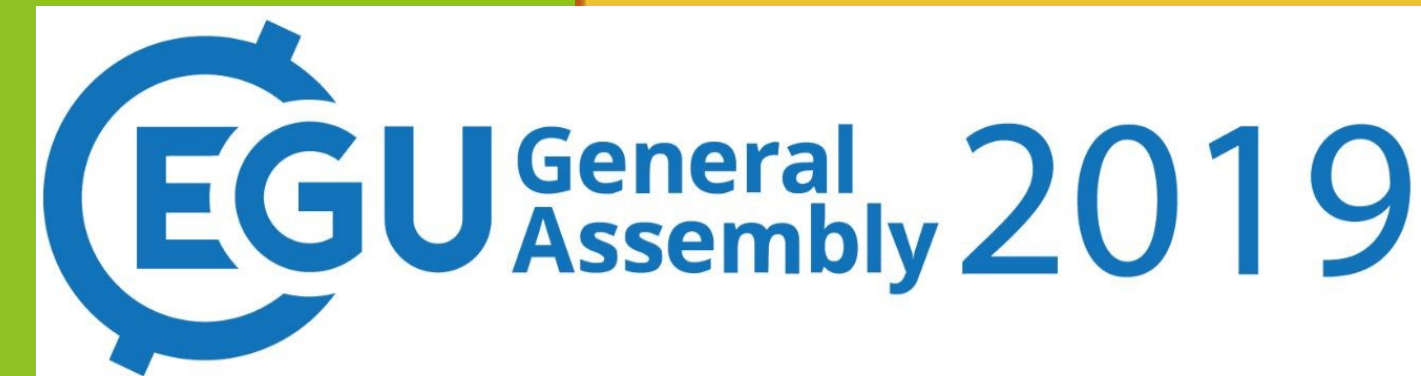


A second life of waste products for a responsible and ethical use of natural resources: evaluations of the use of ashes produced by waste-to-energy plants as aggregated materials

Caterina Caviglia¹, Giorgia Confalonieri¹, Ingrid Corazzari², Enrico Destefanis¹, Giuseppe Mandrone¹, Linda Pastoro¹, Alessandro Pavese¹

¹Earth Sciences Department, Università degli Studi di Torino, via Valperga Caluso 35, 10125 Torino, Italy

²Chemistry Department, Università degli Studi di Torino, via Pietro Giuria 7, 10125, Torino, Italy



INTRODUCTION

In many geographical contexts, the availability of natural mineral resources is not always able to meet the demands and often the supply is carried out at high energetic and environmental costs. This may not only concern fossil fuels but also raw materials used for the production of aggregates and availability of metals for each type of application. It is one of the consequences of the growth of the living standard that involves the construction of an increasing number of infrastructures. For this reason the figures called to solve the problems of supplying raw materials and their use, as geologists and engineers, are necessarily faced with problems different from the normal supply of natural resources, increasingly rare and insufficient to cover the demand or available with very high energy costs and in contrast with the environmental protection issues that we try to apply in many countries.

The research therefore moves from the traditional retrieval through geological and mineral prospecting to the conversion and re-use of materials considered waste or waste deriving from an industrial process.

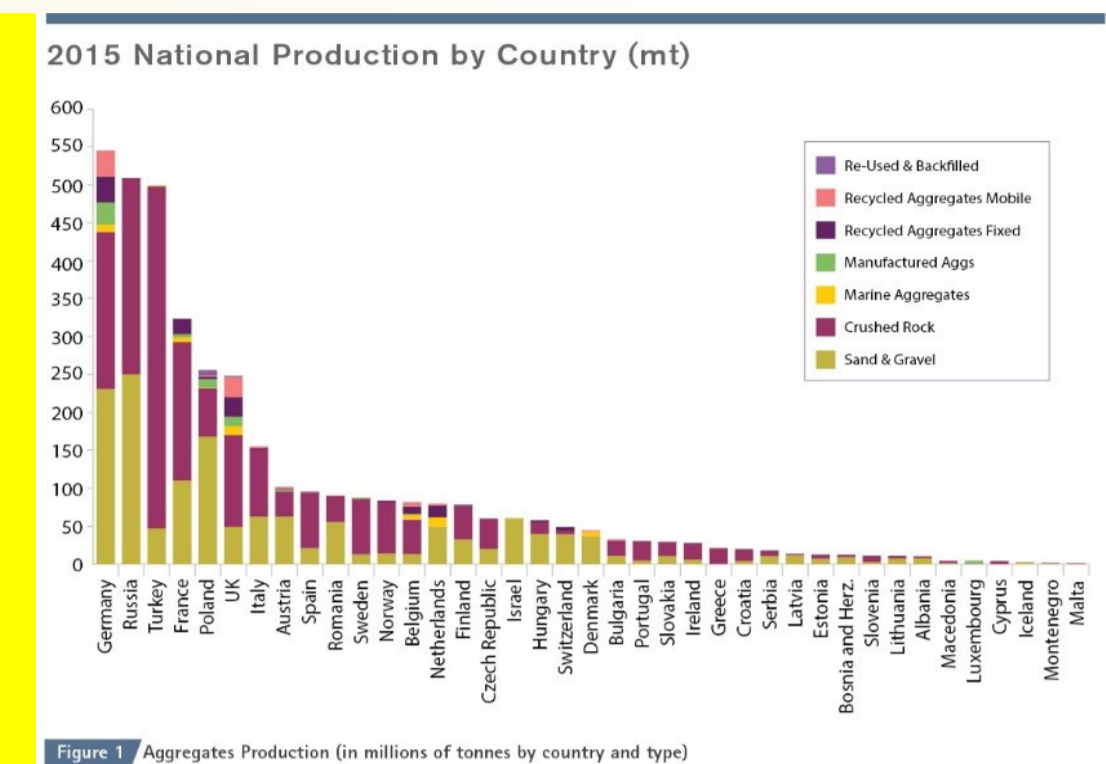
With regard to sustainability, the use of residues from waste-to-energy plants for urban waste is included: after moderate treatments, they can find a role of raw material-second in the construction of works, reducing the need to find additional natural resources and related problems for their disposal or storage.

