Summer School: Biological and Thermal Treatment of Municipal Solid Waste

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CHARACTERIZATION OF DIFFERENT TYPES OF WASTE THERMAL TREATMENT BOTTOM ASH TO ASSESS THEIR RE-USE POTENTIAL

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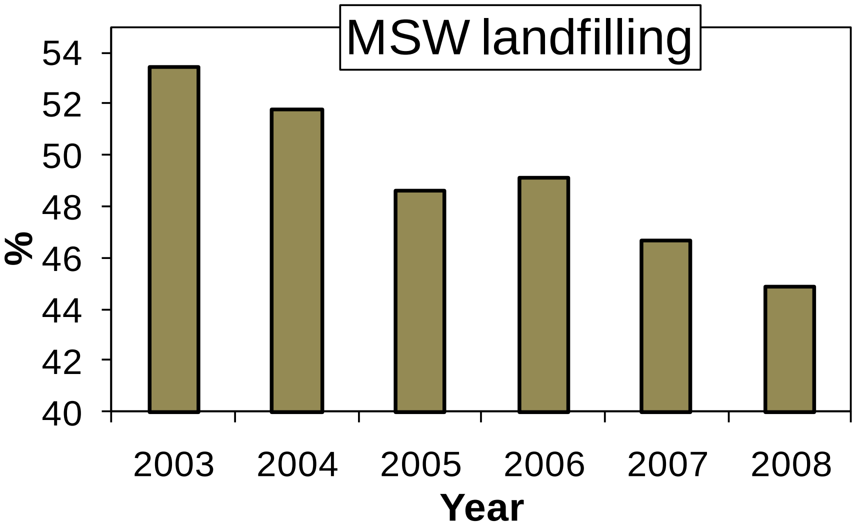
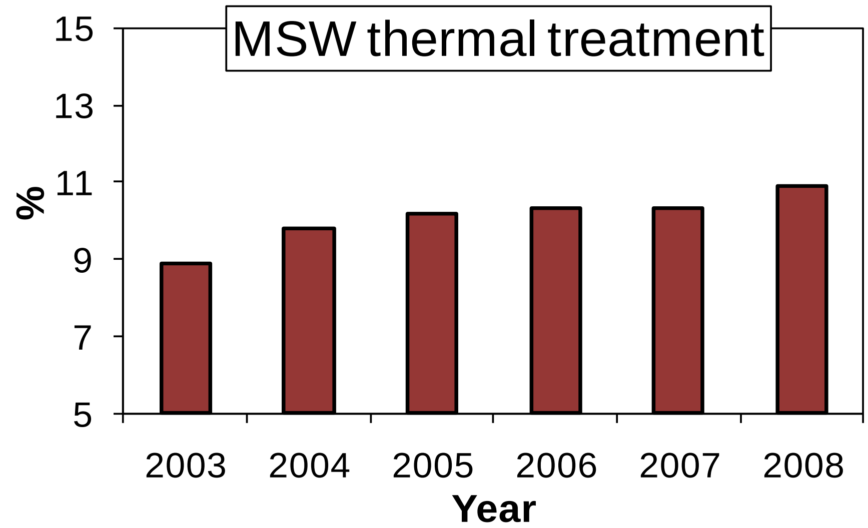
Background (1/5)

- In Italy, MSW landfilling has gradually decreased in recent years while waste thermal treatment has continued to grow (data from ISPRA, 2009)



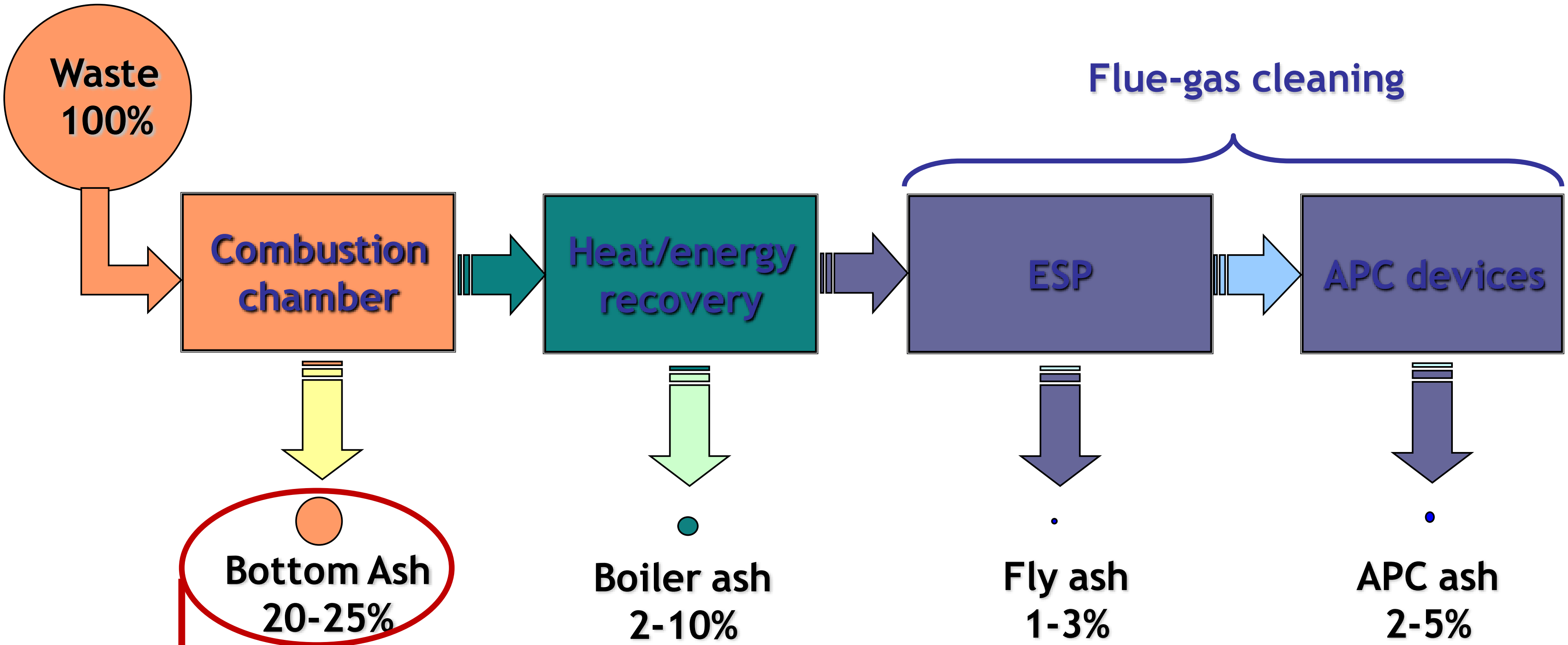


- Since more stringent air emission criteria have been established for waste thermal treatment plants, inorganic pollutants present in the original waste are increasingly transferred to the solid residues produced from these plants

