

Benefits of pre-treatments on MSWI fly ash before the alkali-activation

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Keywords: fly ash; electrodialytic treatment; alkali-activation; leaching

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Municipal solid waste incineration fly ashes (MSWI FA) are classified as hazardous wastes for the high content of heavy metals and soluble salts and their risk of leaching. Nowadays fly ashes are usually collected in hazardous waste disposal sites, but a new possibility is to inertize and eventually recycle them inside construction materials. Geopolymer is an alkali-activated material, belonging to the class of inorganic polymers, and it can be a potential material for this purpose for its environmental properties as low production temperature, lower CO₂ emission compared to cement and for its natural capacity to entrap the heavy metals physically and chemically inside its matrix. However, to improve the properties of the MSWI FA as a raw material for geopolymer, different pre-treatments to reduce the amount and the leaching of metals and salts could be beneficial.

The aim of this study was to investigate how an electrodialytic treatment and a water-washing procedure compared to no pre-treatment of the MSWI FA influenced the environmental and mechanical stability of a metakaolin-based geopolymer.

The fly ash used in this project originated from the Amager Bakke incinerator plant of Copenhagen after the electrostatic precipitator and before addition of flue gas treatment products. The binder used for the alkali-activation was metakaolin (commercial name Argical 1000). The electrodialytic experiment, aiming to reduce the content of heavy metals and salts from the ash, had a duration of 28 days, in a three-compartment cell treating a MSWI FA suspension with L/S of 3.5 and a constant current of 50 mA. For the washing experiment a L/S of 3 and an extracting time of five minutes were used. The treated and untreated ash and metakaolin were characterized for mineralogy, microstructure, particle size, major elements, heavy metals content and leaching. The formulation of geopolymers was 25g of metakaolin where 5, 10 or 20 wt% MSWI FA was added. The alkali activators were a solution of 8M NaOH and 3M Na₂SiO₃. The amount of added alkali-activator depended on the amount of MSWI FA added, so all geopolymers should achieve the rates Si/Al < 3 and Na/Al of 1, considered by literature and previous experiments the best rates for the encapsulation of waste. The samples size of the geopolymers were 2x2x2 cm. All formulations (GEO_metakaolin (0% FA); GEO_raw; GEO_EDR and GEO_wash) were characterized for mineralogy, microstructure and leaching, and the samples with 20 wt% MSWI FA for compressive strength. The leaching tests on crushed geopolymer were made after seven days of curing at room temperature and the leaching results were compared to law limits and the leaching of the ash. Additionally, a monolithic leaching test of the geopolymer samples was made after 7 and 31 days of curing at room temperature. The choice to apply two different leaching tests was to simulate leaching from the geopolymer during two different stages of its life: the disposal as waste (end-of-life) with the first test and the use in the building sector with the latter.

The electrodialytic process induced an acidification of the MSWI FA that resulted in the removal of metals. The removal of Cd, Cu and Zn was between 70% and 90%, while the removal of Cr and Pb was below 30%. pH of the ash after this treatment (named EDR ash) was around 4, compared to the alkaline pH of the raw fly ash of 11, influencing the leaching of the different elements. The leaching of Cd, Cu and Zn in fact increased with the electrodialytic experiment while washing the ash the pH kept an alkaline value and the leaching of these same metals decreased compared to the raw ash. The leaching of chlorides decreased after the treatments bringing the values under the law limits and the X-ray diffractograms showed a pick of Halite (NaCl) for the raw ash that disappeared after the two treatments showing a reduction of chlorides in the matrix. This was also confirmed from the X-ray fluorescence analysis, where the samples showed a decrease of chlorides from 8.5% (raw ash) to 0.1% (EDR ash) and 0.9% (washed ash) and an increase of the Si content from 2.7% in the raw ash to 7.9% after the EDR treatment and 4.1% after the water washing, useful to increase the Si/Al rate for the geopolymerization.

The samples of geopolymers with 20 wt% of FA showed a compact microstructure and a low crystallinity (8%), showing that the geopolymer reactions happened when MSWI FA was added to the metakaolin. The compressive strength (Figure 1) of geopolymers presented values around 11 MPa for the samples without fly ash and the compressive strength increased to 13 MPa by adding the raw ash and the EDR ash. The samples with washed ash had a lower compressive strength, around 7MPa.

