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Antimony in secondary sources - Sb recovery from fly ash

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Master thesis, Environmental technologies

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INTRODUCTION

Metals and metalloids [metal(loid)s] are crucial raw materials in our society. The growing demand for metal(loid)s is posing a risk for future supply and new processes for reuse and recycling have to be developed. Antimony (Sb) was identified as an element with above average economic impact and a high supply risk. Sb is widely applied as a lead-hardening agent or as flame retardant. Fly ash, a waste residual of the waste incineration process, contains considerable amounts of Sb (Fig. 1). State-of-the-art fly ash treatment in Switzerland is the so called FLUWA/FLUREC process, in which heavy metals (e.g. Zn and Pb) are re-covered by acid leaching and liquid/liquid extraction. Sb is not recycled but remains in fly ash, which is costly deposited in landfills for stabilized residues due to the high metal concentration.

Fig. 1: From left to right: Waste incineration plant Zuchwil SO (www.kebag.ch), fly ash (de.academic.ru), antimony, Sb (www.periodictable.com).

CONCEPT

The objectives in this work were on one hand the extraction of Sb from fly ash by means of acidic leaching and on the other hand the reduction of the heavy metal concentrations in the fly ash in order to meet the Technical Ordinance on Waste (TWO) limit values for the deposition as inert waste. The experiments for Sb extraction of fly ash were based on the already existing FLUWA process, in which acidic leaching of fly ash with HCl is performed. According to the FLUWA process, the fly ash was treated first with HCl before additional extractions using different acids were applied. For this purpose, citric acid and different inorganic acids were used. Citrate, as a naturally occurring ligand representing an organic acid with the capability to mobilise metals[1] was used for its known ability to extract Sb, assuming the formation of a soluble Sb-citrate complex. H_3PO_4 was chosen since in literature an exchange mechanism between phosphate and Sb(V) is described[2]. Additionally, it was investigated whether after the extraction steps the fly ash complies with the limit values for the deposition as inert waste.

RESULTS

Preliminary experiments demonstrated the suitability of citric acid for Sb extraction over the pH range 0.6 to 3.0 and 1 M H_3PO_4 extraction between pH 0.6 and 2.0, showing that the Sb extraction was not only H^+ driven but depending on complexing/exchange mechanism (Fig. 2). Compared to Sb, the extraction with 1 M H_3PO_4 between pH 2.5 and 3.0 revealed a relatively high extraction yield for other abundantly present metals, offering the possibility for selective Sb recovery. It was shown that the extraction of Sb from fly ash with citric acid (approx. 3000 mg kg^{-1}, i.e. 79 % of total content) was about 20 times more efficient than solely HCl extraction (approx. 150 mg kg^{-1}, i.e. 4 % of total content) (Fig. 3). However, due to co-extraction of Al (81 %), Cu (57 %), Pb (83 %) and Ti (88 %) citric acid as such was not suitable for selective Sb extraction. To promote selectivity, sequential extraction of fly ash with HCl, H_3PO_4 and citric acid at different pH was studied.