From the plants Waste to Energy, in 2016 only in Europe, around 19 Mtons of bottom ashes have been produced, thus offering a good opportunity for material to be processed to reach the *End of Waste* condition.

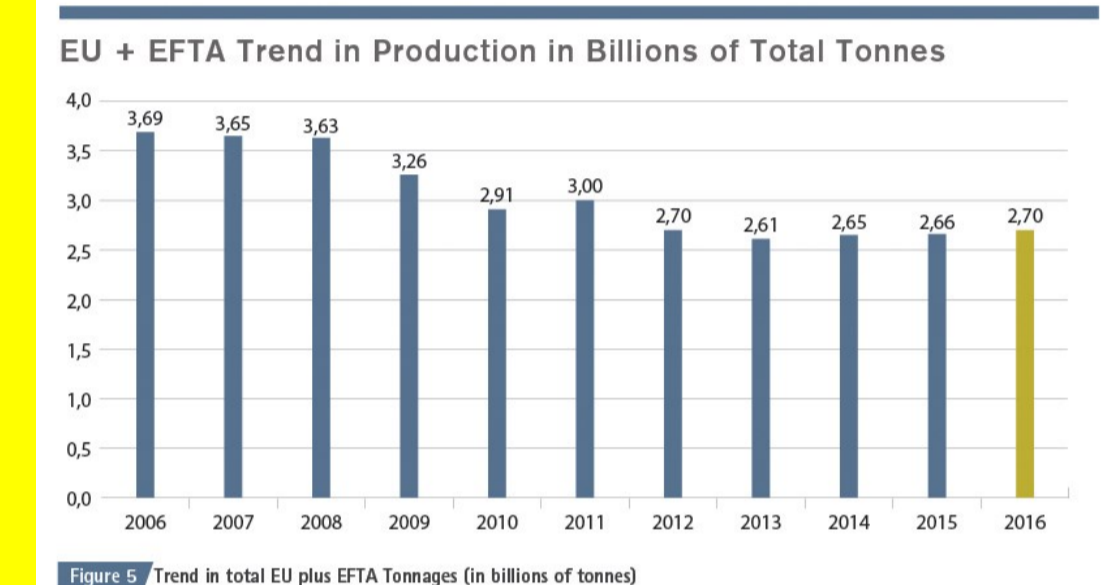
The aim of the present study is to characterize the bottom ashes of municipal solid wastes produces in a plant present in northern Italy by means of a multidisciplinary approach and on the basis of the results we have defined the quotas of material available for re-entry into the "portfolio" of raw materials. We have also tested some inertization techniques to reduce polluting substances release in the environment as natural and accelerated carbonation. The carbonation process involves the absorption of carbon dioxide by an alkaline material, as bottom ash, decreasing pH and making calcite precipitate.

The interaction of carbon dioxide with municipal solid waste incinerator (MSWI) bottom ash has been studied to investigate the resulting changes in pH and bottom ash mineralogy and the impact that these changes have on the mobility of dangerous substances, especially heavy metals. This process can be natural, in an open environment, or accelerated, using laboratories reactors to study the variation of time, temperature and humidity to maximize the carbonation process. We have compared this two methods to evaluate the possibility of a reuse of bottom ashes, respecting the European legislation threshold limits.