- The identification of appropriate management strategies for the solid residues generated in waste thermal treatment plants could contribute in reducing the overall environmental impact of this technology

Background (2/5)

Mass balance in a typical waste to energy plant:



Main solid by-product, accounting for 60-80% by weight of the total solid residues generated in the plant

Background (3/5)

Bottom Ash (BA):

- European production: 20 Mton/y
- Main characteristics: alkaline heterogeneous slag-like mixture of glass, minerals and unburned organic matter
- Its composition depends mainly on:

  - the composition of the waste fed to the plant
  - the operational conditions (mainly the temperature) of the waste thermal treatment plant

- BA natural weathering:

Complex series of reactions that include: dissolution and precipitation of mineral phases, carbonation, sorption, oxidation, etc., that occur over long timeframes from direct exposure of BA to the atmosphere and lead to an alteration of the main physical and chemical properties of these residues

Background (4/5)

- BA reuse options:
  - aggregate substitute for construction of road sub-bases;
  - aggregate substitute in concrete or cement production;
  - filler material for construction of embankements and sound barriers

- Several European Countries (Germany, Sweden, Denmark, The Netherlands) have developed regulations aimed at encouraging BA utilisation

- Pre-treatments applied before reuse: crushing, milling, sieving, metal and aluminum recovery, washing, natural weathering, etc.

- In Italy there is no specific regulation regarding BA reuse, (the M.D. 05/02/1998 for reuse does not apply to BA). The only reuse option that has been extensively adopted is as a secondary material for cement production.

  By far the most adopted management practice is disposal in landfills for non-hazardous waste. However, with the recent decree (205/2010) that implements the EU Directive on waste 2008/98, BA is being classified as a hazardous waste as a precautionary measure due to uncertainties related to its possible classification as an ecotoxic waste (H14)

Background (5/5)

The critical parameter for BA re-use or final disposal is its leaching behaviour, i.e. the mobilization of potentially toxic elements (metals, soluble salts and organic matter) that are present in BA through contact with water

- Main factors affecting the leaching of contaminants from BA:
  - chemical composition: total availability for leaching and effect on pH
  - mineralogical characteristics: main composition and solubility of mineral phases
  - physical properties: particle size of BA (different specific surface area and contaminants dissolution kinetics)
  - weathering processes: chemical (e.g. neutralization of pH) and mineralogical (e.g. formation of secondary minerals) transformations occurring over time in contact with the atmosphere

Objectives

- For different types of **BA from waste thermal treatment plants,** analyze and compare:

  - The main **physical** (water content, grain size distribution, Loss On Ignition (LOI) at 550 °C and at 1000 °C, TGA-MS of the volatile components), **chemical** (elemental composition, anions content and acid neutralization capacity, ANC) and **mineralogical** characteristics (XRD analysis) of the BA

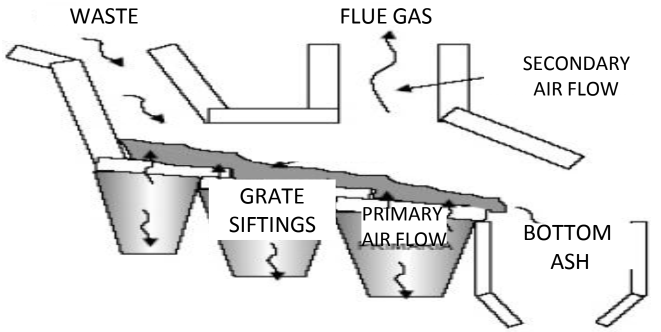
  - The **leaching behavior** of the major and trace elements at natural pH (EN 12457-2), as well as a function of pH (CEN/TS 14429)

- Evaluate the effects of 6 months lab-scale **natural weathering** on the main chemical and mineralogical properties, as well as on the leaching behavior of potentially toxic elements from each type of BA

Materials

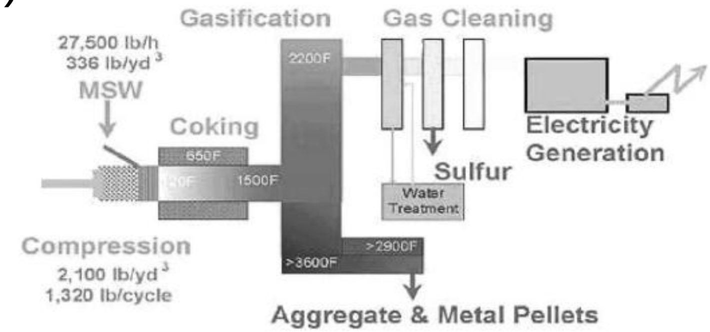
➢ BA from a refuse derived fuel (RDF) incineration plant (**RDF-I BA**):

- Grate-fired combustion chamber
- T: 850-900 °C
- BA production: 10% wt. of the RDF feed
- BA water content: 15-20% wt.



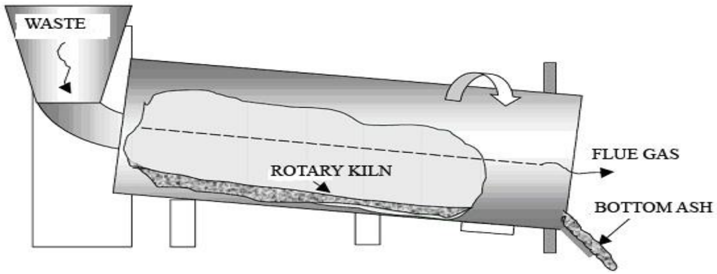
➢ BA from an RDF gasification plant (**RDF-G BA**):

- Fluidised Bed Gasification reactor
- T: 1200 - 1600 °C
- BA production: 5% wt. of the RDF feed
- BA water content: < 5% wt.



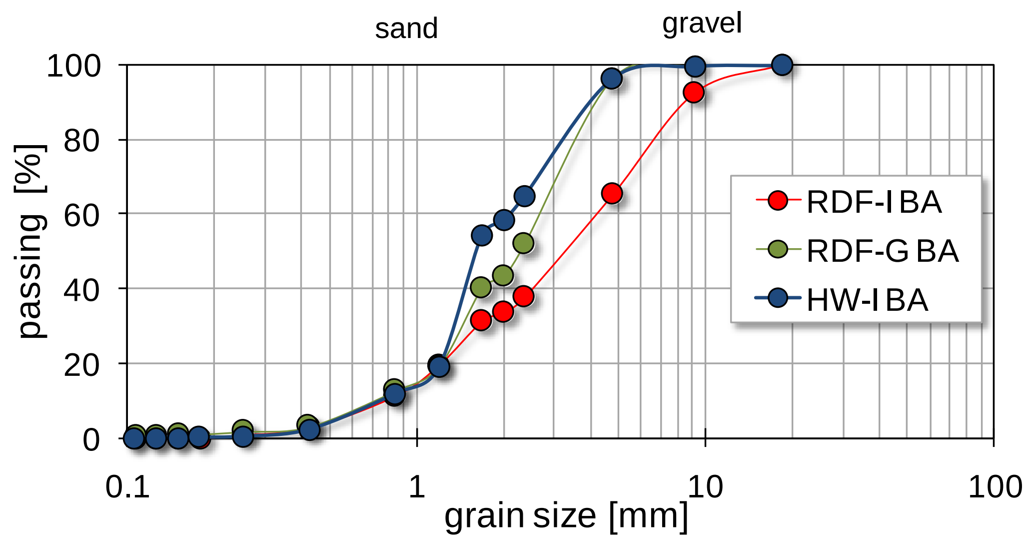
➢ BA from an Hospital waste (HW) incineration plant (**HW-I BA**):

- Rotary kiln combustion chamber
- T: 900-1100 °C
- BA production: 12% wt. of the HW feed
- BA water content: 40% wt.