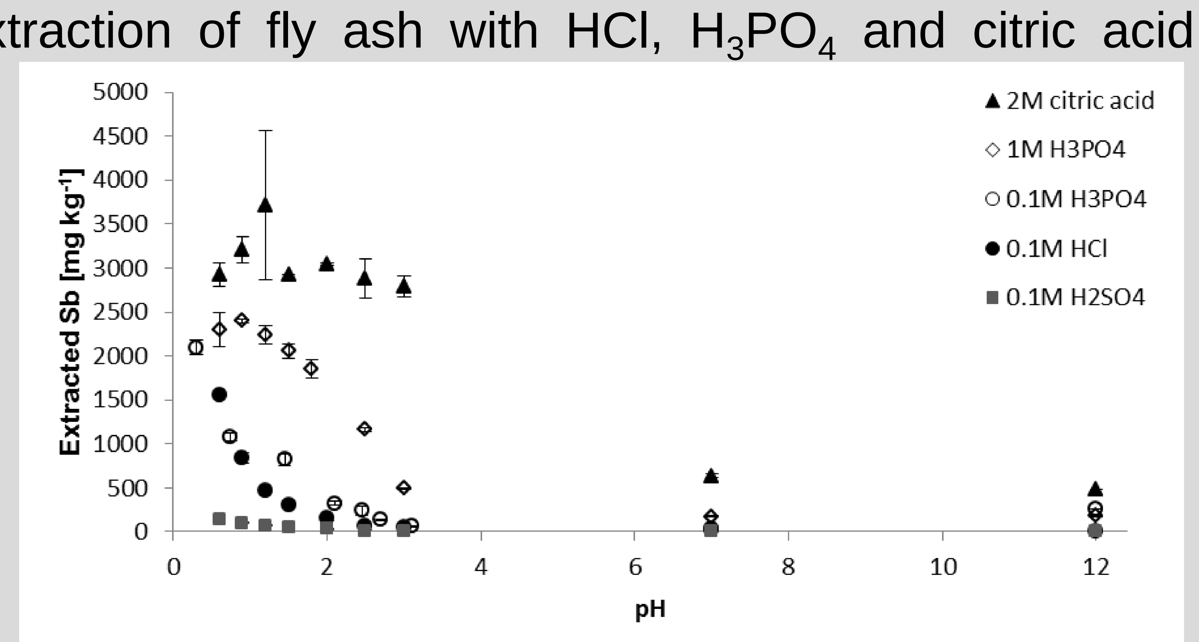

Fig. 2: Preliminary tests for Sb extraction using HCl, H_2SO_4, H_3PO_4 and citric acid at various pH (n=2).

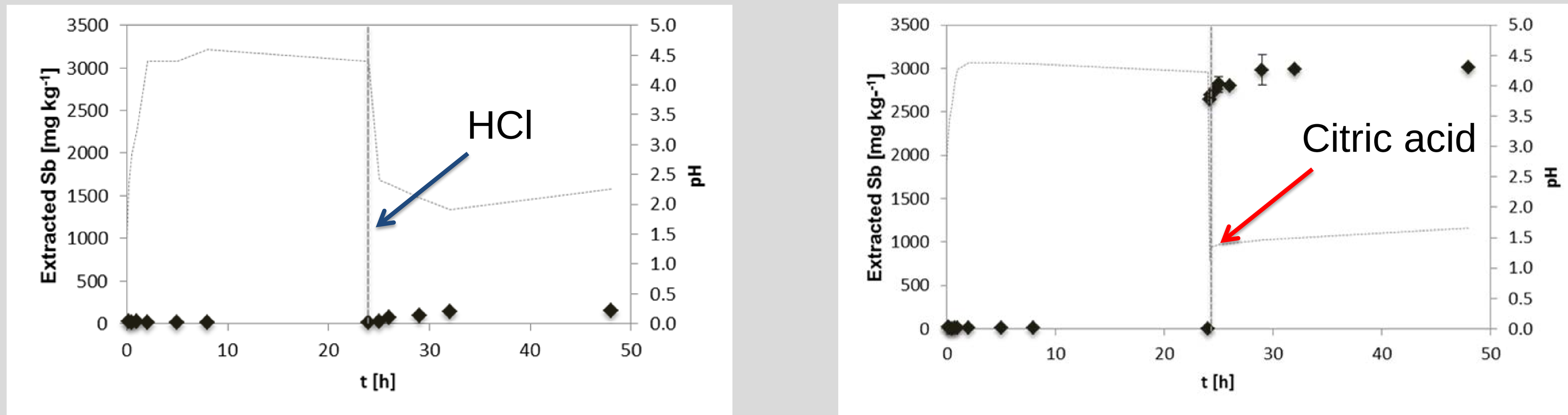

Fig. 3: Extractable Sb from fly ash during HCl 5 % (left figure) and HCl 5 %/citric acid extraction (right figure).

HCl leaching at very low pH (0.6) allowed to separate Sb from other metal(loid)s (Al, Ca, Cd, Cr, Cu, Fe, Mg, Pb) and with further citric acid extraction an approx. 48 % pure Sb solution in relation to the overall metal content was obtained (in a mixture with approx. <1 % As, <1 % Ni, 51 % Ti). Similar results were obtained with HCl/H_3PO_4 extraction also at less acidic condition (approx. pH 2.8). In addition to the recovery of Sb, two strategies for the separation of Sb and As were developed (Fig.4) which are very challenging to separate due to their similar chemical behaviour (using HCl extraction at very low pH<0 or H_3PO_4 at pH>2.5).

