

Recovery of valuable elements from municipal solid waste incineration ashes

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1. Introduction

Incineration of municipal solid waste (MSW), that cannot be recycled, is an effective and established process both to reduce the volume and weight of waste and to recover energy from it. However, significant amount of solid residues are produced from the MSW incineration process, including bottom ash, fly ash, and air pollution control residues. Due to the volatility of heavy metals during waste incineration, they are enriched in the fly ash. These fly ashes are therefore regarded as hazardous waste and have to be disposed of in dedicated landfills [1]. On the other hand, municipal solid waste incineration (MSWI) ashes contain several valuable elements and are an interesting secondary source of for metal recovery. Separation of hazardous elements is one treatment method to produce a less harmful residue [2]. One example is the FLUWA process in which the ash is leached with acidic effluent from the flue gas treatment to produce a zinc-rich sludge, which is further processed [3]. Antimony (Sb), that is both problematic for disposal and a valuable element for different industries is present in MSWI ashes. Most of the primary antimony comes from China, and the EU has listed Sb as an element with high supply risk and a high economic importance [4]. Antimony is used, e.g., as flame retardants, in some plastics, and as a lead-hardening agent [5], and is enriched in MSWI fly ash compared to the content in the earth crust [6]. In this work, the leaching behavior of a fly ash from a waste incinerator was studied. The goal is to develop a concept for the controlled leaching of target elements from fly ashes and at the same time produce an inert non-hazardous residue, Figure 1.

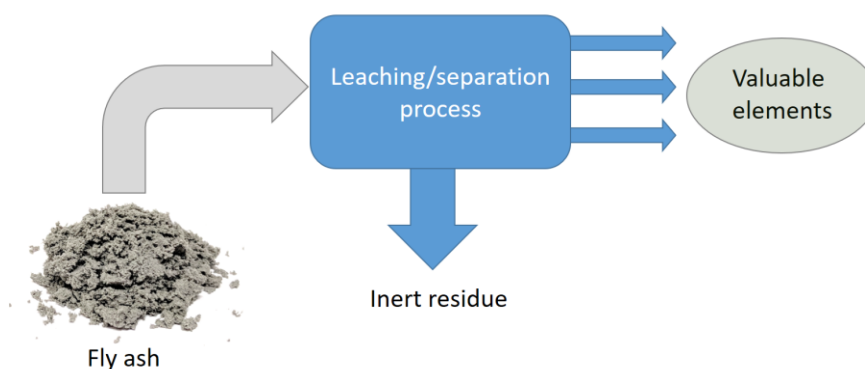


Figure 1. Schematic of leaching process to leach out valuable elements and produce an inert residue.

2. Experimental

Elemental and scanning electron microscope combined with energy-dispersive X-ray (SEM-EDX) analyses of the fly ash were performed to determine the occurrence of valuable and critical elements. Figure 2 shows the elemental composition of the studied fly ash. Of the EU's critical elements, antimony is the most abundant (770 mg/kg ds) in the fly ash sample studied. Figure 3 shows an SEM-EDX area analysis of the fly ash. The EDX analyses suggests that the main compounds of the fly ash are calcium and alkali chlorides and sulfates.

The leaching experiments were conducted in a flow-through reactor using various leaching agents. The leached elements were sampled every 10, 20, 30, 60, 90, 120, 180, 240, and 1440 minutes, and were analyzed with ICP-OES. The leaching agents used were: water, HNO₃, HCl, and citric acid. Three concentrations of the acids were used: 0.1 M, 0.5 M, and 1 M. The setup consists of three flow through reactors, which enables to study three parameters or fly ashes simultaneously.

