Study of pre-treatments of fly ashes aimed to the mineralogical reuse as construction materials: chemical and characterization

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INTRODUCTION

The **management of waste** and its **sustainable reuse** is one of the most important concern in our society in recent years, together with the increasing need to find primary materials without resorting to new extraction of resources. In this context, the thermovalorization of municipal solid waste (MSW) is currently the method that is spreading and replacing landfill disposal; the thermal treatment allows to reduce the volumes significantly, producing energy and returning **bottom ashes (BA) and fly ashes (FA)** in the measure of 20% and 5% of the total waste respectively. The MSW incineration BA are classified as non-hazardous waste and can be reused as a raw material after some physical-chemical treatments 4]. [The **FA**, on the contrary, **are classified as hazardous waste** and according to current legislation, they are usually subjected to vitrification treatments and stored in dedicated landfills; the hazard is due to the high content of soluble salts (chlorides and sulphates) and heavy metals (mainly Zn and Pb). Therefore, for their possible reuse as construction materials [3], [4, [6], [8]. (e.g. ceramic, cement, concrete aggregates) or base roads [5], **a preliminary stabilization step is required** which often **requires the use of significant quantities of energy**.

In the present work, **low energy cost methods are considered to reduce the dangerousness of FA** and consequently make them more easily treatable for their reintegration into the production cycles.

Among the methods, **washing of FA with water is examined**, to find the lowest L/S ratio in the reduction of salts and heavy metals, analysing the dissolution kinetics and the mineralogical content of fly ash before and after each washing treatment.

For a better definition of the kinetics, the FA are previously submitted to particle size separation to understand in which fractions the most dangerous substances are concentrated. Washing treatments can be useful **to remove or reduce soluble salts**, in particular chlorides, by using a different *liquid/solid* (L/S) ratio, in order to obtain a more suitable material for the solidification / stabilization treatments carried out by geopolymerization or in cement. The **eluates of washing** are also taken into consideration to evaluate the **recovery of elemental species** of interest **and** the **purification of the liquid phase with biochar**.

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MATERIAL AND METHODS

Sample FA51

Preliminary Characterization
- Presence of Organic Compounds
- Particle Size Analysis
- Mineralogical Analysis
- Reactivity

Characterization of the release in dissolution
- Leaching test: kinetics and effects
- L/S ratios

Characterization of Treated Material
- Mineralogical Analysis
- Chemical Analysis

Test on Treated Material
- Reactivity
- Treatments of residual washing water

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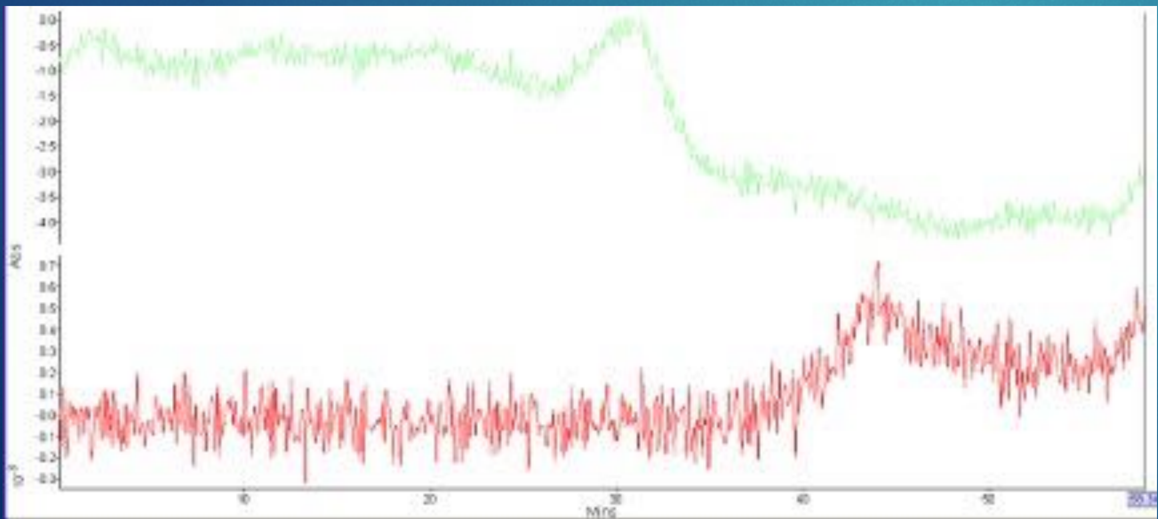
MATERIAL AND METHODS