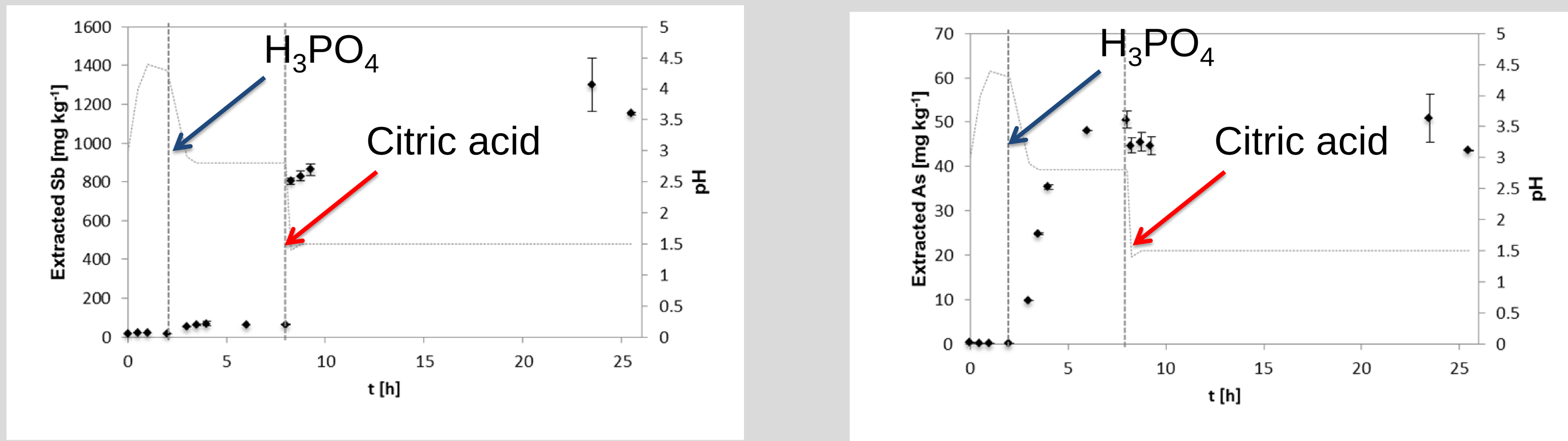

Fig. 4: Sb/As concentrations [mg kg^{-1}] during extraction with HCl/H_3PO_4 and citric acid (n=2).

The aim to decrease elemental concentrations in the fly ash below TOW limit values for the deposition as inert waste was not completely achieved. However, among the experiments performed in this work, continuous extraction with HCl, H_3PO_4 and citric acid showed great potential. The elemental concentrations in the remaining fly ash could be reduced drastically compared to the untreated fly ash: Pb (by 68.9 %), Zn (by 99.5 %), Cu (by 96.7 %), Sb (by 90.7%), Cr (by 82.2 %), Ni (by 62.3 %), Cd (by 97.7 %), and As (by 97.2 %), leaving only Sb above the limit value of the TOW for the deposition as inert waste.

CONCLUSION

Conclusively, a possible strategy for the most selective recovery of Sb could be sequential extraction with HCl at pH 4.5/2.5 in order to remove the bulk parts of the contained metals, followed by H_3PO_4 extraction at pH 2.8 to further remove As and Ni (Fig. 5). Further citric acid extraction would finally solubilise Sb and Ti. The implementation of a sequential extraction with different acids shows high potential for the future to achieve, on the one hand, high Sb recovery rates and on the other hand to further decrease the load of restricted metal(loid)s in fly ash so that a great step towards inert waste seems plausible.

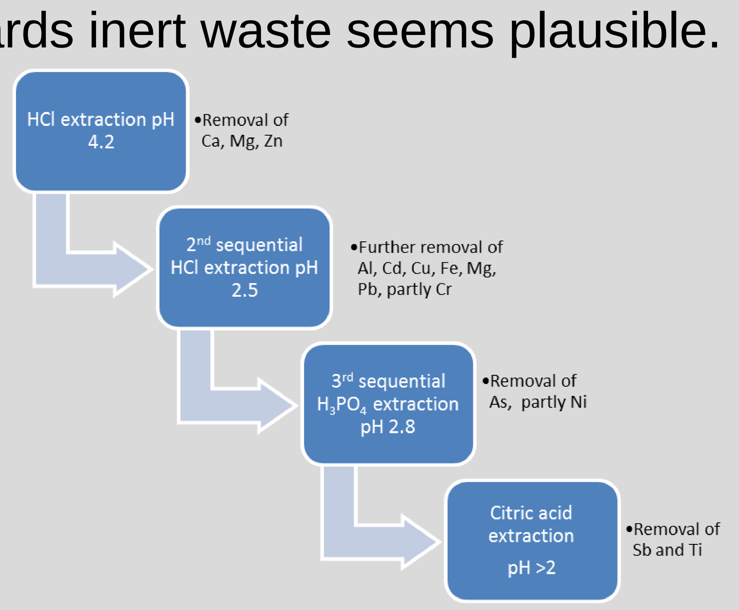

Fig. 5: Extraction scheme for selective Sb recovery from fly ash.

REFERENCES

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