Cr leaching from wood fly ashes before and after hydration/carbonation

L.M Ottosent[1], N.M. Sigvardsen[2]

[1]DTU Sustain, Department of Environmental and Resource Engineering, Technical University of Denmark, 2800 Lyngby, Denmark
[2]Danish Technological Institute, 2630 Tåstrup, Denmark
Keywords: Wood ash, heavy metals, chromium, carbonation.
Presenting author email: limo@dtu.dk

Introduction

The combustion of wood and wood products in combined heat and power plants increases in many European countries, generating vast amounts of wood ash. Wood ashes are often disposed of (Ingerslev et al. 2011); however, different options for utilization have been explored. Most widespread is the use as a fertilizer or additive for fertilizer production for agricultural and forestry applications. Other suggested applications are as an amendment in composting or raw material in the production of construction materials, e.g., concrete (aggregate or partial cement replacement).

Several researchers have reported that the heavy metal concentration is higher in the wood fly ash (WFA) than in the wood bottom ash (Carević et al. 2020). It is important to distinguish between the two fractions concerning utilization. This work focuses on WFAs. Leaching characteristics for heavy metals provide useful information when selecting management and recycling strategies; however, there is neither EU-wide legislation concerning the use as soil fertilizer nor for use in construction materials (as no standard covers such use). The basis of this work is that residues classified as hazardous should not be used as resources to avoid spreading the hazardous substances. Limiting values for non-hazardous waste can be found in Annex 2003/33/EC to the Landfill Directive (1999/31/EC).

Leaching properties of WFAs are likely to change from the ash leaving the combustion plant to the ash stored under ambient environmental conditions. WFAs have self-hardening properties. Complex reactions occur during hydration and carbonation, including forming calcium carbonates, gypsum, and ettringite (Sigvardsen, et al., 2021). These changes in the ash mineralogy during storage will likely influence heavy metal leaching. This work aims to explore the extent of the change in heavy metal leaching caused by hydration and carbonation and to relate the changes to ash characteristics.

Materials and methods

The investigation included eight WFAs from four Danish wood combustion facilities (grate fired) and one Swedish (circulating fluidized bed). Two batches were sampled from three of the plants at different sampling periods.

The heavy metal concentrations in the WFAs were measured according to the US EPA 3015A method. Leaching was evaluated at L:S 2 in accordance with EN 12457/1-4 at L/S = 2 l/kg. The pH and conductivity were measured at L/S 2.5 l/kg. The WFAs were characterized (heavy metal concentration, water content, pH, conductivity, solubility, water-soluble Cl^- and SO_4^{2}, and LoI at 550 °C and 950 °C). Chemometric modeling was used to evaluate the influence of WFA characteristics as variables on the leaching of heavy metals as the responses. The extraction of heavy metals as a function of pH was investigated for one ash from each plant. Closed plastic vials with 1.0 g of WFA and distilled water or HNO_3 of different concentrations (25 ml) were agitated for 1 week. The pH was measured in the suspension with a pH, and the heavy metal concentration was measured in the filtrate.

Five of the WFAs (one from each plant) were hydrated and carbonated: 50 g ash was mixed with 100 ml tap water in petridisches for 30 days in ambient air in the lab. Extra water was added regularly to keep the ashes moist all through the period. Leaching was measured before and after carbonation.

Results and discussion

The WFAs as received

The limiting value for leaching of Cr for waste classified as non-hazardous is 4 mg Cr/kg (2003/33/EC). This limit was exceeded for Cr in four of the eight investigated WFAs. The limiting values were met for Cd, Cu, Ni, Pb, and Zn in all the WFAs. Thus, this abstract focus on Cr. The total concentration varied from 15 – 73 mg Cr/kg.

The pH was between 12.4 and 13.5 in the eight ashes, and the high pH is in accordance with the reported for WFAs in general. The alkalinity of WAs depends on the carbonate, bicarbonate, and hydroxide content.

The chemometric model was based on the characteristics of the eight WFAs as received. It showed that the Cr leaching was positively correlated to: total Cr concentration > water-soluble SO_4^{2-} > WFA solubility > conductivity. It was negatively correlated to the Al concentration, i.e., the less aluminum, the higher Cr leaching. Thus apart from the total Cr concentration, the leaching of Cr depends mostly on solubility-related characteristics.

From the pH-dependent extraction of one WFA batch from each plant (Figure 1a), it was found that Cr had amphoteric behavior (extracted at low and high pH), which is in accordance with, e.g., (Pöykiö et al. 2009). The leaching at high pH needs consideration if the WFA is utilized in concrete since the pH is more than 13 here and at this pH, the extractable Cr indicates mobility.

