017).

Chromium was also originally found in all materials, with MSWI bottom ash having the highest leachable concentration. In the granules, the leachable concentration was reduced in all samples except the sintered granules, which had a dramatically increased chromium leaching. This is contrary to another study on MSWI fly ash and sewage sludge granules (Wei, N. 2015) where heavy metals such as chromium were solidified more efficiently by crystallization and chemical reactions with increasing sintering time and temperature. However, since the aforementioned study did not use an alkali-activator, it is possible something different happens with very high temperatures in the case of our study. They also observed an increase in the leaching rates of heavy metals as MSWI FA content increased, which is also the case in the granules of our study, since the 10 % FA RT and oven samples a much smaller reduction in leaching of chromium. Only the 10 % GBFS granules are within covered structure limits, while the 100 % BA 28-day RT and 24-hour oven samples are also applicable for paved construction. The 10 % FA granules from 28-day RT and 24-hour oven are barely over the paved structure limit of 3,0 mg/kg, reporting leachable concentrations of 3,1 and 3,2 mg/kg, respectively.

Copper was found leaching only in low amounts from MSWI BA and FA (table 5) but a consistent high increase in the leaching of copper is present in all alkali-activated room temperature and oven-cured samples, with the presence of 10 % co-binders reducing leaching a little. Similar results have been reported from MSWI FA based granules (Yliniemi, J. 2017). However, almost complete immobilization of copper is seen in the 800 °C sintered granules, possibly indicating the crystallization or a chemical reaction solidifying and stabilizing the copper into the geopolymer matrix. All granule types are within the Finnish paved structure limit of 6,0 mg/kg leaching of copper, but only the sintered samples are below the covered structure limit.

The results for molybdenum were mixed, but there was a clear correlation with increased leaching by the addition of MSWI FA, since it also had a lot more leachable molybdenum before granulation and alkali-activation. The addition of GBFS only reduced leachable molybdenum in the 24-hour oven sample, but overall, the alkali-activation only worsened its leaching especially in the sintered samples, which had over two times more leachable molybdenum than their other counterparts. None of the granules were within Finnish government limits for covered structures, but all except for the 800 °C sintered 10 % FA granules were within paved structure limits (Table 6).

The leachable values of nickel were very low for all granules, with sintered granules being under the determination threshold (0,01 mg/kg) and others being very similar values of under 0,1 mg/kg. The addition of co-binders barely affected the result but had a small reduction in the 28-day room temperature samples. Nickel was not considered in the Finnish earth construction limits table, but the leachability is very low and similar to other alkali-activated granules (Yliniemi, J. 2017).

The leachability of lead was below the determination limit (0,004 mg/kg) for all sintered samples, but otherwise it was only observed to reduce with the addition of 10 % GBFS, which is logical since slag was the only material which did not contain any lead in the material leachability test. Clearly the alkali-activation combined with the addition of slag stabilized lead much better in a longer 28-day room temperature than oven curing, while pure bottom ash and 10 % FA had a negative effect on leaching. The high temperature sintering seemed to completely immobilize the lead as it did with Cu, Co, and Cd. This

could be due to the crystallization or other chemical bonds forming during the high sintering heat, while the Pb in non-sintered samples is in more soluble form and not incorporated to the geopolymer matrix, as was also discussed in other studies (Wei, N. 2015) (Yliniemi, J. 2017). All granules were within both Finnish construction limits as seen in table 6.

The leachable antimony values increased in all alkali-activated granules except for the sintered 100 % BA and 10 % coal FA granules. Adding 10 % GBFS reduces the leachable value by a larger amount in the case of 28-day room temperature curing and a small amount in oven curing. None of the curing methods were fit to immobilize the antimony, but the sintered 100 % BA and 10 % coal FA granules were within covered construction limits (Table 6) while all the others went over both government limits by a large margin.