Data of aggregates production trend for EU + EFTA (Iceland Liechtenstein, Norway, Switzerland) countries. If European economic growth can be maintained, the EU+EFTA total aggregates production could reach the milestone of 3bnt by 2019, but this would be still much below the pre-crisis 3.7 bnt of 2006.

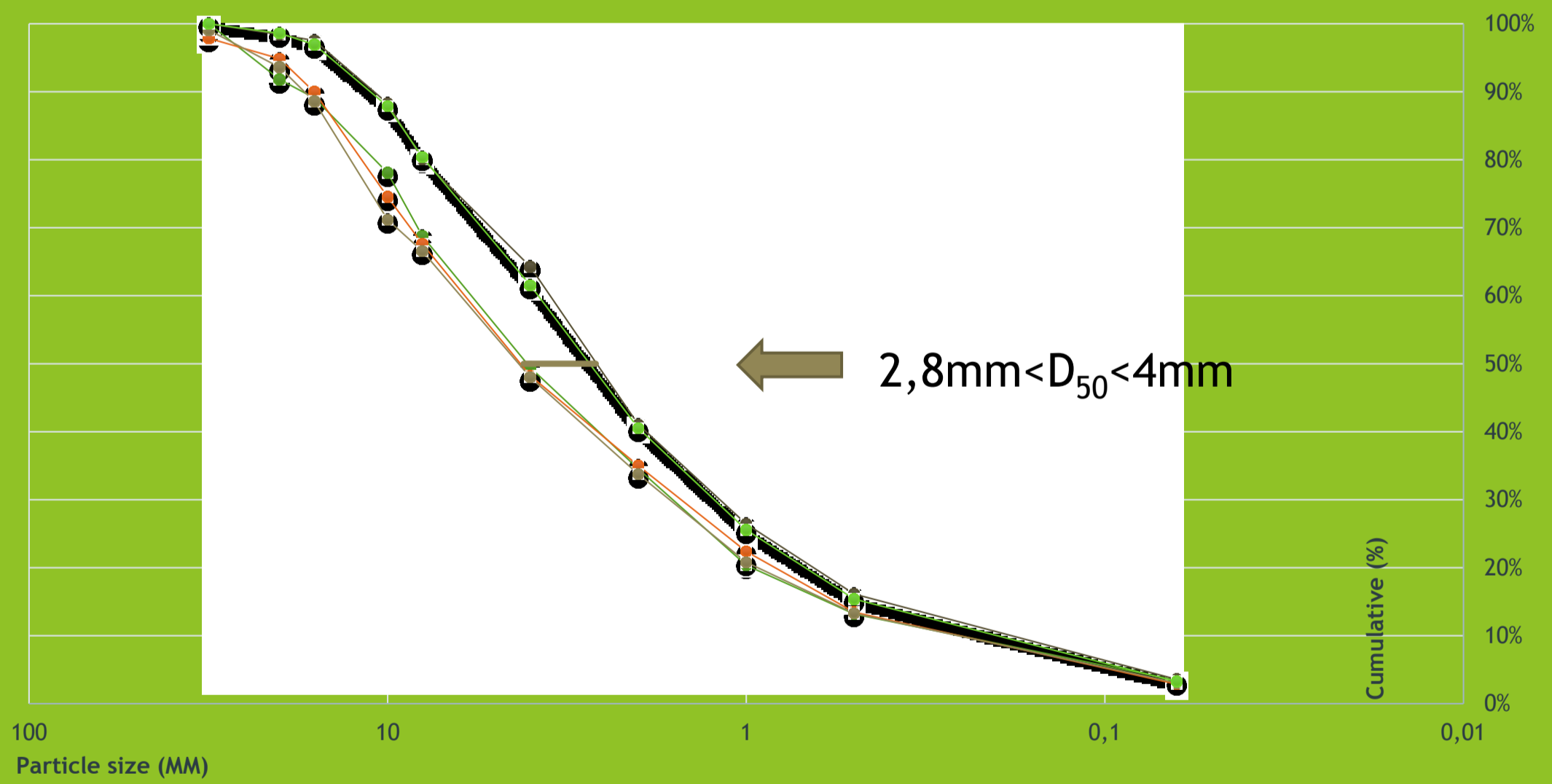


Data of aggregates production from UEPG "Union Européenne des Producteurs de Granulats" annual review 2017-2018.



