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Circular economy perspectives for the valorization of bottom ashes

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1 INTRODUCTION

Each year almost 250 Mt of municipal solid waste (MSW) are generated over Europe. European countries are currently able to incinerate about 67.5 Mt of waste, leaving behind 16-17 Mt of residual material defined *bottom ashes* (BA) (European Commission, 2017a). Considering that the average cost for waste landfilling is 75 €/tonnes (European Environmental Agengy, 2014), complete landfill disposal of BA would cost around 1.3 M€ each year, thereby it appears clear the necessity to find other solutions to manage this material.

Moreover, BA chemical composition and physical properties make them a worthwhile material in terms of reuse and recycling as inert material or "urban mine" for metals (Loginova et al., 2019). Indeed BA treatments would have manifold benefits since they allow to separate the mineral fraction from other components in order to obtain a more pure inert material, recover the metals as secondary raw materials and reduce the waste stream sent to landfills (Verbinnen et al., 2017). Over the years more and more applications for BA reuse have been identified (Bourtsalas, 2012; Dou et al., 2017; Lam et al., 2010; Tang et al., 2016, 2015), although researchers and industry have not yet developed an optimal treatment to recover this material, in particular the fine fraction, which is the richest in terms of metals (Enzner et al., 2017).

Tackling and reducing this loss of resources is the main aim of the project "BASH-TREAT - Optimization of bottom ash treatment for an improved recovery of valuable fractions", that won the call Horizon 2020 ERA-MIN2 "Research and Innovation Programme on Raw Materials to foster Circular Economy" in 2017. This is the framework in which this thesis developed. The samples analysed have been collected after full-scale treatment performed by a mobile plant designed by Heidemann Recycling GmgH. These collected samples have been analysed to investigate the feasibility of secondary raw materials recovery from BA. The experimental work for this thesis was performed under the co-supervision of the research partners of the project, Prof Silvia Fiore at Politecnico of Torino and Prof Kerstin Kuchta at the Technische Universität of Hamburg (TUHH).

2 STATE OF THE ART

Since the composition of BA is strongly related to the solid waste they derive from, the first section of this chapter will be dedicated to an overall framing of the current situation of waste generation and management in Europe, linking these data with common socio-economic indicators. Afterwards BA general characteristics will be presented to account for their possible reuses, also presented in this chapter. Eventually the current state of the art on BA treatment will be described in order to identify technology flaws, that justify the work of this thesis.

2.1 Waste production

The economic growth registered in the developing countries and the consumerist lifestyle adopted by countries worldwide is leading to the production of a quantity of waste larger than what we are actually able to manage. All statistical analyses show a general decrease in waste production in European countries over the years but the targets proposed by the most recent legislations (European Commission, 2008) in terms of waste management still seem unattainable.

The analysis presented in this section is aimed to compare countries with a noteworthy waste incineration capacity, Germany (20 Mt/y) and Sweden (4,5 Mt/y), with Italy (4,7 Mt/y) (CEWEP report, 2012). This choice has been made also because they are the countries of the partners of the project BASH-TREAT.

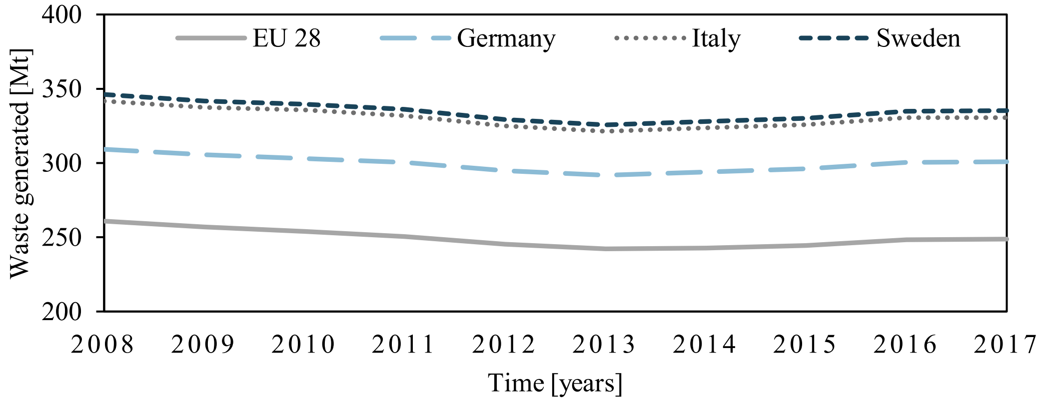


Figure 1 – Waste generated [Mt] from 2008 to 2017 (Eurostat 2019)

According to Figure 1, contrary to the targets set by recent legislations, the amount of waste generated by European countries after a slight decrease, started to rise again in 2014. This period corresponds to the economic upturn following the financial crisis of 2008 and, as will be further discussed in this chapter, several studies have identified a strong correlation between economic wealth and the total amount of waste produced in a country.

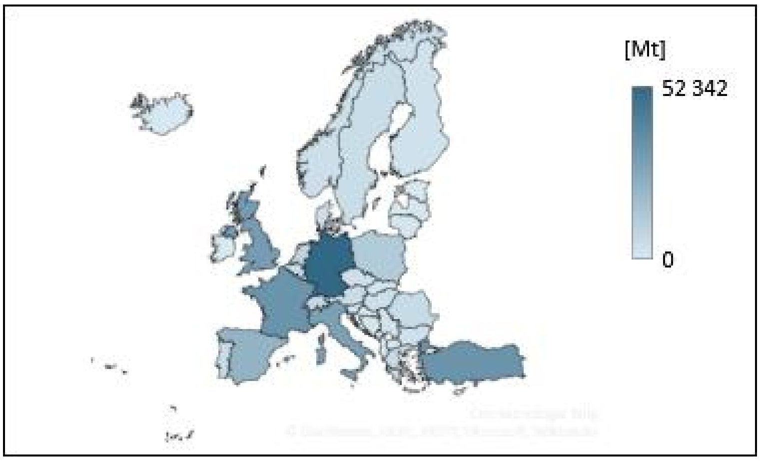


Figure 2 – Waste generation in 2017 [Mt] (Eurostat 2019)

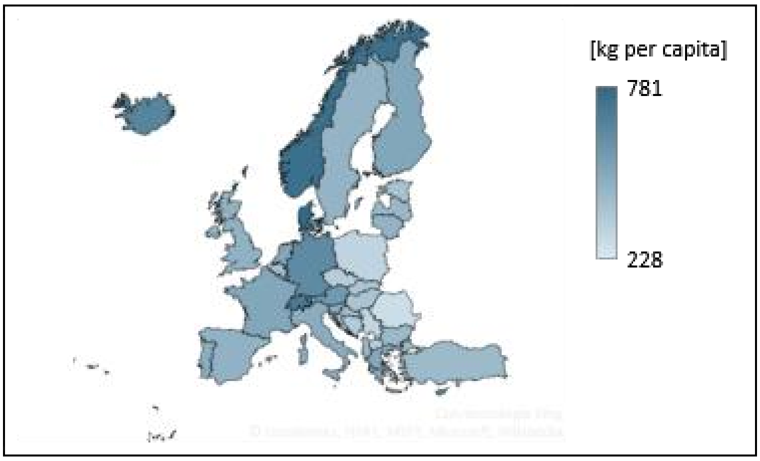


Figure 3 – Waste generation in 2017 [kg per capita] (Eurostat 2019)

As shown in Figure 2 and Figure 3, the total amount of waste produced during 2017 is different among the three countries analysed and it can be due to multiple reasons since population, income and development level play a significant role in the amount of waste originated (Brown, 2015). The analysis of more than 100 countries all over the word has confirmed the intuitive correlation existing between population size and amount of waste originated (Brown, 2015) and this trend can be observed also among the countries analysed in this thesis, as in Figure 3 and Figure 4, where it is possible to notice that the most populated countries are the ones with the higher values of waste generation per capita.

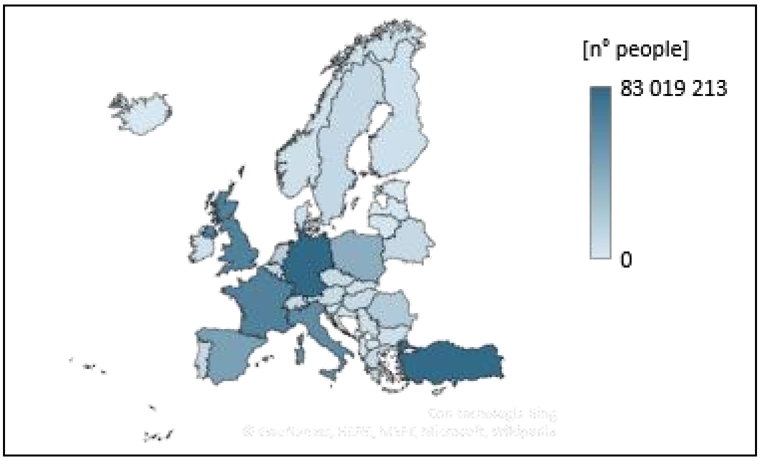


Figure 4 – Population [mln people] (OECP Data 2014)

In addition, in Figure 5 another social indicator, that has been identified as fundamental for the characterization of a country, is presented the population density, that appears to be related also to the virtuosity shown by a country in the management of waste other than to the amount of waste produced, as will be discussed in section 2.2.

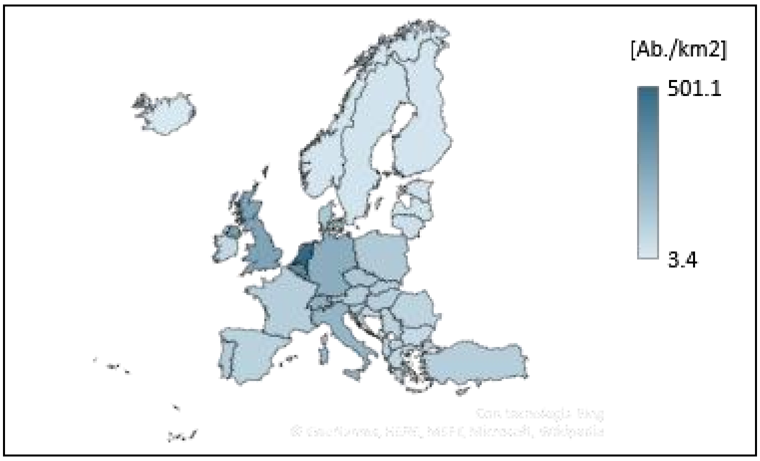


Figure 5 - Population density [people/Km^2] (OECP Data 2014)

Several studies agree that the parameters most strongly related to the production of waste are the economic indicators. In Brown 2015 it has been estimated that the gross domestic product (GDP) of a country is related to the amount of waste generated by a log-log relation with an R^2 of 0.983. This is not the situation of the countries analysed here where, as shown in Figure 6. Sweden is the richest country in terms of GDP but it is also the one with the lowest amount of generated waste, both total and per capita.

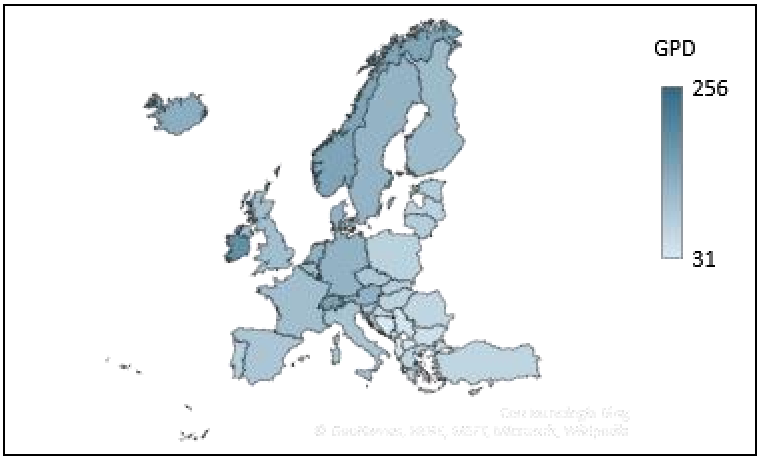


Figure 6 – Gross Domestic Product [€ per capita/year] (OECP Data 2014)

This anomaly can be interpreted applying the “Environmental Kuznets curve” (EKC) to waste production (WKC). EKC represents the relation between the impact on environmental quality and economic growth as a bell-shaped curve, resulting from several driving factors interacting in a complex system (Abrate and Ferraris, 2010). It is a matter of discussion among scholars if the same principle can be applied to waste production (Ercolano et al., 2018). A possible explanation of the data presented for Germany, Italy and Sweden is that all of them have already reached and overcome the critical point after which the relation reverses towards an inverse proportion and an higher GDP corresponds to the possibility of a wiser approach on waste management.

Furthermore, to validate the pattern in the production of waste shown in Figure 3, it can be useful to switch the focus to other economical parameters, no longer to an indicator of income *per se* but to proxies of how this income is evenly distributed among the population, like Gini's coefficient or income distribution.

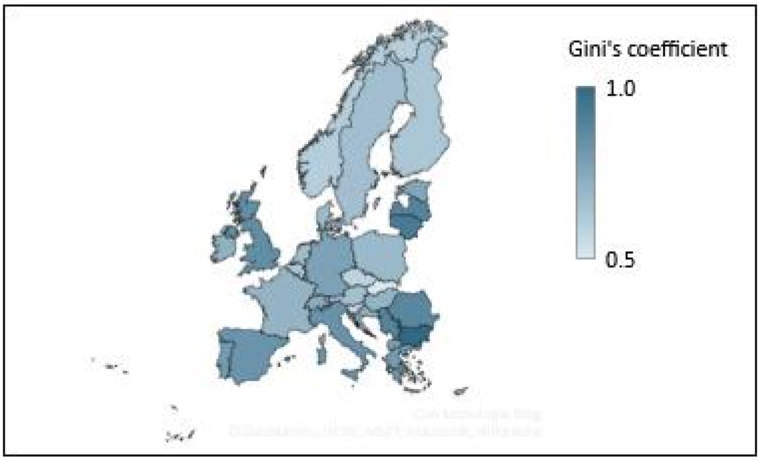


Figure 7 - Gini's coefficient [-] (OECP Data 2014)

Gini's coefficient measures the deviation from a perfectly equal distribution of income among individuals or households within a country. A null value represents absolute equality; a value of 1 absolute inequality and as it is shown in Figure 7 the profile of all the countries analysed is consistent with the European average, but Sweden shows a lower inequality value abreast with the waste generation trends of Figure 3.

2.2 Waste management

Within the general framework presented in paragraph 2.1, MSW generated by households, small businesses and public institutions, represents a small percentage of solid waste. However, due to their heterogeneous composition they represent a complex issue in waste management and at the same time a worthwhile resource to recover energy and secondary raw materials (Malinauskaite et al., 2017).

A considerable amount of potential secondary raw materials is lost as a consequence of the characteristic waste stream of linear economy, where landfilling plays a significant role in waste management. However, the current state-of-the-art technologies offer manifold solutions to this problem in order to follow the principle of end-of-waste fostered by recent legislation, as it is leading to reduce the amount of waste directed to landfills in favour of recycling materials and recovering energy (European Commission, 2008).

The percentages of MSW disposed of in landfills, incinerated and treated with other technologies in the benchmark countries during 2018, are reported in Figure 8.

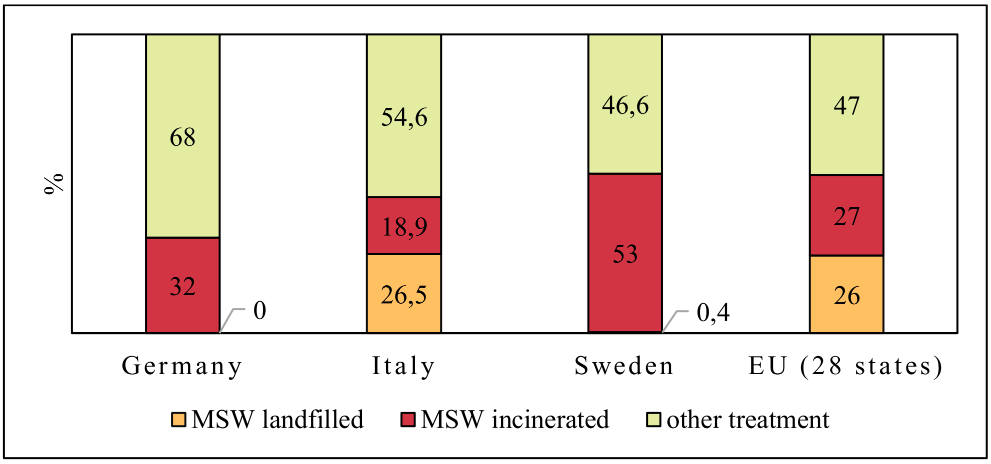


Figure 8 – MSW treatment technologies (BAT on waste incineration, 2018)

Although around Europe almost 30% of waste is disposed of in landfills (European Commission, 2017a). Income levels and social well-being seem to play a key role in the sustainability levels reached in waste management. Indeed, as in Figure 8, more economically prosperous countries like Germany and Sweden almost never resort to landfill to dispose of municipal solid waste choosing instead different treatments involving materials and energy recovery. However, the percentages are different concerning hazardous waste, in Figure 9, where incineration is less applied in favour of landfilling and other treatments.

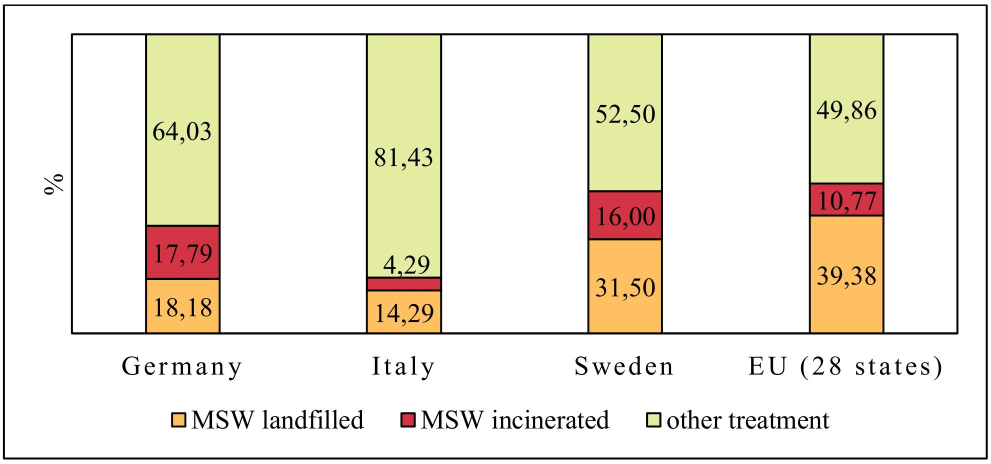


Figure 9 - Hazardous waste treatment technologies (BAT on waste incineration, 2018)

Even though landfilling is still common practice for disposing hazardous and municipal solid waste all over Europe, it has been proven as a detrimental solution in terms of land use, possible soil and groundwater contamination and greenhouse gas production therefore the global trend is going towards other techniques (Daskal et al., 2019). Awareness of these negative impacts on global warming, eco systems, ground and surface water, human health, and land availability resulted in calls for legislation at European level.

Environmental policies enacted in the past two decades are setting the directions for waste management towards a circular system, where environmental and economic aspects can be maximised by transforming waste into secondary raw materials. Following that trend, the most recent directive on this topic, Directive n°2008/850, aims to encourage a progressive reduction in the use of landfill for waste suitable for recycling and recovery, in order to prevent and reduce as much as possible negative effects on the environment.

In order to meet the new legislation requirements, that aim to dismiss the practice of landfilling and increase the amount of material recycled and recovered, the research is focusing on identifying and improving techniques that enable to close material life cycles in a cradle to cradle loop or to create interconnected networks where waste from one process can serve as raw material for another one.

2.3 Incineration with thermal recovery

Incineration is a mature technology and it is present in many European countries, although with different importance with respect to other treatments, as shown in Figure 10.

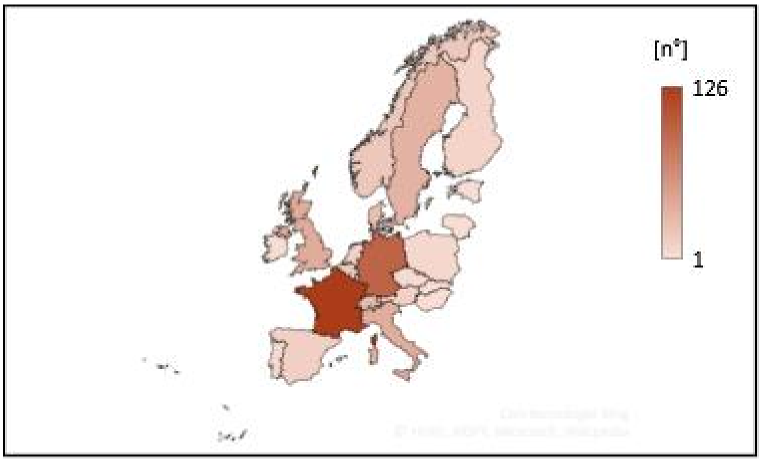


Figure 10 – Waste to Energy treatment plants

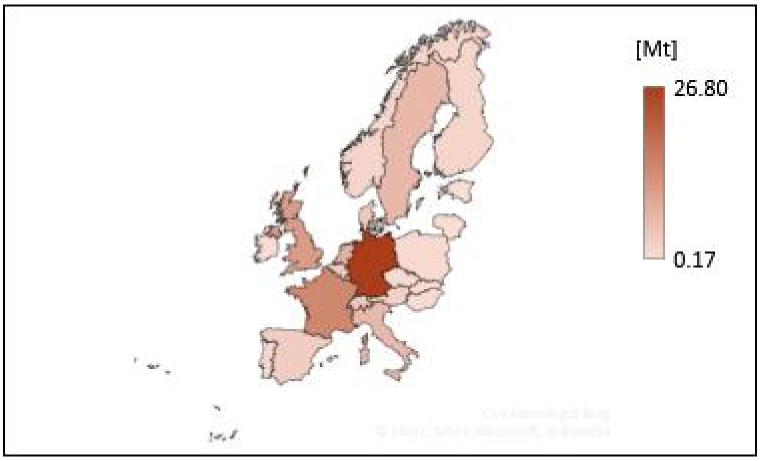


Figure 11 – Amount of incinerated waste [Mt]

The most used technology for thermal treatment of municipal solid waste in Europe is combustion in grate incinerators. This configuration is used by 90% of municipal solid waste incinerators (European Commission, 2017a). In moving grate incinerators, MSW stream is fed to the combustion chamber where it is dried and then incinerated at temperatures up to 950°C (European Commission, 2017a). This treatment does not require any particular pre-treatment of the waste and makes it possible to turn non-reusable, non-recyclable waste into energy, and to reduce the need for landfilling.

The advantages of this technology are manifold and concern both the supply of energy demand with an alternative to fossil fuels based solutions (Malinauskaite et al., 2017) and the more efficient recovery of secondary raw materials. Indeed municipal solid waste heating value is around 10 MJ/Kg and it represents an important alternative source of energy (Malinauskaite et al., 2017) and furthermore after incineration, elementary materials are more easily accessed and, opposed to other destructive processes like shredding or milling that are energy consuming, incineration has a positive energy output as well.

Moreover, incinerators play a key role in emissions restraint both in terms of decreasing CH_4 emissions from landfills, by reducing the amount of waste disposed there, and preventing CO_2 emissions, due to energy production. The environmental impact of this emission restraint is not negligible, because CH_4 has a global warming potential (GWP) 28 times higher than CO_2 and on the other hand energy production from fossil fuels are currently accounted for about 70% of CO_2 emitted each year (source: Climate Analysis Indicators Tool (World Resources Institute, 2017)). This result can be improved with a more efficient recovery of incineration residues, that, as will be further discussed in section 2.5, could replace raw materials in the infrastructure industry.

2.4 Bottom ashes

The solid residues generated by the combustion process are flying ashes (FA) and bottom ashes (BA). Bottom ashes generations is usually 5 times higher than flying ashes (Dou et al., 2017) and represents in terms of weight about the 25% of the total incinerated waste, as in Figure 12.

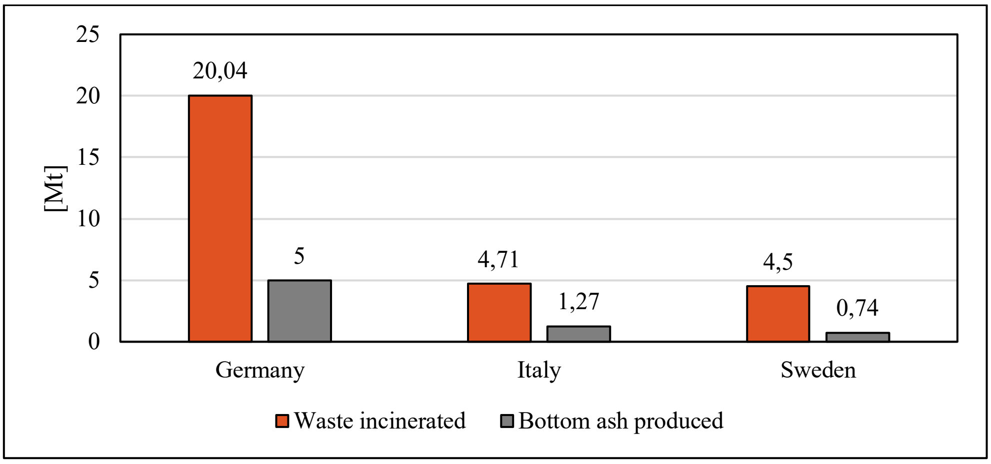


Figure 12 – Incinerated waste and bottom ash produced [Mt] (source: CEWEP Report 2012)

Although the volume reduction is considerable, BA still represent about 20-30% of the weight of the MSWI all over Europe (Caviglia et al., 2019), it is a critical material for landfilling since it may cause contamination problems releasing heavy metals and metalloids, while on the other hand it has shown a great deal of possible applications after some reasonably simple treatments. The investigation of the feasibility of an efficient BA recovery is the rationale of this thesis.

In a Waste-to-Energy plant the bottom ashes are collected on the furnace's grate as non-combustible materials. Even if the waste was sorted before incineration, metals are always present and both ferrous and non-ferrous ones can be taken out of the bottom ashes and recycled. Moreover, the inert fraction could find a market in the construction materials industry (Minane et al., 2017), as feedstock material for ceramic production (Rincon Romero et al., 2018) or as adsorption substrate in particular applications (Fontseré Obis et al., 2017).

Bottom ashes treatments are specifically designed to remove the components that may jeopardise their performance as secondary raw materials: to be recovered as loose construction aggregates or ceramic material, they need to undergo thermal treatments in order to avoid further metals and metalloids release, as detailed in section 2.6.

2.4.1 Physical characterization

The particles size distribution generally belongs to the range within 0.02 and 10 mm, typical values of sand and gravel (Dou et al., 2017). From a physical perspective BA are characterised by a slightly lower density compared to other minerals, the dry bulk density is around 950 Kg/m^3, the moisture content depends on whether the ashes are quenched with water after discharge or not and can vary between 15% and 60% (Dou et al., 2017).

The porous nature of this material grants an adsorptive capacity in line with the values of natural aggregates, and this adsorption property appears to increase in the finest fraction, due to an increase in the specific surface area (Lynn et al., 2017). Many important parameters have shown significant changes within different granulometric classes. However geometrical parameters, such as circularity factor, seem not to change significantly according to the particles dimensions (Yao et al., 2014).

In view of the applications for BA reuse, presented afterwards in section 2.5, engineering characteristics have been studied. BA is a compactable material, even if compaction can often lead to a reduction in the larger fractions due to grinding. It is not possible to define a characteristic range of values for BA's permeability since it is strongly related to moist content and can vary up to 6 orders of magnitude between 10^{-9} and 10^{-4} m/s, but it is almost always suitable to be used as drainage material (Dou et al., 2017). All the parameters to assess the feasibility of aggregates replacement with BA, such as shear strength, freeze thaw resistance and abrasion resistance, are adequate. Besides it is worth-noting that the elastic module presents better performances before ageing, when however BA are not suited for use due to leaching concern (Lynn et al., 2017).

2.4.2 Mineralogical composition

Bottom ashes characteristics depend strongly on the composition of the MSW they were generated from, that is highly variable within a region, and over time. Moreover, the configuration of the incineration plant may also affect BA composition, as the organic content present in the ashes can be linked to the combustion temperature and residence time, and if its concentration is above a certain value it can have a negative effect on the material's density, stiffness and resistance over time (Lynn et al., 2017).