In the case of selenium, the original MSWI BA had a low leachability of 0,04 mg/kg, and after granulation and alkali-activation it was increased with all curing methods and mixes especially with 10 % FA in 800 °C sintering (Table 7). The addition of FA or GBFS increased selenium leaching by a small amount in all except 800 °C sintered 10 % coal FA granules. The granules were all within limits for paved structures according to table 6, but none were under the 0,1 mg/kg required for covered structure limits.

Vanadium was mostly insoluble before alkali-activation with only 0,055 mg/kg leachable vanadium detected by the analysis (Table 5), but after all curing and alkali-activation methods the leachability was increased by a large margin. Especially after using GBFS as a co-binder, the leachability of vanadium dramatically increased compared to other samples. Similar findings were reported by other studies (Yliniemi, J. 2017) and the much higher leachability of vanadium in the initial leaching test on GBFS powder supports this outcome. The addition of MSWI FA also increased vanadium leaching, but by a much smaller amount than slag. For the Finnish earth construction limits (Table 6), all except for the GBFS-based granules were within paved structure limits and only non-sintered 100 % BA and all sintered granules were within covered structure limits.

The last notable leachable metal was zinc, which was earlier reported to be 25 times more leachable from MSWI FA than BA and was by far the most leachable metal from MSWI FA. Therefore, it is surprising to see from alkali-activated results that the addition of 10 % MSWI FA reduced the leachability of zinc in 28-day room temperature curing. In sintered and 24-hour oven granules, the leachability was higher with the addition of any co-binder, but in 28-day RT-curing both co-binders had reduced the leachable fraction, especially with GBFS addition. The same kind of behaviour was reported in another study (Yliniemi, J. 2017) and the almost completely immobilized Zn in sintered granules was explained by volatilization due to its low boiling point in high temperature sintering by Wei Na in his study on sintered LWAs (Wei, N. 2015). Overall, the leachability was reduced in all types of granules except for the 100 % BA 28-day RT sample, which had almost the same leachable value as the original sieved MSWI BA (Table 5). All the granules also were very much within both Finnish government limits on earth construction (Table 6).

# 4   SUMMARY

The purpose of this thesis was to study how bottom ash from the incineration of municipal solid waste could be used as a main aluminosilicate precursor for geopolymerization in the form of granules, so that they would be fit as a recycled construction material to create circular economy. The geopolymer granules were made by using sodium silicate solution as an alkali-activator which also would help in stabilizing the hazardous components such as heavy metals by physical encapsulation or chemical bonds in the geopolymer matrix. The effects of alkali-activation on leaching, bulk density, water absorption and compressive strength was tested with different curing methods and co-binders.

In this thesis, MSWI bottom ash, MSWI fly ash, GGBFS and coal fly ash were used as raw materials for the granulated geopolymers. The granulation was done by tumbling granulator with a pelletizing disk, which easily resulted in mostly spherical granules, but since the addition of binding liquid and alkali-activator was done with a dropper bottle, the liquid-to-solid ratio varied between every sample to get enough surface-dry granules.

After successful granulation, all the granules were subjected to different curing methods, which were 28-day curing in room temperature and 28-day curing in a 60 °C oven for the first part of the study, or microwave curing and high heat sintering at 400 – 800 °C after initial oven curing in the second part of the study. The resulting granules were all classified as lightweight aggregates (LWA) with their bulk density according to the EN 13055-1 standard. The water absorption of sintered granules was much higher than other studies reported, but most of the granules, especially the samples of 10% coal fly ash were close to the absorption properties of LECA.

The compressive strength of granules did not improve with time in other granules other than 10 % GGBFS granules during 28 days of mild curing in room temperature or an oven, and even then, 7 days of curing had a better or similar effect to 28 days. Sintering mostly had a positive effect on the strength properties for the 10 % MSWI FA mix at 800 °C but otherwise sintering at all temperatures had a surprisingly bad effect on the strength, even though it was expected to get a lot stronger by the crystallization. A possible

explanation for the low strength performance is the void areas in structure caused by irregular formation in granulation or cracks formed during curing, especially by high heat in sintering. Also, it was known that the metallic aluminium could cause pores in the structure due to hydrogen gas producing during alkali-activation, causing changes in bulk density, water absorption and strength. The strength performance in general was similar to a tested LECA pellet and good enough for landfilling, but much weaker than other commercial LWAs such as Lytag.