TGA + FTIR analysis research of secondary organic compounds generated by not optimal combustion processes.

The presence of such compounds (e.g. dioxins and furans) would make the treatment very difficult.



Analysis parameters: heating in an inert atmosphere from 35 to 900 °C; this temperature was maintained for 15 minutes in an oxidizing atmosphere (N_2/O_2 ratio 3: 1).

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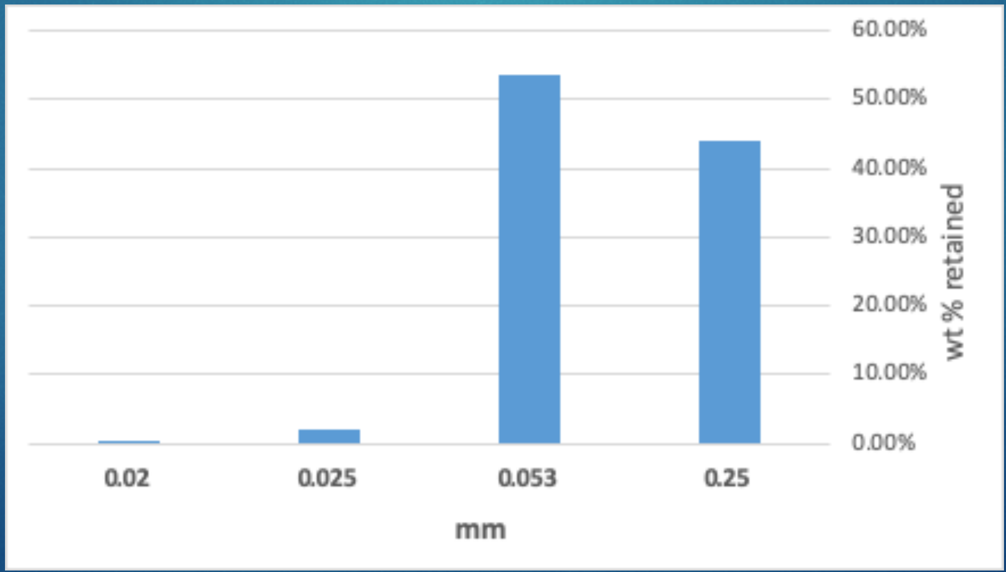
MATERIALS AND METHODS

Particle Size Analysis

The FA51 sample was subjected to granulometric analysis for its dimensional characterization, the purpose of the approach was to evaluate any relationship between composition and size. Four sieves were used to define the average size of the FA. More than 50% by weight of the analysed sample falls in the class between 0.025 and 0.053 mm.