BA physical characterization

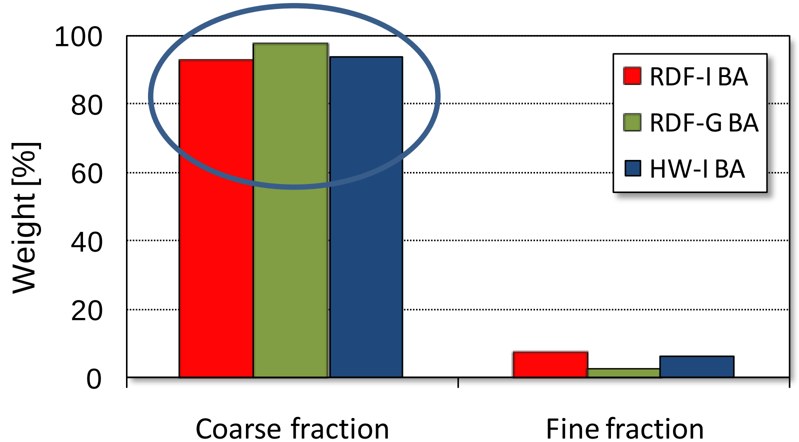
- Pre-treatment: homogenization through quartering; removing of fractions >5 cm; oven-drying at 60 °C and sieving
- Particle size distribution:



- Production of the following size fractions:

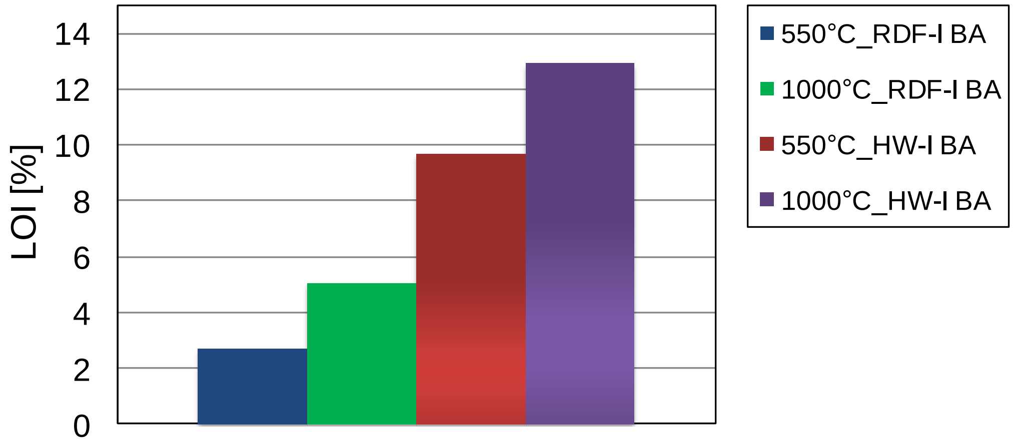
  - φ> 12 mm → *Removed*
  - φ= 12 – 0.425 mm → **Coarse fraction**
  - φ< 0.425 mm → **Fine fraction**

All the results presented hereafter are referred to the coarse fraction



BA physical characterization

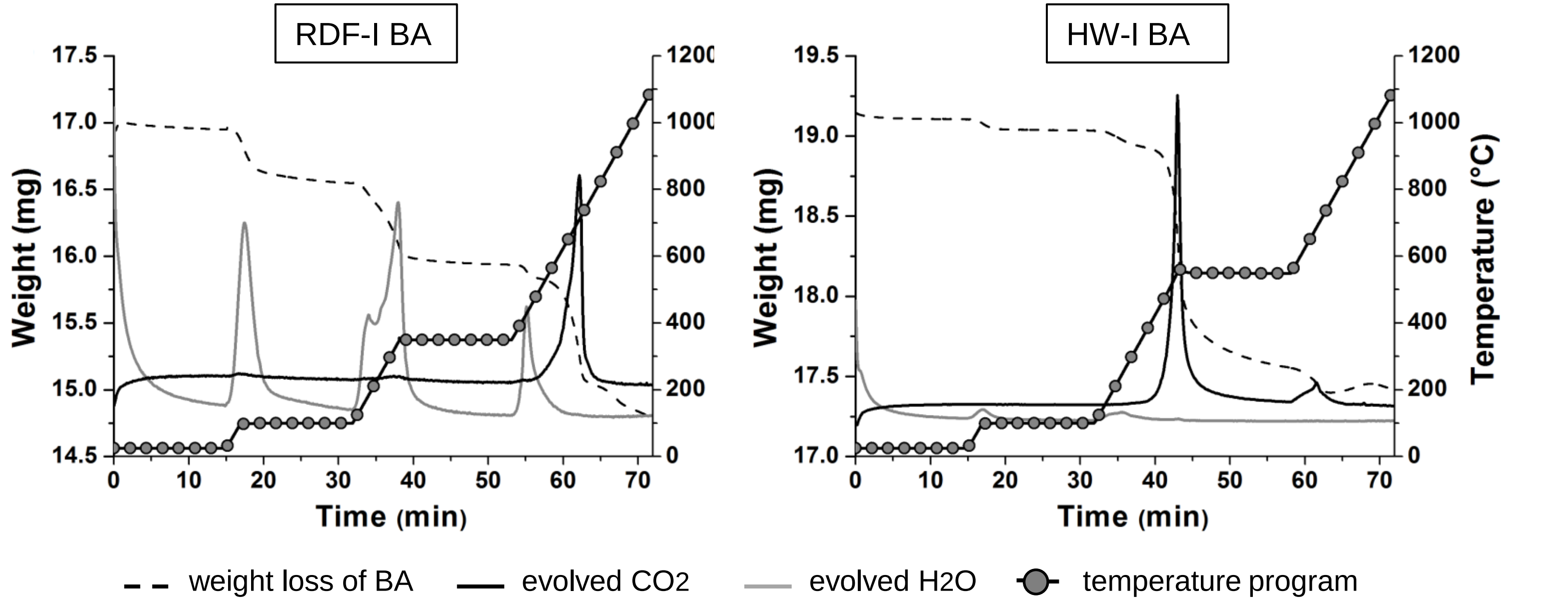
- LOI at 550 °C (UNI EN 15169) and 1000 °C (ASTM C-25):