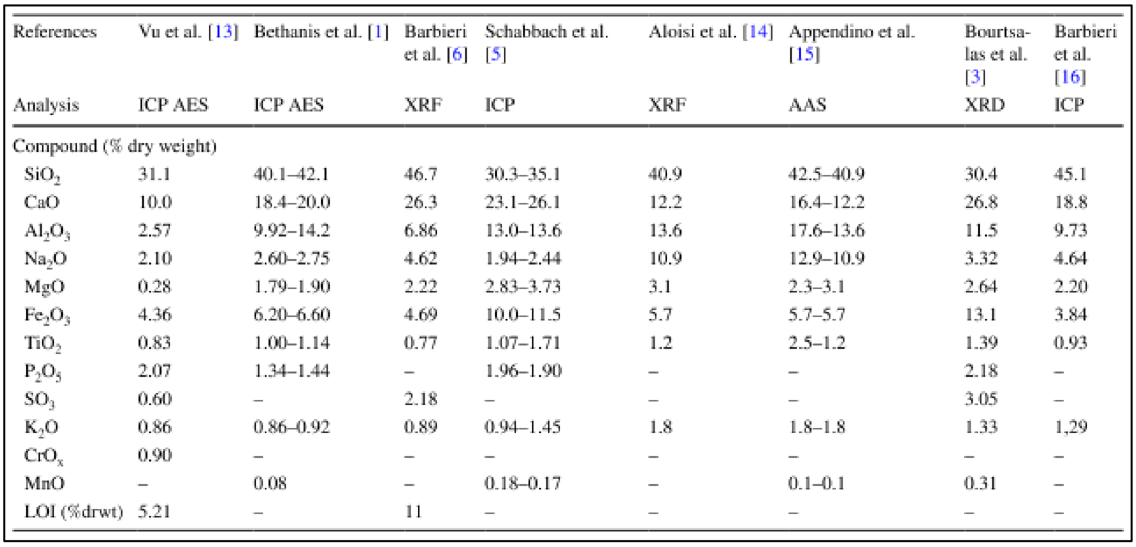
Albeit estimations of solid waste composition are always uncertain, and combustion operative conditions depend on the specific plant, it is always possible to identify some general characteristics. BA always correspond to the inert and metallic components of the waste and generally present as a granular material with a relevant amorphous phase and a characteristic particle size distribution within 0.02-10 mm. The typical composition of bottom ashes may be identified as around 60 % SiO_2, 20% CaO, 10% metal oxides (Fe_2O_3, Al_2O_3, Na_2O) and residual amounts of trace metals Pb, Cu, Zn, Cd, Cr, Ni (Dou et al., 2017).

Across all granulometric classes, quartz is the most abundant mineralogical specie even in the finest fractions (Minane et al., 2017). However, since it is a mechanically resistant mineral, its presence is wider in the largest fraction (Loginova et al., 2019). Zeolites, on the other hand, are rarely found in the fraction between 4 and 22 mm, mainly due to the fact that they present as a powder in the fine fraction *per se* or attached to greater particles (Loginova et al., 2019). The most common Calcium minerals in BA are Calcite and Anhydrite, the former is commonly found in all granulometric classes while the latter is characteristic only of the finest fractions (< 500 μm), where it is the main responsible for sulphate leaching (Loginova et al., 2019).

2.4.3 Elemental composition and leaching behaviour

Several studies have tackled the characterisation of bottom ash composition and their results are shown below in Table 1. However, BA's chemical composition seems to be strongly related to particle size: Si appears to decrease with particle size while Ca and heavy metals show an increase upon particle size decrease (Caviglia et al., 2019), as shown in Figure 14. Moreover, metals like Pb, Zn, Cd and Sn have been found in high concentration in fraction below 8 mm (Allegrini et al., 2014).

Table 1 - Composition of MWIBA characterization studies (Lopez Ferber et al., 2019)



References	Vu et al. [13]	Bethanis et al. [1]	Barbieri et al. [6]	Schabbach et al. [5]	Aloisi et al. [14]	Appendino et al. [15]	Bourtsalas et al. [3]	Barbieri et al. [16]
Analysis	ICP AES	ICP AES	XRF	ICP	XRF	AAS	XRD	ICP
Compound (% dry weight)								
SiO_2	31.1	40.1–42.1	46.7	30.3–35.1	40.9	42.5–40.9	30.4	45.1
CaO	10.0	18.4–20.0	26.3	23.1–26.1	12.2	16.4–12.2	26.8	18.8
Al_2O_3	2.57	9.92–14.2	6.86	13.0–13.6	13.6	17.6–13.6	11.5	9.73
Na_2O	2.10	2.60–2.75	4.62	1.94–2.44	10.9	12.9–10.9	3.32	4.64
MgO	0.28	1.79–1.90	2.22	2.83–3.73	3.1	2.3–3.1	2.64	2.20
Fe_2O_3	4.36	6.20–6.60	4.69	10.0–11.5	5.7	5.7–5.7	13.1	3.84
TiO_2	0.83	1.00–1.14	0.77	1.07–1.71	1.2	2.5–1.2	1.39	0.93
P_2O_5	2.07	1.34–1.44	–	1.96–1.90	–	–	2.18	–
SO_3	0.60	–	2.18	–	–	–	3.05	–
K_2O	0.86	0.86–0.92	0.89	0.94–1.45	1.8	1.8–1.8	1.33	1,29
CrO_x	0.90	–	–	–	–	–	–	–
MnO	–	0.08	–	0.18–0.17	–	0.1–0.1	0.31	–
LOI (%drwt)	5.21	–	11	–	–	–	–	–

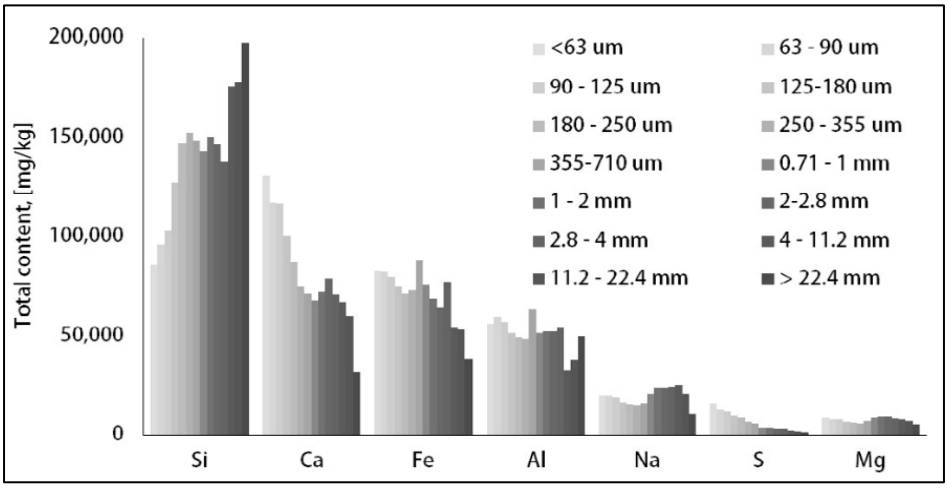


Figure 13 - Major elements content in different granulometric classes (Loginova et al., 2019)

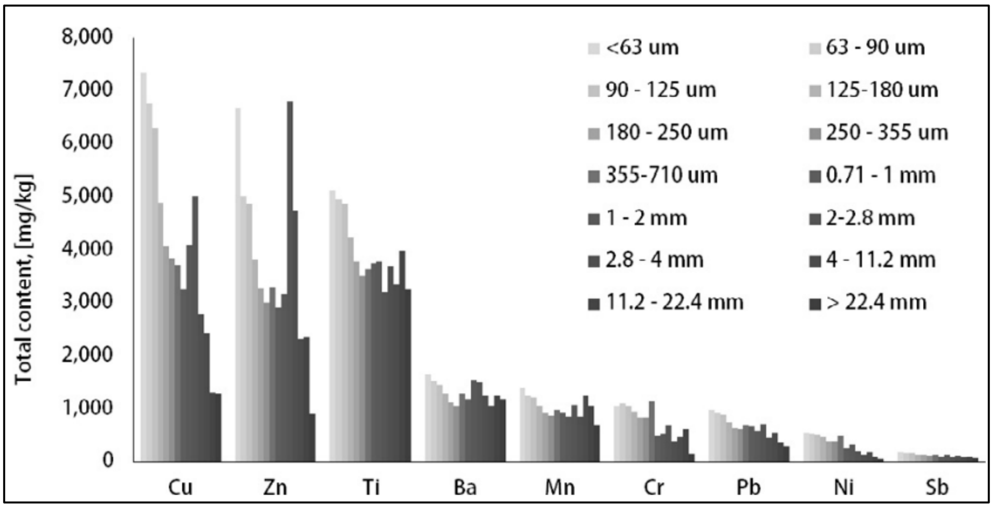


Figure 14 – Trace metals content in different granulometric classes (Loginova et al., 2019)

Different studies have investigated presence and release mechanisms of metals in BA as they represent an interesting opportunity for "urban mining"(Xia et al., 2017), with all the environmental and economic advantages that result from it, but also from the possible recovery of the inert fraction (Alam et al., 2019b). BA leaching characterization is mostly concerned on determining heavy metals release mechanisms, since other substances that may pose a threat on health and environment, like dioxins and furans, are rarely found in BA. From several experimental analyses it was possible to develop a log-log linear model to estimate metals leaching potential based on the total amount present in BA (Dou et al., 2017).

$$\log C_{\text{leaching}} = 0.618 \cdot \log C_{\text{total}} - 1.92 \qquad (1)$$

Leaching is not constant over time since it depends on the present concentration but also because during ageing CO_2, diffusing into the solid matrix, facilitates the transformation of CaO into calcite ($CaCO_3$) and ettringite ($Ca_6Al_{12}(SO_4)_3(OH)_{12}\cdot 26H_2O$) leading to a pH decrease that inhibits metal release (Dou et al., 2017).

Furthermore, metals releasing has been related to other factors, such as liquid-to-solid (L/S) ratio and bulk content. The particle shape factor has an interesting effect on metal release since a higher specific surface area (SSA) facilitates the metal solubility and mineral dissolution that leads to an increase in metals leaching (Dou et al., 2017).

Relying again on the model previously presented, the mineral composition of the incinerated waste has to be taken into account as it affects the partition of metals between BA and flue gasses and thereby the total amount present in BA. If chloride is present it is possible for the metals to form compounds with small size and low boiling point that evaporate during combustion, on the other hand sulphur stabilizes the metals as sulphates into the matrix of BA (Verholst et al., 1996). Additionally geochemical reactions naturally occurring over time, like precipitation of gypsum and aluminosilicates and formation of Al and Fe oxides induce variation in acid neutralization capacity, pH, redox potential, sorption and ion exchange capacity, affecting metals release (Polettini and Pomi, 2004).

Besides, REEs can be found within BA with a concentration around 88 and 124 mg/kg (Funari et al., 2016). Their presence is greater in bottom ash compared to fly ash since they have high boiling points. This value is too low to justify their recovery from an economical point of view, however they are easily detectable by correlation with other parameters such as P_2O_5 and Al_2O_3 concentration or magnetic susceptibility, that can be quickly measured on site, in order to evaluate from case to case if the recovery is economically feasible (Funari et al., 2016).

2.5 Current management of bottom ash

Nowadays, BA exiting from MSW incinerators are either disposed of in landfills or recovered as secondary raw materials (Lam et al., 2010). Over the years the market for treated BA has spread from recovery of inert fraction, reused in the construction field, to metals mining (Enzner et al., 2017). Other than a source for metals recovery, BA, thanks to their chemical composition and physical properties, as described in the paragraph 2.4.3, are suitable for use as base and sub-base materials in road construction, cement and concrete production and low-cost adsorption substrate (Dou et al., 2017).

BA, since their composition is generally rich in CaO and SiO_2 , are a potential replacement for raw materials in concrete and cement production (Sorlini et al., 2011). The decarbonation process of lime, in order to transform calcium carbonate ($CaCO_3$) into lime (CaO), is the most critical step in cement production due to the amount of CO_2 released and of energy required, hence using as raw material BA, which are naturally rich in CaO, entails an environmental and economic advantage (Lam et al., 2010). On the other hand the main issues with the concrete application are early cracking, induced by the presence of metallic aluminium or zinc, and corrosion of steel reinforcements caused by chlorides that can however easily be averted by wet or semi-dry separation processes and washing treatments (Verbinnen et al., 2017).

Other than concrete and cement production, one of the earliest application proposed for BA reuse has been asphalt paving, where the material, appropriately treated, may replace natural gravel or crushed rocks in the base and sub-base layers of road pavement (François and Pierson, 2009). Considering that the main limitation is the concern for eventual contaminations, caused by the release of the metals present in the BA, it is necessary to operate washing or separation treatments to reduce metals concentration before their posed (Van Praagh et al., 2018).

Another construction application of BA has been as ceramic materials, since they have shown the appropriate characteristics in terms of density, strength and adsorption properties (Verbinnen et al., 2017). Likewise cement and concrete, BA chemical composition makes it suitable to replace clay in ceramic production (Lam et al., 2010). While to assume the characteristic amorphous structure of glass a vitrification treatment is required (Rincon Romero et al., 2018).

In the recent years, the high level of porosity and specific surface area, discussed in the paragraph 2.4.1, have lead research to focus on the reuse of BA as adsorption material to treat gaseous and liquid waste stream (Lam et al., 2010). BA have been found particularly suitable for removing dyes, like alizarin yellow, fast green, and methyl violet from industrial waste water with adsorption capacity comparable with other adsorbents like perlite (Gupta et al., 2005). Besides, BA have shown an interesting behaviour in gaseous phase treatment, where they selectively adsorbed H_2S, finding a proper fit as daily cover material for landfills (Fontseré Obis et al., 2017). Adsorption and cation exchange capacity have been proved to increase in the smaller fraction of the BA (Lam et al., 2010), that are the most difficult to recover and therefore this is one of the less used application (Dou et al., 2017).

However, all these potential applications require the BA to undergo a series of treatments, which has the main goal of removing metals from the bulk material. In several European states metals recovery is common practice for BA treatment, even though the efficiency reached is often trivial (Bourtsalas, 2012).

2.5.1 Environmental impacts

Seen the possible applications of recovered BA previously discussed, the main environmental concern for their reuse is about their leaching behaviour (Schafer et al., 2019), but recent studies are starting to take into account other aspects such as life cycle assessment and greenhouse gas emission (Silva et al., 2019).

Regarding the replacement of aggregates in cement production and road pavement realization the most critical environmental issue has always been leaching. Asphalt pavement was one of the first application to be implement for bottom ash reuse and extensive literature handled their leaching characterisation (Bourtsalas, 2012; François and Pierson, 2009; Lynn et al., 2017; Silva et al., 2019; Van Praagh et al., 2018). The main environmental issues for this application are salt dissolution and metal release (François and Pierson, 2009). However it has been observed that blending BA with other aggregates hinders metals release (Schafer et al., 2019).

Moreover, since they represent a cluster of metals that can be mined through physical and chemical separation, as discussed afterwards in section 2.6, resource recovery form BA is a noteworthy action. This possibility has been compared with regular extraction of raw materials, that could be also found in BA, such as steel, aluminium alloys, Cu and aggregates, using the usual life cycle assessment methodology. Since conventional metal extraction and melting activities requires a considerable amount of energy, often provided by fossil fuels, recovery of metal from BA result in a decrease of global warming potential (GWP) and also a decrease of potential impact acidification (TA), due to SO_2 release from metal smelters.(Allegrini et al., 2015).

2.6 Bottom ash treatment

The possible configurations of BA treatments are composed of dry and wet processes that follow dry or wet discharge. The differences between these configurations and their advantages or disadvantages will be presented in this section.

Nowadays bottom ashes could be discharged with different technologies, either a wet or a dry system. The former system is the most used all over Europe and it enables to contain dust released during BA movement from the moving grate, but it could slightly compromise the quality of the recovered metals. Dry bottom ash discharge on the other hand is more challenging since it requires an enclosed system, constantly under suction in order to prevent dust release (Kahle et al., 2015). This technique has been adopted by only two industrial plants in Europe, however it has been proven to be economically viable since it increases the effectiveness of metal separation, therefore it maximises revenues from metal recovery (non-ferrous metals, above all) while reducing disposal costs as a result of weight reduction, and associated lower transport costs (Koralewska, 2011).

The different processes that BA undergo are aimed to minimise the environmental impact in case of landfilling and to allow the recovery of valuable materials. Past research has identified several possibilities to treat BA, including separation processes, based on different composition or behaviour, stabilization, either natural or artificially accelerated and thermal methods (Dou et al., 2017).

2.6.1 Discharge systems

The most common practice in Europe is wet discharge, where the unburnt materials are moved through a moving grate to a water tank in order to extinguish burning lumps and cool down the ashes. In this case the final water content of the bottom ashes may vary from 15% in case a pressing and draining system is present, to 20% if the extraction from the water basin is carried out by a loading bucket. Nowadays, wet discharge is a consolidated technology that allows to easily reduce ash temperature, to wash out salts or chlorides and to prevent fine dusts spreading. However, this practise may compromise the quality of the extracted metals, since when in contact with water BA may react and change pH, inhibiting further metal release. Moreover, water eases fine particle agglomeration hindering the recovery of particles with dimension between 5 and 8 mm (Riva et al., 2016).

A more recent trend is to change the configuration of the discharge system to a dry one, where the cooling of the ashes is carried out by recycle of air from the outside in order to better exploit the thermic energy gained during the incineration and guarantee a more efficient combustion of the organic matter. Furthermore, corrosion reactions and agglomeration of fine particles are not occurring due to the lack of water, and the fine fraction, which is the one with more metals content, results more easy to separate (Martin et al., 2015). The main issue with this configuration is the difficulty in containing the dust released during ash transport. Currently in Europe, there are only two waste incineration plants that use the dry ash extraction system: SATOM in Monthey (CH) and KEZO in Hinwill (CH).

Metal recovery is more difficult from wet-discharged BA due to different factors. As previously stated, the flowing air in the dry discharge system increases the efficiency of the combustion and decreases the quantity of organic matter present in the ash. Moreover the contact with water causes an increase in the difficulty of metals recovery due to a lumping effect and to the generation of a thin layer of silicon and calcium oxides, that need a treatment with acids in order to be removed (Kahle et al., 2015).

2.6.2 Stabilization - Weathering

Notwithstanding the processes undergone by the BA, in the majority of treatment plants the first step after discharge is a weathering phase when, as a consequence of exposure to atmospheric conditions, different mineralogical alterations occur (Polettini and Pomi, 2004). During this phase the original mineralogy is altered as a result of different processes: hydrolysis of Ca, Al, Na and K oxides, hydroxides dissolution or precipitation and absorption of atmospheric CO_2 that leads to carbonation (Meima and Comans, 1999). These alterations cause changes in macroscopic aspects like an increase in crystallinity index (Polettini and Pomi, 2004) and chemical properties like acid neutralization capacity, pH and sorption and iron exchange capacity (Meima and Comans, 1999).

During ageing, the main reaction kinetics are influenced by the natural diffusion of CO_2 and the $Ca(OH)_2$ dissolution, that can be described with an unsteady transport and reaction model, in which porosity ε and effective diffusion coefficient D_{eff} are assumed to be constant over time (Meima and Comans, 1999).

$$\varepsilon_{air} \cdot \left(\frac{\partial C_{CO_2}^2}{\partial t} \right) = D_{eff} \cdot \left(\frac{\partial^2 C_{CO_2}^2}{\partial x^2} \right) - R_{CO_2} \tag{2}$$

This carbonation process is due to the interaction of CO_2 with naturally alkaline materials like the alkaline metal oxides present in BA and leads to the reaction below.

$$Ca(OH)_{2(aq)} + CO_{2(aq)} \rightarrow CaCO_{3_{(s)}} + H_2O_{(l)} \tag{3}$$

The formation of calcium carbonates causes several alterations in physical and chemical properties of BA. The capture of CO_2 is linked to a mass increase and a porosity decrease, however, creation of micropores has been observed since $CaCO_3$ has a higher molar volume than CaO. As for the chemical characteristics pH is reduced from 11-12 to 8-9 while acid neutralization capacity may rise, leading to heavy metals stabilization (Dou et al., 2017).

Carbonation kinetics seem to improve with higher CO_2 concentration and a specific range of moisture, in order to create water layers thin enough to limit diffusion distance. Moreover recurring to pressurised conditions apparently aids carbonation kinetics, without affecting however the overall CO_2 uptake (Santos et al., 2013). Besides natural ageing, research has investigated feasibility and effectiveness of reagents addition to improve bounding of metals and solid matrix in order to reduce leachability (Lam et al., 2010) but these works mainly concerned fly ashes, where leachable heavy metals concentration is higher (Wang et al., 2015) due to processes like metals vaporisation and adsorption on the surface of fly ash particles (Lam et al., 2010) . Moreover, the curbing of leaching potential obtained during weathering is due to the formation of mineral coatings around the particle surface and that has been proven to be detrimental in terms of mineral recovering (Holm and Simon, 2017).

2.6.3 Physico-mechanical treatment

After been discharged the bottom ashes undergo a series of treatments aimed to separate the inert fraction from the metallic components in order to obtain more pure secondary raw materials. The configuration of the system varies from plant to plant, but treatments involved are generally aimed to classify the mineral fraction and separate ferrous metals and non-ferrous metals as well as organic matter. Separation could be implemented based on particle size, shape, density, surface wettability, magnetic properties, colour, physicochemical property, and solubility, the efficiency of the separation relies on these differences (Xing and Hendriks, 2006).

The most conventional method in European WtE plant is a dry separation process following wet discharge. This process employs manual sorting, screening, magnetic and eddy current separation to achieve a recovery of metals (both ferrous and non-ferrous) that makes it worthwhile (Koralewska, 2011). Nevertheless, a more innovative approach is to treat wet discharged ash adding more water in order to further improve the quality of the recovered metals. This process involves a screening of different granulometric classes (< 2 mm, 2-6 mm, 6-20 mm, 20-40 mm) that are then treated separately to recover valuable fraction. In Figure 15 it is represented the percentage of application for the different treatments, described later in this section, all over Europe.

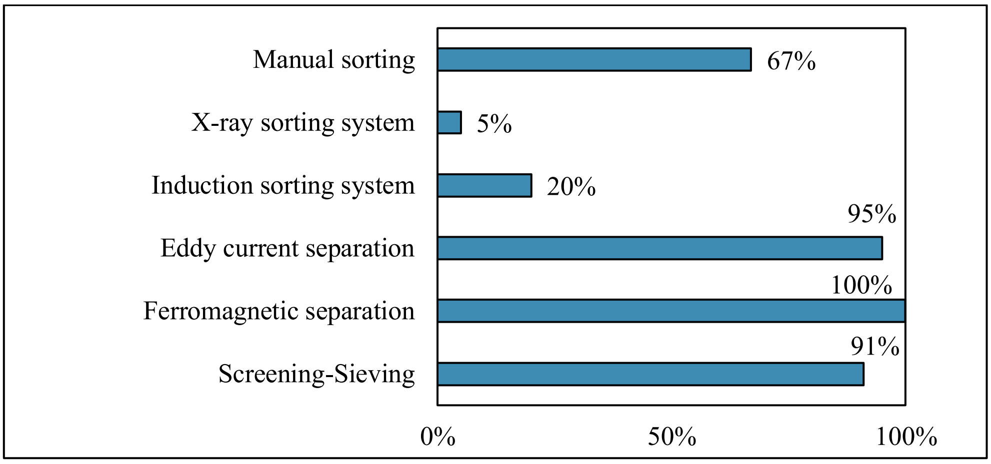


Figure 15 - Application of different separation techniques

Since each granulometric class has one or more characteristic components, it has been proven effective to always operate sieving and screening to classify the ashes in groups with different particle size and therefore different behaviour, in order to subsequently direct them to the most appropriate treatment sequence. The main issue with this step is the formation of lumps in the fine fraction of the bottom ashes. Generally, this treatment is carried out in a closed environment since even in wet-discharged BA if the water content is lower than 10% it causes problems of dust releasing.

It is possible to notice that ferromagnetic metals are always subject to recover since the technique for their separation is easily implemented and because even if their market value is lower compared to other elements, iron scraps can be found in significant amounts (Morf et al., 2013). The configuration for this treatment varies according to material flow size, velocity and particle size. However, eventual stainless steel present cannot be separated with this principle because it does not assume magnetic behaviour even if the main element of its alloys is iron.

Non-magnetic metals are generally separated from the ashes using an eddy current separator where a set of rotating magnets induces eddy currents that cause a magnetic deflection force to act on ferrous metals while non-magnetic metals are guided by friction, gravitational, centrifugal and drag (air resistance) forces. This causes a separation in ferrous and non-ferrous material trajectories and allows their separation. The efficiency of eddy current separators can be improved with a more precise interval in the fractioning, that simplifies the calculation of the ballistic curves, as well as having a configuration of multiple separation in series. The key parameter in this process is repulsiveness [$m^2/\Omega \cdot Kg$], which is the ratio of electrical conductivity [$1/\Omega$] and density [Kg/m^3].

Typically, in a state-of-the-art plant, following magnetic and eddy current separation an Induction Sorting System (ISS) is installed to separate non-magnetic materials with low repulsiveness like stainless steel. This machine uses sensors to detect metallic objects with magnetic induction and with compressed air it throws them away from the conveyor belt. A similar principle is the one on which X-ray sorting is based, where the sensors detecting metallic items are replaced by an X-ray module that recognise specific shapes that are more likely to be metallic and separate them from the ash stream again with compressed air.

The treatments that the ash undergoes are similar to the ones used in reclamation of polluted sites, they are very energy-demanding but achieve remarkable yields in metals recovery and leachate reduction (Bourtsalas, 2012). Efficiency in non-ferrous metals recovery ranges between 29% and 75% with a dry-sorting system but can increase up to 79% with wet sorting (Rem et al., 2004).

2.6.4 Thermal treatment

Thermal treatments rely on two different processes to reduce metals leaching: separation through evaporation or immobilisation to stabilise metals in the solid matrix, resorting to vitrification, melting, sintering and microwaving (Dou et al., 2017).

Evaporation of suitable metals, like Cd, Pb and Zn, is generally induced by heating the ashes to a temperature of 1000°C, higher than the one reached during MSW incineration but still below their melting points. Higher temperatures are needed in order to more stably embed metals in the solid matrix, but this step does not usually requires long residence time (Dou et al., 2017).

As for thermal immobilisation, several techniques could be implemented: melting, vitrification, sintering or microwaving (Dou et al., 2017). Melting and vitrification are similar processes in which, due to high temperature (between 1000°C and 1500°C), inorganic species present in the residues chemically bond together and therefore volatilization of metals like Hg, Cd, Pb and Zn is inhibited (Stabile et al., 2019). Sintering instead relies on increasing temperature or pressure, without reaching the melting point, to produce glass-ceramic products characterized by low porosity and high resistance, suitable for use as cementitious composites (Yang et al., 2018). The most recent developed thermal treatment is microwaving: heating with a non-ionizing electromagnetic radiation between 300 MHz and 300 GHz (Dou et al., 2017).

2.7 Research gap: feasibility of recovery for fine fraction

The treatment processes described in the paragraph above, allow to recover a noteworthy amount of secondary raw materials, which would otherwise be lost with the waste stream sent to landfills. Nevertheless, some resource potential is still unexploited. The limit of current state-of-the-art treatment corresponds with the difficulty met in recovering the finest fraction.

In Figure 16 it is summarised the finest particle size for which recovery is still feasible in different European countries. All the source from these data are listed in table 1 of "The characterisation of the fine fraction of MSWI bottom ashes for the pollution and resource potential" of V. Enzner, O. Holm, M. Abis, K. Kuchta.

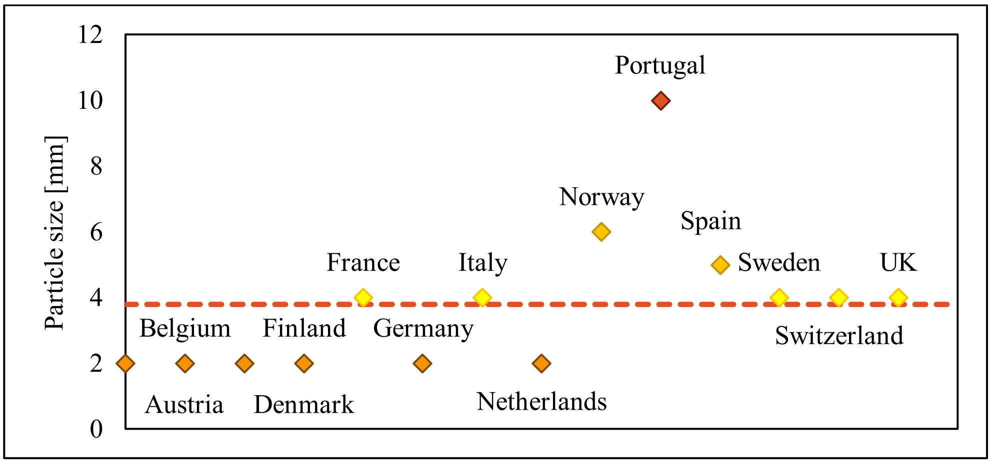


Figure 16 - Finest particle size treated in state-of-the-art European plants (Enzner et al., 2017)

The recovery feasibility gap is significant, as some more upstanding countries, among which Germany, are able to treat BA with particle size as fine as 2 mm while other countries leave a greater amount of material untreated. The latter is the case of Portugal, which performance is particularly sub-standard considering that all the materials with dimension lower than 10 mm is sent to landfills.

The finest fraction, that is currently not recovered, is critical to manage, since in this fraction the higher concentration of heavy metals is gathered. Hence it is crucial treating it to reduce pollution potential in case of landfilling and to recuperate metals to make the process profitable (Allegrini et al., 2014).

The resources present in this fraction are manifold considering that, as detailed in paragraph 2.4.3, BA's elementary composition is strongly related to the particle dimension. For instance, leaching capacity of elements like Ni or Sb does not show significant dependence on particle size, while Cu , Zn and the others show an increasing concentration in the fine fractions of BA (Loginova et al., 2019). Indeed, presence of these metals in the finest fractions represent an unaddressed criticality when it comes to landfilling and a lost resource as secondary raw materials. The aforementioned metals have not negligible market values and their recovery could be economically favourable. Even if it is important to underline that these values are mere approximations since market values are subject to change.

These economic aspects, combined with the environmental advantages described in section 2.5.1, are the grounds for optimising the recovery of residual metals and minerals, in particular for the fractions still unexploited, which is the rational of this work.

