

FLY ASH OF MUNICIPAL WASTE INCINERATOR: LEACHABILITY OF METALS AFTER SFE WITH CO₂

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Aiming the removal of metal contamination of chemical solid waste or harbour sludge, supercritical fluid extraction from fly ash is a successful example. Large quantities of heavy metal contaminated fly ash are generated due to the growing amount of municipal solid waste and its incineration. Currently, expensive deposition of the ash is required because contact with (rain) water leads to leaching of these metals and subsequently to pollution of ground water. One way to reduce the leachability of the ashes is supercritical fluid extraction (SFE) with CO₂ and extractants. The extractants, such as e.g. (Bis(2,4,4-trimethylpentyl)monothio-phosphinic acid (*Cyanex 302*), Tributylphosphate (*TBP*), Di-(2-ethylhexyl)phosphoric acid (*D₂EHPA*) are dissolved in CO₂ and form CO₂-soluble metal-complexes. Extraction was carried out in a rotating vessel of about 12 l volume at 16 MPa and with a constant CO₂-flow. Afterwards, the metal leachability of the extracted ash was studied with standardised column leaching tests.

The resulting cumulative leaching curves showed a better leachability reduction of *Mn* in particular when the CO₂ extraction efficiency was better. The leachability of metals such as e.g. *Pb* and *Mo*, initially above the legislative leaching limit, was reduced significantly while *Pb* was reduced below this limit. Despite a dramatic leachability increase of some metals (such as e.g. *Sb*) SFE and a combination of treatment steps have a potential to reduce the leachability below legislative values allowing even re-use of fly ash as construction material.

INTRODUCTION

Large volumes of fly ashes are produced by municipal solid waste incinerators (MSWI). The amount of produced fly ash is increasing due to an increasing number of incineration plants. Combustion of the estimated annual 250 million tons of municipal solid waste only in Europe, has a potential of about 12 million tons of MSWI fly ash. The waste is burnt in the furnace, where the bottom ash is collected. The lighter fly ash and evaporated metals flow upward with hot combustion flue gases. In cooler regions of the incinerator the volatile compounds cool down, and precipitate or condense on the surface of non-volatile particles [1]. This leads to accumulation and enrichment of toxic heavy metals on fine ash particles. A particle that is formed by vaporisation and condensation consists of an oxide rich core surrounded by an exterior hull containing predominantly (sparingly) water soluble compounds such as *NaCl*, *KCl*, *CaSO₄* and *CaCO₃* [1]. These compounds form a thin crust of aggregates on the surface [2]. Depending on the surface composition and structure, the (toxic) metals leach out after contact with water, and pollute the groundwater. Therefore, isolated and

expensive disposal of the ash is required. In addition, it is becoming increasingly important to find ways of utilising this fly ash. For reuse of ash as filler for cement or pavements only a minimal leachability of metals is allowed by national legislation. SFE offers a method to reduce the metal content to such an extent, that leachability is reduced and the demands of legislation are observed. In this study the leachability is compared with exemplary values of a Dutch decree on building materials [3] considering infiltration rates of 300 mm/year.

Supercritical CO₂ in combination with suitable extractants is advantageous for extraction of metals from solid particles such as e.g. fly ash [4], because CO₂ is a benign and cheap solvent. SFE does not require any expensive drying of the final product as evaporation of solvent CO₂ by release of pressure results in both a solvent free matrix and a separate metal-extractant complex. Aiming the development of a scaled up process for the treatment of fly ash or other solid material, this paper concentrates on the release of metals from fly ash after SFE by means of a standardised leaching test [5]. The differences in release of exemplarily four metals (*Pb*, *Mn*, *Sb*, and *Mo*) is shown after (i) SFE with various extractants (*Cyanex 302*, *TBP*, *D₂EHPA* or mixtures of *TBP-D₂EHPA*) and after (ii) SFE from water pre-leached fly ash.

MATERIAL AND METHODS

MSWI fly ash was supplied by AVR, Rotterdam. SFE was carried out using the extractants *Cyanex 302* (Bis(2,4,4-trimethylpentyl)monothiophosphinic acid, Cytec Inc.), *TBP* (Tributylphosphate, British drug house), and *D₂EHPA* (Di-(2-ethylhexyl)phosphoric acid, Alfa).