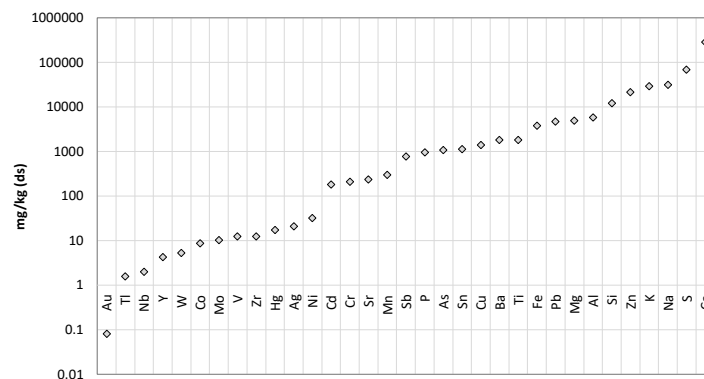


Figure 2. Elemental composition of the fly ash.

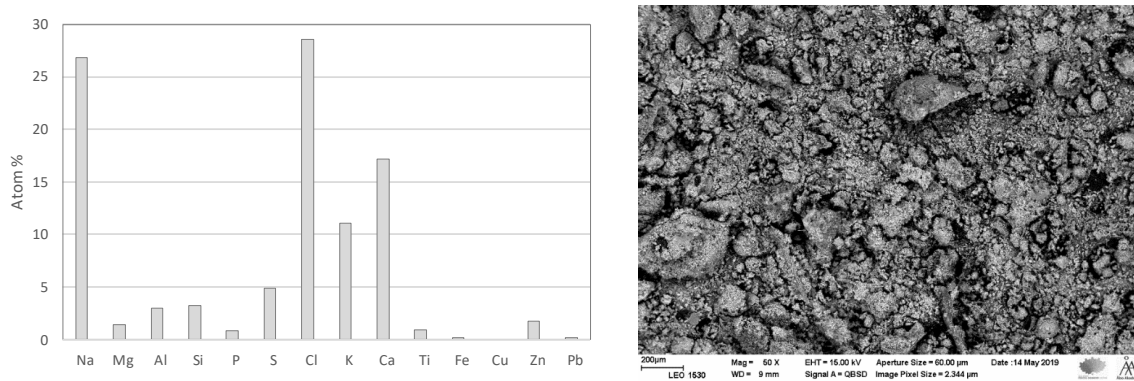


Figure 3. SEM-EDX area analysis and SEM backscatter image of the ash.

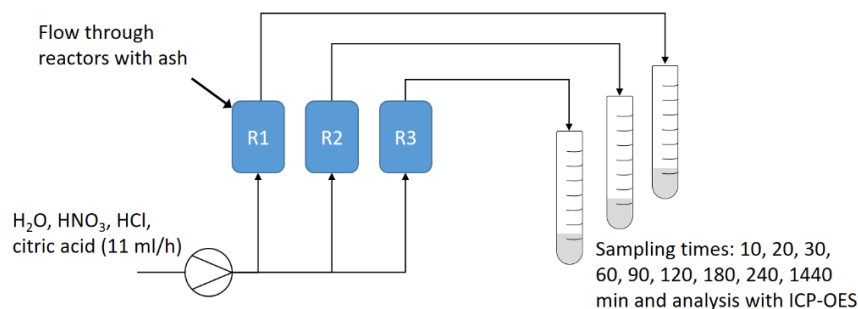


Figure 4. Experimental setup of the leaching method.

3. Results and discussion

The results from leaching of water-soluble Ca, K, Na, and S is shown in Figure 5. During the first 20 minutes virtually all the Na and K was leached and most of the Ca. The initial leaching rates were significantly higher than that of sulfur and accordingly it is assumed that these elements were present as highly soluble chlorides. After the initial leaching, no K or Na was leached out anymore, while Ca continued to be soluble with about the same rate as sulfur, assumably as CaSO_4 . A large share of the fly ash was leached out in the water leaching.

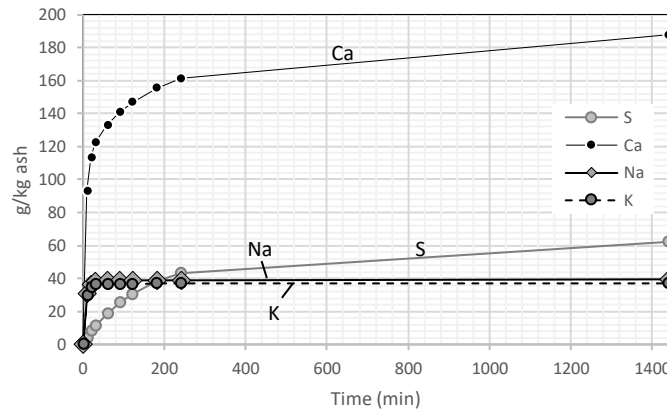


Figure 5. Water leachable Na, K, S, and Cl.