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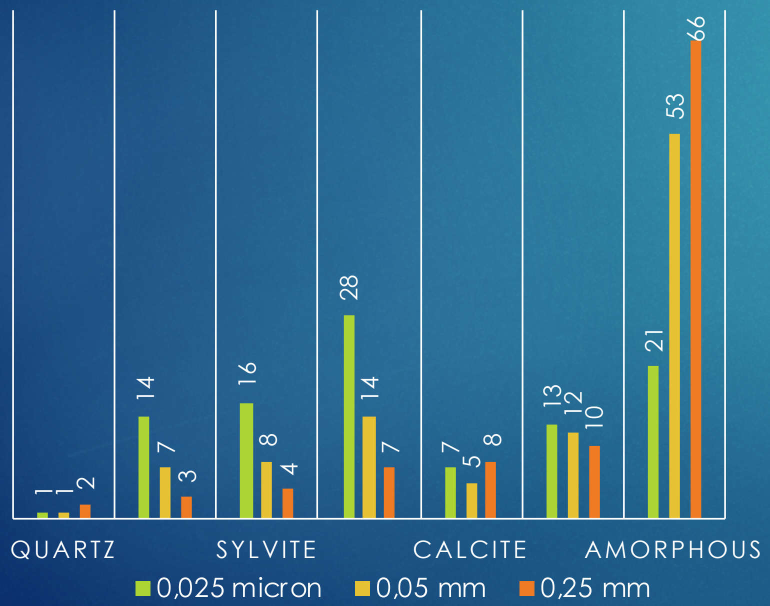
MATERIALS AND METHODS

Mineralogical Analysis

The sample was analyzed in XRD analysis using a Rigaku Miniflex system to define the main mineralogical phases that make up the particle size fractions.



FA are mainly made up of phases with an alk-chloride and Ca-alk-sulfate chemistry; subordinately from CaCO3 and quartz. In particular in fig. the mineralogical phases are reported in detail and it is observed that in the finer fractions, the mineralogical phases defined at the expense of the amorphous fraction increase; among these in particular Halite and Sylvite for chlorides and Syngenite for sulphates. Less notably, an increase in Calcite and Anydrite is observed. Quartz is slightly more abundant in the fraction> 0.25 mm.

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MATERIAL TREATMENTS

Water Washing

The water washing was tested at different L/S ratios in order to define the value corresponding to the maximum efficiency. Experiments were carried out with values of the L/S ratios between 2 and 50 to evaluate the kinetics of the dissolution reaction. FA samples were dissolved in ultrapure water.

The indicator parameters taken into consideration were the electrolytic conductivity of the solution and the weight loss detected on the residual FA sample.

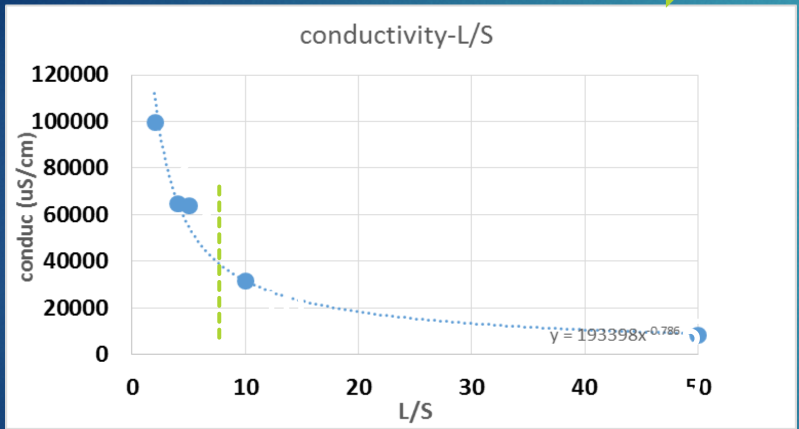
The table shows the quantities of FA used for the washing tests.

$V(H_2O)/m(FA)$	L/S
100 ml/2 g	50
100 ml/10 g	10
100 ml/20 g	5
100 ml/25 g	4
100 ml/50 g	2