- Higher **LOI** values **at 550 °C** were measured for **HW-I BA** compared to **RDF-I BA** possibly due to the volatilization of elemental carbon, hydrated phases or organic matter that decompose at moderate temperature
- Increases of 3-5% wt. of the **LOI at 1000 °C** were registered for both the RDF-I and the HW-I BA, possibly due to the contents of carbonates and volatile compounds with a decomposition temperature between 550-1000 °C
- No LOI at either temperature was measured for the **RDF-G BA** due to its formation at temperature > 1200 °C

BA physical characterization

- TGA-MS : thermo-gravimetric analysis coupled with mass spectrometry of the gaseous decomposition products for the interpretation of LOI



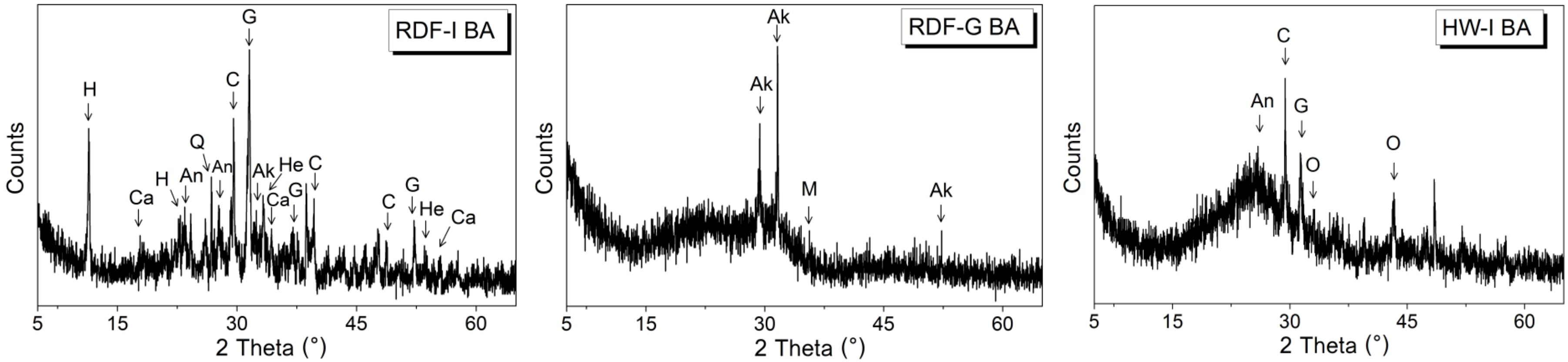
- **RDF-I BA**: significant weight loss steps due to the release of H_2O from moisture evaporation (100° C) and possibly from hydrated phases decomposition; large CO_2 peak from decomposition of carbonates

- **HW-I BA**: weight loss mainly resulted from decomposition of elemental carbon (550° C)

- **RDF-G BA**: no weight loss was registered

BA mineralogical characterization

- XRD analysis



H: *Hydrocalumite* ($Ca_4Al_2Cl_2O_6 \cdot 10H_2O$); **Ca**: *Calcium hydroxide* ($Ca(OH)_2$); He: *Hematite* (Fe_2O_3); **Q**: *Quartz* (SiO_2); **Ak**: *Akermanite* ($Ca_2MgSi_2O_7$); **An**: *Anorthite* ($CaAl_2Si_2O_8$); **G**: *Gehlenite* ($Ca_2Al_2SiO_7$); **C**: *Calcite* ($CaCO_3$); **Si**: *Calcium and magnesium silicate* ($Ca_2MgSi_2O_7$); **M**: *Magnesite* (Fe_3O_4); **O**: *Silicon and Iron oxide* (Fe, SiO_2)

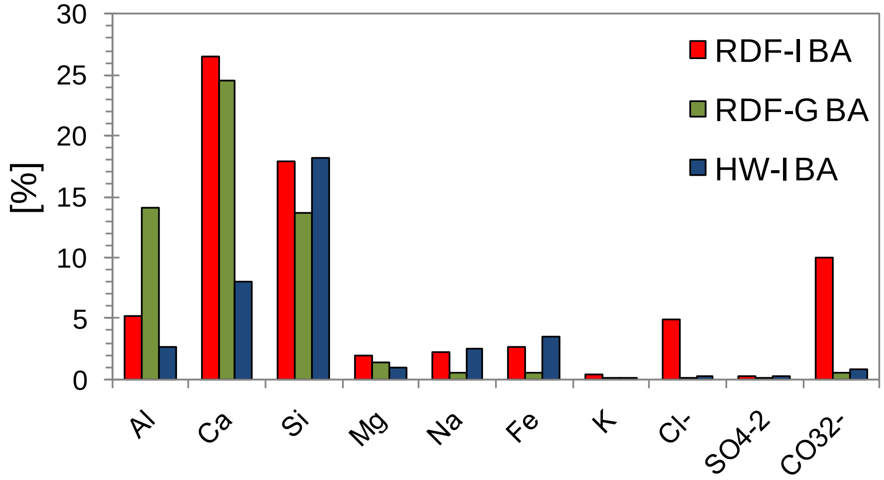
<u>RDF-I BA</u>: large variety of crystalline phases were detected, among which the most abundant corresponded to Ca and Al silicates, as well as Ca carbonate; further intense peaks corresponded to Ca and Al hydrated phases

<u>RDF-G BA</u>: mainly composed by glassy and amorphous phases, with the only detectable crystalline phases being Ca and Mg silicates and Fe oxides

<u>HW-I BA</u>: consistent glassy and amorphous phases were detected with the small amount of crystalline phases being Ca and Al silicates, Ca carbonate, as well as Si and Fe oxides

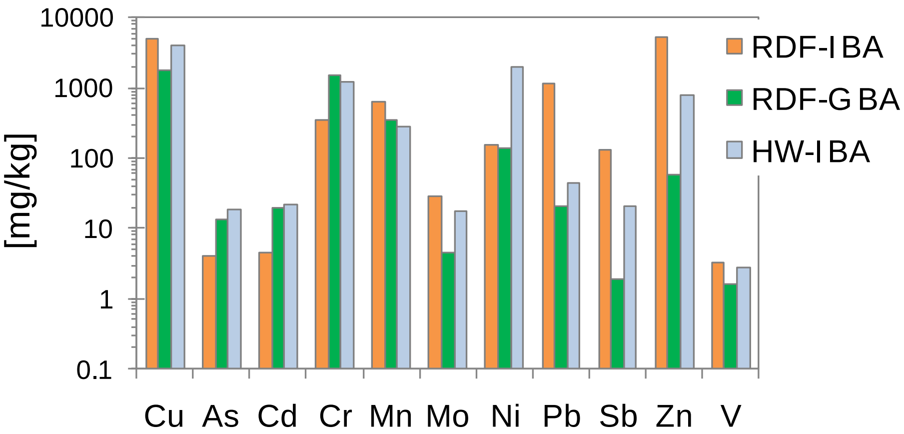
BA chemical composition

❑ **Major elements** (% dry wt.)