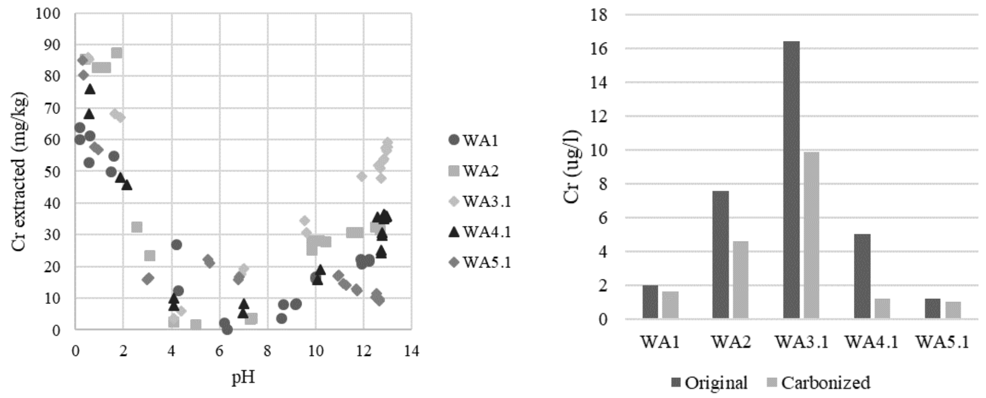

Figure 1: (a) pH-dependent extraction of Cr and (b) leaching of Cr before and after hydration/carbonation in wood ashes from five different wood combustion plants.

Changes in characteristics by hydration/carbonation

The pH decreased during the hydration/carbonation to 10-11. The conductivity also decreased in every of the WFAs. Thus, it was evident that the characteristics changed during hydration and carbonation. From the literature, it is known that calcium carbonates, gypsum, and ettringite can be expected to form. The ettringite formation demands the presence of sulfate, soluble aluminate, and $Ca(OH)_2$. The prevalence of ettringite or gypsum is determined by the content of Al in the specific wood ash (Sigvardsen et al., 2021). Thus, the chemometric modeling indicated that the Cr leaching from the WFA as received was highest in the ashes where gypsum must be expected to prevail during hydration/carbonation; high content of water-soluble SO_4^{2-} and low Al content. From Figure 1b it is seen that the Cr leaching decreased from every WFA during the hydration/carbonation (though still above the limiting value for two of the WFAs). This decrease can be because Cr is built into the new phases or it can be because of the decreasing pH (as illustrated in Figure 1a). It is important to understand the change in leaching behavior to ensure safe utilization in the different applications under development.

Conclusions

The leaching of heavy metals from eight WFAs was investigated. Cr was the only heavy metal where leaching exceeded the limiting value for classification as non-hazardous. This was in four of the WFAs. Thus, the Cr leaching may hamper safe utilization. Extraction of Cr from WFAs is amphoteric, and Cr is readily extracted both at low and high pH. During storage under ambient conditions, the characteristics of WFAs will change due to hydration and carbonation. It was found that the leaching of Cr decreased during these reactions; however, the leaching still exceeded the limit as non-hazardous in some of the ashes. For future safe utilization of WFA in, e.g., concrete, it is important to investigate if this decrease in leaching is due to Cr being included in the new phases or the decrease in pH. Concrete has a high pH, and the Cr leaching may increase if utilized here, specifically in the latter case.

Acknowledgments

The work is part of the AshCycle project (Grant No. 101058162), funded by the European Union.

References

Ingerslev, M., Skov, S., Sevel, L., Pedersen, L.B. (2011). Element budgets of forest biomass combustion and ash fertilisation - A Danish case-study, Biomass and Bioenergy. 35, 2697–2704.

Carević, I., Baričević, A.., Štirmer, N., Šantek Bajto, J. (2020) Correlation between physical and chemical properties of wood biomass ash and cement composites performances, Constr. Build. Mater. 256

Pöykiö, R., Rönkkömäki, H., Nurmesniemi, H., Perämäki, P., Popov, K., Välimäki, I. (2009) Release of metals from grate-fired boiler cyclone ash at different pH values, Chem. Speciat. Bioavailab. 21, 23–31

Sigvardsen, N.M., Geiker, M.R., Ottosen, L.M. (2021) Phase development and mechanical response of low-level cement replacements with wood ash and washed wood ash. Construction and Building Materials. 13 p., 121234