MATERIAL TREATMENTS

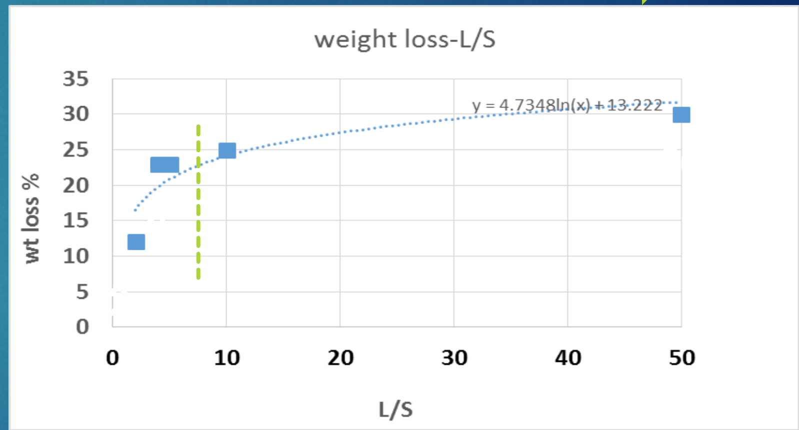
Leaching tests: reaction kinetics as a function of electrolytic conductivity and weight loss

2 Increasing L/R ratio 50



The conductivity values of the solutions range from 100 mS for lower L/S to 8.5 mS for higher L/S.

2 Increasing L/R ratio 50



The (%) weight loss values measured on the solid residues range from 12% for lower L/S to 30 for higher L/S.

The most suitable L/S range for the dissolution of the FA is therefore between 5 and 10. With L / S> 10, the use of water is too high compared to the amount of dissolution detected.

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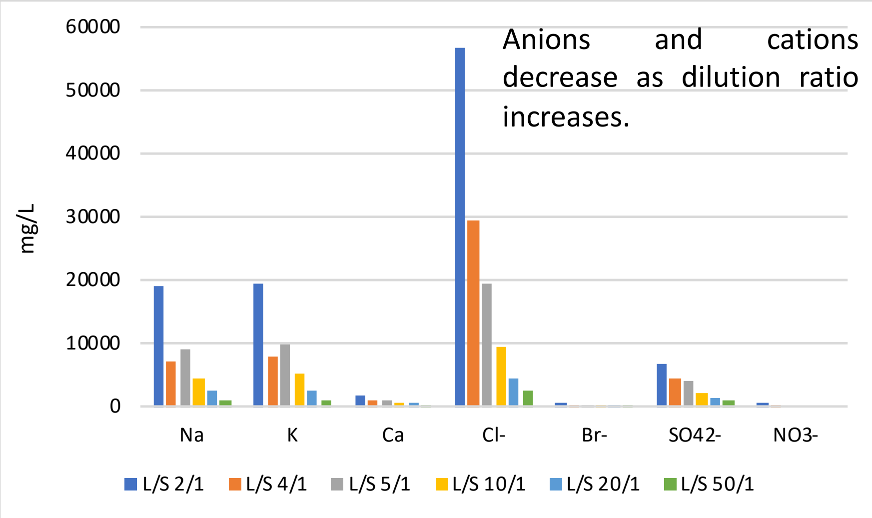
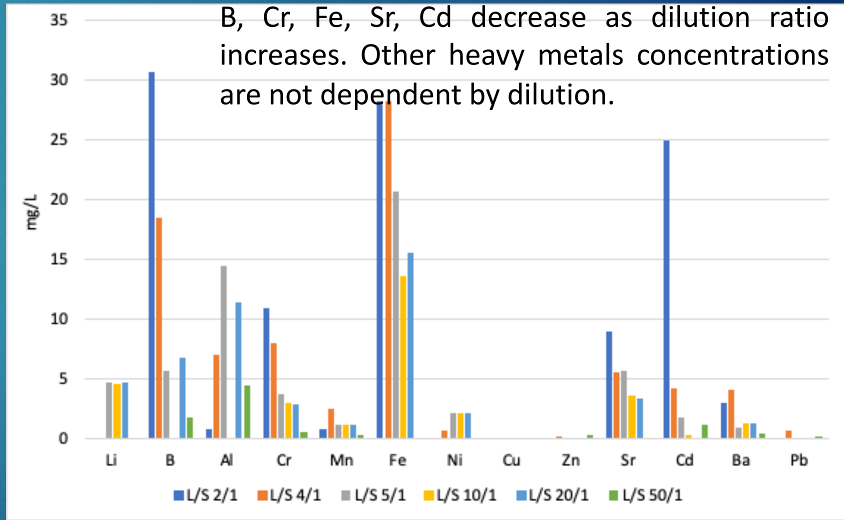
MATERIAL TREATMENTS