- **Ca** content is fairly similar for both the RDF-I BA and the RDF-G BA possibly depending on the characteristics of the RDF fed to the plants
- **Si, Al** and **Mg** content were retrieved in similar concentrations for the three BA samples (apart from the higher content of Al for RDF-G BA)
- High concentration of $\mathbf{Cl^-}$ and $\mathbf{CO_3^{2-}}$ were measured for RDF-I BA, while for RDF-G and HW-I BA the higher temperature formation of the ash possibly volatilised these components

❑ **Trace elements** (mg/kg dry wt.)



- Significant contents of **Cu** and **Cr** (around 1 g/kg) were measured for each type of BA
- Higher **Pb** and **Zn** were measured for RDF-I BA possibly depending on the lower temperature formation of this ash compared to the other samples
- HW-I BA was enriched in **Ni** that might be related to the characteristics of the medical waste materials

BA leaching properties (1/4)

- Compliance leaching test at natural pH (EN 12457-2)

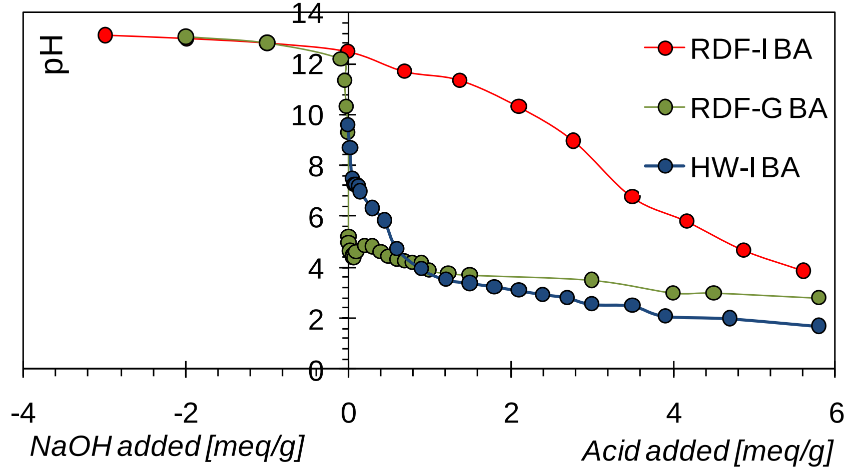
Parameter	RDF-I BA	RDF-G BA	HW-I BA	EU LFD			Italian Reuse
				Inert	non-Hazardous	Hazardous	
pH	12.39	9.3	9.97	–	–	–	5.5 - 12
As	0.001	0.003	0.002	0.5	2	25	0.5
Cd	< 0.02	< 0.02	< 0.02	0.04	1	5	0.05
Cr	0.129	0.099	0.037	0.5	10	70	0.5
Cu	**2.60**	0.19	0.23	2	50	100	0.5
Mo	0.225	0.039	0.180	0.5	10	30	–
Ni	0.111	0.032	0.022	0.4	10	40	0.1
Pb	**3.15**	0.17	0.077	0.5	10	50	0.5
Sb	**0.539**	0.013	**0.073**	0.06	0.7	5	–
V	0.167	< 0.04	< 0.04	–	–	–	2.5
Zn	**4.52**	1.05	1.08	4	50	200	30
Chlorides	**5726.1**	228.7	426.9	800	15000	25000	1000
Sulfates	55.4	21.9	627.8	100(	20000	50000	2500
DOC	32.4	3.9	4.5	500	800	1000	300

EU LFD: European Landfill Acceptance criteria (2003/33/EC); Italian reuse: Reuse Limits for non Hazardous waste (M.D. 05/02/1998) . All concentration values are expressed in mg/kg BA

- **RDF-G BA**: complied with both the limits for inert waste landfilling and for re-use
- **HW-I BA**: complied with the limits for re-use but, since Sb slightly exceeded the limit for inert waste landfills, should be disposed of in non-hazardous waste landfills
- **RDF-I BA**: given its high alkaline pH, significant leaching of metals (Cu, Pb and Zn) was found; further chloride release showed to limit the re-use potential of BA which can be accepted at landfills for non-hazardous waste

BA leaching properties (2/4)

❑ Acid/Basic Neutralization Capacity (ANC/BNC) (CEN/TS 14429): information on pH conditions imposed by external influences

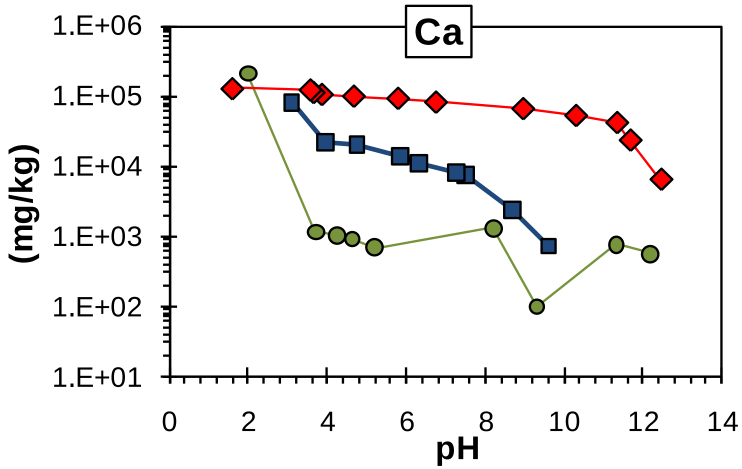


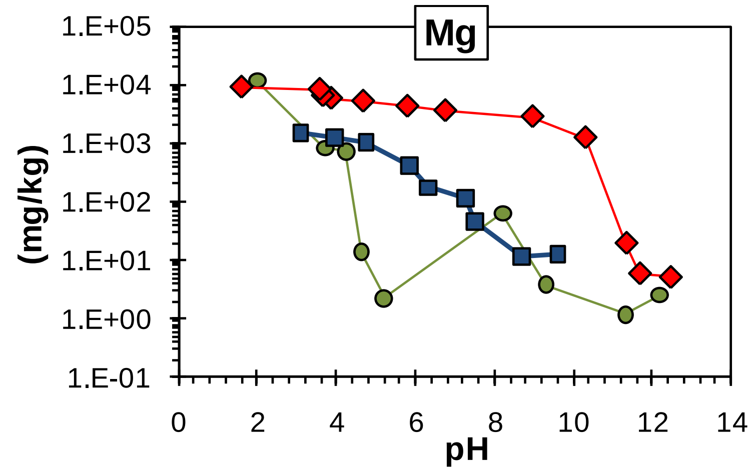
• **RDF-I BA**: a significant ANC was found which may be attributed to the large amount of crystalline phases, namely: Ca carbonate, as well hydrated compounds with relevant buffering properties at alkaline conditions, in accordance to XRD and TGA-MS results