The extraction of 2 kg fly ash was carried out in a revolving vessel, while the extractants were added continuously into the constant CO₂-flow (8-18 kg/h) of 20 MPa at 40°C. After extraction, a rinsing step with pure CO₂ removes the remaining complexing agent and metal complexes. The sample handling and the extraction procedure have been presented earlier [6]. The experimental conditions of the SFE experiments are listed in Table 1. Pre-leaching with a liquid/solid (L/S) mass ratio of 10 was carried out batch-wise (2-3.5 kg of fly ash) prior to SFE (exp. C2 and C3) for about 1 h with water (pH 7, 60°C) as described more elaborately elsewhere [7]. The initial humidity of the ash prior to C2 and C3 was 38 wt.% while it was 4 wt.% prior to all other SFE experiments.

Table 1 : Experimental conditions of SFE from MSWI, at $T=40^{\circ}\text{C}$, $p=20$ MPa

Exp.	Extractant concentration in CO ₂	Extraction		Rinsing step	
		t_{ext}	CO ₂ flow	t_{wash}	CO ₂ flow
C1	0.11 mol% <i>Cyanex 302</i>	1 h	10 kg/h	2.5 h	10 kg/h
C2	0.06 mol% <i>Cyanex 302</i> *	"	18 kg/h	"	"
C3	0.11 mol% <i>Cyanex 302</i> *	6 h	10 kg/h	3.5 h	"
T1	0.2 mol% <i>TBP</i>	1 h	8 kg/h	2 h	19 kg/h
D2	0.2 mol% <i>D₂EHPA</i>	"	"	"	"
TD1	0.2 mol% <i>TBP</i> + 0.2 mol% <i>D₂EHPA</i>	"	"	"	"
TD4	0.35 mol% <i>TBP</i> + 0.2 mol% <i>D₂EHPA</i>	"	"	"	"

* after pre-leaching

RESULTS AND DISCUSSION

The leachability of *Pb*, *Mn*, *Sb*, and *Mo* from both original (Ori) MSWI fly ash and from fly ash after SFE with *Cyanex 302* (exp.'s C1, C2, C3), *TBP* (exp. T1), *D₂EHPA* (exp. D2) and mixtures of *TBP-D₂EHPA* (exp.'s TD1, TD4) was determined with column leaching tests [5]. In Figures 1-4 the cumulative amount of leached metals is plotted versus the liquid/solid (L/S) mass ratio of total leachate and tested ash, showing a spontaneous leaching response for all metals.

Pb-leaching: The leaching of *Pb* increased with the addition of leaching acid (Figure 1), while most *Pb* was leached for L/S<1. The leached amount of *Pb* from the original ash exceeded the legislative limit. This leaching was reduced after SFE with *TBP* and *D₂EHPA* (exp.'s TD4, D2, and T1) and significant reduction to 10% and 40% of the maximum allowed value was obtained by water pre-leaching and subsequent SFE with *Cyanex 302* (C2, C3). In these cases the pre-leaching not only removed some *Pb* it also changed the availability of *Pb*. In cases of enhanced *Pb*-leaching (C1, TD1) the removal of retarding surface compounds by SFE apparently enabled an easier access of water in the leaching test.

Mn-leaching: As shown in Figure 2, the leachability of *Mn* either did not change significantly (C2, T1) or it decreased to about 50% (C1, D2, TD1, TD4), which harmonised for the latter with the degree of SFE of about 50%. Only after exp. C3 (with water pre-leaching) the leachability increased about 5 times with a trend to even higher values. Apparently the availability of *Mn* in the leaching was strongly enhanced by the pre-leaching.