Fly ashes leaching chemical composition: results of the leaching test at different dilution ratios

2 Increasing L/R ratio 50



2 Increasing L/R ratio 50



The most suitable L/S range for the decrease of chlorides and sulfates is between 5 and 10. With L / S> 10, the use of water is too high compared to the amount of dissolution detected.

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MATERIAL TREATMENTS

XRD results after leaching test: analysis of residual phases at different L/S

Untreated fly ashes	L/S=2	L/S=4	L/S 5	L/S=10	L/S=20	L/S 50
Amorphous	Amorphous	Amorphous	Amorphous	Amorphous	Amorphous	Amorphous
Halite	Halite					
Anidrite	Anidrite	Anidrite	Anidrite	Anidrite	Anidrite	Anidrite
Syngenite	Syngenite	Syngenite	n.d.	n.d.	n.d.	n.d.
Sylvite	Sylvite	n.d.	n.d.	n.d.	n.d.	n.d.
Calcite	Calcite	Calcite	Calcite	Calcite	Calcite	Calcite
Quartz	Quartz	Quartz	Quartz	Quartz	Quartz	Quartz

KCl and NaCl are not detected by XRD in the residual solid with a ratio > of L/S 4.

The amorphous decreases from L/S 2 to 20 Syngenite

MATERIAL TREATMENTS

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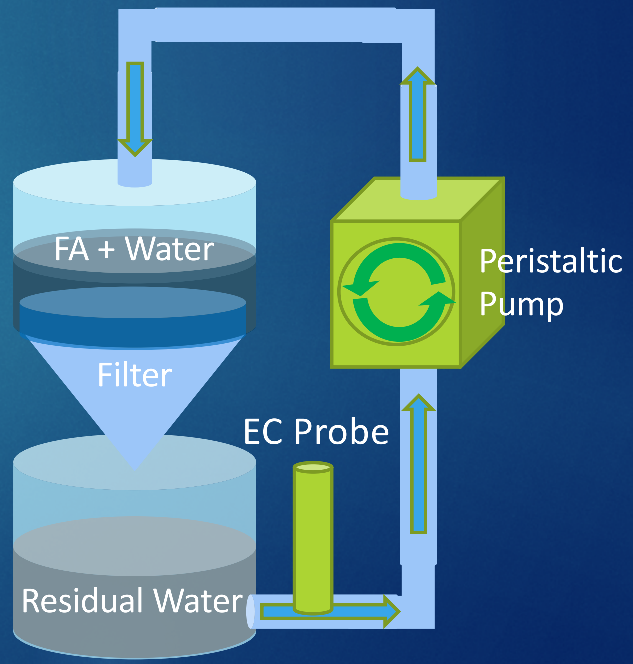
Washing Treatment: (L/S 10 = 5 mg fly ash/50 mL deionized water), 15 minutes

In this test fly ashes are washed in 5 steps. After the first step water has been reuse for the next washing step without any addition of volume. Total time: 15 min.

step	conductivity	total filtered volume (from 50 ml)
1	36200	45,2
2	34600	43,9
3	35000	43,4
4	35000	42,4
5	35000	41,1

L/S 10 at the step 1; L/S 8 at the step 5: no water volume added. Final volume of residual water: 41 ml.

The treatment system allows the water to recirculate.
The electrolytic conductivity of the residual water is measured at the end of each wash and is brought back into the tank in contact with the FA with a peristaltic pump for a new wash. The treatment ends when there are no increases in EC value.