MATERIALS AND METHODS

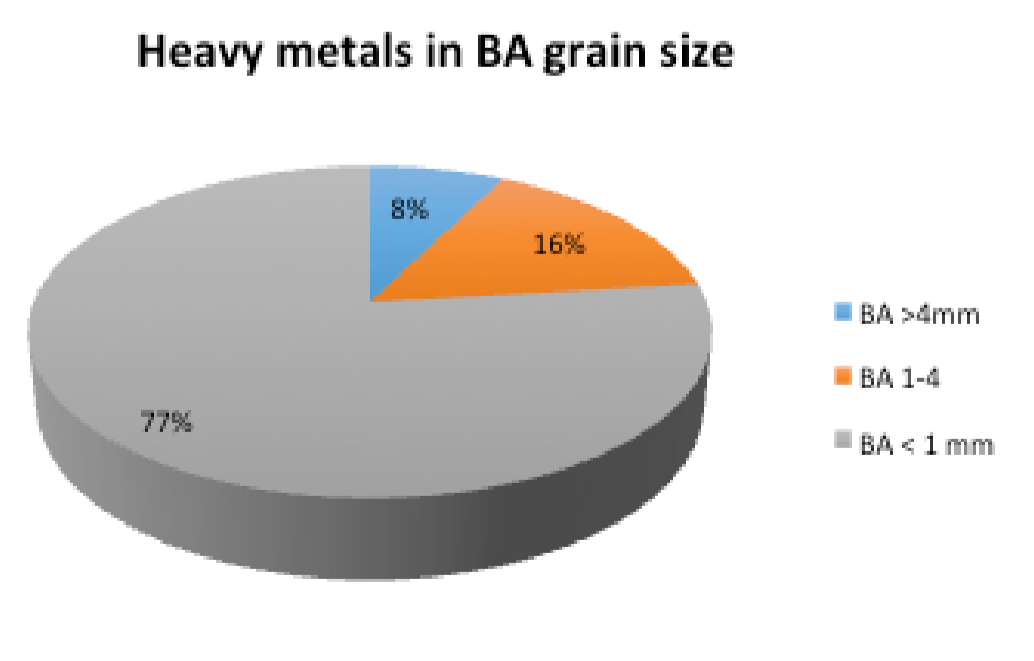
Some bottom ashes samples were taken from the accumulation deposits of a waste-to-energy plant located in northern Italy. The material leaves the incineration process as it is and is rather heterogeneous and contains a significant fraction of metal elements. BA are divided in a fraction over and under 1 mm to perform the best treatments for each grain size.



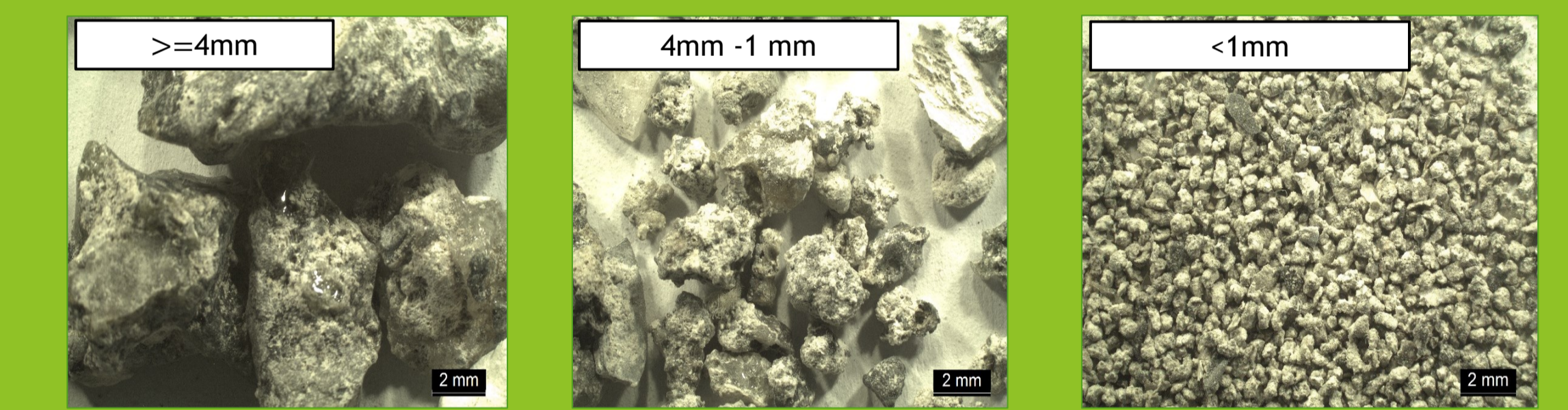
| >4 mm | 4 -1 mm | <1 mm | water content | loose bulk density |
|-------|---------|-------|---------------|--------------------|
| % wt | % wt | %wt | %wt | kg/l |
| 36 | 38 | 26 | 17 | 1,095 |

AVERAGE HEAVY METALS CONCENTRATION IN WATER AFTER RELEASE TESTS OF BA

After leaching test concentrates mainly in the finer fraction <1 mm, especially Cu, Pb, Zn.