The environmental impact assessment done by leaching analysis found varying results dependent on the hazardous components and what type of curing and co-binders were used. Generally, it was found that some metals such as barium were only stabilized well by milder curing conditions, indicating alkali-activation alone being enough to reduce leachable concentrations of certain metals. On the other hand, some metals were only stabilized and solidified by the high heat of 800 °C sintering in addition to the alkali-activation, while sintering also allowed many metals such as chromium in very high amounts to leach even though they were stabilized before sintering. Also, even the mild room temperature curing with alkali-activation was enough to increase leachability of some hazardous components such as lead.

To find better explanations for the changes in compressive strength, bulk density, water absorption and leaching, a further analysis should be done by optical methods and scanning electron microscopy (SEM) to observe possible changes in the surface and morphology of the granules. Due to time constraints, it was not possible to include a thorough SEM analysis for this thesis.

# REFERENCES

Abdullah, M. M. A. B., Jamaludin, L., Hussin, K., Bnhussain, M., Ghazali, C. M. R. & Ahmad, M. I. 2012. Fly ash porous material using geopolymerization process for high temperature exposure. International journal of molecular sciences, 13(4), pp. 4388-4395.

Azim, M. A. M., Azhar, A. T. S., Tarmizi, A. K. A., Shahidan, S. & Nabila, A. T. A. 2017. Enhancing the compressive strength of landfill soil using cement and bagasse ash

Bröckl, M. et al. 2021. Jätteenpolton kiertotalous- ja ilmastovaikutuksiin vaikuttaminen eri ohjauskeinoin. Valtioneuvoston kanslia 27.01.2021

Cheeseman, C., Makinde, A. & Bethanis, S. 2005. Properties of lightweight aggregate produced by rapid sintering of incinerator bottom ash. Resources, conservation and recycling, 43(2), pp. 147-162.

Chindaprasirt, P. & Cao, T. 2015. 5 - Setting, segregation and bleeding of alkali-activated cement, mortar and concrete binders.

Cioffi, R., Colangelo, F., Montagnaro, F. & Santoro, L. 2011. Manufacture of artificial aggregate using MSWI bottom ash. Waste management (Elmsford), 31(2), pp. 281-288.

del Valle-Zermeño, R., Formosa, J., Chimenos, J., Martínez, M. & Fernández, A. 2013. Aggregate material formulated with MSWI bottom ash and APC fly ash for use as secondary building material. Waste management (Elmsford), 33(3), pp. 621-627.

FINLEX® 331. Government Decree 331/2013 2013. http://www.finlex.fi/fi/laki/alkup/2013/20130331 [accessed March 8, 2021].

FINLEX® 591. Government Decree 591/2006. http://www.finlex.fi/en/laki/kaannokset/2006/20060591 [accessed March 8, 2021].

Franus, M., Panek, R., Madej, J. & Franus, W. 2019. The properties of fly ash derived lightweight aggregates obtained using microwave radiation. Construction & building materials, 227, p. 116677.

Garcia-Lodeiro, I., Palomo, A. & Fernández-Jiménez, A. 2015. 2 - An overview of the chemistry of alkali-activated cement-based binders.

Kirby, C. S. & Rimstidt, J. D. 1993. Mineralogy and surface properties of municipal solid waste ash. Environmental science & technology, 27(4), pp. 652-660.

Liew, Y., Heah, C., Li, L., Jaya, N. A., Abdullah, M. M. A. B., Tan, S. J. & Hussin, K. 2017. Formation of one-part-mixing geopolymers and geopolymer ceramics from geopolymer powder. Construction & building materials, 156, pp. 9-18.