3 BASH-TREAT PROJECT

The H2020 project "BASH-TREAT - Optimization of bottom ash treatment for an improved recovery of valuable fractions", won the call ERA-MIN2 "Research and Innovation Programme on Raw Materials to foster Circular Economy" (May 2018-May 2021), is coordinated by Technical University of Hamburg and involves DIATI Politecnico di Torino as partner. The main goal of BASH -TREAT is the optimization of a physico-mechanical process, implemented at full-scale on a mobile plant (fed by 50 t/h of bottom ash), for the recovery of metals and inerts. Three full-scale industrial tests, performed in municipal solid waste (MSW) incineration plants in Germany, Sweden and Italy are planned in the project.

The samples analysed in this thesis have been collected in 2 bottom ash treatment plants. The treatment trains implemented in the two facilities, shown in Figure 17 and Figure 18 consist in a series separation steps based on magnetic properties, particle size and inductive characteristics. The materials exiting from these plants have been afterwards fed to a mobile treatment plant, designed by Heidemann Recycling GmbH, described in paragraph 3.3.

3.1 BA treatment plant 1 (Germany)

In the treatment plant installed in Germany, the BA firstly undergo a magnetic separation to recover iron, (with a 99% purity) from the waste stream, that it is afterwards sent to sieving. The first sieve separates the particles above 40 mm, sending them to a wind shifter, from the particles with dimension below 40 mm, that are again sent to magnetic separation and sieving at 8 mm. Both the particles with size above and below 8 mm undergo a series of eddy current separations, with however the different configurations shown in Figure 17.

After the last step, the remaining mineral fractions, slags between 0-2 mm, 2-8 mm and 8-40 mm, are collected partly to be analysed and partly to be fed to the mobile plant to investigate the feasibility of a further separation of recoverable fractions.

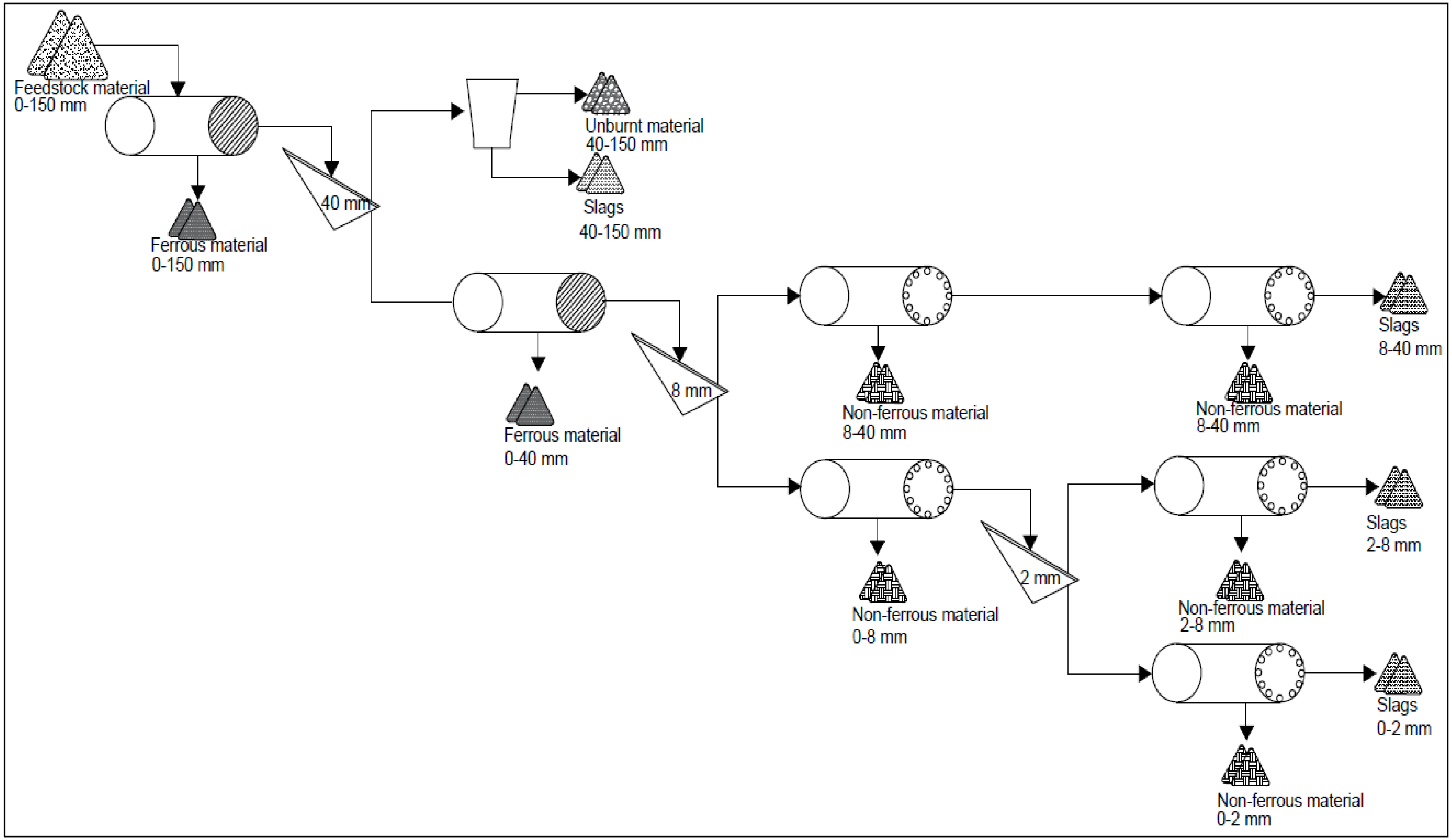


Figure 17 - Work chart of BA treatment plant 1 (Germany)

3.2 BA treatment plant 2 (Sweden)

BA treatment plant 2 (located in Sweden) implements a first magnetic separation of the ferrous metals with greater particle dimension and then operates a series of dimension classifications to better recover the non- ferrous materials (Figure 17). The slags with dimension between 0-4 mm and 4-26 mm have been sent to the mobile treatment plant to be processed and analysed in the labs.

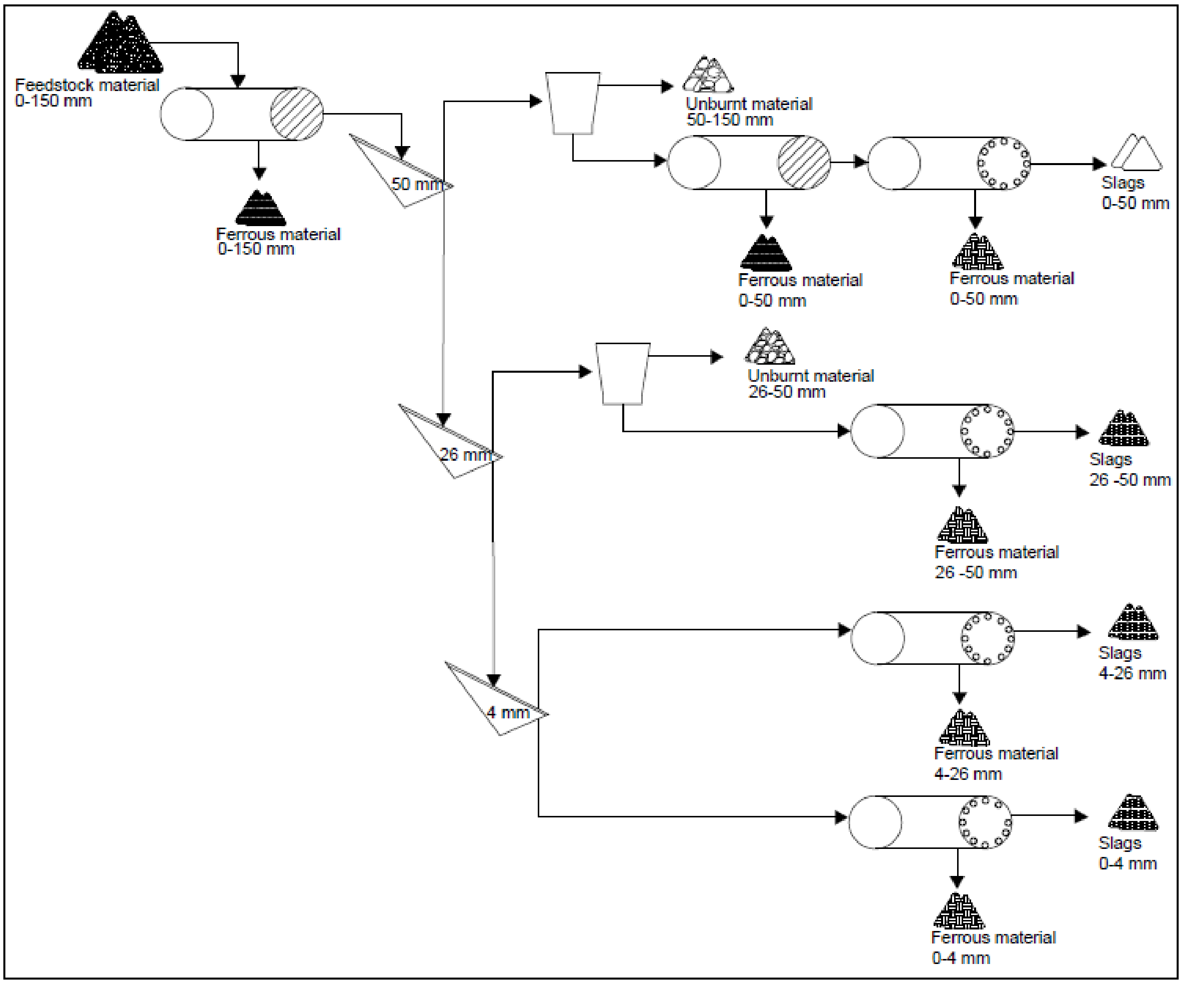


Figure 18 - Work chart of BA treatment plant 2 (Sweden)

3.3 Mobile treatment plant

The fine fraction refinery tests have been additionally implemented with the mobile treatment plant Sortatec PRO M1, designed by Heidemann Recycling GmbH, shown in Figure 19 and which specific characteristics are listed in Table 2.

Figure 19 - Mobile treatment plant Sortatec PRO M1

Table 2 - Mobile treatment plant characteristics

Characteristic	Value	m.u.
Transport length	13.77	m
Transport height	3.97	m
Transport width	3.00	m
Throughput (0-40 mm)	50	t/h
Operating voltage	400	V
Control voltage	230	V
Total weight	28	t
Support load max.	5	t
Acoustic level	72	dBa

Hence, the finest fractions have been treated with this innovative system that uses an enhanced magnetic field, generated by a forefront coil, to separate ferrous materials from the dry BA stream on the conveyor belt. The specific configuration of this treatment involves a rotating drum magnetic separator that improve the recovery of the magnetic fraction, dividing the iron oxides that are not recoverable using standard treatments. Then the material, depurated of this fraction, undergoes an eddy current separation, that relies on 38 rotating magnetic poles and is able to enhance the separation yield of non-ferromagnetic components.

The treatment is carried out in a dry environment, skipping weathering and crushing steps, since it has been observed that wet conditions lower sieve separation efficiency (Holm and Simon, 2017). The operational settings adopted in this treatment are aimed to the recovery of metals fractions, both ferrous and non-ferrous, as pure as possible, sacrificing recovering rates in place of grade of the recovered metals. Thereby a necessary loss of metals has to be expected in the mineral output, as illustrated in Figure 20.

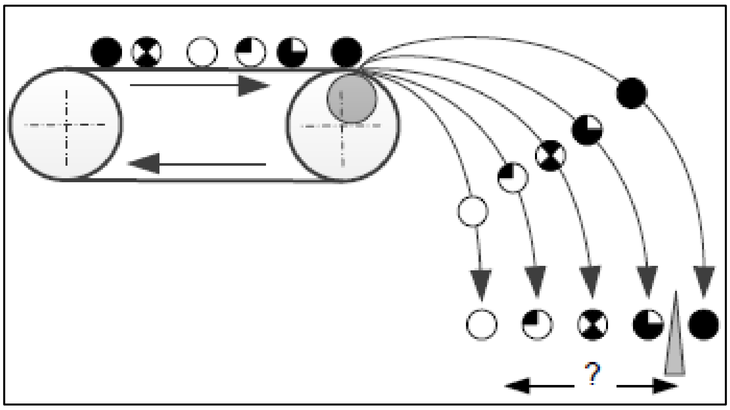


Figure 20 – Metals and mineral particle trajectories overlap (Bunge, 2015).

The mineral material, contaminated by the presence of these residual metals, has been the subject of this study, as it will be discussed in the next chapter.

4 MATERIALS AND METHODS

The aim of this work is the assessment of the current solutions for bottom ash treatment implemented in full scale treatment plants and in an innovative mobile plant designed by Heidemann Recycling GmbH.

The characterization of the samples of bottom ash collected at the treatment plants described in chapter 3 has been carried out at TUHH and at Politecnico di Torino. This analyses allowed to evaluate the efficiency of metal separation from the bottom ash stream in the mobile treatment plant by comparing the composition of the fine fractions entering the mobile treatment plant and the outputs of the magnetic oxides separation and the residual mineral fraction; the composition of the last output, the non-ferrous metals collected with the eddy current separator, has been estimated in the mass balance.

Besides, the elemental analysis of these different categories has been compared with the results obtained from the analyses of the fine fraction. This comparison allowed to determine the origin of the different elements in order to spot which materials would be necessary to separate from the waste stream to avoid the presence of undesired components or to better recover secondary raw materials.

Eventually the feasibility of a further treatment to recover critical raw materials (CRMs) and valuable fraction from the analysed bottom ash have been tested in the laboratories of TUHH. The recovery potential has been assessed by comparison with the characteristic composition of commercial materials, also measured through XRF spectrometer, while recovery of mineral fractions as construction aggregates has been teste by performing leaching tests in batch condition and analysing the leachate with ICP-OES spectrometry. The analyses with ICP-OES have been also used to complete the sample composition characterization for those elements that the XRF spectrometer is not able to detect.

4.1 Samples

The samples that were analysed have been collected between May and September 2019 at the bottom ash treatment plants 1(Germany) and 2 (Sweden), described in chapter 3.

The sampling procedure for each of the samples has been implemented according to the standard DIN EN 932-1 “Test for general properties of aggregates - Part 1: Methods for sampling”. The samples have been collected picking up 15 incremental masses of treated BA at regular time intervals and mixing them. All the sampling has been taken two times. The preparation of the samples had the aim to select significant and representative specimens, the procedure used was coning and quartering. The sub-sampling technique consisted in piling up the loose material, flattening the tip of the pile and splitting it in four identical parts. Then two opposite quarters were discharged while the two complementary ones were combined to form a specimen, repeating these steps until the desired dimension of the specimen was reached. The analysed samples have been shown in Figure 21.

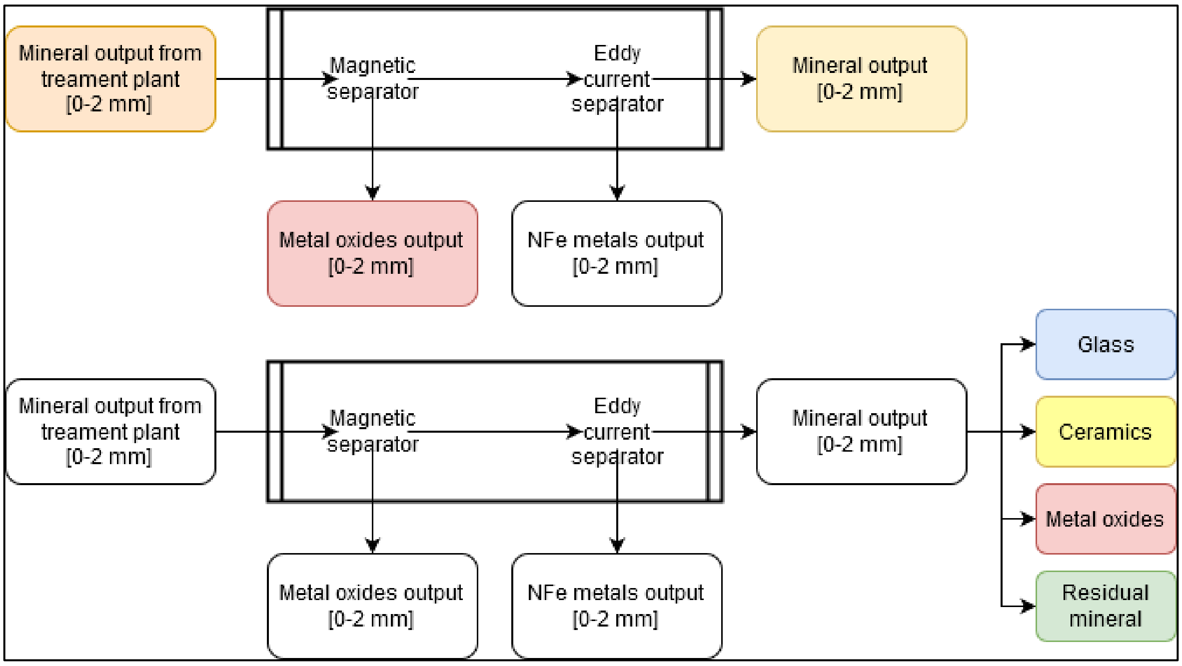


Figure 21 – Analysis scheme

The materials analysed belong to two different granulometric classes: a coarse one (between 2 mm and 40 mm) that corresponds to the one that is already valorised and a fine one (below 2 mm) that is still unrecovered in all countries.

The sampling of the fines in plant 1 has involved the mineral fraction entering the mobile treatment plant and the output materials: the oxides separated by the magnetic collector and the final mineral fraction.

Among the coarse fraction of bottom ash, different material classes have been identified through manual sorting (such as Glass, Ceramics, Oxides and a remaining unsorted fraction named Others). The classification of the sample components with manual sorting has been performed following the standard defined by the norm DIN EN 1744-8 "Tests for chemical properties of aggregates – Part 8: Sorting test to determine metal content of Municipal Incinerator Bottom Ash (MIBA) Aggregates".

In particular the fraction between 2 and 4 mm have been washed with an acid solution to clean the particles surface and improve the classification with manual sorting. The dried samples have been weighted and placed in a stainless-steel colander to be submerged with the acid solution. This solution has been prepared mixing water and hydrochloric acid (37%) with a ratio of 9:1. After a contact time of 60 seconds the samples have been removed from the acid bath and rinsed with water, placed again in the oven at 105°C to dry and weighted a second time to evaluate the loss of material due to the washing.

After this procedure the samples from the mineral fraction of both bottom ash samples have been categorized in the same classes previously defined. The magnetic metals have been removed with a hand-guided magnetic separator characterized by an attraction force of 60 Kg, while all the other components have been selected by hand-picking. The remaining material has been sorted based on its appearance: it has been identified as "glass" the material which presented transparency to light and as "ceramics" the fragments which broke along straight planes.

The results of this material component analysis are shown in Figure 22, where the terms fines identifies the granulometric class below 2 mm for which it was not possible to identify the different material classes present.

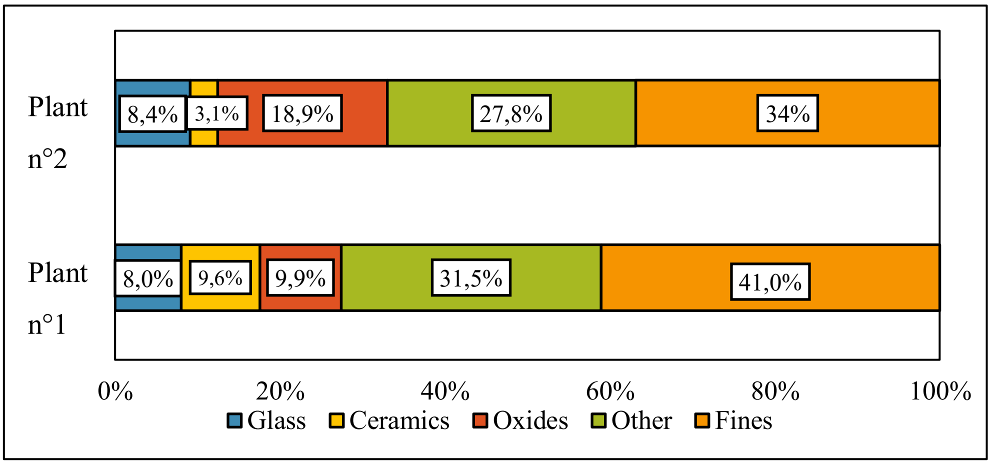


Figure 22 – Material classes distribution of bottom ash mineral fractions

Since it was not possible to identify the different material components in the fraction with particle size below 2 mm, this class has been categorised only according to the granulometric distribution. The fine fraction from treatment plant 2 and from the mobile plant in both tests have been sieved at 63 µm, 0.1 mm, 0.2 mm, 0.63 mm and 1.0 mm, the results of this analysis are shown in Figure 23

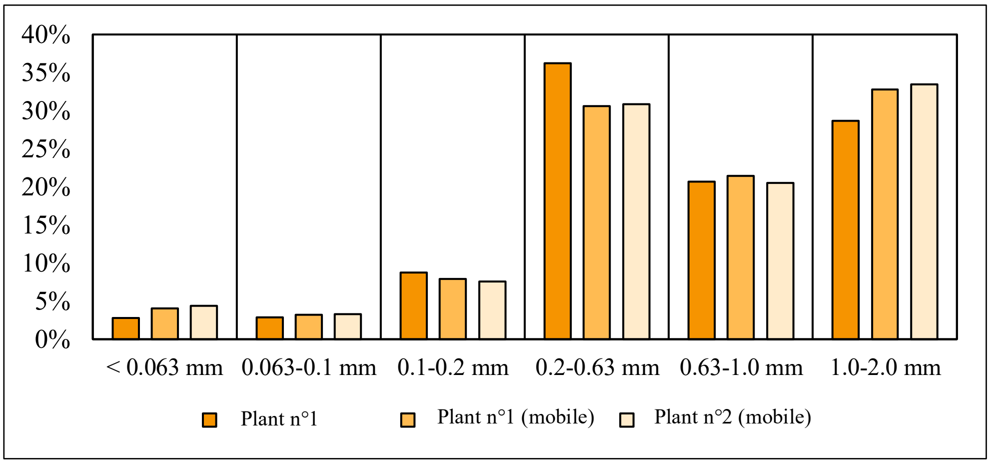


Figure 23 – Particle size distribution of fine mineral fractions

The values in the previous figure represent for each size range the percentage of material retained by the sieve normalised by the total weight of the sieved sample. In all the following analysis, the results have been normalised considering that for the samples collected after the mobile treatment plant the fine fraction represent 41% of the total sample from plant 1 and 34% of the sample from plant 2. However, since the percentage of the fine fraction of bottom ash from plant 1 before the mobile treatment plant was not available, the percentages shown in Figure 23 sums up to 100% of fine fraction (below 2 mm) and not to 100% of bottom ash.

4.2 Sample characterization

4.2.1 X ray spectrometry analyses

The samples collected in both sites described in the previous section have been analysed with XRF spectrometry in order to determine their element composition both to spot criticalities, due to the presence of hazardous compounds, and to enlighten potentially unexploited secondary raw materials.

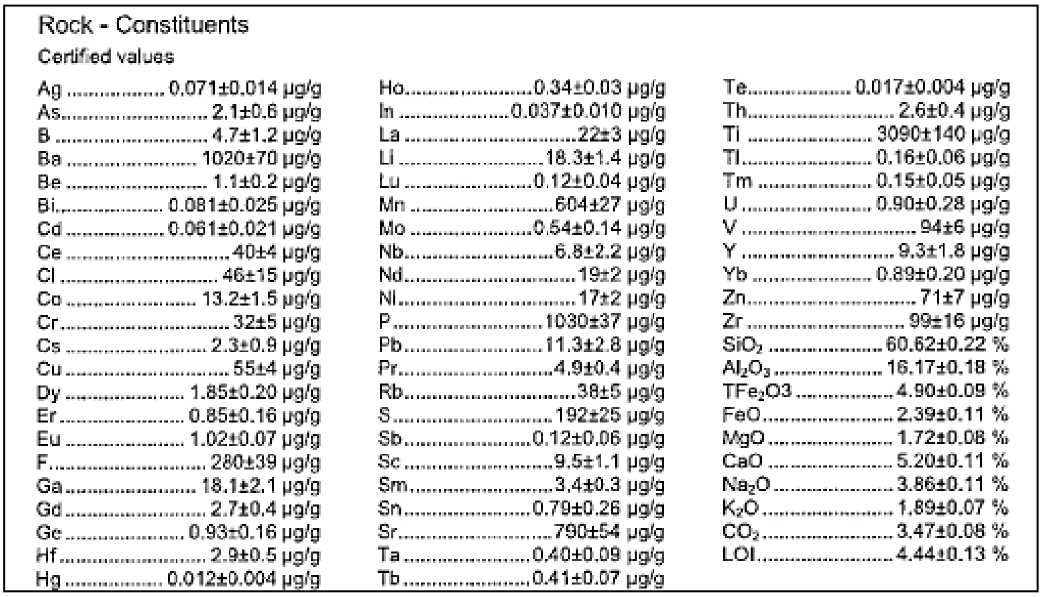
The procedure for XRF analyses stems from the standard defined in the reference norm DIN EN 15309 “Characterization of waste and soil - Determination of elemental composition by X-ray fluorescence”. The different categorises identified by manual sorting have been finely ground, according to procedure, and analysed with X-ray spectrometry.

The instrument used for analysing the samples is the XRF spectrometer “VEX DE VS” from Rigaku, that with minimum preparation returns a complete element analysis of a powdered sample.

The results of these measurements have been integrated for the elements too light to be detected (in order of atomic weight Li, B, Na and Mg), with the values measured with ICP-OES. ICP-OES.

Calibration

The quantitative analysis of samples is generally carried out by comparison with standards containing elements of known and certified concentration, consisting of matrices similar to those of the samples to be analyzed. In case of BA, there are not default standards to compare the analysis results, therefore it was necessary identifying a sample that was acceptably similar, even if not flawless. The constituents of the chosen standard sample are listed in Figure 24.



Rock - Constituents

Certified values

Ag	0.071±0.014 µg/g	Ho	0.34±0.03 µg/g	Te	0.017±0.004 µg/g
As	2.1±0.6 µg/g	In	0.037±0.010 µg/g	Th	2.6±0.4 µg/g
B	4.7±1.2 µg/g	La	22±3 µg/g	Ti	3090±140 µg/g
Ba	1020±70 µg/g	Li	18.3±1.4 µg/g	Tl	0.16±0.06 µg/g
Be	1.1±0.2 µg/g	Lu	0.12±0.04 µg/g	Tm	0.15±0.05 µg/g
Bi	0.081±0.025 µg/g	Mn	604±27 µg/g	U	0.90±0.28 µg/g
Cd	0.061±0.021 µg/g	Mo	0.54±0.14 µg/g	V	94±6 µg/g
Ce	40±4 µg/g	Nb	6.8±2.2 µg/g	Y	9.3±1.8 µg/g
Cl	46±15 µg/g	Nd	19±2 µg/g	Yb	0.89±0.20 µg/g
Co	13.2±1.5 µg/g	Ni	17±2 µg/g	Zn	71±7 µg/g
Cr	32±5 µg/g	P	1030±37 µg/g	Zr	99±16 µg/g
Cs	2.3±0.9 µg/g	Pb	11.3±2.8 µg/g	SiO_2	60.62±0.22 %
Cu	55±4 µg/g	Pr	4.9±0.4 µg/g	Al_2O_3	16.17±0.18 %
Dy	1.85±0.20 µg/g	Rb	38±5 µg/g	TFe_2O3	4.90±0.09 %
Er	0.85±0.16 µg/g	S	192±25 µg/g	FeO	2.39±0.11 %
Eu	1.02±0.07 µg/g	Sb	0.12±0.06 µg/g	MgO	1.72±0.08 %
F	280±39 µg/g	Sc	9.5±1.1 µg/g	CaO	5.20±0.11 %
Ga	18.1±2.1 µg/g	Sm	3.4±0.3 µg/g	Na_2O	3.86±0.11 %
Gd	2.7±0.4 µg/g	Sn	0.79±0.26 µg/g	K_2O	1.89±0.07 %
Ge	0.93±0.16 µg/g	Sr	790±54 µg/g	CO_2	3.47±0.08 %
Hf	2.9±0.5 µg/g	Ta	0.40±0.09 µg/g	LOI	4.44±0.13 %
Hg	0.012±0.004 µg/g	Tb	0.41±0.07 µg/g		

Figure 24 - Sample for XRF calibration (Nordtest catalog)

As described in section 2.4,the main components of BA are SiO_2, CaO, metal oxides and trace elements, and their characteristic percentages have been the benchmarks in the selection of the standard sample.

Sample preparation

The samples with particle size between 0.63-1 mm and 1-2mm have been further milled with a tungsten carbide planetary mill to reduce their grain dimension in order to be analysed. The settings applied to the planetary mill are listed in Table 3.

Table 3 - Milling settings for bottom ash

Parameter	Value	u.m.
N° of spheres	2	-
Frequency	24	Hz
Time	10	min

The samples with greater particle dimensions have been separated into different categories, milled and gathered within material classes to be analysed with XRF spectrometer. Whereas, the different subsamples for each material class were already milled and reduced t the dimension required by the XRF spectrometer.

4.2.2 Leaching batch test

As it will be discussed in the next chapter the main recovery application for bottom ash mineral fraction is reuse as construction material, however this requires the leachate water to comply with regulatory thresholds, defined by law. In order to estimate the leachate concentration values of the samples a batch test with L/S=10 has been performed.

The samples used for this test are the fine fractions of bottom ash collected in Bremen before and after the mobile treatment plant and the “other minerals” fraction, resulted from manual sorting of the mineral output of the mobile treatment plant, both between 2-8 mm and 8-40 mm.