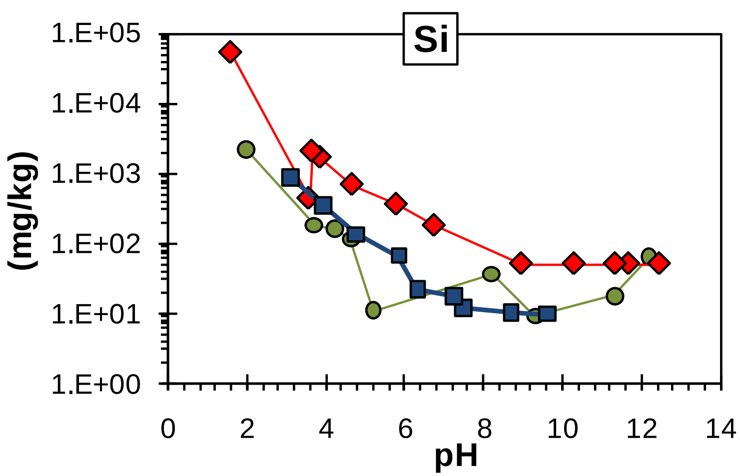
• **RDF-G and HW-I BA**: low level of ANC was measured as pH rapidly dropped; these results might be related to the lack of alkaline phases with buffering capacity and the abundance of amorphous-glassy phases in these types of BA, as detected by XRD and TGA-MS

BA leaching properties (3/4)

- Leaching properties as a function of pH (CEN/TS 14429) - Major components



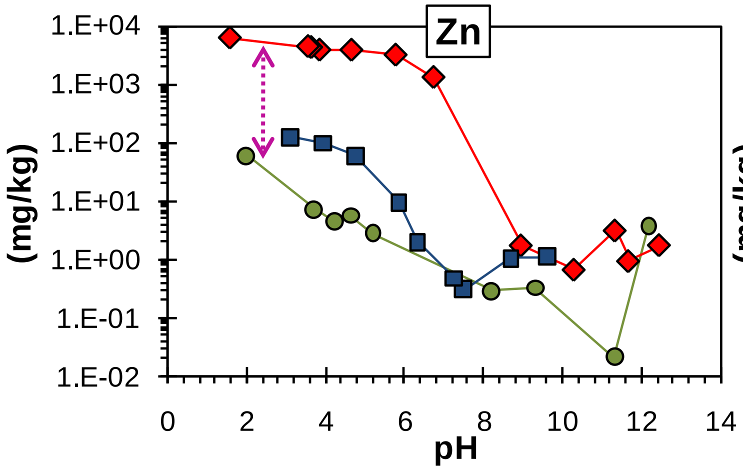


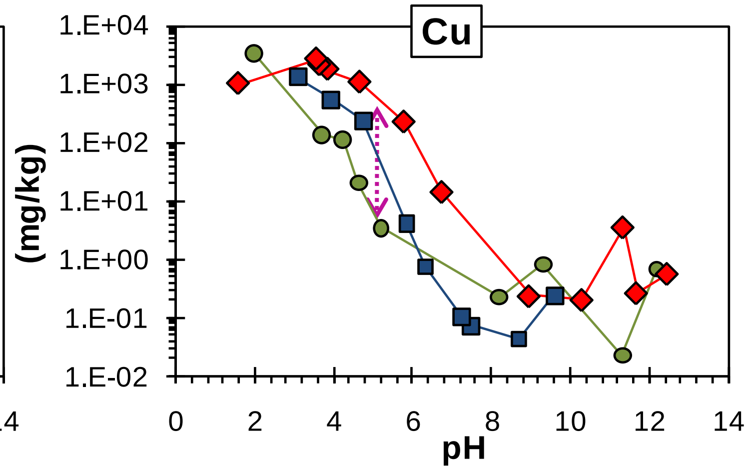


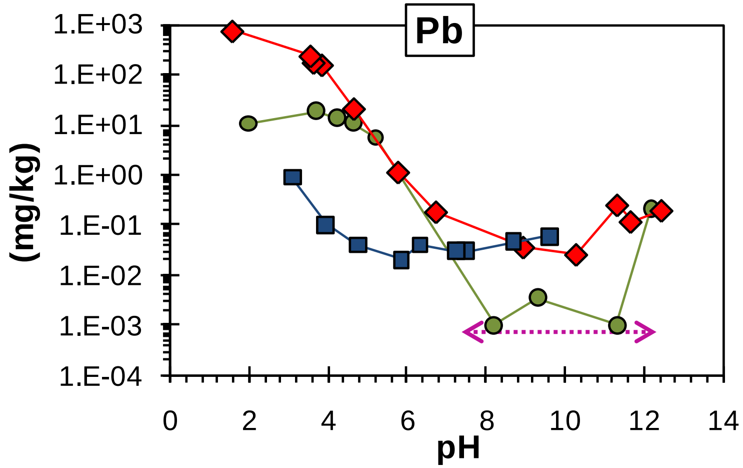
- **Ca and Mg:** lower leaching was measured for **RDF-G BA and HW-I BA** compared to the **RDF-I BA,** over the pH range >4 due to their different mineralogical composition, solubility of minerals and availability of these elements for leaching.
- **Si:** lower leaching for **RDF-G BA and HW-I BA** compared to **RDF-I BA** was found almost over the entire pH range that could be related to its low availability for leaching.

BA leaching properties (4/4)

- Leaching properties as a function of pH (CEN/TS 14429) - Trace contaminants







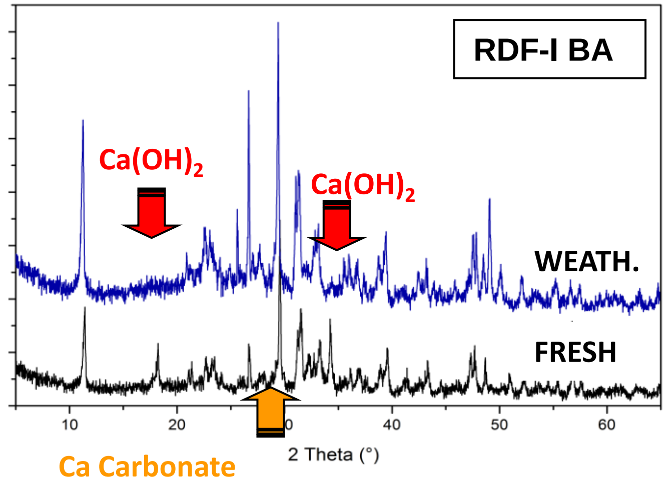
• **Zn:** lower leaching was measured for **RDF-G BA and HW-I BA** compared to the **RDF-I BA,** almost over the entire pH range, possibly due to its low availability.