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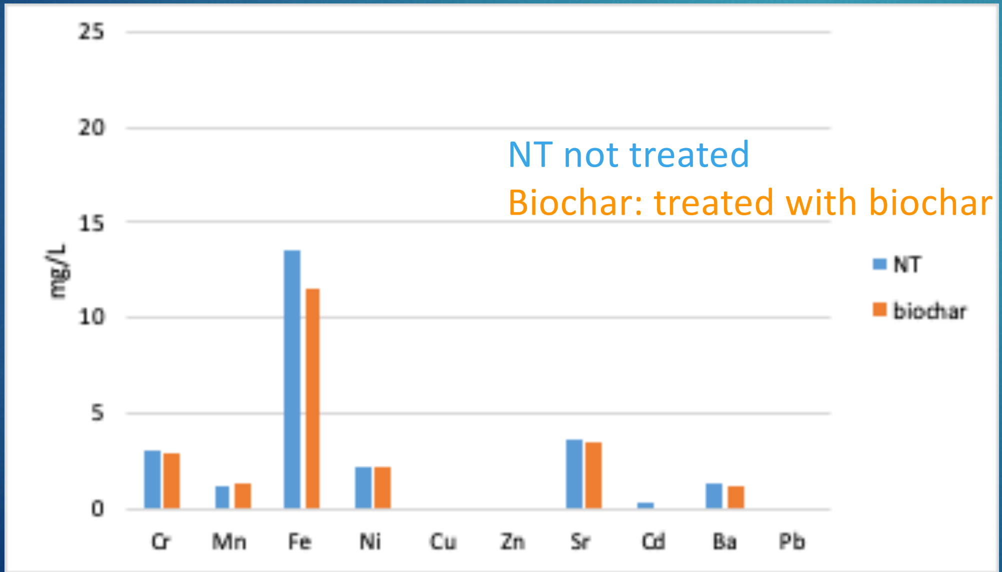
TEST ON TREATED MATERIAL

Residual water purification: addition of BIOCHAR

Vegetal biochar was mixed to fly ashes leachates in a ratio 4:1 mixed into the solution for 24 h and then filtered. The reduction is very effective on Cd. A 20-30% reduction of chlorides and sulphates occurs, too.