The test has been performed by pouring 90 gr of material and 900 ml of deionised water in different bottles, that have been then agitated for 24 hours at room temperature. After this first step the samples have been left settle for 30 minutes and filtered. Afterwards, from the filtrate three sub-samples have been collected: 20 ml to measure pH, electrical conductivity and redox potential, each one with a specific datalogger, 20 ml to measure Chlorides and Sulphates and a remaining part has been analysed with ICP-OES in order to determine the composition of the leachate. In the last sub-sample, it was necessary to add 100 µl of HNO_3^- to slightly decrease the pH of the liquid in order to keep in solution the metal species in order to be able to detect them with ICP-OES.

4.3 Sensitivity analysis

The statistical analysis of the measured data has been implemented by calculating the Pearson product-moment correlation coefficient (or Pearson correlation coefficient), which is a measure of the strength of a linear association between two variables and is denoted by r, defined in Equation (4).

$$r = \frac{n(\Sigma xy) - (\Sigma x)(\Sigma y)}{\sqrt{[n\Sigma x^2 - (\Sigma x)^2][n\Sigma y^2 - (\Sigma y)^2]}} \tag{4}$$

The correlation between two variables is directly proportional to the absolute value assumed by the coefficient "r", which itself can be either positive or negative depending whether the relationship between the variables is respectively positive or negative. While, when "r" assumes a value close to zero the variables analysed have to be considered not correlated.

Eventually, all the correlation coefficients presented have been tested with a p-value lower that 0.05 (5%), whereas the p-value represents the probability of finding the same result in case of a null hypothesis, when the correlation coefficient were actually zero.

4.4 Recovery potential assessment

The feasibility of several recovery possibilities has been studied, as it will be described in the following sections.

4.4.1 Material recovery as aggregates

Several past studies (Keulen et al., 2016; Lynn et al., 2017; Silva et al., 2019, 2017; Sorlini et al., 2011; Tang et al., 2016; Yang et al., 2018; Yin et al., 2018) have examined the possibility of recovery mineral fraction of bottom ash as construction aggregates.

Having the analysed material already undergone an advanced treatment for the removal of magnetic metallic oxides and electroconductive metals, the feasibility of its recovery as construction material has been investigated.

The leachate concentration have been measured according to the procedure described in section 4.2.2 and compared to the leaching limit values for utilisation of waste-derived aggregates in several EU Member States (Saveyn et al., 2014). In particular, the thresholds used to determine the recovery feasibility have been the limits define by German law *"Referentenentwurf des Bundesministeriums für Umwelt, Naturschutz, Bau und Reaktorsicherheit"* from 2017 and "*Regolamento recante modifiche al decreto ministeriale 5 febbraio 1998 «Individuazione dei rifiuti non pericolosi sottoposti alle procedure semplificate di recupero, ai sensi degli articoli 31 e 33 del decreto legislativo 5 febbraio 1997, n. 22*" updated in date 5th April 2006 .

Moreover, despite the finest fraction of bottom ash have been identified as the most contaminated and is usually disposed of in landfill without being recovered, past studies (Alam et al., 2019b) have been able to identify a cut-off particle size above which the material could still comply with regulatory limits for reuse as non-shaped construction material. Leaching tests have not been performed on the different granulometric classes below 2 mm but only on generic samples with particle size between 0 mm and 2 mm. However, these results have been used to identify elements exciding legal limits and, using the total concentration of the particles below 2 mm represent almost half of the collected sample.

4.4.2 Specific material recovery

In order to further evaluate the recovery feasibility for the different material classes identified through manual sorting the analyses performed on the glass and ceramics components of bottom ash have been compared with samples of glass and ceramic collected from commercial products, such as glass bottles and ceramic mugs. This comparison between the elemental compositions of the fractions of bottom ash identified as glass or ceramic and commercial materials allowed to identify which element is present on behalf of the incineration process that the ashes overwent or was a characteristic component of the material from the beginning.

Comparison with reference commercial materials

Since XRF spectrometry requires samples in the form of fine powders, hence comminution is a fundamental step in the preparation of the samples. Each object has been washed in the sink and manually crushed to obtain fragments with proper dimensions for the following step of milling. The dimensions of the container and of the milling spheres adopted required a maximum dimension of the input material of 6 mm.

To remove impurities as much as possible the fragments have been cleansed with deionized water. Before being insert in the milling equipment the fragmented samples have been dried in the oven at 105°C for one hour. The milling has been performed according to the following settings: 2 tungsten carbide spheres, frequency of 24 Hz and milling time of 10 minutes. The final milled samples have then been analysed through x-ray fluorescence spectrometry.

Addressing the difficulty in collecting a representative sample of different glass a further step for the identification of the element alien to the characteristic composition of glass has been made by comparing the XRF spectrometry with the standard concentration values found on literature (Lopez Ferber et al., 2019; Puertas et al., 2015).

4.4.3 Urban mining potential evaluation for oxides fraction

Despite the concentration of metals in bottom ash are generally not comparable to mineral ores, the metal oxides fraction identified with manual sorting results richer on these valuable components, hence the feasibility of metal mining from this fraction has been estimated.

This computation stems from the characterisation of the material classes with XRF spectrometry, although these values have been remodelled using the available data about the granulometric distribution and material composition of the sample. Eventually these concentration values, referred not to 1 Mg of glass, ceramics, oxides or mineral but to 1 Mg of overall bottom ash, have been linked up with their price range (Bunge, 2015; US Geological survey, 2019).

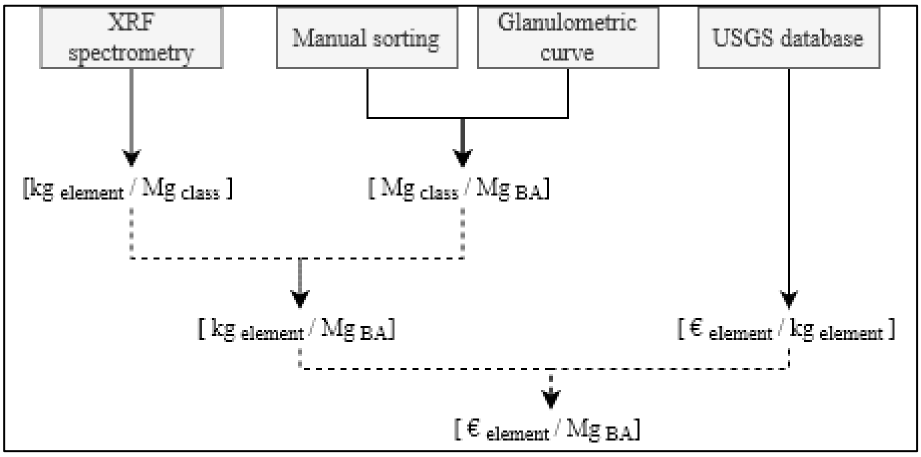


Figure 25 – Procedure for economic value assessment

4.5 Economic evaluation

The last analysis presented is a simple cost/gain assessment for the different recovery possibilities investigated. These possibilities have been combined in different scenarios as following (Table 5):

0. Landfilling:
    a. All the material is sent to a hazardous waste landfill, without treatment or separation processes
    b. After a step of magnetic separation, the non-magnetic (less contaminated) fraction of bottom ash is sent to a landfill for non-hazardous waste, while the metal oxides and fine fractions are sent to a hazardous waste landfill
    c. Other than the magnetic separation, a further sieving step is implemented for the fine fraction and the class above 0.5 mm is sent, along with the non-magnetic fractions, to a landfill for non-hazardous waste
1. Material recovery as aggregates:
    a. After a step of magnetic separation, the non-magnetic (less contaminated) fraction of bottom ash is recovered as recycled aggregates, while the metal oxides and fine fractions are sent to a hazardous waste landfill
    b. After a step of magnetic separation and the sieving of the fine fraction at o.5 mm, the non-magnetic fraction and the fraction between 0.5 mm and 2 mm is recovered as recycled aggregates, while the metal oxides and fine fractions are sent to a hazardous waste landfill
2. Specific material recovery:
    a. A more complete material sorting is performed to separated not only the metal oxides from the coarse fraction but also glass and ceramic material. Glass and ceramics are recycled, and the mineral fraction is recovered as aggregates while metal oxides and fine fraction are sent to an hazardous waste landfill

   b. Glass and ceramics are recycled, the mineral fraction and the fine fraction sieved at 0.5 mm are recovered as aggregates while metal oxides and the remaining fines are sent to a hazardous waste landfill
3. Specific material recovery and metal mining:
   a. After a complete material sorting glass and ceramics are recycled, the mineral fraction is recovered as aggregates and the metal oxides undergo further treatments to extract metals and critical raw material while the fine fraction is sent to an hazardous waste landfill
   b. Glass and ceramics are recycled, the mineral fraction and the fine fraction sieved at 0.5 mm are recovered as aggregates and metal oxides undergo further treatments to extract metals and critical raw material while the fine fraction is sent to an hazardous waste landfill

Table 4 – Recovery scenarios

Scenario		Glass	Ceramics	Oxides	Others	Fines (0.5-2mm)	Fines (0-0.5 mm)
0	0.a	Landfill	Landfill	Landfill	Landfill	Landfill	Landfill
	0.b	Inert landfill	Inert landfill	Landfill	Inert landfill	Landfill	Landfill
	0.c	Inert landfill	Inert landfill	Landfill	Inert landfill	Inert landfill	Landfill
1	1.a	Aggregates	Aggregates	Landfill	Aggregates	Inert landfill	Landfill
	1.b	Aggregates	Aggregates	Landfill	Aggregates	Aggregates	Landfill
2	2.a	Glass	Ceramics	Landfill	Aggregates	Inert landfill	Landfill
	2.b	Glass	Ceramics	Landfill	Aggregates	Aggregates	Landfill
3	3.a	Glass	Ceramics	Metal rec.	Aggregates	Inert landfill	Landfill
	3.b	Glass	Ceramics	Metal rec.	Aggregates	Aggregates	Landfill

The economical evaluation of these scenarios has been performed considering an average cost of landfilling for non-hazardous (75 €/t) and hazardous waste (150 €/t) (European Environmental Agengy, 2014). The revenue from the sale of the material as aggregates, recycled glass and recycled ceramics have been estimated based on literature data (Mugoni et al., 2020; Release, 2018), while the economic value of the metal oxides class has been estimated as the total value of the different metals and critical raw material present in it, according to the scheme in Figure 25.

5 RESULTS AND DISCUSSION

5.1 Bottom ash characterisation

The analysis with XRF spectrometry has been performed on the different classes of materials identified through sieving (above and below 2 mm) and manual sorting (Glass, Ceramics, Oxides and Others), hence the concentration values refer to the single material class and not the overall samples of bottom ash.

5.1.1 Bottom ash fine fraction: treatment efficiency

The fine fraction (below 2 mm) treated in the mobile treatment plant has been characterised with XRF spectroscopy. The samples analysed are the mineral fraction treated in plant 1 and fed to the mobile treatment plant and the outputs of metal oxides collected by the magnetic separator and the final mineral fraction, cleared of ferrous and non-ferrous metals, as shown in Figure 26.

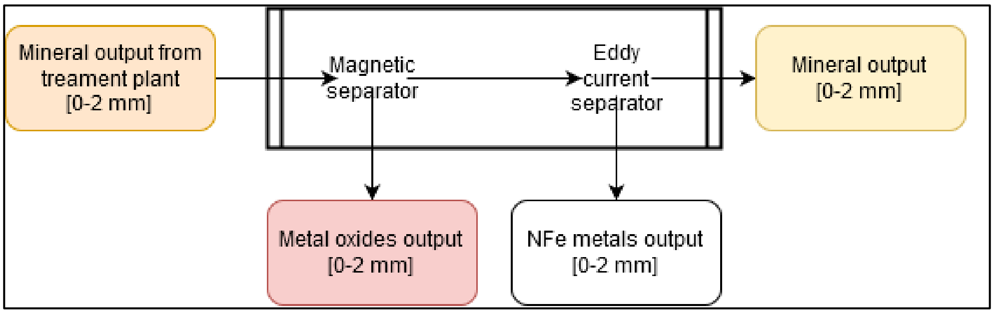


Figure 26 – Analysed samples in the fine fraction

Different granulometric fractions of each samples have been analysed in order to observe how metals and mineral concentration varies with particle dimensions (Figures 26, 27, 28).

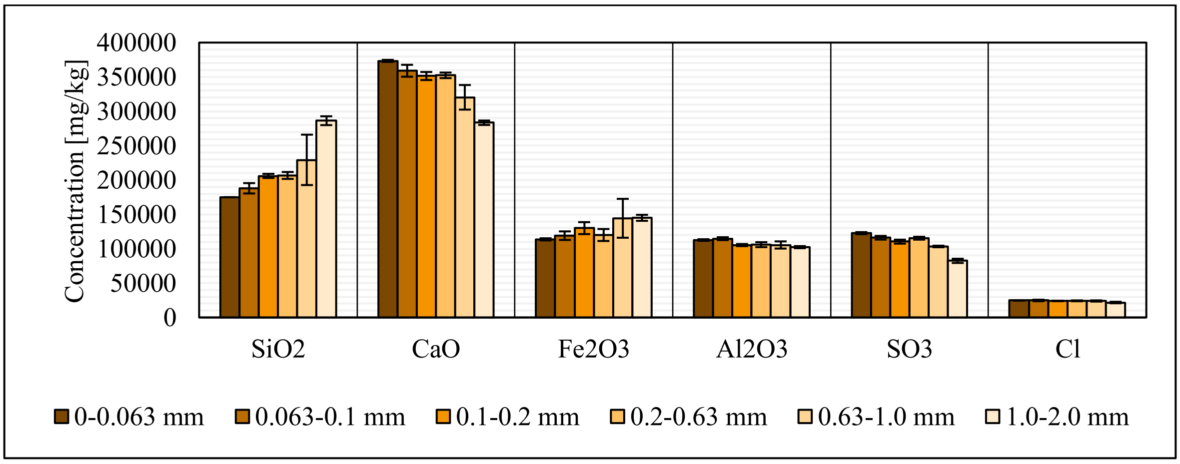


Figure 27 – Fine mineral fraction from plant 1 fed to the mobile plant (1)

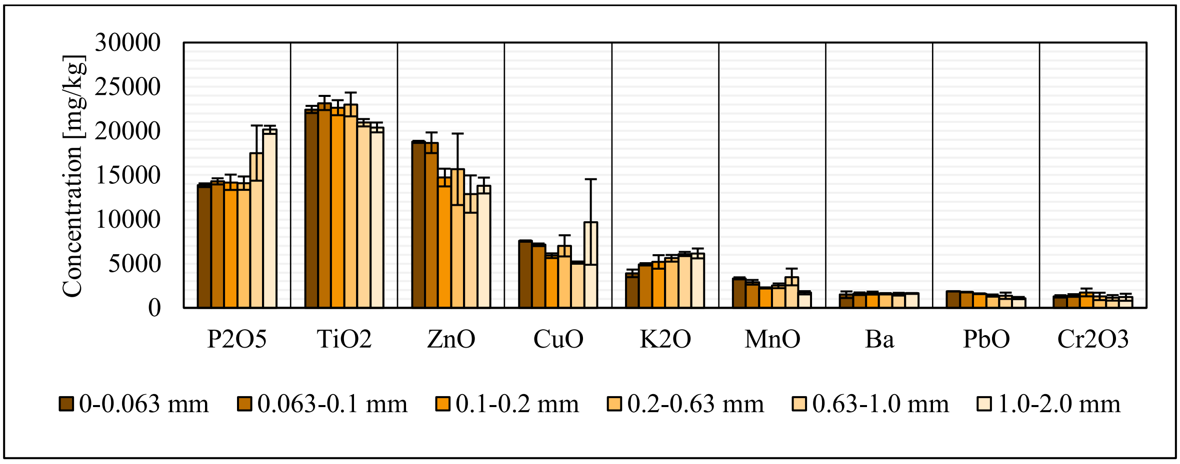


Figure 28 Fine mineral fraction from plant 1 fed to the mobile plant (2)

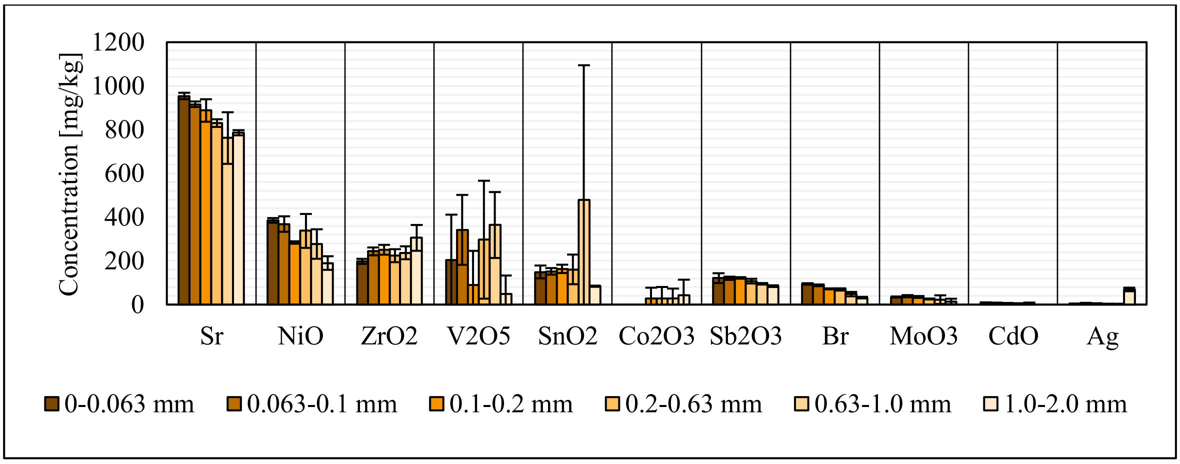


Figure 29 Fine mineral fraction from plant 1 fed to the mobile plant (3)

The material analysed in the graphs above is the output of the state-of-the-art treatment plant in Bremen and it already underwent several treatment steps, consisting mainly in sieving and magnetic and inductive separations. The samples analysed belong to the finest fraction of bottom ash treated, which is the most contaminated, since metals in ionic form tend to deposit on fine particles, that have a high specific surface. Moreover, state-of the art separation techniques have been proved to have lower efficiency on materials with smaller particle size. Hence this material, which is the mineral output of plant 1, still contains ferrous and non-ferrous metals that hinder its recovery and has been fed to the mobile treatment plant where an innovative solution to collect non-ferrous metals is implemented.

The first output of the mobile treatment plant is the magnetic fraction, which is separated from the bottom ash in order to streamline the mass flow directed to the eddy current separator and increase the efficiency of that treatment step.

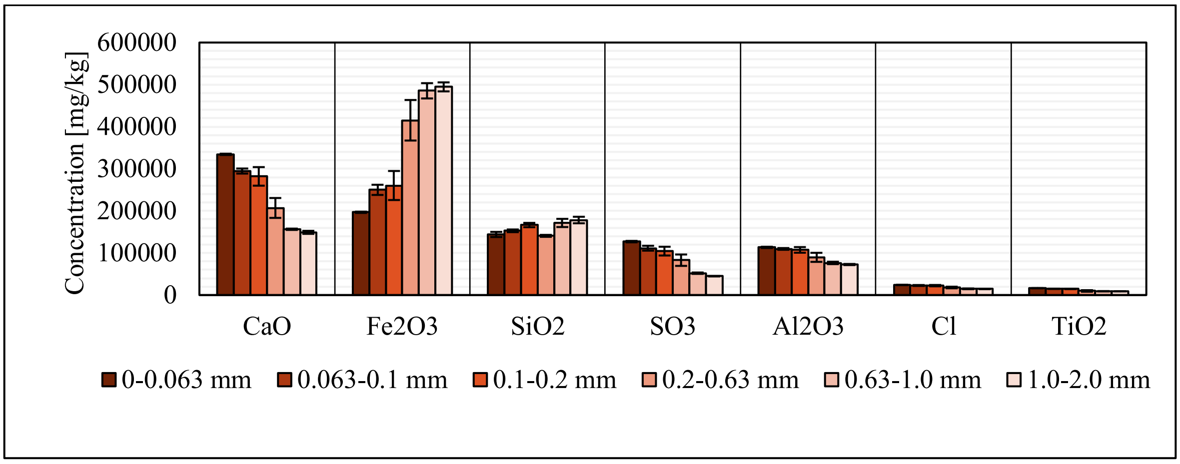


Figure 30 – Fine metal oxides removed by mobile plant (1)

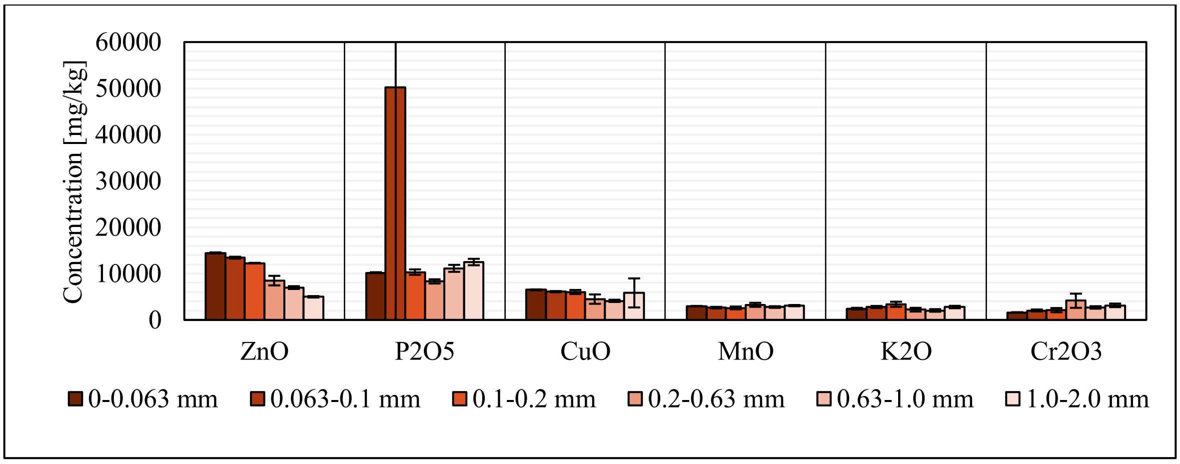


Figure 31 Fine metal oxides removed by mobile plant (2)

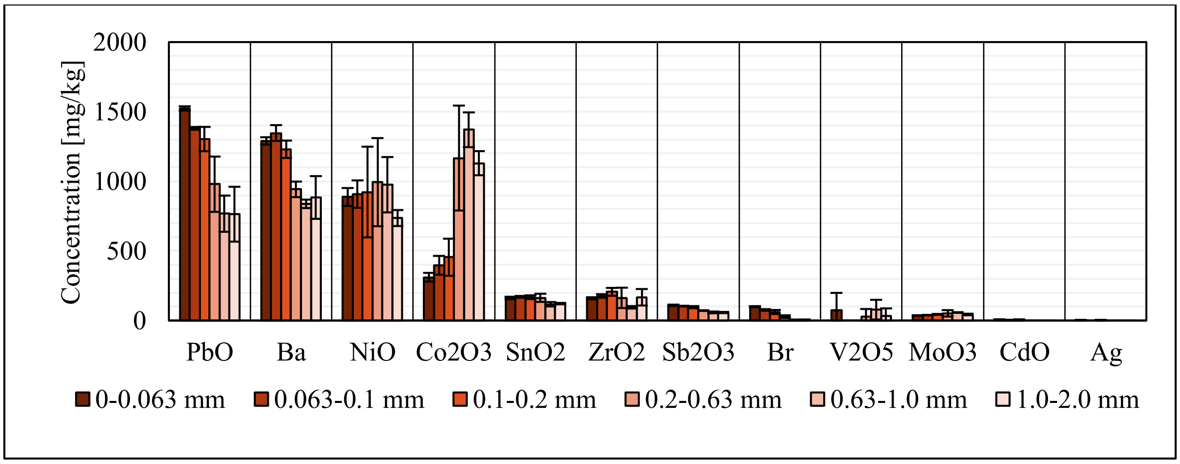


Figure 32 Fine metal oxides removed by mobile plant (3)

The separation of this material stream is operated with a magnetic collector, thereby its composition results higher in magnetic elements, such as Iron, Nickel and Cobalt. Whereas the concentration of elements, constituent the mineral phases of bottom ash, such as Calcium, Sulphates and Chloride tends to decrease. This behaviour is less marked in the finest fractions, below 0.1 mm, where separation based on magnetic properties is no more efficient.

Eventually the final mineral output of the mobile treatment plant has been characterised. The main aim of this enhanced treatment is not the creation of a pure mineral fraction, but rather the collection of non-ferrous metals, then metal contamination in the mineral fraction is not completely removed but substantially reduced.

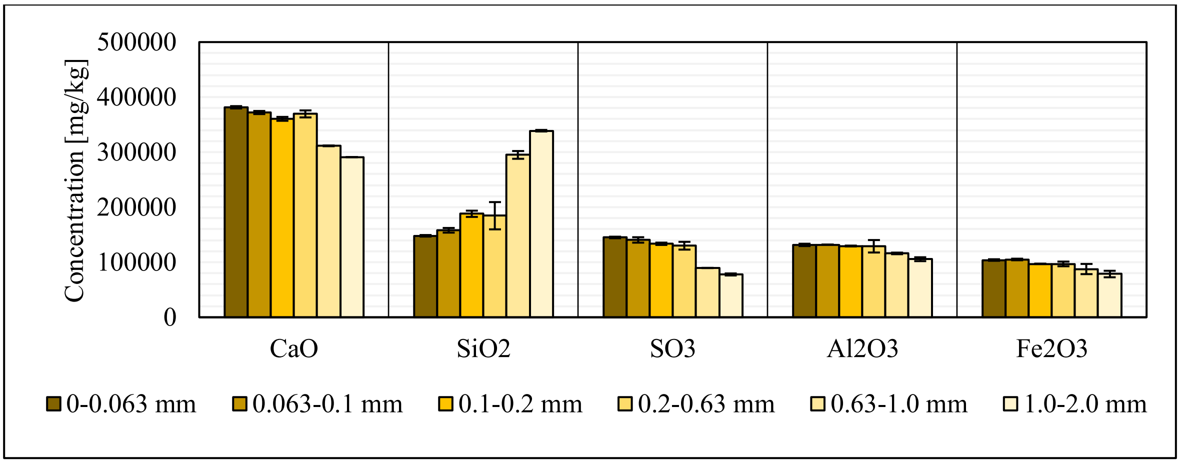


Figure 33 – Fine mineral fraction after the treatment of BA from plant 1 into the mobile plant (1)

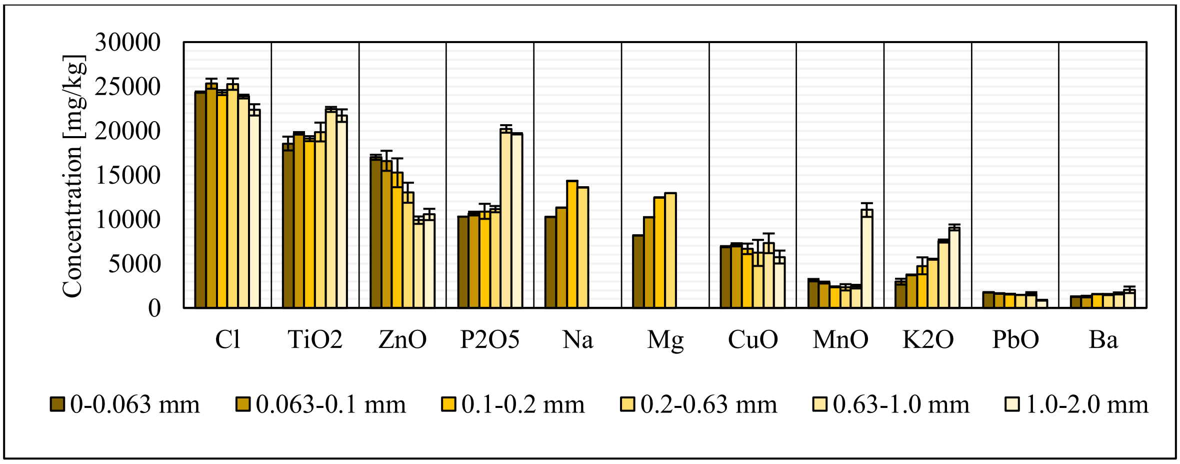


Figure 34 Fine mineral fraction after the treatment of BA from plant 1 into the mobile plant (2)

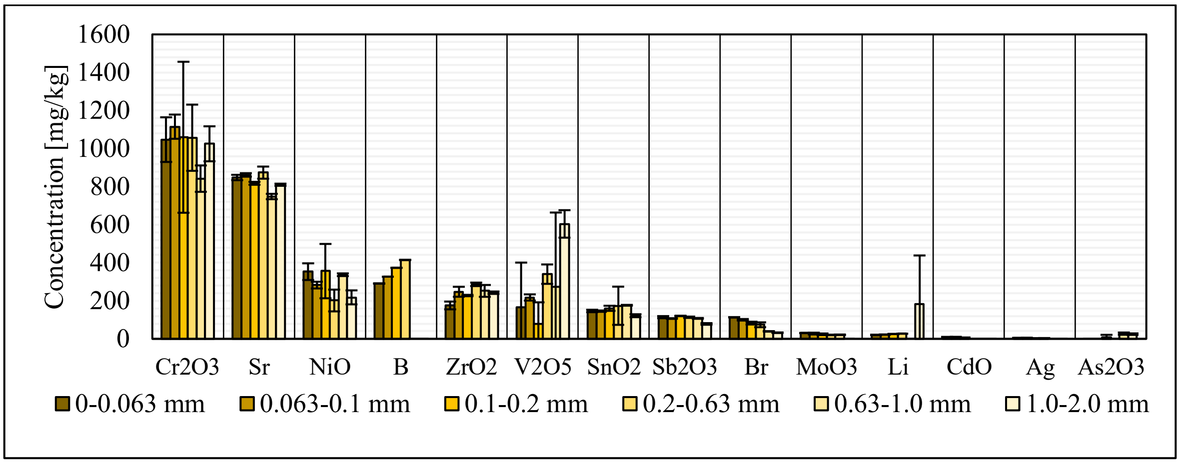


Figure 35 Fine mineral fraction after the treatment of BA from plant 1 into the mobile plant (3)

The composition of this fraction is similar to the first sample analysed, however the concentration of native metals such as Aluminium, Copper, Lead and Zinc is lower. Likewise also the concentrations of metals like Iron, Nickel and Tin are reduce. Cobalt is completely removed from all granulometric classes and Silver results completely collect from the fractions between 0.63 mm and 2 mm. The concentration of potentially toxic elements (PTEs), like Copper, Nickel, Antimony and Zinc appears lower after the treatment implemented in the mobile plant.