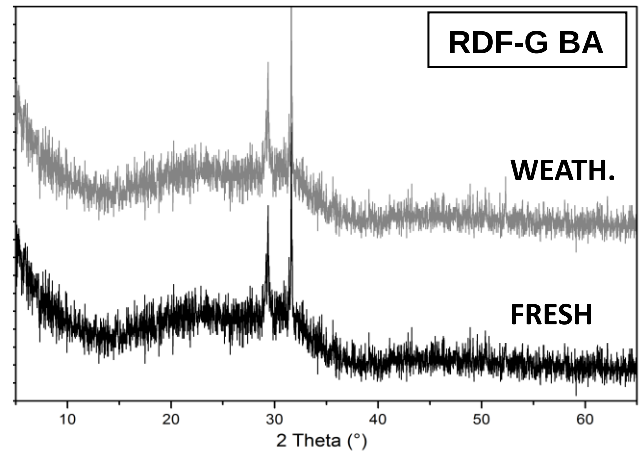
• **Cu:** lower leaching was found for **RDF-G and HW-I BA** compared to **RDF-I BA** mainly at pH 4-8.

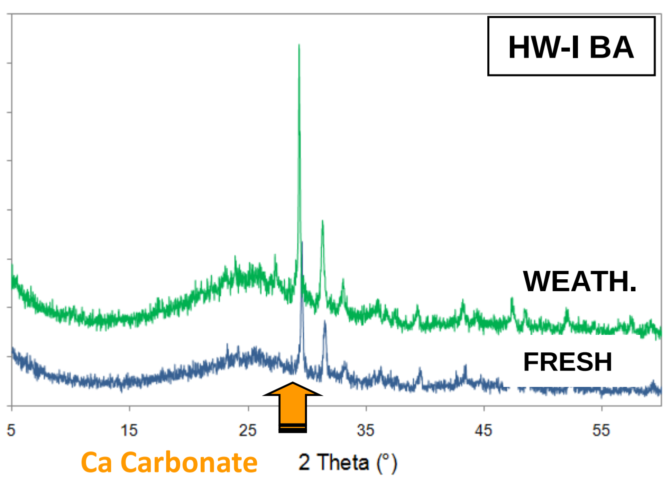
• **Pb:** lower leaching for **RDF-G BA** was found at pH 8-12 compared to the other samples; while under acidic conditions **HW-I BA** showed lower concentrations than those of the other samples.

Effect of weathering (1/3)

- Mineralogical composition (XRD)





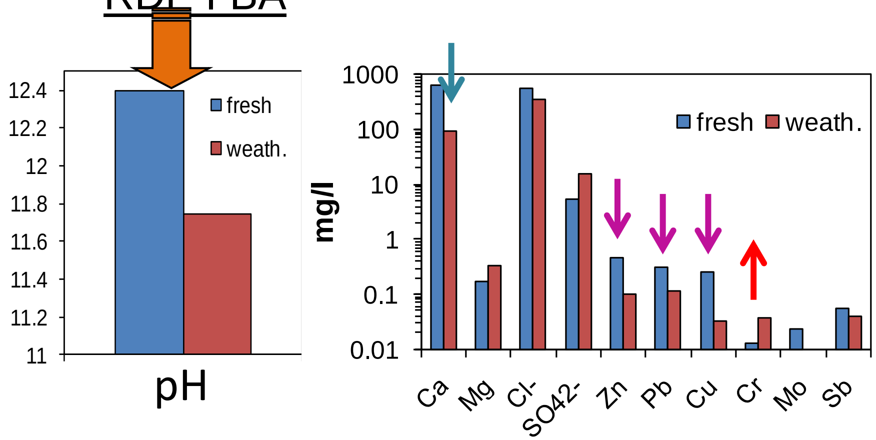


- <u>RDF-I BA</u>: decrease of **calcium hydroxide** and increase of **Ca carbonate** as a result of carbonation ($Ca(OH)_{2(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O$) under atmospheric conditions
- <u>RDF-G BA and HW-I BA</u>: No significant differences were detected (apart from an increase of Ca carbonate in HW-I BA) as these samples mainly contained glassy phases

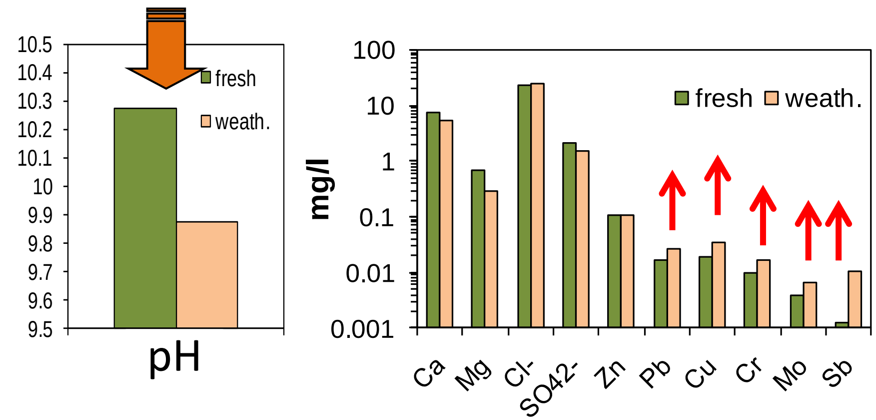
Effect of weathering (2/3)

- Compliance leaching test at natural pH (EN 12457-2)