This study is still in progress, using different ratios of liquid/ biochar

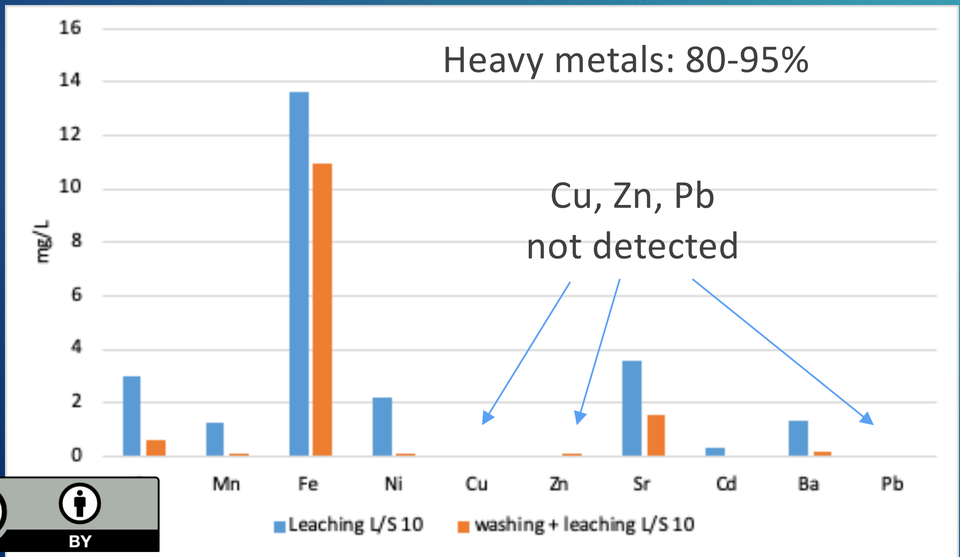
TEST ON TREATED MATERIAL

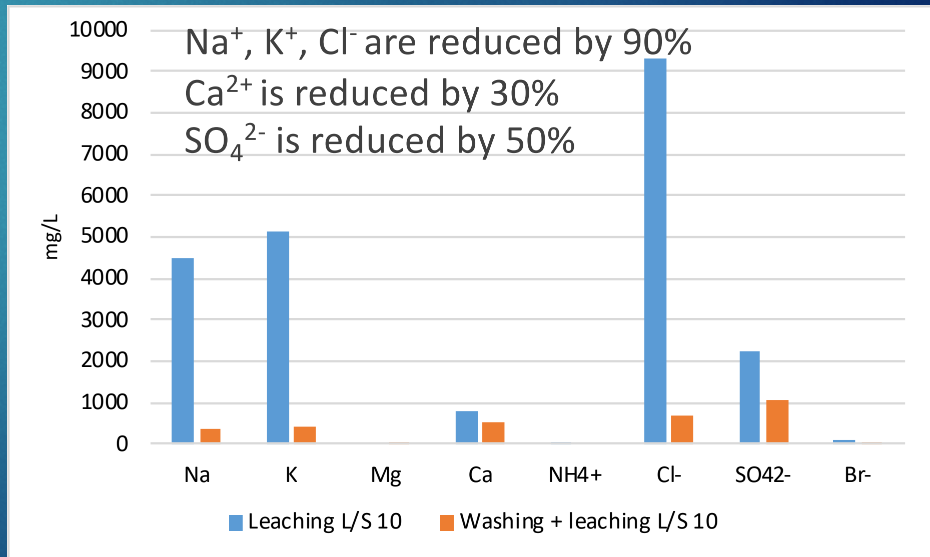
Heavy metals and anions concentrations after washing treatment + leaching test L/S 10

Fly ashes were submitted to leaching test after the washing treatment

Before treatment: blue **After washing: orange**

XRD tests after the washing test + leaching test are not available because of the stop caused by the COVID19...





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TEST ON TREATED MATERIAL
treatment products on FA material

Treatment products on FA material

SOLID RESIDUE
80 % *(wt)* after washing

- **STABILIZATION**
- **GEOPOLYMERIZATION**
- **CEMENTS**

LIQUID RESIDUE

High concentrations of chlorides and sulphates; biochar added to the solution **can reduce** heavy metals as **Cd** by 100%
Less effective on Cr and Ni reduction. Cu, Pb, Zn not detected.

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Solid Residue: applications

The solid residue of fly ashes after a washing treatment shows a lower content of anions and cations (chlorides, sulphates, Na^{+}, K^{+}, Ca^{2+}, and some heavy metals). The presence of soluble salts (e.g. chloride and sulphates) is especially important for the reuse of fly ash as construction aggregates because it could have a negative impact by decreasing the mechanical properties of concrete and causing corrosion [1], [2], [3] .

After the treatment fly ashes residues can be applied for:

- Cements [5], [6]
- Geopolymerization [7]
- Civil engineering applications, as roads, embankment…
- Brick and construction materials [8]

Results and discussion

Washing treatments can be useful to remove most of the soluble salts and main heavy metals from fly ashes:

- The residual solid after leaching has a wt % from 15% to 20% depending to the leaching ratio of water/ solid

- After a leaching test with a ratio of L/S=4 NaCl and KCl are not detected by X-Ray diffraction in the solid residues. Soluble salts and heavy metals significantly decrease.

- The washing treatment with L/S 10 is required to reduce leaching concentrations up to 95% for chlorides and 50% for sulphates. Cr, Ni, Cd significantly decrease.

- Waste water can be treated by the mixing or filtration with biochar (the study is in progress) which reduces heavy metals like Cr, Cd, and Mn.

- The residual solid can be reused for civil engineering applications and construction materials.

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