The leaching rates of Zn, Pb, and Cu with water, 0.1, and 1 M HNO_3 are shown in Figure 6. No Zn and Cu was leached out with water, however some Pb was. With 1 M HNO_3 , Zn and Cu were leached out during the first 60 min, while Pb was leached out at a lower rate. With 0.1 M HNO_3 , the leaching was significantly slower.

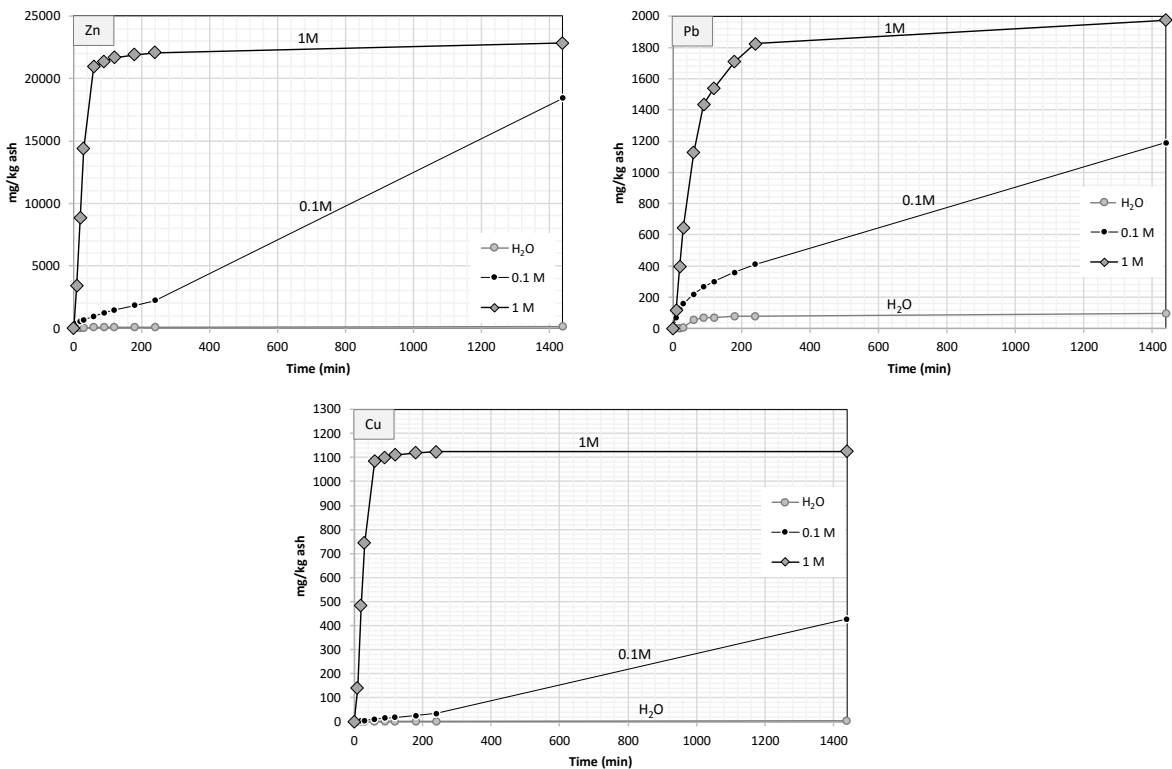


Figure 6. Leaching of Zn, Pb, and Cu with 0.1 M HNO_3 , 1 M HNO_3 , and water.