The granulometric classes below 0.63 mm, from this mineral material, have been analysed also with ICP-OES spectrometry, hence their characterisation includes also Sodium, Magnesium, Boron and Lithium.

5.1.2 Bottom ash coarse fraction

Moreover, the characterization of the coarse fraction of bottom ash produced by plant 1 is presented for each one of the material classes identified with manual sorting, in order to identify where the different elements concentrate.

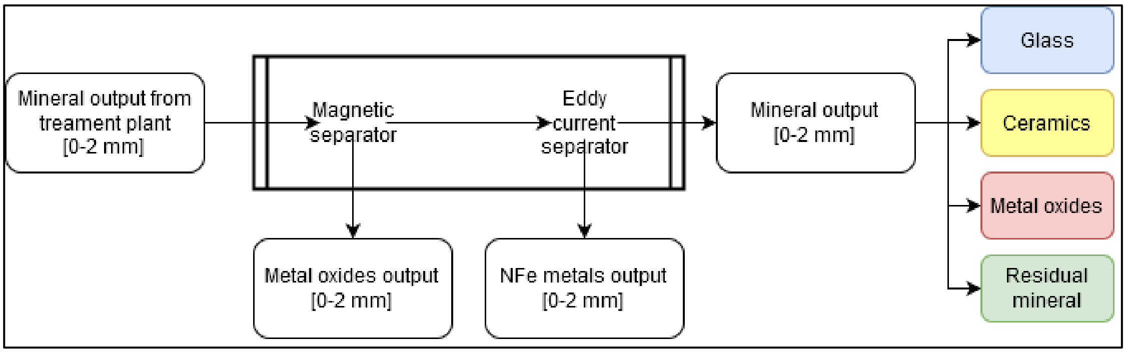


Figure 36 – Analysed samples in the coarse fraction

The composition shown in the figures below, would not be complete with only the results of XRF spectrometry, which, as address in section 4.2, is not able to detect Na, Mg, B, and Li, thereby the concentration values for those elements have been taken from the ICP analyses performed at TUHH laboratory.

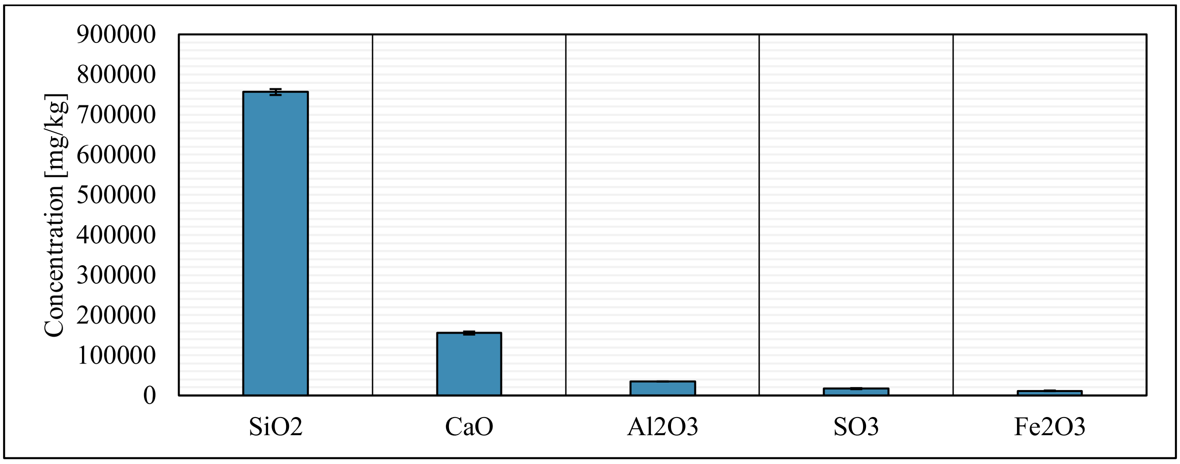


Figure 37 – Characterisation of glass fraction (1)

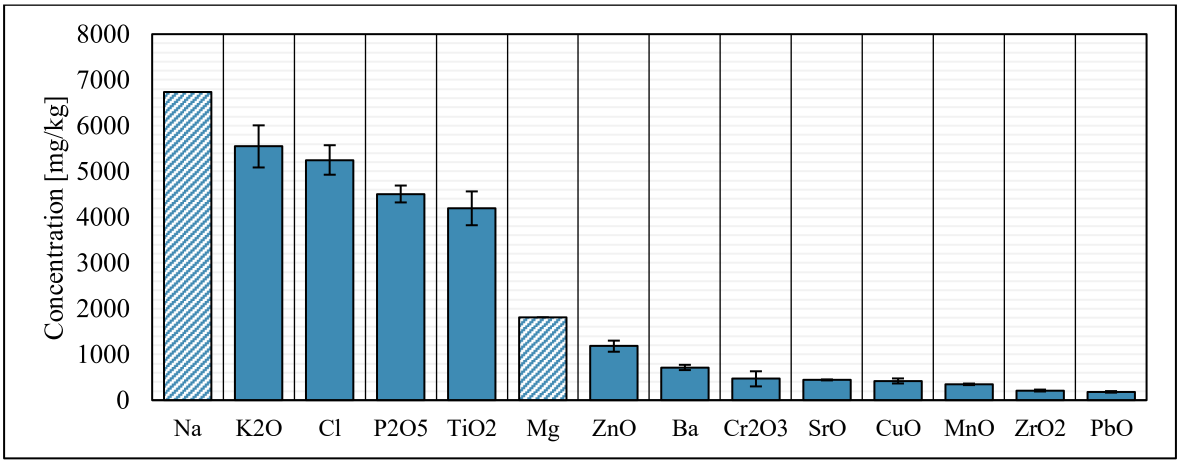


Figure 38 – Characterisation of glass fraction (2)

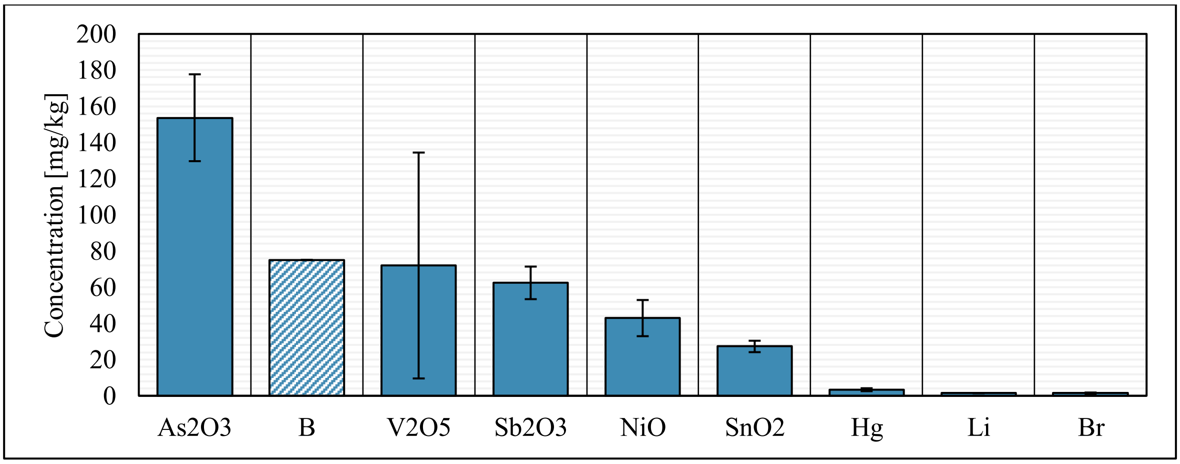


Figure 39 – Characterisation of glass fraction (3)

The composition of the class identified as glass is consistent with the typical concentration values of commercial glass, whereas the main components are quartz, SiO_2, sodium or potassium compounds, which lower the fusion temperature of the material and calcium and magnesium carbonates, that prevent the material from melting again. In particular the most common type of glass, soda-lime, has a composition of 70–75 wt% SiO_2, ,12–16 wt% of Na_2O and 10% CaO, while lead glass typically contains 55–65 wt% SiO_2, 18–38 wt% of PbO, and 13–15 wt% Na_2O or K_2O and 10–15 wt% CaO, aluminosilicate glass 52–58 wt% SiO_2, 15–25 wt% of Al_2O_3 , and 4–18 wt% CaO and borosilicate 70–80 wt% SiO_2, 7–13 wt% of B_2O_3, 4–8 wt% Na_2O or K_2O and 2–8 wt% of Al_2O_3 (Hasanuzzaman et al., 2015).

Besides, glass composition may change with the addition of other metals or minerals in order to bestow specific properties to the material: for example barium carbonate is added to increase the refraction index of the material, while boron enhance its thermic behaviour and some metals are used to confer different colours to the glass: iron and chromium for green, nickel and cobalt for blue and copper oxides for lighter shades of blue, titanium for brown or yellow and tin, arsenic and antimony oxides for a matt white hue. However, these metals are present only as trace elements and, since the analysed samples have been collected from a incineration plant located in Germany where green and brown glass is subject to specific incentives for material recycling, iron, chromium and titanium concentrations are expected to be lower than in samples from other countries.

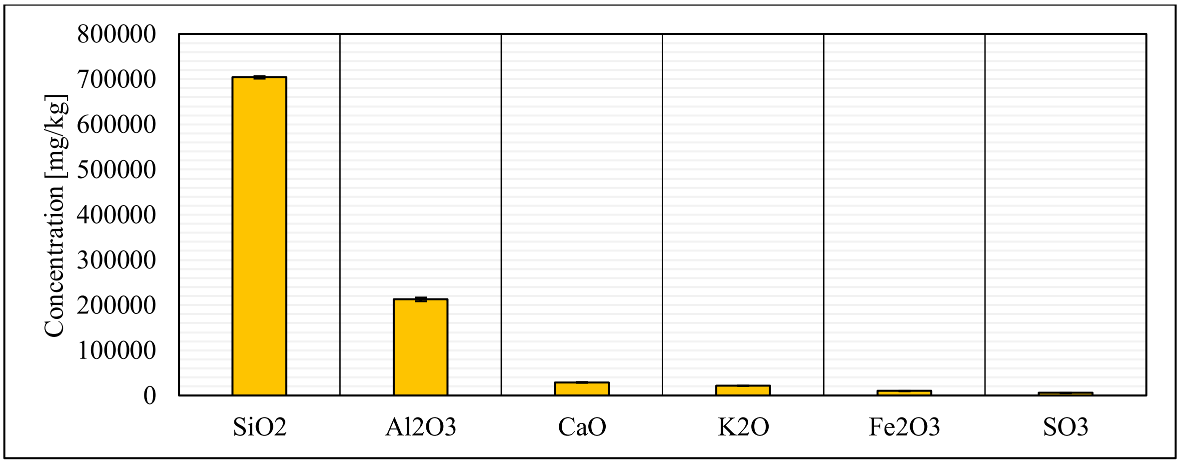


Figure 40 – Characterisation of Ceramics fraction (1)

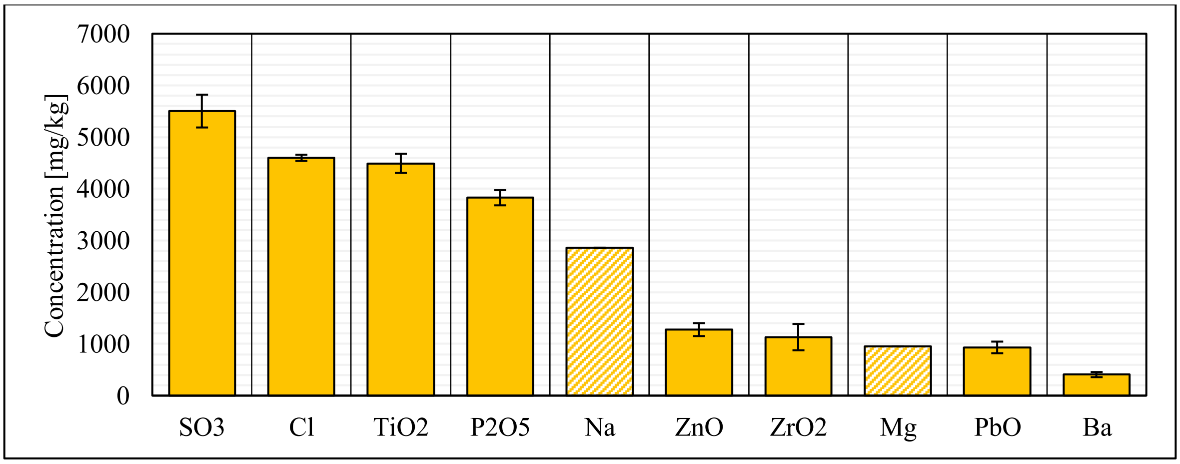


Figure 41 - Characterisation of Ceramics fraction (2)

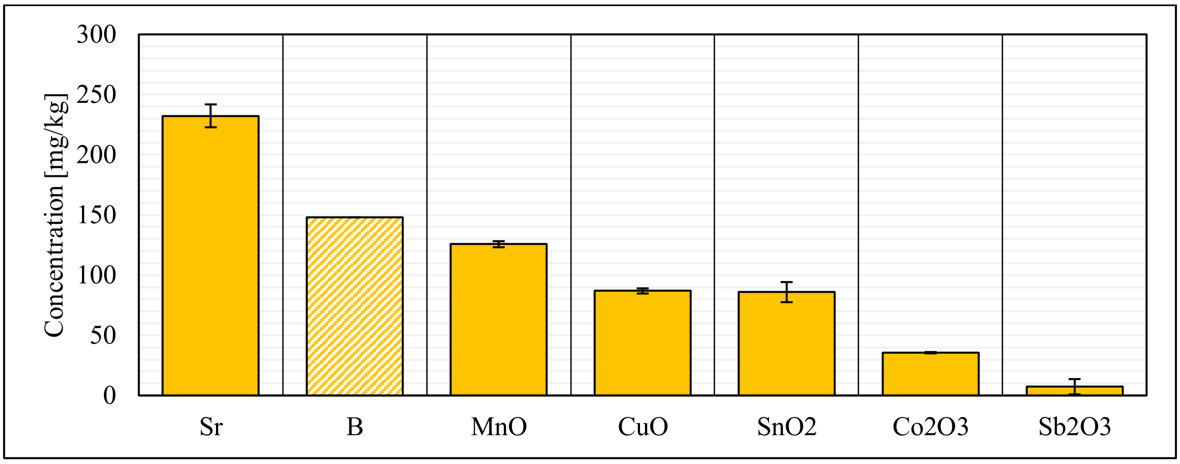


Figure 42 - Characterisation of Ceramics fraction (3)

According with the literature data about ceramics composition the main elements are silica SiO_2 and alumina Al_2O_3, followed by calcium, iron, magnesium, sodium, potassium and titanium (Lopez Ferber et al., 2019). The difficulty of comparing these results to the generic composition of ceramic materials is due both to the wide concentration ranges of different elements among the numerous types of existing ceramic materials and in the unavailability of data about which of these materials is actually sent to incineration instead of being directly recycled or sent to landfill.

The presence of strontium in the first two classes of material may be related to the presence of intensely performing materials such as glasses with enhanced strength and optical properties containing strontium oxide or ceramic glazes where strontium carbonates or oxides are used to replace barium or lead (Singerling and Ober, 2018).

Furthermore, Tungsten has been found only in these first classes. Due to the abrasive nature of these materials it is possible that this value represents a contamination of the sample occurred during the process of size reduction in a tungsten carbide planetary mill, step necessary for XRF analysis. Instead the plastic behaviour of the metals in the class oxides and the fragile structure of the minerals in the residual mineral fraction may have prevented this from happening in those classes. Therefore, from now on, tungsten has not been considered as a matrix component of the material and it has not been taken into account in the assessment of the economic value of the material.

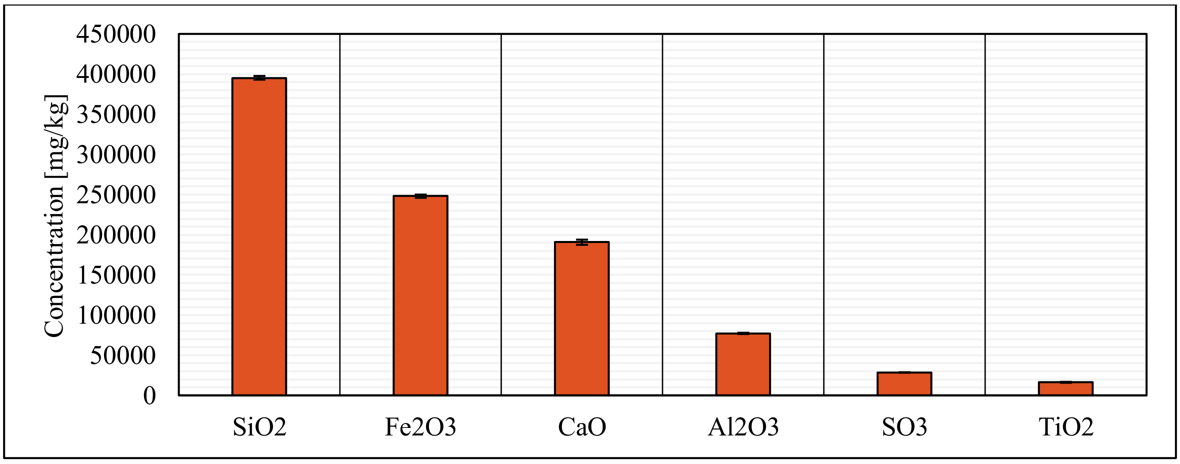


Figure 43 – Characterisation of metal oxides fraction (1)

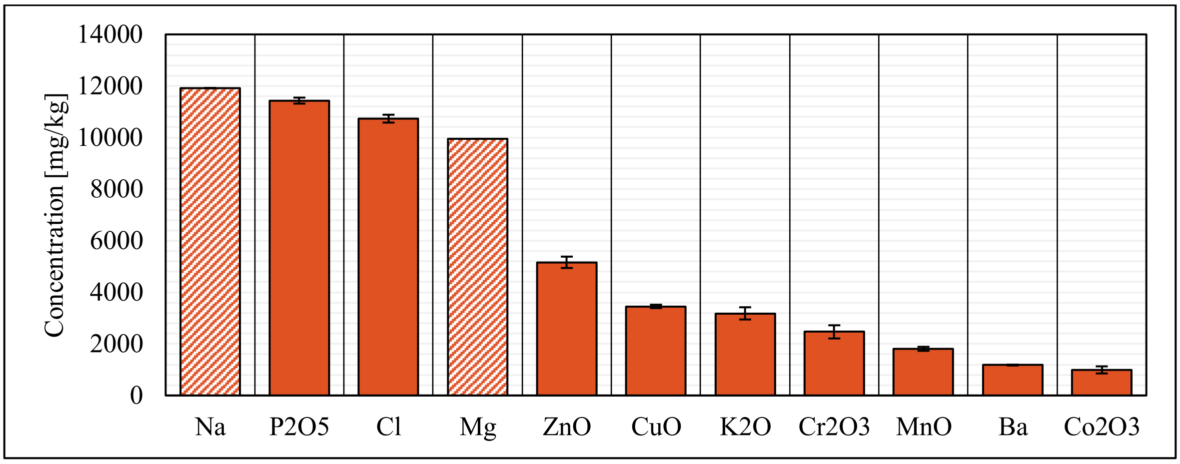


Figure 44 – Characterisation of metal oxides fraction (2)

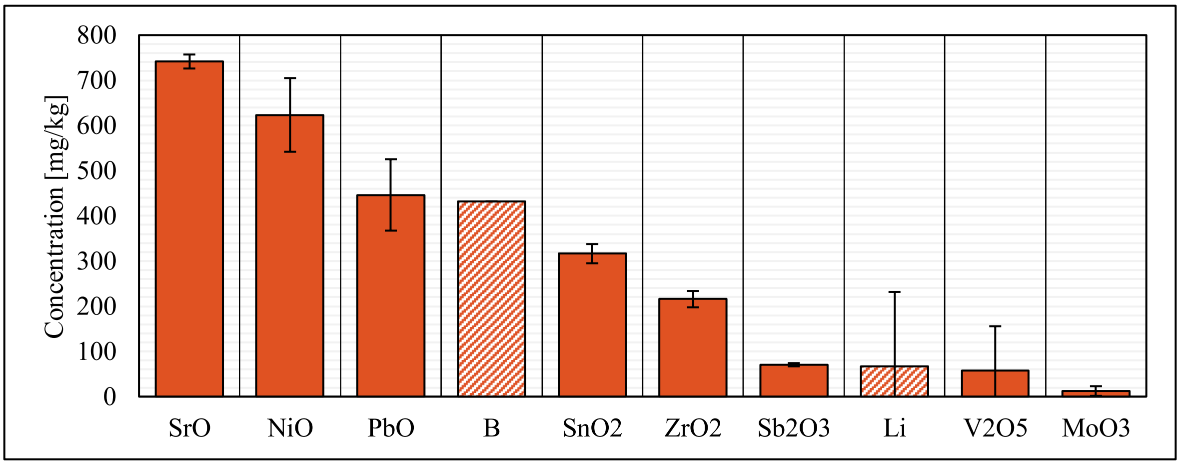


Figure 45 – Characterisation of metal oxides fraction (3)

The class defined as oxides, which has been separated in the manual sorting process with the aid of a magnet, is richer in concentration of metals with magnetic properties, such as Fe, Ni and Co, and of metals commonly found in their alloys, like Zn, Ti, Cu and Cr (Schulte, 2020). This particular class, after the separation from the rest of the bottom ash, appears to be enriched in Fe, Zn, Ti, Cu, Mg, Mn, Cr, Ni, B, Co, Li and Sb and, because of that observation, this class has been identified as a potential resource for metal mining, as it will be discussed further in paragraph 5.4.3.

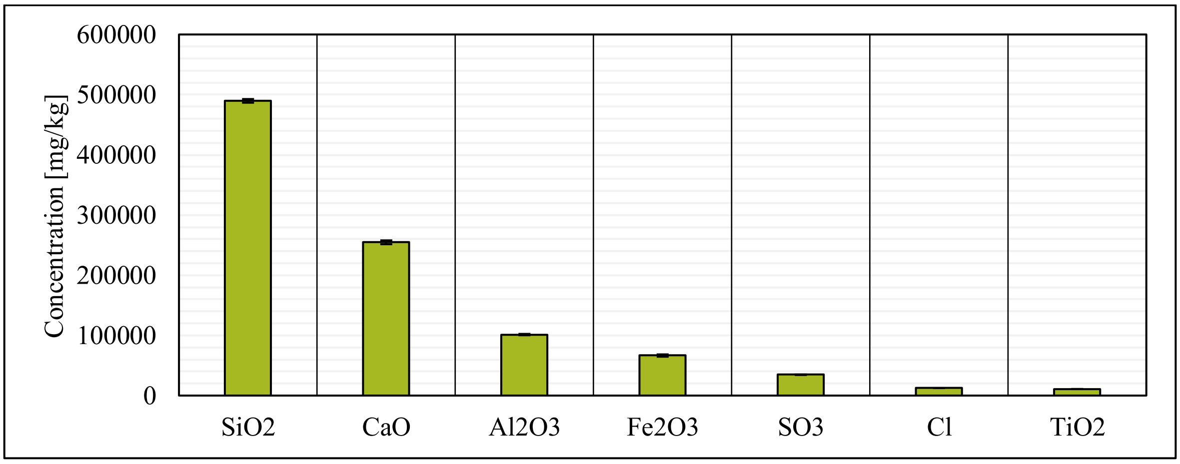


Figure 46 – Characterisation of residual mineral fraction (1)

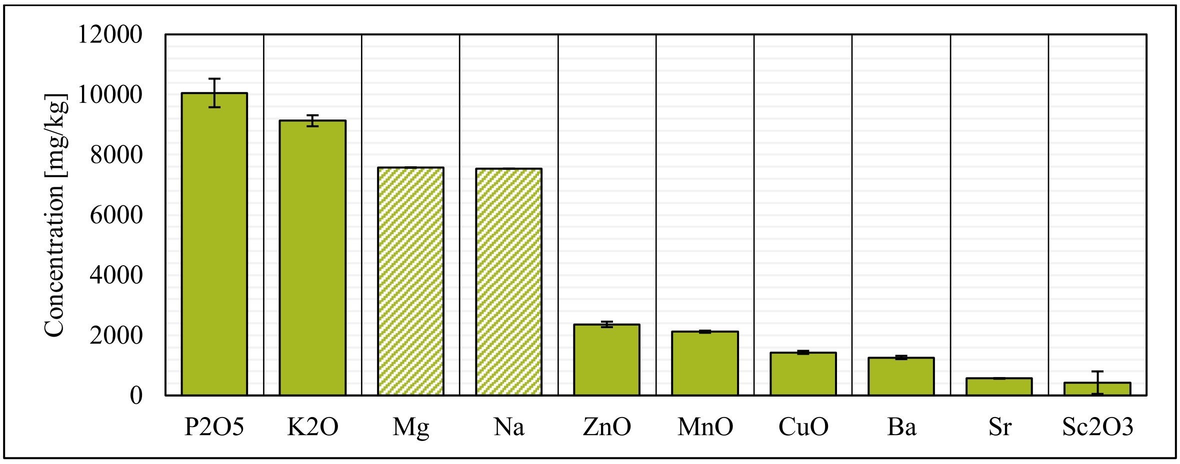


Figure 47 – Characterisation of residual mineral fraction (2)

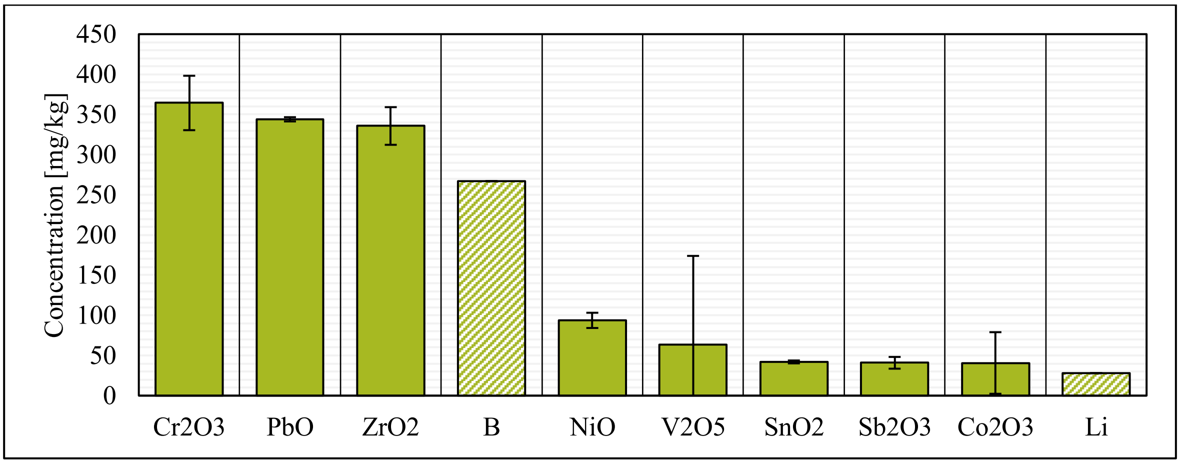


Figure 48 – Characterisation of residual mineral fraction (3)

Whereas the remaining mineral fraction composition is coherent with the general mineralogical composition of weathered bottom ash, containing: quarts SiO_2, ghelenite $Ca_2Al_2SiO_7$, magnetite Fe_3O_4, hematite Fe_2O_3, calcium carbonates $CaCo_3$, Anhydrite $CaSO_4$, ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}$ $6H_2O$, Goethite FeOOH, Corundum Al_2O_3 (T. Astrup, A. Muntoni, A. Polettini, R. Pomi, T. Van Gerven, 2016).

5.2 Element distribution and enrichment factors

Using the mass balance shown in Figure 22 it was possible to calculate the weighted average concentration of the coarse fraction of bottom ash produced by plant 1. The estimation of this weighted average concentration values has been compared to the characterisation of each material class identified in order to evaluate how the different compounds distributes themselves among the materials and identify the most contaminated and the most valuable components of bottom ash.