BOTTOM ASHES TREATMENTS



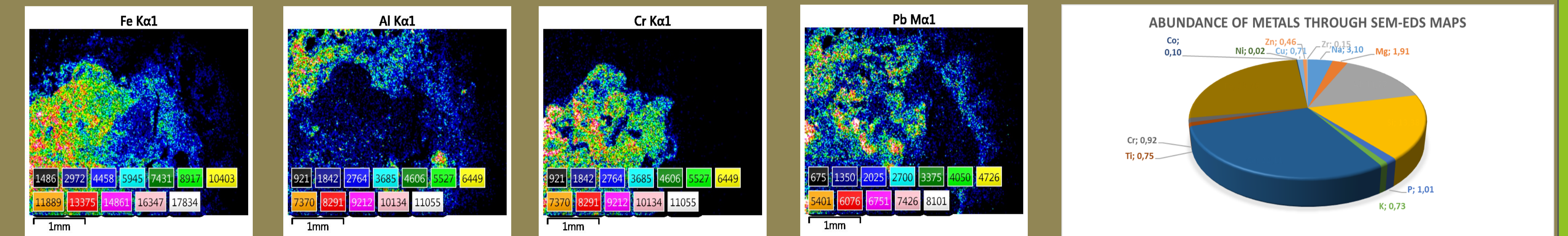
Washing Washing/ Accelerated carbonation Accelerated carbonation

Accelerated carbonation was performed using 20g of BA, applying different conditions of temperature, water content, pressure of CO₂ and time. The fraction up to 4 mm was excluded from carbonation since it doesn't contain high concentrations of dangerous substances, as already recognized in previous works (Um et al.,2017), and it only requires moderate treatments as washing. Accelerated carbonation tests were applied to the grain size fraction between 4 mm and 1 mm, and on the fraction <1 mm.

The following results are relative to the fraction < 1 mm because most of the heavy metals and polluting substances concentrates in it. In fact heavy metals detected in the <1 mm fraction of BA are three times higher than in the coarser fraction >1 mm. Different set of parameters were applied in the accelerated carbonation tests, as indicated by previous work on BA carbonation (Bertos et al., 2004; Van Gerven et al., 2005; Baciocchi et al., 2010; Nam et al., 2012; Pan et al., 2012): the water to solid ratio (L/S) in the samples has been maintained in the range 0,2-0,4 L/S, temperature variation has been set from 25 to 50 °C, time from 60 to 120 minutes and P CO₂ from 1 to 3 bar.

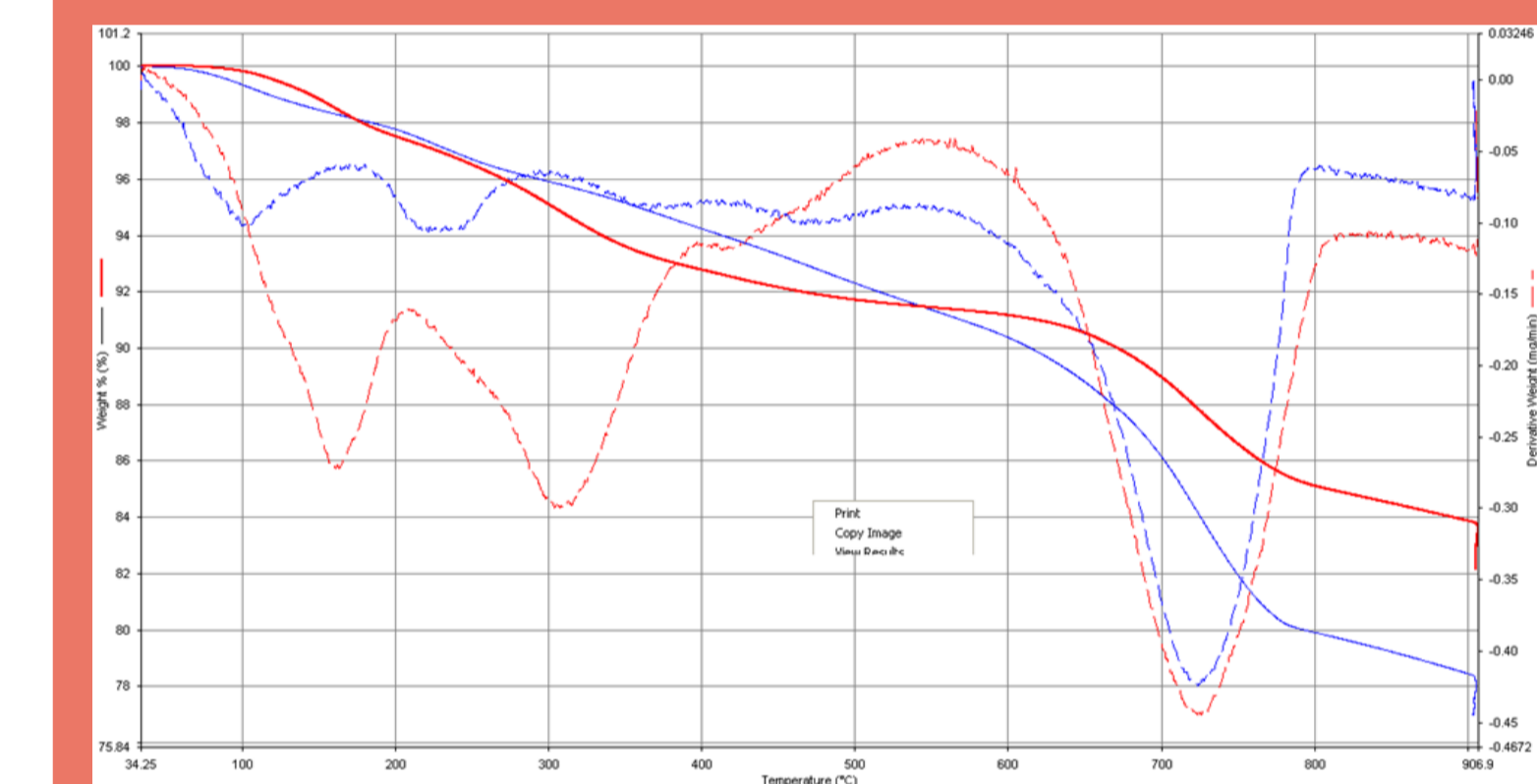
CHARACTERIZATION OF THE METALLIC FRACTION