The leaching results for antimony are shown in Figure 7. Antimony was leached out more slowly than, e.g., Zn and Cu. The leaching rate was much faster using HNO_3 and HCl with 0.5 M and 1 M acids. The leaching was even faster with the stronger citric acid. Interestingly, the yield with 0.1 M citric acid was much better than for 0.1 M HCl and HNO_3 . Most of the Sb was leach out from the ashes with the stronger acids and even with the 0.1M citric acid. The results support the previous study by Fabienne [7], who reported that Sb can be efficiently leached with citric acid up to pH 3.

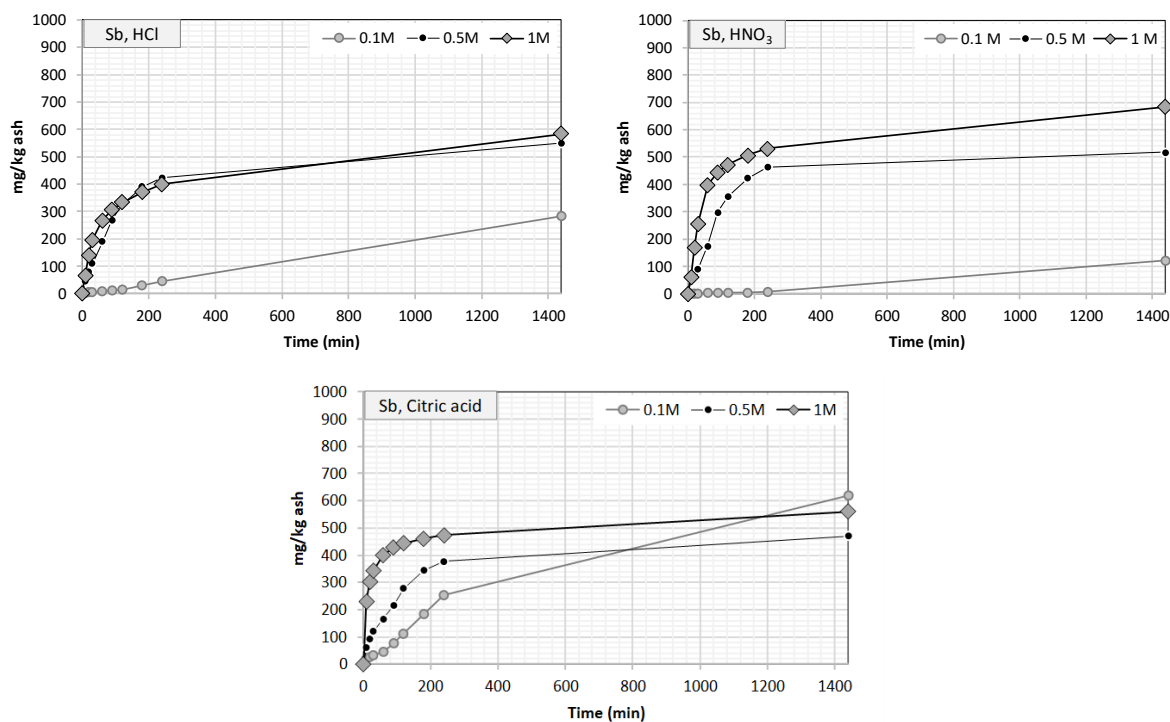


Figure 7. Leaching of Sb with HCl , HNO_3 , and citric acid.

4. Conclusion

In this work, the leaching behavior of metals in a MSWI fly ash was studied. A leaching method was built, in which flow through reactors are used. The sampling was done with certain intervals to obtain leaching rates of various elements. Using a flow through reactor gives the maximum leaching rate, compared to batch reactors where solubility and pH play a significant role.

In the experiment with water as leaching agent, Ca, K, and Na chlorides were quickly leached out, while calcium sulfate leached out more slowly. Water leaching prior to an acid leaching step would make the recovery of acid leaching elements more effective and simple. The acid concentration had a significant effect on the leaching rates of metals. Antimony leaching with citric acid led to a high recovery degree even with a 0.1 M citric acid solution. A multi-step, controlled leaching to recover specific elements of interest appears possible, which would greatly contribute to the concept of circular economy.

Acknowledgements

This work has been funded by the WtE 2030 project. The WtE 2030 project is co-funded by the Research Council of Norway, Enova and industry partners.

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