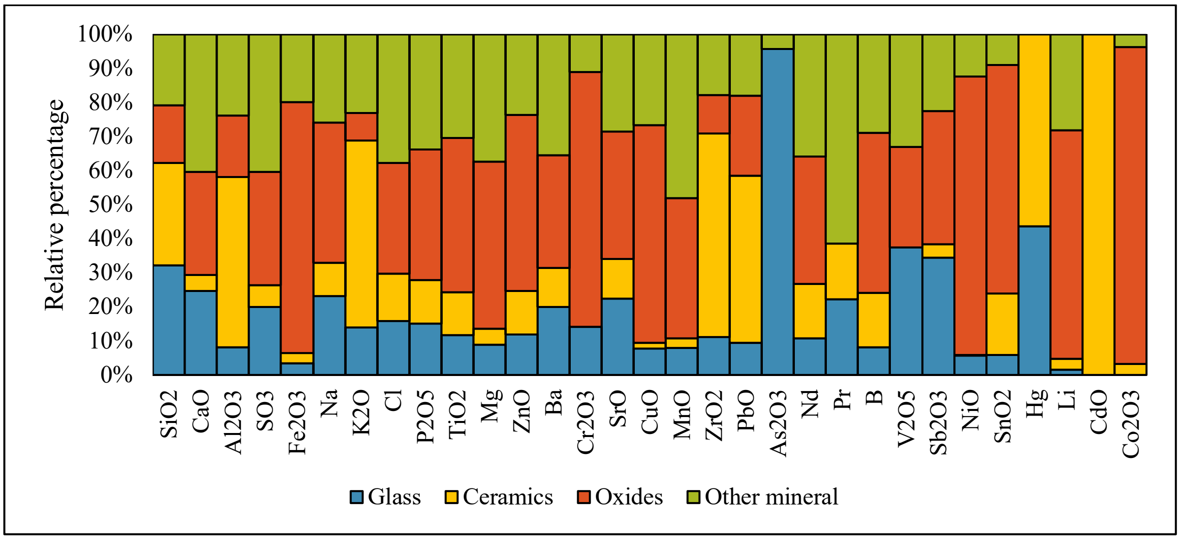


Figure 49 – Element distribution among BA produced by plant 1

Furthermore, the enrichment on different components of each material class has been estimated considering the values above 1, from the graph above, indicating that the concentration of the single element in that class is higher than the average.

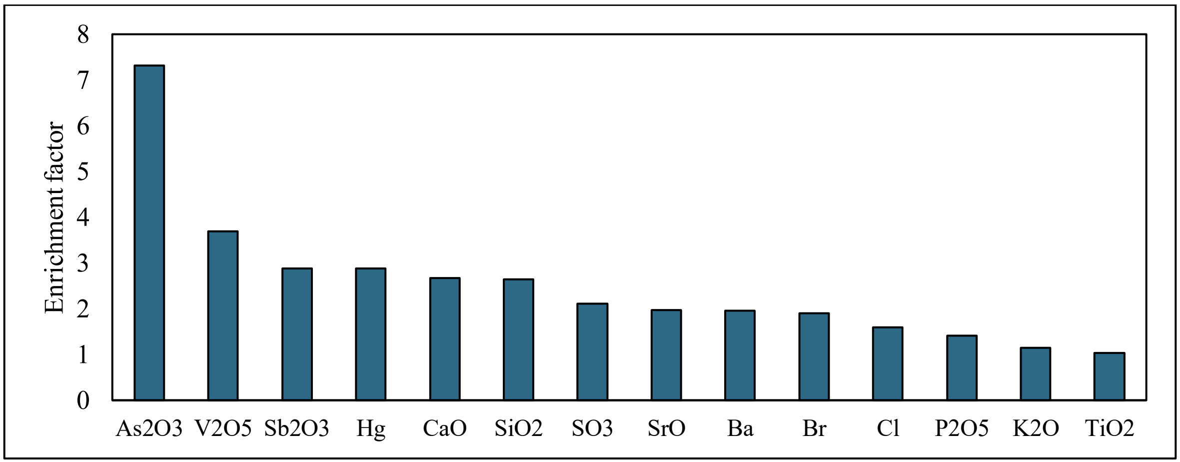


Figure 50 – Enrichment factor of glass fraction

From the previous figure, it is possible to observe that the glass fraction of bottom ash results enriched in elements like silica, Calcium and Potassium that are among the main constituent of glass and elements like Barium and Strontium that are used in glassmaking industry to increase thermic and optic characteristics of this material. Moreover, the high concentration of Vanadium, Antimony and Chlorides is in line with the results obtained by batch leaching test with L/S=2, performed during previous analyses.

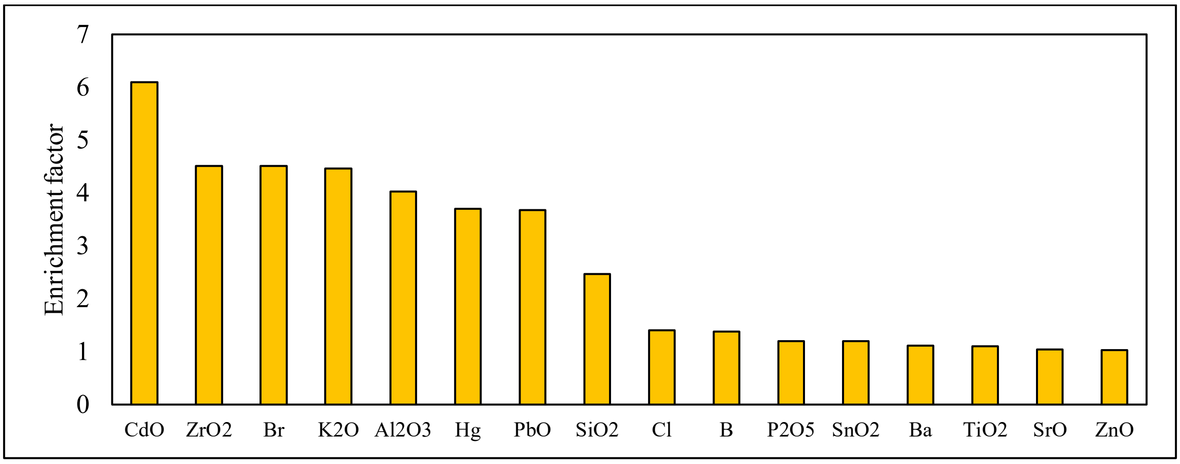


Figure 51 – Enrichment factor of ceramics fraction

Likewise, the ceramics materials separated from bottom ash result richer in Silica and Alumina, Potassium and Zirconium, which are common constituents of the material and at the same time it appears to have high concentration of extraneous metals. Moreover, the higher superficial contamination of this class compared to glass fraction can be justified by the porous nature of ceramic materials.

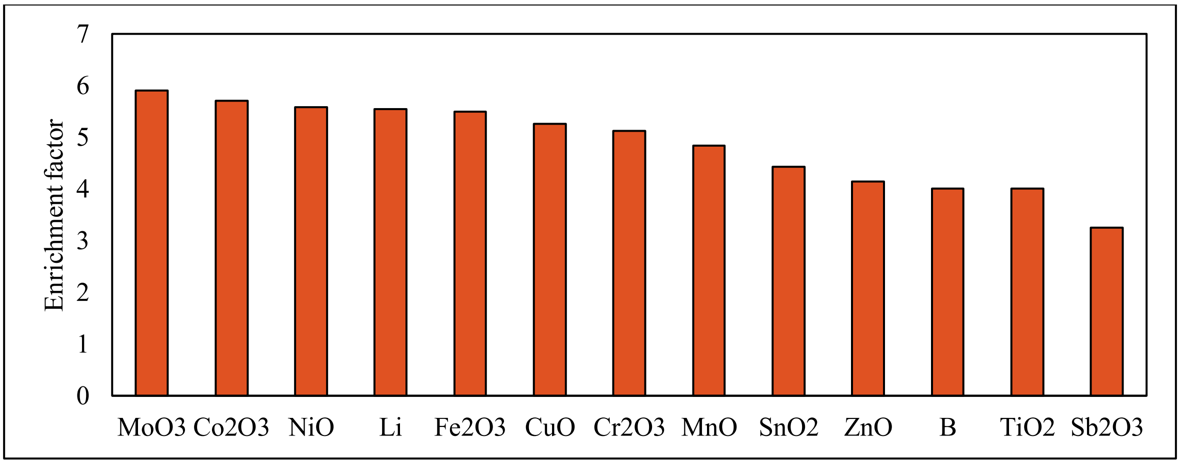


Figure 52 – Enrichemnt factor of metal oxides fraction

The class of metal oxides has been separated from other bottom ash material with a strong neodymium magnet, thereby it results a concentrated cluster of magnetic metals, Iron, Nickel and Cobalt, and other metals that are generally used in alloys with the ones previously listed. Molybdenum and Chromium release from bottom ash has been found to compromise the possible recovery of this material as construction aggregates (Verbinnen et al., 2017). The fact that those elements, as well as other potentially toxic elements like Copper, Nickel and Antimony, tend to concentrate in the metal oxides class, allows to define this class as the one that is necessary to remove in order to improve the leaching characteristic of the material and guarantee the possibility of its recovery as construction aggregates. On the other hand, seen how valuable metals and critical raw materials content increases by separation of this class from the rest of bottom ash, metal oxides has been identified as a possible "urban mine" and a different recovery path has been considered for this material.

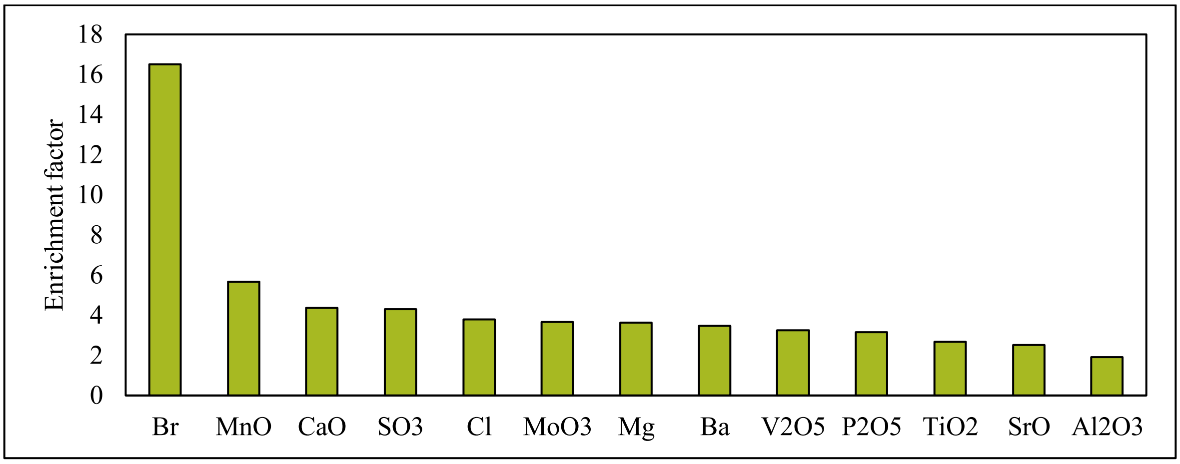
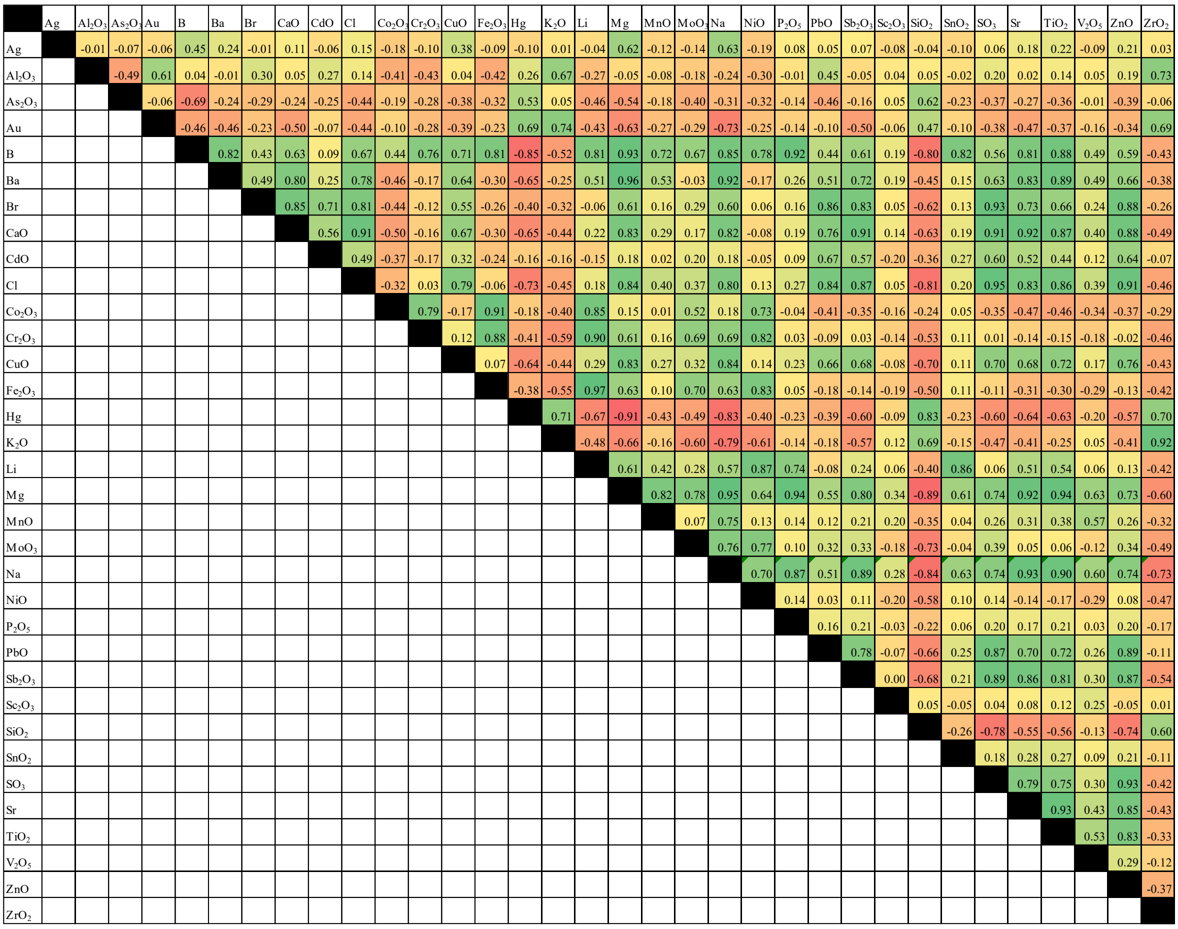


Figure 53 – Enrichemnt factor of residual mineral fraction

The last class of residual minerals, like the metal oxides class, formed during the incineration process and it is constituted by the combination of the flame-resistant materials non-refractories, like ceramics or glass, and non-magnetic, since those have been separated through manual sorting. This class in characterised by the presence of Manganese, Calcium, Sulphates, Chlorides, Magnesium, Barium and Aluminium in mineral forms like Halite, Melilite, Plagioclase and Pyroxene (T. Astrup, A. Muntoni, A. Polettini, R. Pomi, T. Van Gerven, 2016).

5.3 Sensitivity analysis

The results of the analysed previously discussed have been used to perform a sensitivity analysis using Pearson correlation coefficient, as define in Equation **(4)**. The results of this analysis are shown in Figure 54.



	Ag	Al_2O_3	As_2O_3	Au	B	Ba	Br	CaO	CdO	Cl	Co_2O_3	Cr_2O_3	CuO	Fe_2O_3	Hg	K_2O	Li	Mg	MnO	MoO_3	Na	NiO	P_2O_5	PbO	Sb_2O_3	Sc_2O_3	SiO_2	SnO_2	SO_3	Sr	TiO_2	V_2O_5	ZnO	ZrO_2
Ag		-0.01	-0.07	-0.06	0.45	0.24	-0.01	0.11	-0.06	0.15	-0.18	-0.10	0.38	-0.09	-0.10	0.01	-0.04	0.62	-0.12	-0.14	0.63	-0.19	0.08	0.05	0.07	-0.08	-0.04	-0.10	0.06	0.18	0.22	-0.09	0.21	0.03
Al_2O_3			-0.49	0.61	0.04	-0.01	0.30	0.05	0.27	0.14	-0.41	-0.43	0.04	-0.42	0.26	0.67	-0.27	-0.05	-0.08	-0.18	-0.24	-0.30	-0.01	0.45	-0.05	0.04	0.05	-0.02	0.20	0.02	0.14	0.05	0.19	0.73
As_2O_3				-0.06	-0.69	-0.24	-0.29	-0.24	-0.25	-0.44	-0.19	-0.28	-0.38	-0.32	0.53	0.05	-0.46	-0.54	-0.18	-0.40	-0.31	-0.32	-0.14	-0.46	-0.16	0.05	0.62	-0.23	-0.37	-0.27	-0.36	-0.01	-0.39	-0.06
Au					-0.46	-0.46	-0.23	-0.50	-0.07	-0.44	-0.10	-0.28	-0.39	-0.23	0.69	0.74	-0.43	-0.63	-0.27	-0.29	-0.73	-0.25	-0.14	-0.10	-0.50	-0.06	0.47	-0.10	-0.38	-0.47	-0.37	-0.16	-0.34	0.69
B						0.82	0.43	0.63	0.09	0.67	0.44	0.76	0.71	0.81	-0.85	-0.52	0.81	0.93	0.72	0.67	0.85	0.78	0.92	0.44	0.61	0.19	-0.80	0.82	0.56	0.81	0.88	0.49	0.59	-0.43
Ba							0.49	0.80	0.25	0.78	-0.46	-0.17	0.64	-0.30	-0.65	-0.25	0.51	0.96	0.53	-0.03	0.92	-0.17	0.26	0.51	0.72	0.19	-0.45	0.15	0.63	0.83	0.89	0.49	0.66	-0.38
Br								0.85	0.71	0.81	-0.44	-0.12	0.55	-0.26	-0.40	-0.32	-0.06	0.61	0.16	0.29	0.60	0.06	0.16	0.86	0.83	0.05	-0.62	0.13	0.93	0.73	0.66	0.24	0.88	-0.26
CaO									0.56	0.91	-0.50	-0.16	0.67	-0.30	-0.65	-0.44	0.22	0.83	0.29	0.17	0.82	-0.08	0.19	0.76	0.91	0.14	-0.63	0.19	0.91	0.92	0.87	0.40	0.88	-0.49
CdO										0.49	-0.37	-0.17	0.32	-0.24	-0.16	-0.16	-0.15	0.18	0.02	0.20	0.18	-0.05	0.09	0.67	0.57	-0.20	-0.36	0.27	0.60	0.52	0.44	0.12	0.64	-0.07
Cl											-0.32	0.03	0.79	-0.06	-0.73	-0.45	0.18	0.84	0.40	0.37	0.80	0.13	0.27	0.84	0.87	0.05	-0.81	0.20	0.95	0.83	0.86	0.39	0.91	-0.46
Co_2O_3												0.79	-0.17	0.91	-0.18	-0.40	0.85	0.15	0.01	0.52	0.18	0.73	-0.04	-0.41	-0.35	-0.16	-0.24	0.05	-0.35	-0.47	-0.46	-0.34	-0.37	-0.29
Cr_2O_3													0.12	0.88	-0.41	-0.59	0.90	0.61	0.16	0.69	0.69	0.82	0.03	-0.09	0.03	-0.14	-0.53	0.11	0.01	-0.14	-0.15	-0.18	-0.02	-0.46
CuO														0.07	-0.64	-0.44	0.29	0.83	0.27	0.32	0.84	0.14	0.23	0.66	0.68	-0.08	-0.70	0.11	0.70	0.68	0.72	0.17	0.76	-0.43
Fe_2O_3															-0.38	-0.55	0.97	0.63	0.10	0.70	0.63	0.83	0.05	-0.18	-0.14	-0.19	-0.50	0.11	-0.11	-0.31	-0.30	-0.29	-0.13	-0.42
Hg																0.71	-0.67	-0.91	-0.43	-0.49	-0.83	-0.40	-0.23	-0.39	-0.60	-0.09	0.83	-0.23	-0.60	-0.64	-0.63	-0.20	-0.57	0.70
K_2O																	-0.48	-0.66	-0.16	-0.60	-0.79	-0.61	-0.14	-0.18	-0.57	0.12	0.69	-0.15	-0.47	-0.41	-0.25	0.05	-0.41	0.92
Li																		0.61	0.42	0.28	0.57	0.87	0.74	-0.08	0.24	0.06	-0.40	0.86	0.06	0.51	0.54	0.06	0.13	-0.42
Mg																			0.82	0.78	0.95	0.64	0.94	0.55	0.80	0.34	-0.89	0.61	0.74	0.92	0.94	0.63	0.73	-0.60
MnO																				0.07	0.75	0.13	0.14	0.12	0.21	0.20	-0.35	0.04	0.26	0.31	0.38	0.57	0.26	-0.32
MoO_3																					0.76	0.77	0.10	0.32	0.33	-0.18	-0.73	-0.04	0.39	0.05	0.06	-0.12	0.34	-0.49
Na																						0.70	0.87	0.51	0.89	0.28	-0.84	0.63	0.74	0.93	0.90	0.60	0.74	-0.73
NiO																							0.14	0.03	0.11	-0.20	-0.58	0.10	0.14	-0.14	-0.17	-0.29	0.08	-0.47
P_2O_5																								0.16	0.21	-0.03	-0.22	0.06	0.20	0.17	0.21	0.03	0.20	-0.17
PbO																									0.78	-0.07	-0.66	0.25	0.87	0.70	0.72	0.26	0.89	-0.11
Sb_2O_3																										0.00	-0.68	0.21	0.89	0.86	0.81	0.30	0.87	-0.54
Sc_2O_3																											0.05	-0.05	0.04	0.08	0.12	0.25	-0.05	0.01
SiO_2																												-0.26	-0.78	-0.55	-0.56	-0.13	-0.74	0.60
SnO_2																													0.18	0.28	0.27	0.09	0.21	-0.11
SO_3																														0.79	0.75	0.30	0.93	-0.42
Sr																															0.93	0.43	0.85	-0.43
TiO_2																																0.53	0.83	-0.33
V_2O_5																																	0.29	-0.12
ZnO																																		-0.37
ZrO_2																																		

Figure 54 – Pearson correlation coefficients

The distribution of valuable elements like Silver and Gold does not app to be related to any other component. On the other hand, mineral elements like Calcium, Chloride and Sulphates seem to be strongly correlated, as shown in Figure 55 with vale of the parameter r up to 0.91.

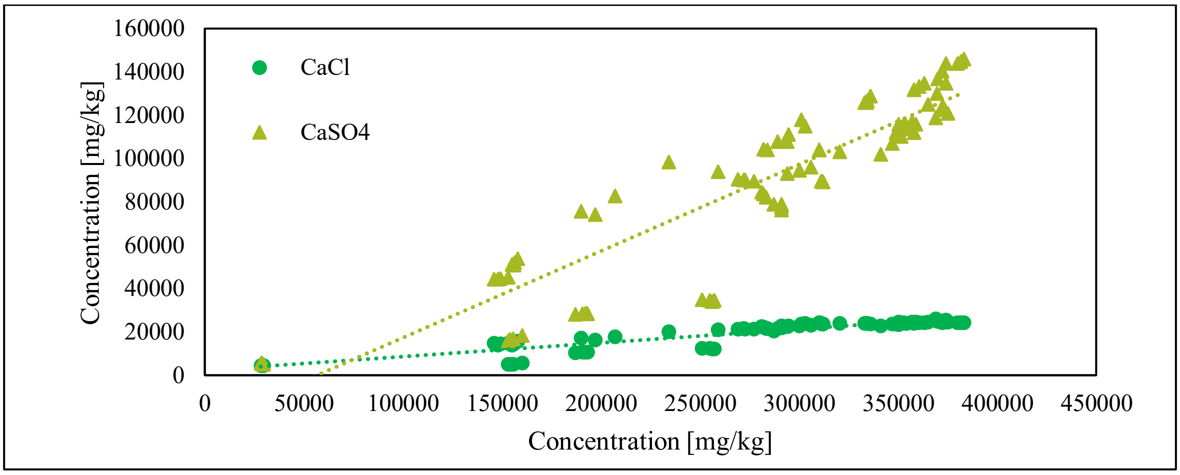


Figure 55 –Correlation Calcium-Chloride and Calcium-Sulphates

The presence of these relationships may be due to the formation of mineral phases during incineration, as in Melilite (Calcium, Sodium, Potassium, Strontium and Magnesium) and Plagioclase (Sodium, Calcium, Potassium and Barium mineral), or during weathering/aging phase, as for instance Gypsum (Calcium sulphates) Halite (Sodium chloride) or Zeolite (Calcium, Potassium, Sodium, Barium and Strontium mineral). In this case the presence of these elements is strongly related to their released, considering that ionic bonding formed by those salts are easily dissolved in water.

Yet at the same time, some of the correlations identified have been linked to the feedstock of incinerated municipal solid waste composition. For example Cobalt and Lithium show a Pearson coefficient r of 0.85, and this is in accordance with the estimation that more than half of Lithium production is destined to produce batteries alongside with Cobalt (US Geological survey, 2019). The determination of the correlation Lithium-Cobalt can be used to determine Lithium concentration based on detected amount of Cobalt, without recurring to ICP-OES spectrometry. Moreover, the enrichment of Lithium in the metal oxides fraction, as observed in Figure 52, may be justified by the strong relation existing between this element and Cobalt, which is strongly magnetic.

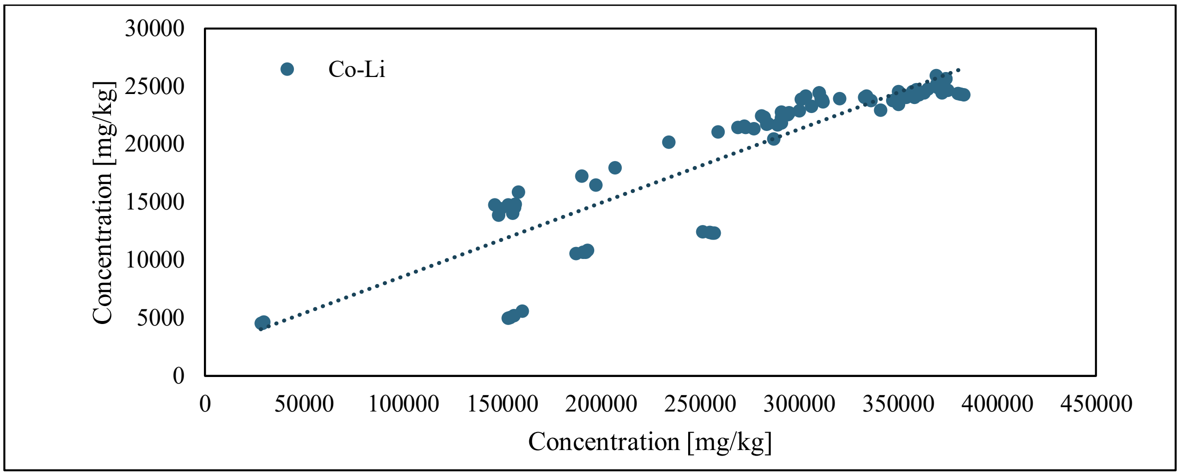


Figure 56 –Correlation Cobalt-Lithium

In the same way Chromium concentration in the metal oxides fraction is justified by the strong correlation existing between this element and Iron, which presents a Pearson coefficient r of 0.88.

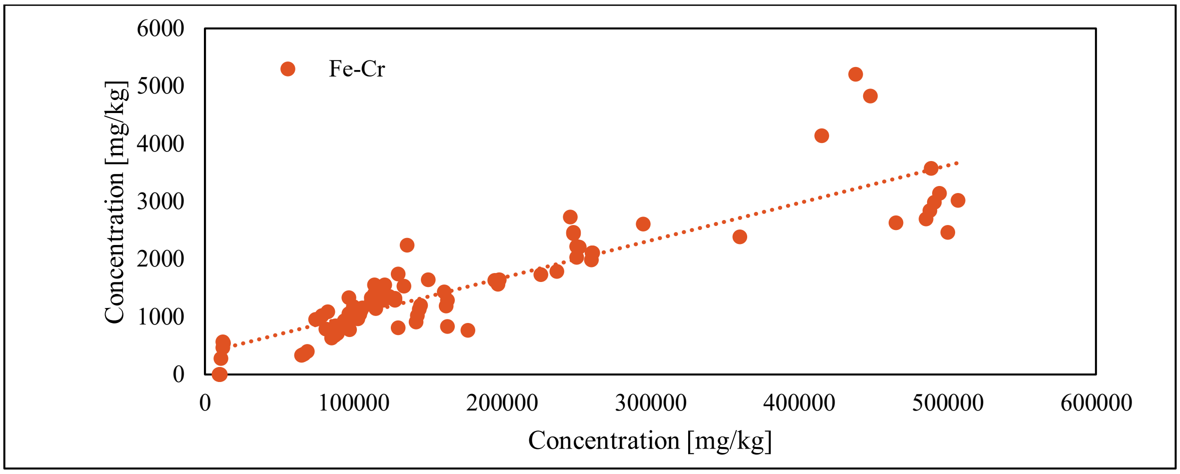


Figure 57 –Correlation Iron-Chromium

On the other hand, Antimony, which is widely used in plastic manufacture due to its action as flame-retardant, has been found to be correlated with other components of plastic materials like Chlorides (r = 0.87) or Bromine (r = 0.83).