Within the coarser granulometric fraction (> 4mm) ferromagnetic granules have been identified and separated by a magnet. This rate sometimes exceeds 10% of the total weight of the sample. The separated material was analyzed by electronic scanning microscopy with EDS to obtain compositional maps capable of providing preliminary information on the metallic species present.



The compositional maps, considered in the total data collected by EDS, provide an elemental metallic set expressed in % of oxides reported in the pie chart.

TGA + FTIR QUANTIFICATION OF ACCELERATED CARBONATION



TG (continuous line) and derivatives (dashed lines) measured in function of the temperature for BA not treated (red line) e BA carbonated (blue line)

BA not treated vs BA carbonated

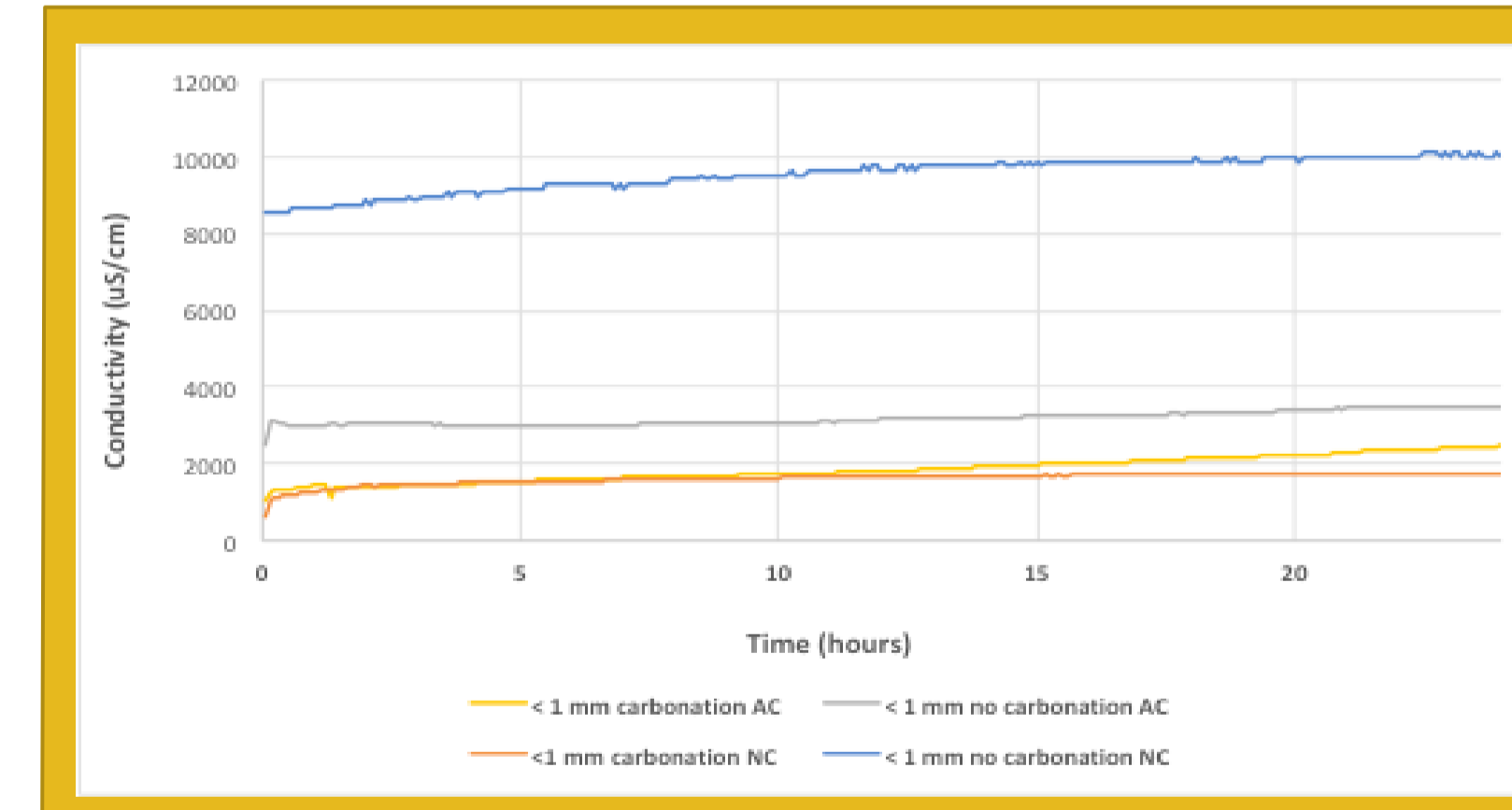
Weight loss can be due to the CO₂ release. Temperature and CO₂ release is compatible with the thermal decomposition of carbonates.