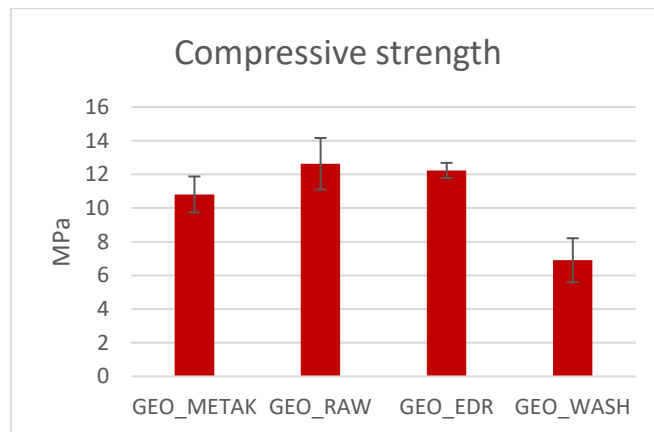


Figure 1: Compressive strength of different samples of geopolymers using treated and untreated fly ash (20 wt%) cured for 28 days.

The leaching tests applied to the geopolymers confirmed the effectiveness of the pre-treatments especially on some metals, but also showed low leaching of geopolymers with raw MSWI FA. The final pH was for all geopolymer samples alkaline (pH 11-12) and all leaching results were under the law limits. The leaching of all the elements was already under the law limits in the raw FA before the treatments and after the pre-treatments leaching of some metals decreased, as shown in Fig. 2a related to Cr. After the alkali-activation the leaching in the GEO_raw was even lower than in the fly ash itself and the leaching was even lower in the GEO_EDR especially using 10% and 20% of FA (Fig. 2b), meaning an immobilization of Cr (and other metals) in the geopolymer matrix. An opposite result of increased leaching (mobilization) was only seen for Cr in the GEO_wash sample (Fig. 2b). Contrarily to the Cr leaching, the leaching of Zn in the EDR ash was extremely high (77mg/l) and over the law limit after the treatment due to the low pH of the EDR ash, but achieved leaching values under the detection limit in GEO_EDR, also showing immobilization in the geopolymer matrix. The results from the static monolithic leaching test showed comparable and low leaching both after 7 and 31 days of geopolymer curing. However, after 31 days the leaching of Cr increased for all the samples, while it was stable or lower for the other metals.

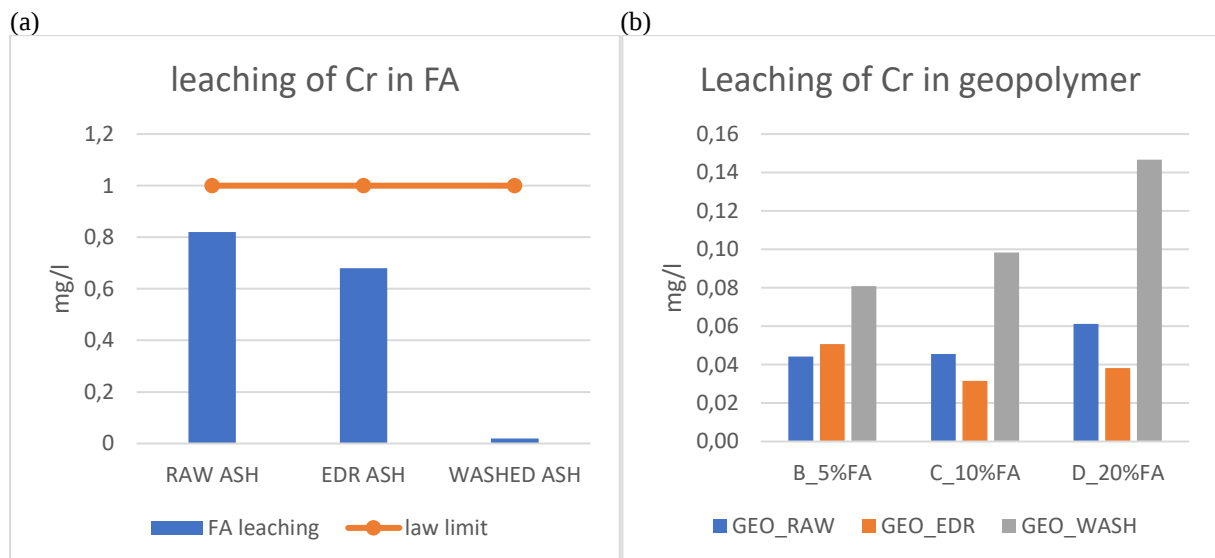


Figure 2: Comparison leaching of Cr in the different types of FA before (a) and after (b) the alkali-activation.

The pre-treatments removed Cl from the MSWI FA and electrodialytic treatment also removed metals. In conclusion, stable and environmentally friendly geopolymers can be created using both the raw and pre-treated fly ash, meaning that geopolymers can represent a good solution for the reuse of the FA. However, the EDR treated ash in geopolymers have comparable or lower leaching value for all the metals except for Cd, where the washed ash has a better result. It could be interesting to modify the setting of the electrodialytic treatment obtaining a lower value of leaching before the use of the treated ash or to increase the amount of ash to more than 20 %, to see if the final metal leaching and stability changes significantly.