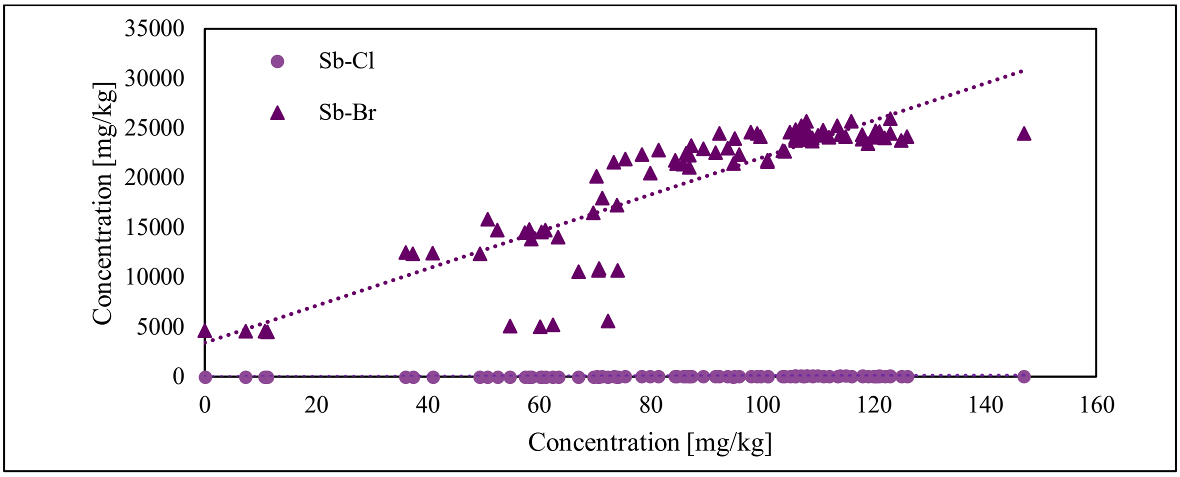


Figure 58 –Correlation Antimony-chlorides and Antimony-Bromine

A linear relation has been observed also among mineral stemming from organic residues, as for instance Magnesium and Manganese (r = 0.82), Magnesium and Sodium (r = 0.95) and Magnesium and Potassium (0.94).

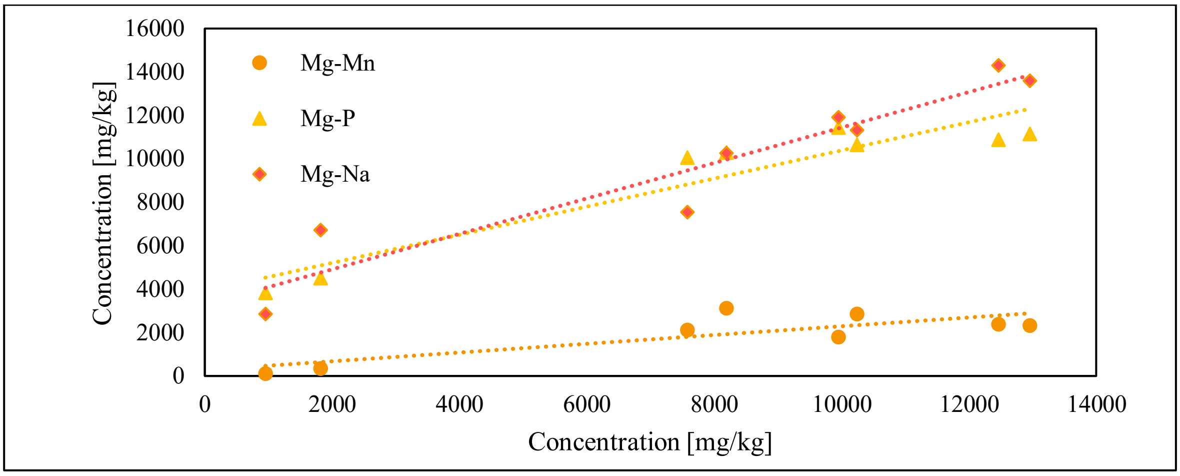


Figure 59 –Correlation Magnesium-Manganese, Magnesium-Sulphates and Magnesium-Sodium

5.4 Recovery potential assessment

5.4.1 Recycling of Glass

Glass is a stable material, formed in combustion chambers with temperature higher than the one reached into municipal solid waste incinerators. Hence it is assumed that this material is not altered during the combustion and the contamination present in this class is due to the melting of metals or plastic during the incineration or to the deposition of a superficial layer in the ageing phase. Anyway, these elements, external to the general composition of glass, are the main limits to recycle this material. In order to study the composition of this external contamination, the glass fraction separated from bottom ash has been compared to literature data on glass composition, in Figure 60, and to the analyses of a sample of different glass materials collected before incineration, in Figure 61 and Figure 62.

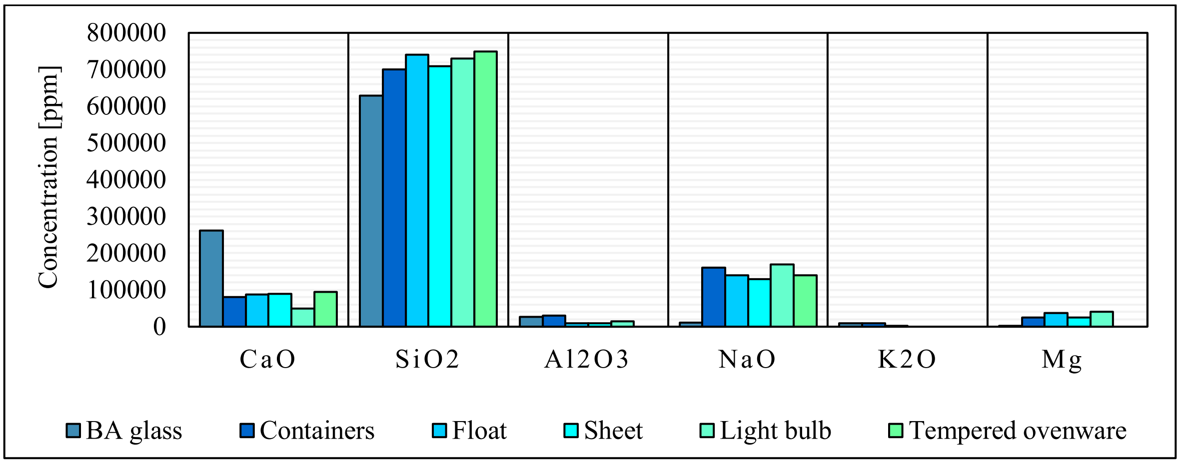


Figure 60 – Composition of bottom ash glass (XRF) and soda-lime glass (Puertas et al., 2015)

The data collected from literature review refer to the composition of soda-lime glass that is the most commonly found in waste and thereby in bottom ash. The main components seems to be unaltered by the incineration process, except for calcium which concentration in bottom ash is twice the standard value for glass. This result is in line with the assumption of the presence of a superficial layer composed by salts like Calcium sulphates, carbonates and chlorides.

However literature composition do not specify the concentration ranges for trace components and this comparison has been performed by analysing with XRF a sample of glass material different from the one collected from the bottom ash, in Figure 61 and Figure 62.

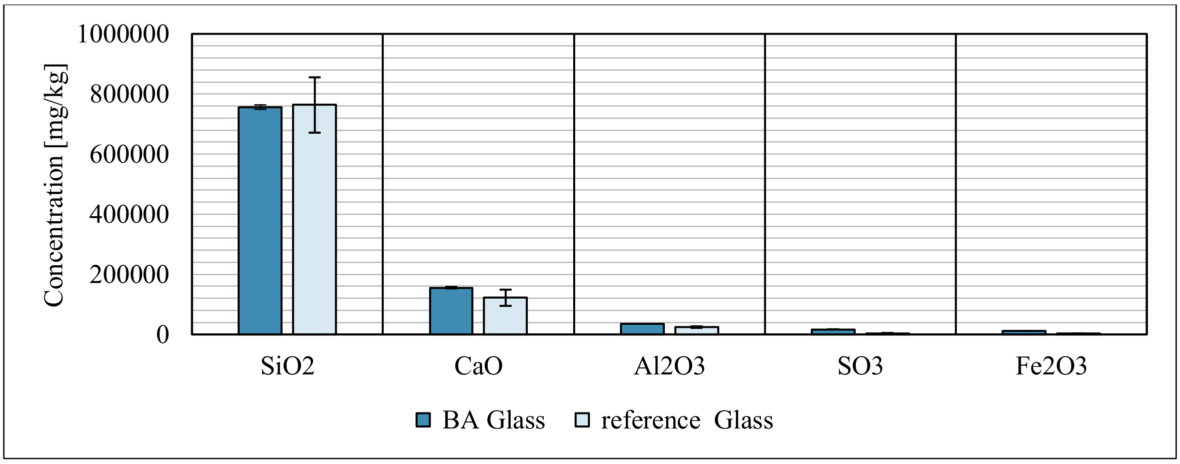


Figure 61 - Composition of bottom ash glass and waste glass (main components)

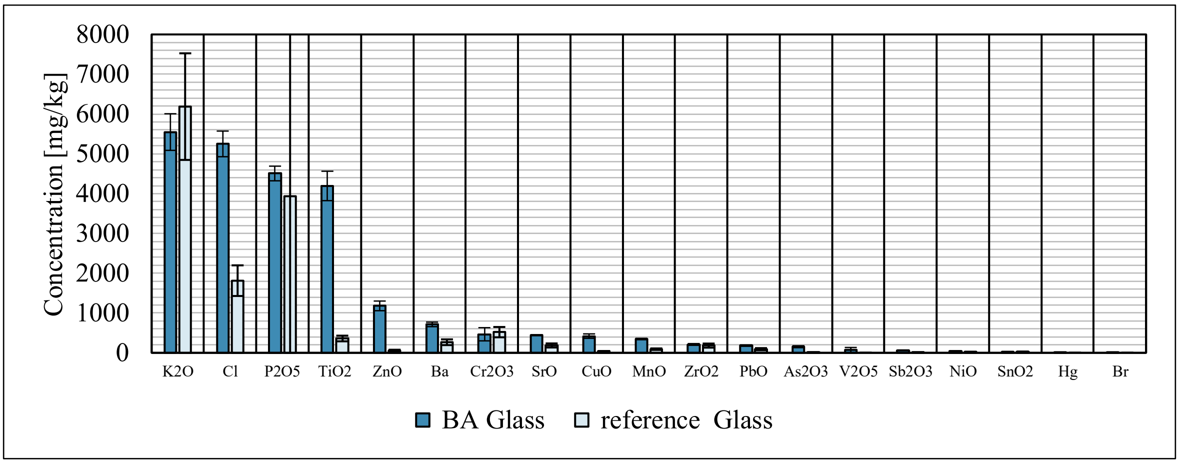


Figure 62 – Composition of bottom ash glass and waste glass (trace components)

The difference in the composition of the main components is comparable to the one observe with literature data. Whereas the bottom ash glass fraction results richer in chlorides, phosphates, and Barium that form the mineral fraction of bottom ash and some other metals, like Titanium, Zinc Copper, Vanadium and Antimony. The last elements are metals with low melting temperature or components of plastics like polyethylene and may have sticked to the surface of glass particles during the incineration of the waste.

The feasibility of the removal of these elements from glass surface has been estimated comparing the concentration released into water, in a Batch test with L/S=2, and digested with aqua regia. In both cases the concentration values have been measured with ICP-OES spectrometry.

5.4.2 Recycling of ceramics

Ceramics, just like glass, belong to a class of materials, called refractories, which are not altered in mineralogy and thermal expansion if subjected to thermal processes between room temperature and 1000°C (Lopez Ferber et al., 2019). Hence the incineration process does not alter the characteristic composition or mechanic behaviour of those materials. The class of bottom ash selected as ceramic material has been compared to literature data on characteristic composition of ceramic materials, in Figure 63.

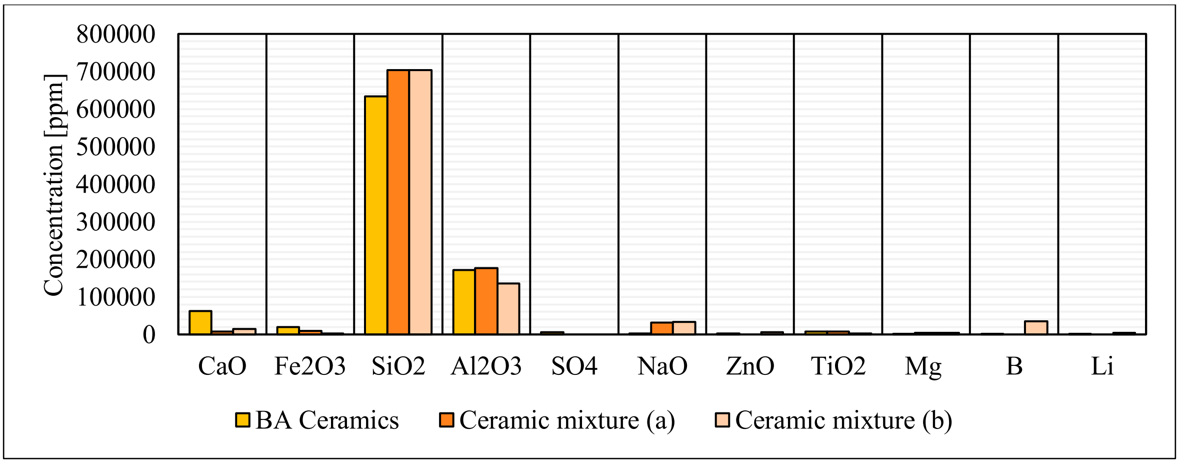


Figure 63 – Composition of bottom ash ceramics (XRF) and traditional ceramic mixtures (Mugoni et al., 2020)

In the previous figure, it is possible to observe how similar the composition of those materials is; however, from these data it is not possible to address the presence of low concentration of metals and minerals due to the deposition of a superficial layer during weathering phase. Like already discussed for glass materials, a sample of waste ceramic mixture has been created in the lab purposely to be analysed with XRF spectrometry and to be compared with the materials separated from bottom ash.

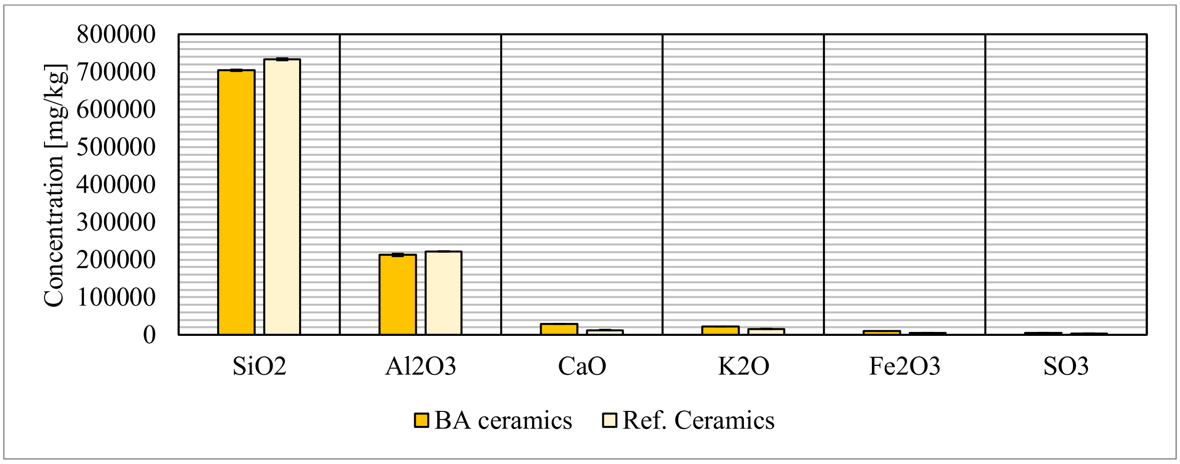


Figure 64 – Composition of bottom ash ceramics and waste ceramics (main components)

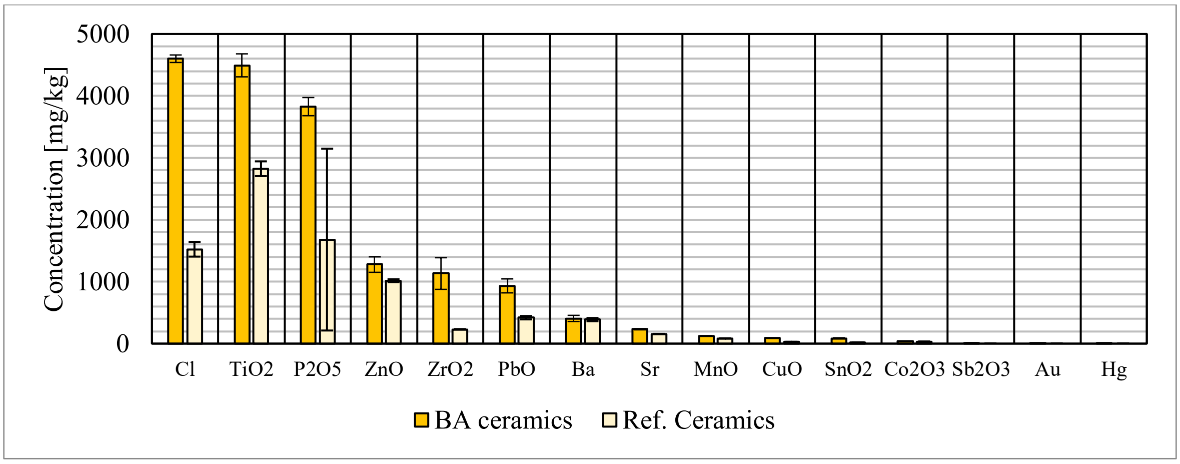


Figure 65 – Composition of bottom ash ceramics and waste ceramics (trace components)

The higher contamination appears to be Chlorides, Posphates, Titanium, Zirconium, Lead and Mercury; however information on the types of ceramics materials (crockeries, kitchenware, tiles and bricks) and their relatively percentage are scares and it is difficult to define a representative sample of reference ceramic mixture to evaluate the effect of incineration process on this class of material.

5.4.3 Urban mining from metal oxides

As already mentioned in section 5.2, the separation of the magnetic components form the mineral fraction of bottom ash generated a class of metal oxides enriched in valuable metals and critical raw materials. Thereby harvesting these components from this class may result more economically favourable than it would be from the total mineral fraction. The economic value of the total fraction and of the magnetic component is presented in Figure 66 and Figure 67.

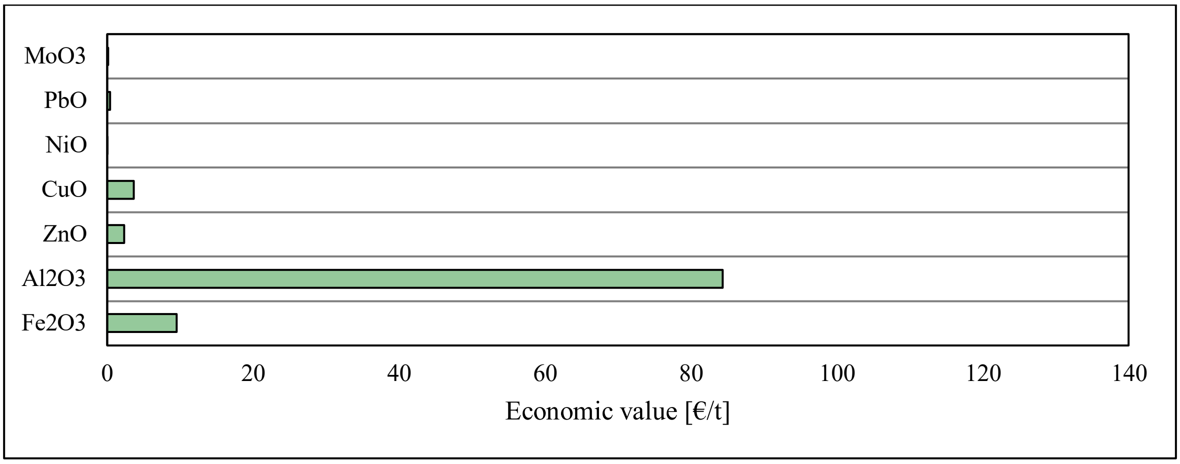


Figure 66 – Economic value of metals in the total mineral fraction

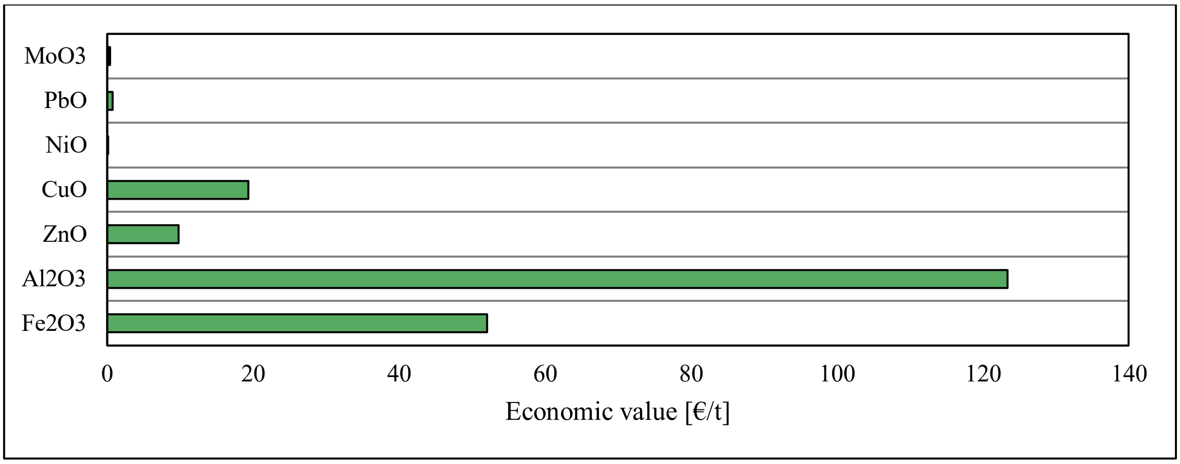


Figure 67 – Economic value of metals in the metal oxides fraction

Previous researches established that approximately 85% of bottom ash economic value stems from the collection of iron scraps and non-ferrous metals recovery (Bunge, 2015). Since all of these components result more concentrated in the metal oxides fraction, the increase in the economic value is significant. The most abundant metal present in the material analysed is iron, that represents around 10% or the total bottom ash sample and this concentration values increase almost at 25% in the metal oxides class, where iron concentrates. Despite being one of the most common metal present on the planet crust, mining within the European countries accounts barely to 12% of the global iron production, despite the presence of important steel industries like the ones in Germany, Italy and France (European Commission, 2017b).

Copper concentration increase is also noteworthy and although it is not currently listed as critical raw material, the only European country in which copper is mined is Poland, accounting only for

2.6% of the global production. Since this is not enough to meet demand, Europe relies almost completely on imported copper from south America (27.6% Peru, 22.1% Chile, 9.5% Brazil and 9.1% Argentina) and Indonesia (10.9%) and recycling it from end-of-life products is encourage (European Commission, 2017b). Moreover the energy saved by recycling copper is 75% less than what is required to mine a virgin material (D. Giurco et al., 2014). Whereas the requested energy to recycle aluminium is 95% less than extraction from mineral ores (D. Giurco et al., 2014). In particular it is necessary to point that the Aluminium presence in the total mineral fraction is overestimated due to the alumina (aluminium oxides) content in the ceramic and mineral components, which is not recoverable with metal mining. Moreover, despite the significant enrichment of Molybdenum and Nickel registered in the metal oxides fraction, as previously shown in Figure 52, their concentration is still too low to considerably increase the economic value of the magnetic fraction. Low concentration values registered for silver, gold, Bismuth, molybdenum, Thallium and Zinc is due to the high transfer rate into flying ash that those element show (Funari et al., 2015).

The economic value of bottom ash is also strongly dependent from the presence of critical raw materials, that tend to concentrate in the metal oxides fraction.

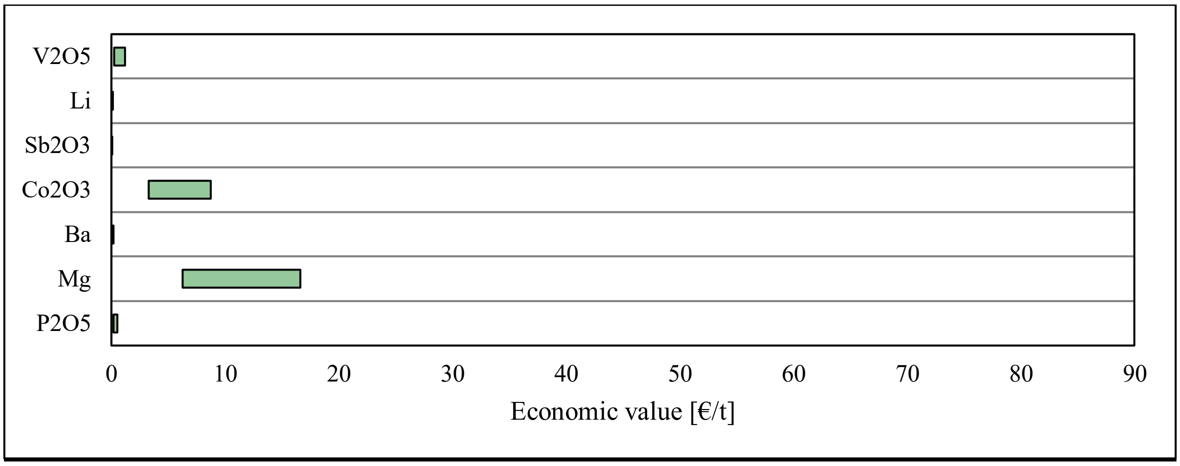


Figure 68 – Economic value of CRMs in the total mineral fraction

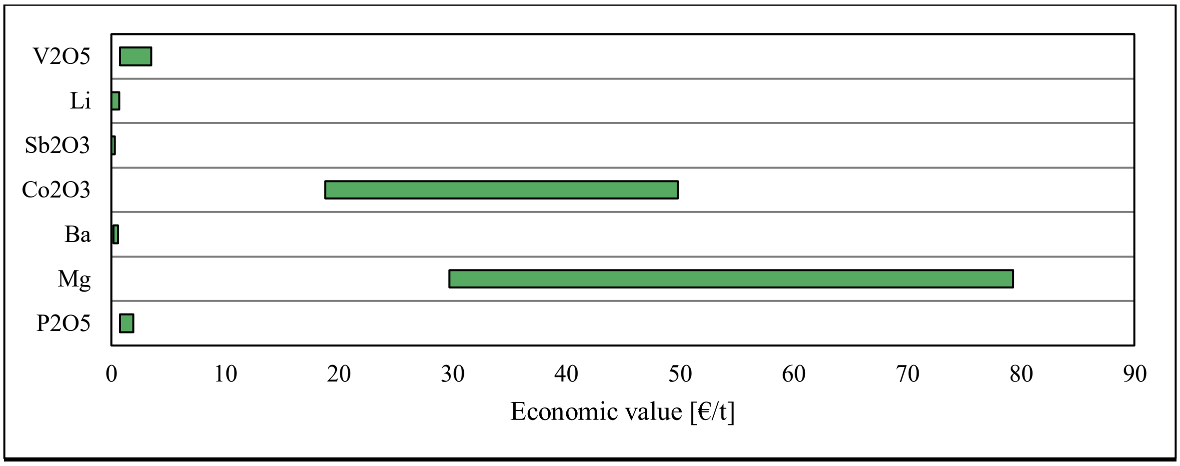


Figure 69 – Economic value of CRMs in the metal oxides fractions

Phosphate in mineral form is mainly mined to produce Phosphoric acid, used a fertilizer, however the concentration in bottom ash is too low compared to mineral ore grade. Magnesium is the main driver, among the critical raw materials present, of the value increase registered separating the metal oxides fraction, and the economic importance of this element resides in the wide range of metallurgical application available for it: reduction of titanium and other metals (32%); alloying aluminium (24%); diecasting (16%); and desulfurization of iron and steel (15%).

Barium is used as powder coatings and filler in paint and plastics. Plastic production is also one of the main applications of Antimony, which provides better behaviour to plastic material acting as flame-retardant. Lithium and Cobalt have a high market value since they are necessary materials for battery production. Likewise Vanadium is used in battery production and in steelmaking to provide additional strength to ferrous alloys (US Geological survey, 2019).

Table 5 – Economic value estimation from metal and CRMs recovery (Funari et al., 2015; Allegrini et al., 2014)

Element	**Total mineral**	**Metal oxides**	**Literature data on bottom ash**[1]		**Concentration ore**[2]		**Active mines**[3]		**u.m.**
			min	**max**	**min**	**max**	**min**	**max**	
Fe_2O_3	4.52	24.80	0.40	15.00	-	-	27	54	%
Al_2O_3	5.27	7.71	1.90	11.00	-	-	-	-	%
P_2O_5	0.32	1.14	0.10	2.40	-	-	1	18	%
Mg	0.21	1.00	0.04	2.49	10	40	-	-	%
ZnO	1244.67	5163.33	-	2.00	50000	150000	4400	110000	mg/kg
CuO	656.15	3453.33	0.02	2.50	5000	20000	1000	26700	mg/kg
Ba	364.31	1180.00	-	0.40	590000	-	-	-	mg/kg
Co_2O_3	173.77	992.33	-	-	500	3000	150	2300	mg/kg
PbO	253.33	446.33	74	13000	300000	400000	-	-	mg/kg
Sb_2O_3	21.68	70.60	7.00	432.00	-	27000	1000	25000	mg/kg
Li	12.09	67.00	-	0.01	-	-	-	-	mg/kg
V_2O_5	19.49	57.00	20.00	122.00	500	13000	-	-	mg/kg
MoO_3	2.09	12.37	2.5	280	-	10000	-	-	mg/kg

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[1] (Funari et al., 2015)

[2] (Allegrini et al., 2014)

[3] Geological Survey of Finland (GTK-website: http://en.gtk.fi/). (Funari et al., 2015)

Unfortunately, despite the significant accumulation of metals in the oxide fraction (Lead and Vanadium double their concentration, Barium and Antimony concentration increases by three times while Magnesium and Molybdenum almost by five times) their presence is not comparable to the grade of mineral ore necessary to mine those elements. Iron oxides concentration, after collection of the magnetic fraction, gets closer to the ore grade, like also Phosphorous, Zinc and Copper. Cobalt concentration in the total sample results already comparable with the grade of mined mineral ore, nevertheless the concentration in the metal oxides fraction is five times higher.