The accelerated carbonation process has been quantified by thermogravimetric analysis coupled with FTIR, to quantify the amount of carbonates produced. Two samples of grain size < 1 mm were chosen, one not treated and one carbonated, and were heated in N₂ atmosphere from 35 to 900 °C (ramp 20 °C/min). At 900 °C, they were kept for 15 minutes in oxidizing atmosphere(N₂/O₂ 3/1).

RESULTS

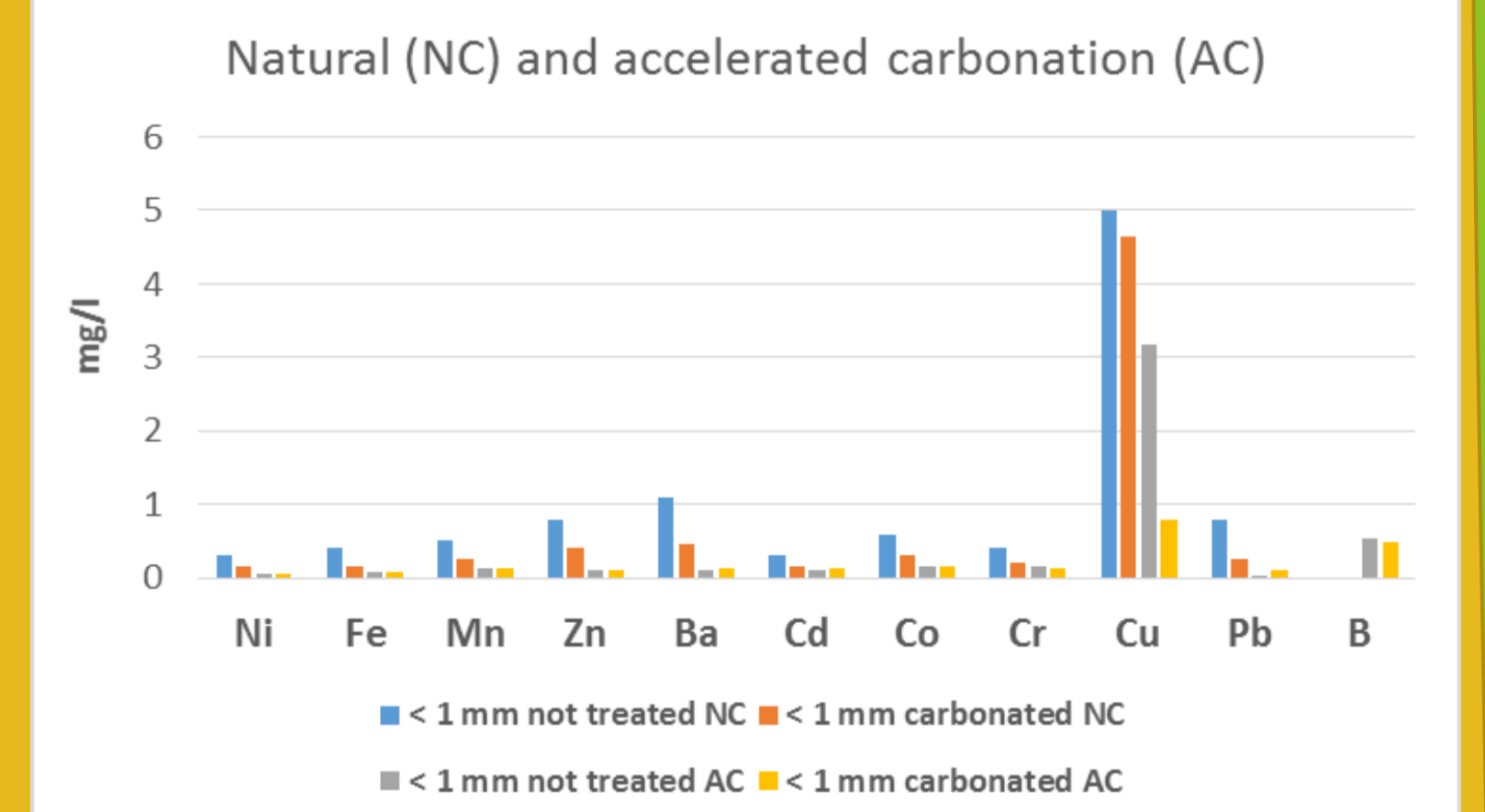
- Weight loss for BA: 6,5%
- Weight loss for BA carbonated: 11,5%
- The difference of 5% is compatible with the weight increase (measured in laboratory) after carbonation of 4-5 %