Liu, Y., Zheng, L., Li, X. & Xie, S. 2009. SEM/EDS and XRD characterization of raw and washed MSWI fly ash sintered at different temperatures. Journal of hazardous materials, 162(1), pp. 161-173.

Luukkonen, T., Abdollahnejad, Z., Yliniemi, J., Kinnunen, P. & Illikainen, M. 2018. One-part alkali-activated materials: A review. Elsevier.

Matjie, R., Bunt, J. & van Heerden, J. 2005. Extraction of alumina from coal fly ash generated from a selected low rank bituminous South African coal. Minerals engineering, 18(3), pp. 299-310.

Müller, U. & Rübner, K. 2006. The microstructure of concrete made with municipal waste incinerator bottom ash as an aggregate component. Cement and concrete research, 36(8), pp. 1434-1443.

Nazari, A. & Sanjayan, J. G. 2015. Modelling of compressive strength of geopolymer paste, mortar and concrete by optimized support vector machine. Ceramics international, 41(9), pp. 12164-12177.

Oghbaei, M., & Mirzaee, O. 2010. Microwave versus conventional sintering: A review of fundamentals, advantages and applications. Journal of Alloys and Compounds, 494(1-2), pp. 175–189.

Pacheco-Torgal, F., Labrincha, J., Leonelli, C., Palomo, A. & Chindaprasit, P. 2014. Handbook of Alkali-Activated Cements, Mortars and Concretes.

Rafiza, A. R., Al Bakri, A. M. M., Kamarudin, H., Khairul Nizar, I., Hardjito, D., Badaruzzaman, W. H. W., & Yahya, Z. 2013. Microstructure Study on Volcano Ash Geopolymer Aggregate at Different Sintering Temperature. Key Engineering Materials, pp. 594-595, 83–87.

Ren, P., Ling, T. & Mo, K. H. 2021. Recent advances in artificial aggregate production. Journal of cleaner production, 291, p. 125215.

SFS EN 13055-1. Lightweight Aggregates for Concrete, Mortar and Grout. 2002.

SFS-EN 12457-3. Characterisation of waste. Leaching. 2002.

Sommer, K. 1991. Powders: Granulation. Concise Encyclopedia of Advanced Ceramic Materials, pp. 373–375

Suomen virallinen tilasto (SVT). 2020b. Yhdyskuntajätteet Suomessa käsittelytavoittain 2018-2019.
https://pxnet2.stat.fi/PXWeb/pxweb/fi/StatFin/StatFin__ymp__jate/statfin_jate_pxt_12cv.px/table/tableViewLayout1/ [accessed May 9, 2021].

Tajra, F., Elrahman, M. A., Chung, S. & Stephan, D. 2018. Performance assessment of core-shell structured lightweight aggregate produced by cold bonding pelletization process. Construction & building materials, 179, pp. 220-231.

Tang, P. & Brouwers, H. 2017. Integral recycling of municipal solid waste incineration (MSWI) bottom ash fines (0–2mm) and industrial powder wastes by cold-bonding pelletization. Waste management (Elmsford), 62, pp. 125-138.

Terzić, A., Pezo, L., Mitić, V. & Radojević, Z. 2015. Artificial fly ash based aggregates properties influence on lightweight concrete performances. Ceramics international, 41(2), pp. 2714-2726.

Their, J. M. & Özakça, M. 2018. Developing geopolymer concrete by using cold-bonded fly ash aggregate, nano-silica, and steel fiber. Construction & building materials, 180, pp. 12-22.

Vegas, I., Ibañez, J., San José, J. & Urzelai, A. 2008. Construction demolition wastes, Waelz slag and MSWI bottom ash: A comparative technical analysis as material for road construction. Waste management (Elmsford), 28(3), pp. 565-574.

Wei, N. 2015. Leachability of heavy metals from lightweight aggregates made with sewage sludge and municipal solid waste incineration fly ash. International journal of environmental research and public health, 12(5), pp. 4992-5005.

Yliniemi, J. 2017. Alkali activation-granulation of fluidized bed combustion fly ashes. Oulu: University of Oulu.