Phosphate in bottom ash is still far from the concentration of the mineral reserves, however nowadays there no known substitutes for it in agriculture and recovering from secondary raw materials is a trending topic in research.

Exploitation of bottom ash as "urban ore" is usually defined as not economically favourable, since the concentration values for most of the metals is too low to justify further treatments, and especially in this case the recovery of ferrous and non-ferrous metals has already been performed with state-of-the-art equipment. Anyway the results demonstrate the existence of components still recoverable, considering that this components are present in bottom ash already in granulated form and the energy required for their extraction is lower than from mineral deposit, therefore separation techniques different from the one already implemented in the mobile treatment plant, like gravimetric collection of Wilfley shaking table, should be investigated.

5.4.4 Recovery of mineral fraction as construction material

In order to assess the feasibility of material recovery as construction aggregates for the class of bottom ash identified as residual mineral after manual sorting and the fine fraction (below 2 mm), a leaching test in batch condition has been performed.

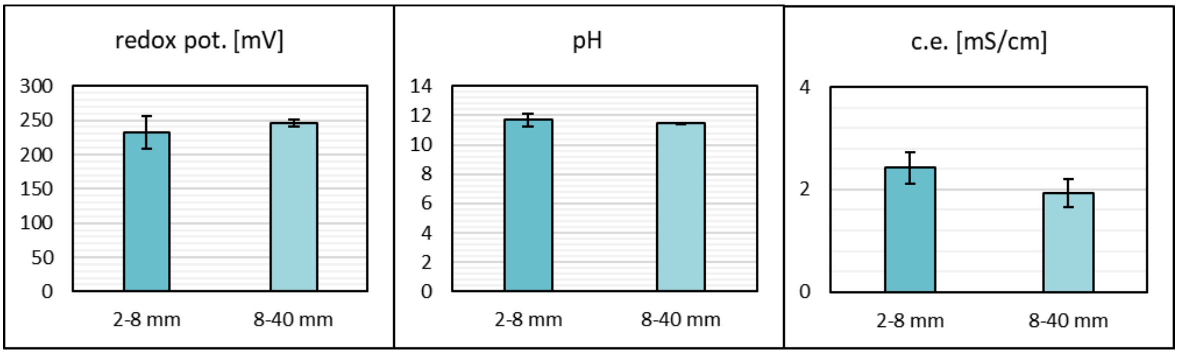

Figure 70 – Leachate characteristic after batch test L/S=10 on coarse fraction

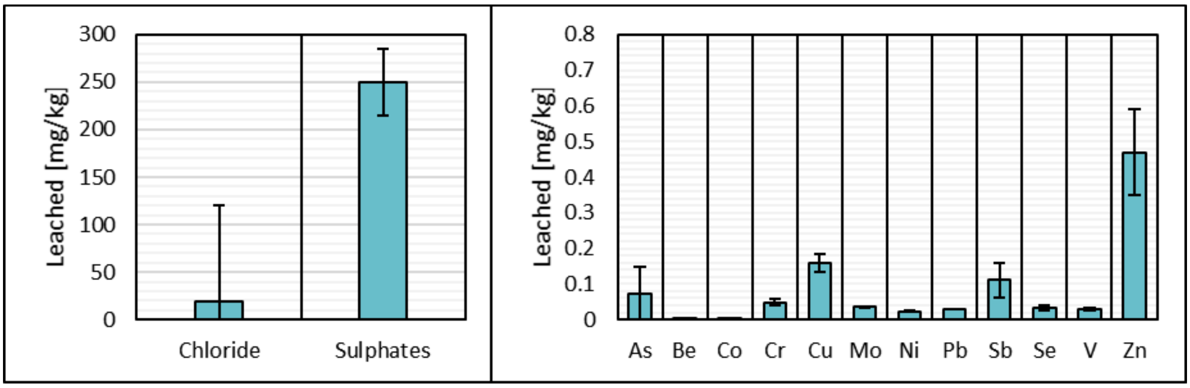

Figure 71 –Leachate composition after batch test L/S=10 on coarse fraction (2-8 mm)

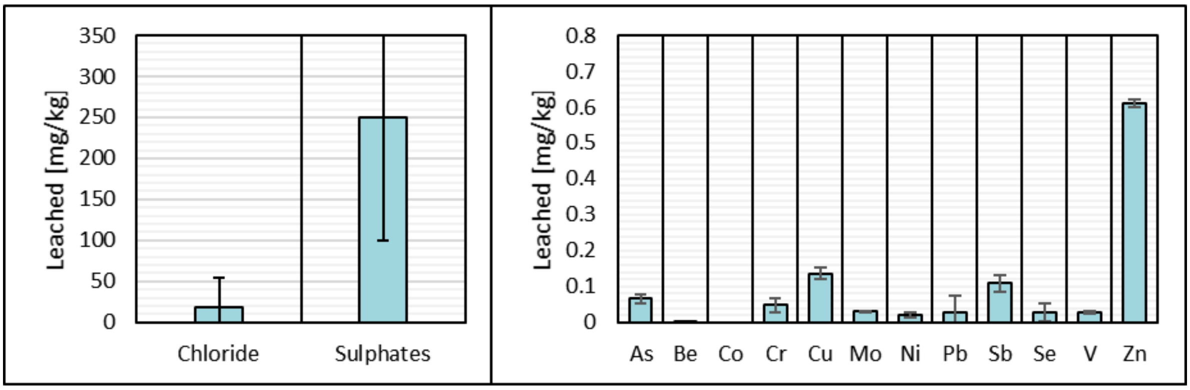

Figure 72 –Leachate composition after batch test L/S=10 on coarse fraction (8-40 mm)

The leachate characteristic of the mineral fraction of bottom ash seems not to be dependent from particle size, the only considerable difference between the fraction 2-8 mm and 8-40 mm is that the former releases four time more sulphates compared to the latter. Despite this disparity and a small increase in Chromium and Copper released by the fraction 8-40 mm, the results of the leaching tests performed on those samples appear similar.

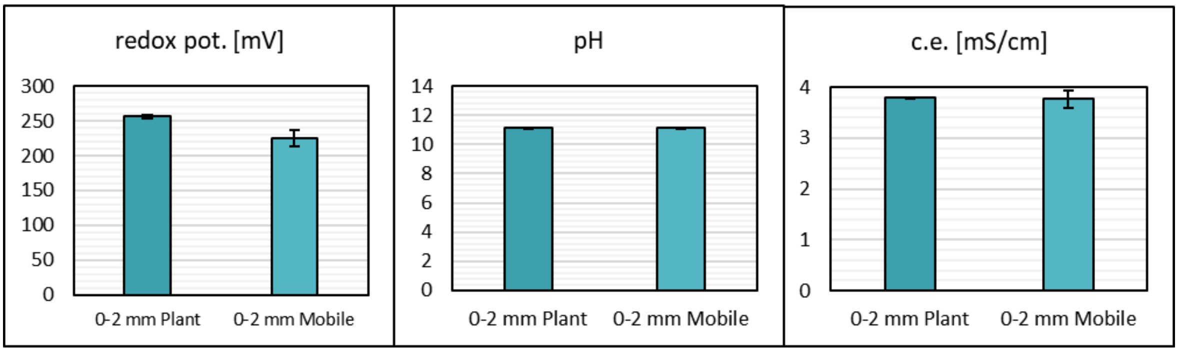

Figure 73 – Leachate characteristic after batch on fine fraction before and after mobile plant

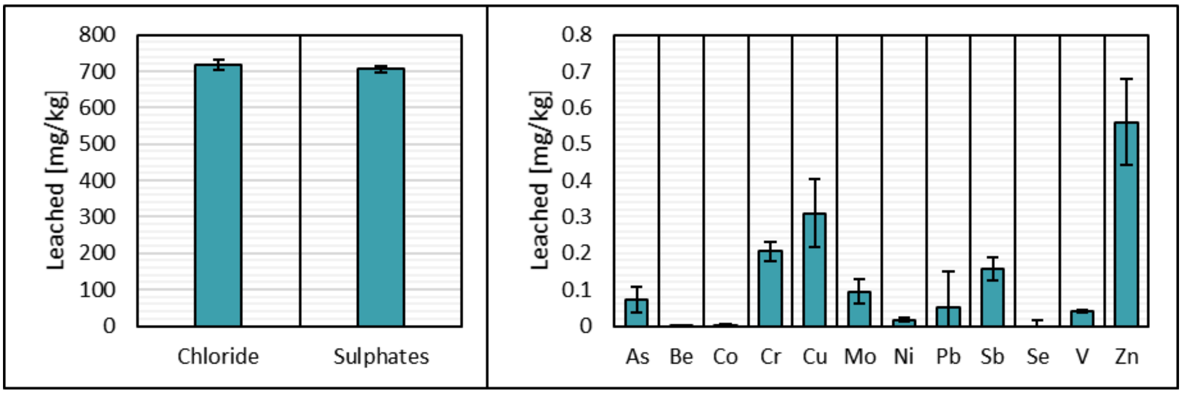

Figure 74 –Leachate composition after batch test L/S=10 on fine fraction before mobile plant

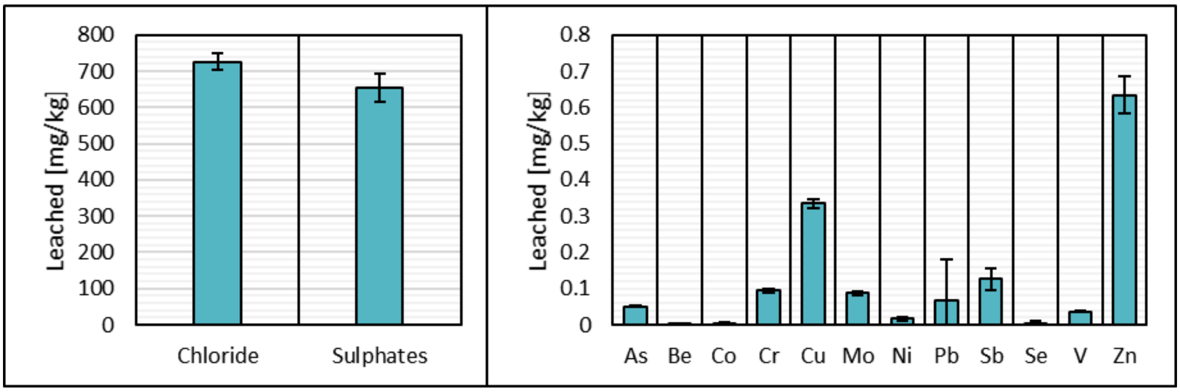

Figure 75 –Leachate composition after batch test L/S=10 on fine fraction after mobile plant

From the results of the leaching test performed on the fine fraction of bottom ash prior the treatment in the mobile plant, Figure 74, and after it, Figure 75, it is possible to notice how the removal of the magnetic and non-magnetic metals plays a role in decreasing the amount of metals released in water, especially for Chromium, Molybdenum and Antimony. The concentration of element released have been compared with the limits defined by Italian law (D. Lgs. 152, 2006), in Table 6, and German legislation in Table 7, Table 8 and Table 9 for recovery as construction material.

Table 6 – Comparison with Italian legislation (D. Lgs. 152, 2006)

	Law limit [mg/kg]	2-8 mm (M) [mg/kg]	8-40 mm (M) [mg/kg]	0-2 mm (P) [mg/kg]	0-2 mm (M) [mg/kg]
Cl	**100**	19±101	250±35	716.67 ± 13.61	725.33 ± 22.94
SO4-	**250**	76±109	483±151	706.33 ± 9.07	653.33 ± 39.72
As	**0.05**	0.07 ± 0.07	0.07 ± 0.01	0.07 ± 0.04	0.05 ± 0.001
Ba	**1**	0.11 ± 0.01	0.1 ± 0.007	0.09 ± 0.005	0.09 ± 0.003
Be	**0.01**	0.00 ± 0	0.00 ± 0	0.001 ± 0	0.001 ± 0
Co	**0.25**	0.004 ± 0	0.00 ± 0	0.003 ± 0	0.005 ± 0
Cr	**0.05**	0.05 ± 0.01	0.05 ± 0.019	0.21 ± 0.03	0.09 ± 0.005
Cu	**0.05**	0.16 ± 0.03	0.14 ± 0.016	0.31 ± 0.09	0.33 ± 0.013
Ni	**0.01**	0.023 ± 0.003	0.02 ± 0.007	0.02 ± 0.004	0.02 ± 0.004
Pb	**0.05**	0.029 ± 0	0.027 ± 0.048	0.05 ± 0.098	0.07 ± 0.088
Se	**0.01**	0.033 ± 0.006	0.027 ± 0.025	0.00 ±0.017	0.004 ± 0.017
V	**0.25**	0.03 ± 0.003	0.027 ± 0.003	0.04 ± 0.004	0.04 ± 0.004
Zn	**3**	0.46 ± 0.12	0.61 ± 0.012	0.56 ± 0.117	0.63 ± 0.117

According to Italian legislation, the main barriers for reuse as construction aggregates are Chloride, Sulphates, Arsenic, Copper, Nickel and Selenium. The fine fraction present also released above the authorized thresholds for Chromium and Lead; meanwhile Arsenic release appears to be hindered in the fine fraction after the treatment in the mobile plant.

Table 7 – Comparison with German legislation (HMVA-1)

	HMVA-1 [mg/kg]	2-8 mm (M) [mg/kg]	8-40 mm (M) [mg/kg]	0-2 mm (P) [mg/kg]	0-2 mm (M) [mg/kg]
Cl	**160**	19±101	250±35	716.67 ± 13.61	725.33 ± 22.94
SO4-	**820**	76±109	483±151	706.33 ± 9.07	653.33 ± 39.72
Cr	**0.15**	0.05 ± 0.01	0.048 ± 0.019	0.21 ± 0.026	0.09 ± 0.005
Cu	**0.11**	0.16 ± 0.03	0.14 ± 0.016	0.31 ± 0.094	0.33 ± 0.013
Mo	**0.055**	0.036 ± 0	0.03 ± 0.002	0.095 ± 0.032	0.087 ± 0.032
Sb	**0.01**	0.11 ± 0.05	0.11 ± 0.023	0.156 ± 0.032	0.13 ± 0.03
V	**0.055**	0.029 ± 0.003	0.027 ± 0.003	0.04 ± 0.004	0.04 ± 0.004

Table 8 – Comparison with German legislation (HMVA-2)

	HMVA-2 [mg/kg]	2-8 mm (M) [mg/kg]	8-40 mm (M) [mg/kg]	0-2 mm (P) [mg/kg]	0-2 mm (M) [mg/kg]
Cl	**5000**	19±101	250±35	716.67 ± 13.61	725.33 ± 22.94
SO4-	**3000**	76±109	483±151	706.33 ± 9.07	653.33 ± 39.72
Cr	**0.46**	0.05 ± 0.01	0.048 ± 0.019	0.21 ± 0.026	0.09 ± 0.005
Cu	**1**	0.16 ± 0.03	0.14 ± 0.016	0.31 ± 0.094	0.33 ± 0.013
Mo	**0.4**	0.036 ± 0	0.03 ± 0.002	0.095 ± 0.032	0.087 ± 0.032
Sb	**0.06**	0.11 ± 0.05	0.11 ± 0.023	0.156 ± 0.032	0.13 ± 0.03
V	**0.15**	0.029 ± 0.003	0.027 ± 0.003	0.04 ± 0.004	0.04 ± 0.004

Table 9 – Comparison with German legislation (HMVA-3)

]	**HMVA-3 [mg/kg]**	2-8 mm (M) [mg/kg]	8-40 mm (M) [mg/kg]	0-2 mm (P) [mg/kg]	0-2 mm (M) [mg/kg]
Cl	**5000**	19±101	250±35	716.67 ± 13.61	725.33 ± 22.94
SO4-	**3000**	76±109	483±151	706.33 ± 9.07	653.33 ± 39.72
Cr	**0.6**	0.05 ± 0.01	0.048 ± 0.019	0.21 ± 0.026	0.09 ± 0.005
Cu	**2**	0.16 ± 0.03	0.14 ± 0.016	0.31 ± 0.094	0.33 ± 0.013
Mo	**1**	0.036 ± 0	0.03 ± 0.002	0.095 ± 0.032	0.087 ± 0.032
Sb	**0.15**	0.11 ± 0.05	0.11 ± 0.023	0.156 ± 0.032	0.13 ± 0.03
V	**0.2**	0.029 ± 0.003	0.027 ± 0.003	0.04 ± 0.004	0.04 ± 0.004

Materials identified as HMVA-1 have the widest range of applications among the three classes of material, as they can be used also in protective walls under cultivated soil Backfilling of structures and dams in the embankment area under cultivable soil Bedding sand under pavement or under slabs. However, the results of the leaching tests both on coarse and fine fractions are too high in the analysed samples to be considered for these applications.

The possible uses identified by German legislation for materials belonging to the class HMVA-3 and HMVA-2 are base course bitumen bound, substructure under foundation or floor slabs, ground consolidation under bound top layer, base layer with hydraulic binders under bound topcoat or backfilling of construction pits. The difference between these two classes is that HMVA-2 material can be used also in substructure up to 1 m from the subgrade under bound Topcoat and backfilling of structures and dams in the embankment area under cultivable soil.

Samples collected after the treatment in the mobile plant, belonging to all granulometric classes 0-2 mm, 2-8 mm, 8-40 mm, comply with the requirements for HMVA-3 application. While instead HMVA-2 requirements are not fulfilled for Antimony in the coarse fraction and a specific treatment for this material should be considered.

5.5 Economic evaluation

Eventually, after the assessment of the different proposed recovery scenarios feasibility, detailed in the previous sections, the economic aspects have been investigated, in order to identify a sustainable management system for this fraction of bottom ash. All the following consideration have been estimated for a total amount of 100 tonnes of bottom ash. The identification of the scenarios refers to Table 4.

In Figure 76 the outcomes and incomes determined by the different handling possibilities are presented. Whereas the differences between incomes and outcomes is presented as net revenue in Figure 77.

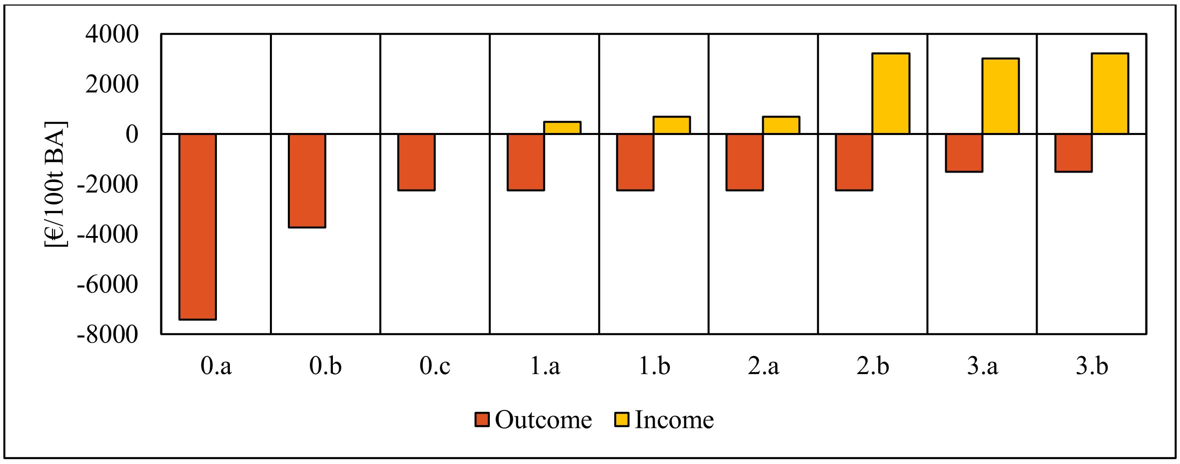

Figure 76 – Outcomes and incomes of different recovery scenarios

Specifically, the worst scenarios from an economic point of view are the one defined scenario “0”, in which landfill disposal is considered. In scenario “0.a”, all the considered amount of bottom ash (100 tonnes) are sent to a landfill for non-hazardous waste; in scenario “0.b”, on the other hand, the less contaminated material classes of the coarse fraction, and in scenario “0.c” also the fine fraction between 0.5 and 2 mm, are sent instead to a landfill for inert waste, which requires lower landfill tax rates and gate fees. The total cost of landfilling has been estimated based on the data collected for different European countries, the tax cost considered for non-hazardous waste landfill has been 75 €/t while for inert waste has been 5 €/t (European Environmental Agengy, 2014).

In scenario “1” the fraction previously identified as inert waste have been supposed to be recovered as construction aggregates with a market value of 10 €/t (Brown, 2019). While the eventual profit collected from the separation of different materials from the coarse fraction of bottom ash has been estimated considering an economic value of 20 €/t for recycled glass (Rincon Romero et al., 2018) and, in absence of more specific data, a value of recycled ceramics equivalent to the market price of aggregates. Eventually, the overall economic value of the metal oxides class, which recovery is assumed in scenario “3”, has been estimated. The data used in this case corresponds to the average between the minimum and maximum values reported in section 5.4.3.

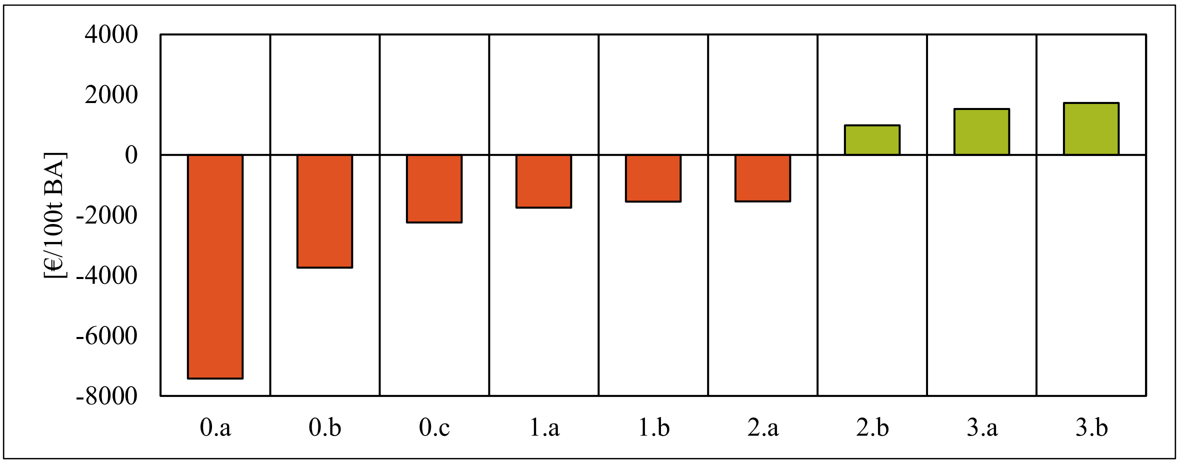

Figure 77 – Net revenue of different recovery scenarios

It is possible to observe how the last possibilities presented, where the amount of material directed to landfill is as little as possible, present a positive revenue While the worst solution, from a merely economic point of view, is the case in which the entire amount of bottom ash is sent to hazardous waste landfill (scenario 0). Thereby the differences between the cost of any solution and scenario 0 has to be intended as potential savings, as in Figure 78.

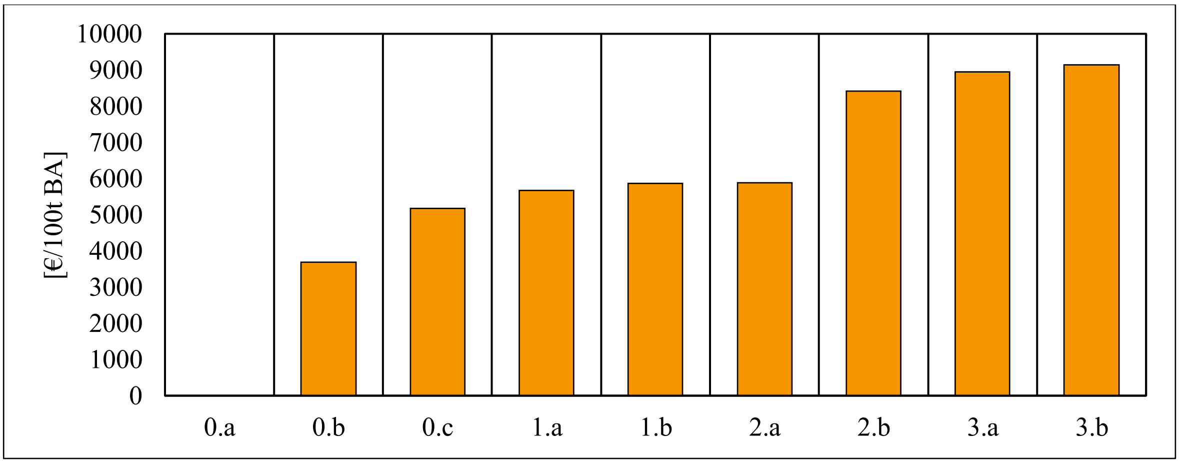

Figure 78 – Potential saving compared to scenario 0

Material-based recovery for the mineral fraction of bottom ash (as in scenarios 2 and 3) has been proven to increase the income margin and the last three scenarios present not only less cumbersome solutions compared to complete landfill but also a positive overall economic flux. The treatment cost required by these solutions has not been estimated in this study; hence, the margin shown in Figure 78 should serve for a future and economically more detailed study, as the upper edge below which treatment cost should place in order to define this process as economically justifiable.

6 CONCLUSIONS

According to several previous studies (Alam et al., 2019a; Allegrini et al., 2014; Funari et al., 2015; T. Astrup, A. Muntoni, A. Polettini, R. Pomi, T. Van Gerven, 2016), the characterisation of municipal solid waste incineration bottom ash (BA) performed in this thesis has highlighted the twofold nature of this material, which represents at the same time an environmental hazard and an exploitable resource. Hence the correct recovery of bottom ash has been once again proven to be a key step toward reaching circular economy. Nowadays, the main application for bottom ash, whether it is not directly sent to landfill, is as raw material in cement and concrete production. This application is fostered by the fact that aggregates cost is strongly dependent on the distance between aggregate mining sites and the construction sites where they are sent; and municipal solid waste incineration plants on the other hand are usually located close to urban areas, where construction materials are more required (Bourtsalas, 2012). Although previous studies have estimated how the recovery of bottom ash as construction aggregates can hypothetically replace only 0.6% wt. of primary aggregates in the European market, the removal of this material from the waste stream directed to landfill results in a 7– 8 vol% decrease each year (Blasenbauer et al., 2020). Thereby the main drivers towards bottom ash recovery appear to be the necessity to comply with the EU Landfill Directive and to reduce management costs due to Landfill tax.

From the starting point of an already well-developed research literature on the topic of sustainable management of municipal solid waste incineration bottom ash, the main contributions brought by this work have been:

- the assessment of the recovery feasibility of the BA fine fraction as construction material after a treatment with the cutting-edge technology of Sortatec PRO M1 plant (Holm and Simon, 2017), although the fine fraction of BA has always been defined as the most critical component to recover;
- the identification of a more innovative material-based recovery system for the mineral fraction, depurated of ferrous and non-ferrous metals by Sortatec treatment plant. The different materials sorted from this fraction were: glass, ceramics, metal oxides and a residual mineral fraction.

Refractory materials like glass and ceramics have been proven, as detailed in sections 5.4.1and 5.4.2, to remain substantially unaltered after incineration, aside from minimal increases in trace elements concentration that, based on the correlation reported in section 5.3, have been linked to superficial contamination, which can be easily removed either with water washing or dry abrasive treatments. Then, a more proper recycling process has been identified for these materials instead of being used as construction aggregates.

Meanwhile the conventional solution of recovery as aggregates has been proposed only for the mineral materials formed during incineration. However, among this fraction, a further class of metals oxides has been identified and separated from the residual mineral fraction, in order to remove hazardous components or elements that may hinder its performance as construction material, as explained in 5.4.4.

From the characterisation of the metal oxides, in section 5.4.3, it has been observed how this class concentrates not only the dangerous components but also the most valuable elements in terms of metals (Iron, Zinc and Copper) and critical raw materials (Phosphorous and Cobalt). The grade of these elements are rather low compared to mineral ore, however their recovery may be justified by the reduction of energy consumption and greenhouse gas emissions linked to metal mining from this already available form instead of from virgin metal extraction.

Eventually, the fine fraction of bottom ash (below 2 mm) has been proven to benefit from the enhanced treatment performed by the mobile plant Sortatec PRO M1, to the extent that the results of the leaching test performed on this sample comply with the regulatory limits for recovery as construction material defined by German legislation, as detailed in section 5.4.4. However, thresholds reported in the Italian legislation are not respected by this fraction of bottom ash. Nonetheless, despite the fact that leaching tests have been performed only on the total fine fraction between 0-2mm, from the characterization of different granulometric classes among the fines in terms of total content, as presented in section 5.1.1, the concentrations of the critical elements appear to decrease with the increase of particle size. Thereby, leaching test of different granulometric ranges of the fine fraction of bottom ash should be performed in order to identify a possible cut-off particle size above which fine bottom ash can comply with other countries regulations.

In conclusion, the existence of different solutions for sustainable management of on municipal solid waste incineration bottom ash has been proven. However, the legal framework on this topic at European level is still lacking homogeneity and specificity, and currently this one of the main barriers that jeopardize the closure of the loop for the management of this material within a circular economy approach.

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