LEACHING TESTS BEFORE AND AFTER CARBONATION



Electrolytic conductivity/ time diagram of the leaching test

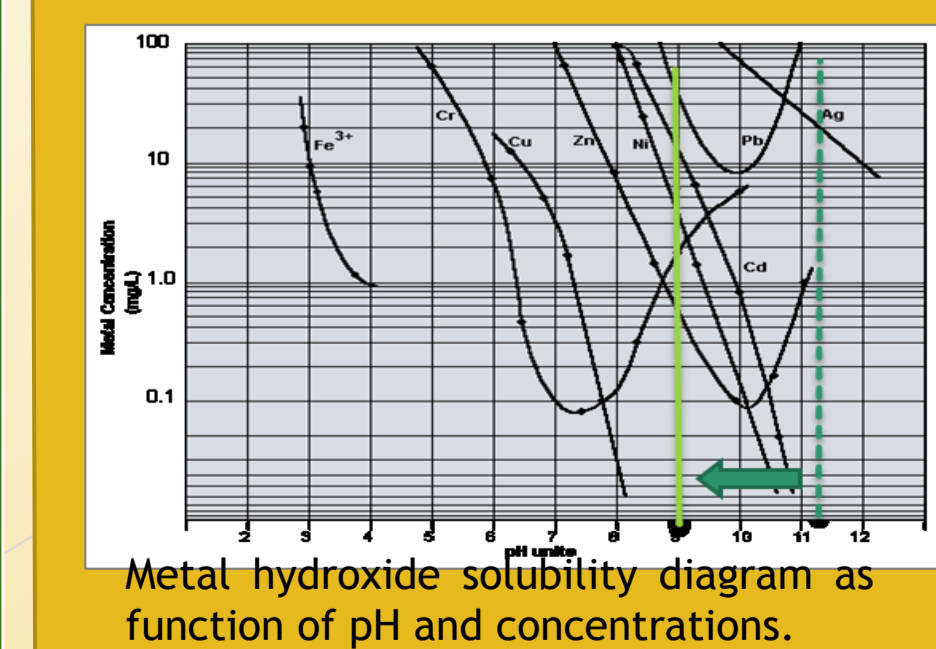
The diagram shows the difference between the samples treated with natural carbonation NC and accelerated carbonation (AC). The conductivity of the two carbonated samples are very similar. The high conductivity value of the NC sample before treatment is probably due to the presence of a very fine fraction which is reduced by the carbonation by grain agglomeration.



CONCLUSIONS

Heavy metals concentrate mainly in the finer grain size of BA (< 1 mm). The accelerated carbonation is effective in the reduction of heavy metals but requires an optimization of the parameters that influence pH in the release in the natural environment.

Removing metals from the coarser grain size of ash is essential to improve their reuse and treatments; moreover it can represent a source of metal recovery



The comparison between the leaching test after natural and accelerated carbonation show the decrease in both the situation of most of the heavy metals, especially copper, zinc, chromium, nickel and lead. In the case of natural carbonation Ni, Cr, and Pb decrease by 50%, while Cu by 7%. pH of the solution decreases, for untreated BA, from 12,5 to 11,5. In the case of accelerated carbonation, Cu decrease by 75%, while the Ni and Cr by 15%. pH decrease from 11 to 9.5. The decrease of pH to 9.5 after the accelerated carbonation strongly affects the solubilization of some heavy metals like Pb, Zn, Cd, Ni which are more soluble at lower pH.

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