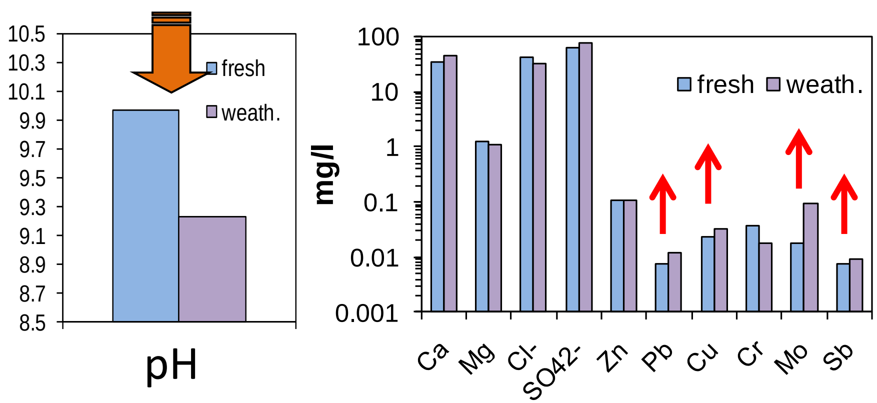
• RDF-I BA



• RDF-G BA



• HW-I BA

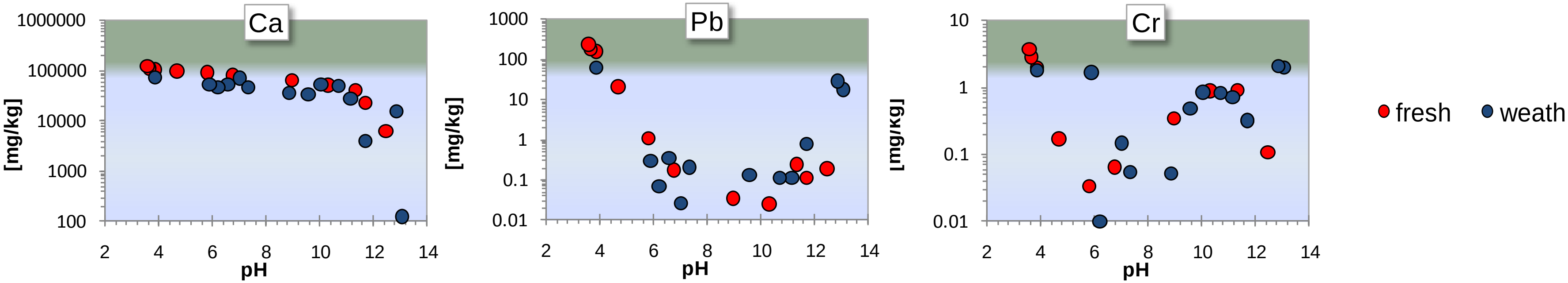


•**RDF-I BA**: significant reduction in the mobility of metals (mainly Cu) as an effect of the decrease of pH and Ca leaching (possibly due to carbonation of BA). Slight increase of Cr and SO_4^{2-}. Leaching values still above the limit for re-use and inert waste landfilling

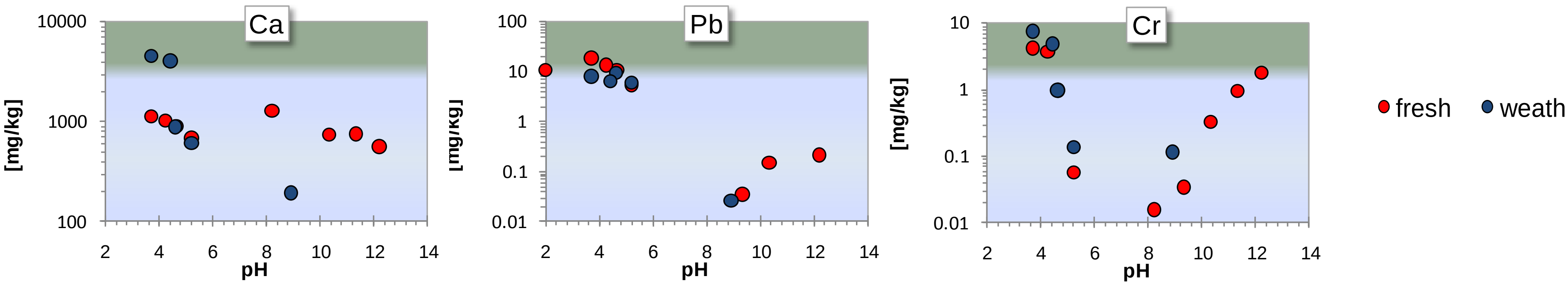
•**RDF-G BA and HW-I BA**: slight increase of metals (e.g. Pb) as an effect of the decrease in pH. Slight increase of oxyanions forming metals (e.g. Sb and Mo) although eluate concentrations remained below the limits for re-use of non hazardous waste

Effect of weathering (3/3)

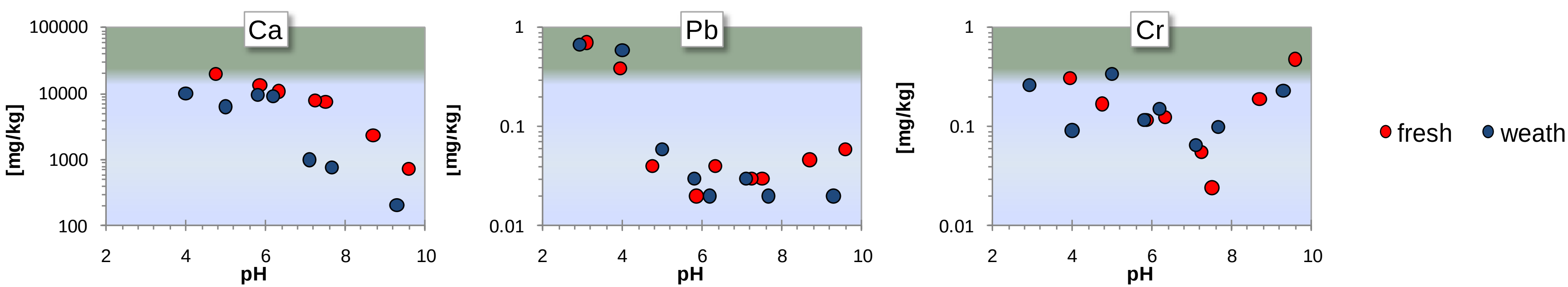
- RDF-I BA



- RDF-G BA



- HW-I BA



Conclusions

- This work, focusing on **RDF-I, RDF-G** and **HW-I bottom ashes**, indicated that the operational conditions (i.e. temperature) of the waste thermal treatment have a great influence on total content of major and trace components, mineralogy, as well as leaching of the produced BA

- **RDF-G BA and HW-I BA**, showed high re-use potential, due to the lower leaching of contaminants from the glassy matrix at natural pH (around 9-10) (compliance leach. test).

- Natural weathering modifies the mineralogical and chemical properties of the **RDF-I BA**. Results mainly showed decrease in pH and, consequent decrease of metals leaching (e.g. Pb), as well as increase of oxyanion forming metals (e.g. Cr).

Ongoing work

- **Geochemical modeling**: study of the leaching mechanisms and processes occurring in BA; prediction of long-term risks (migration and/or bioavailability) from BA re-use or disposal and improvement of the quality of this residue

- **TGA-MS measurements**: evaluation and interpretation of the weight losses of the different types and size fractions of BA at specific temperature steps

Implications for future research

- **Percolation column tests (lab-scale and full-scale measurements)**: assessment of the short-term leaching behaviour of this waste material in disposal or re-use scenarios

- Study of the **Technical properties** and **leaching behaviour** of BA (mainly for RDF-G samples due to the lack of information) relevant for its re-use applications, e.g. in concrete production