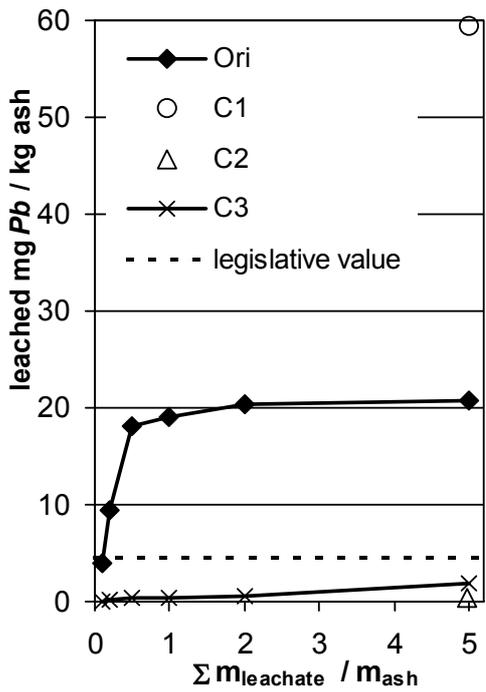
Sb-leaching: Although the SFE of *Sb* was good (60-98%), the leachability increased dramatically (Figure 3). While the leachability of the original ash was only 1% of the maximum value, it rose to values slightly (C1), 3-5 times (T1, D2, TD4) or to values up to about 115 times (C3) above the maximum value. Obviously water pre-leaching (C2, C3) in particular increased the availability of *Sb* for the leaching liquid (pH 4) during the standardised test. It seemed that the lowest leaching and highest SFE (98%) was obtained with an equal amount of *TBP* and *D₂EHPA* (TD1).

Mo-leaching: The leachability was not reduced significantly after SFE with dry ash (Figure 4), despite a good extraction efficiency (70-95%). Since SFE had little influence on *Mo*-leachability, it seemed that the water leachable *Mo*-compounds were removed best by water pre-leaching. Although pre-leaching prior to SFE only resulted in 50% extraction with CO₂, the leachability was reduced by about 75%. The leachability was not reduced below its maximum allowed value. Therefore (i) longer pre-leaching and/or (ii) pre-leaching with a higher L/S ratio may keep the *Mo*-leachability below that value.

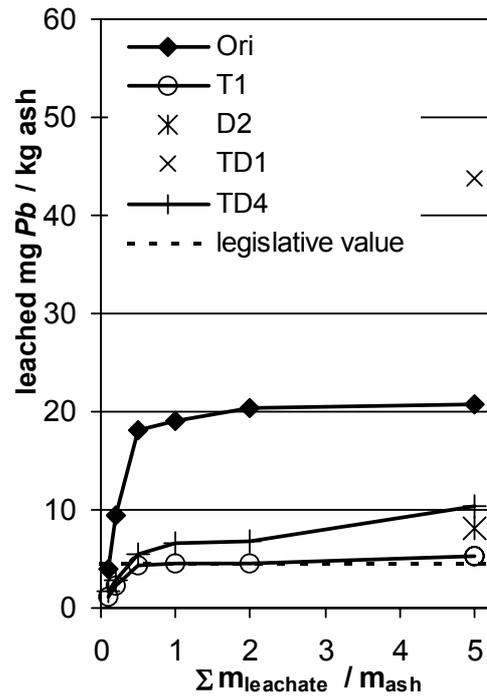
CONCLUSION

Pre-leaching did not necessarily result in reduced (as e.g. for *Pb*, *Mo*) or enhanced (*Mn*, *Sb*) leachability or did not generally improve the results of SFE. A general relation between the SFE-results and leachability was not evident for the studied metals.

However, the leachability of metals exceeding the leaching limit was reduced. Therefore, SFE along with a combination of treatment steps has the potential to reduce the leachability below legislative values.

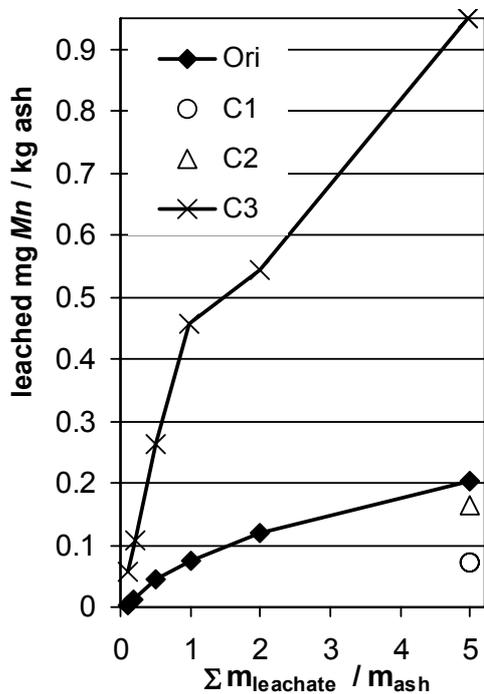


(a)

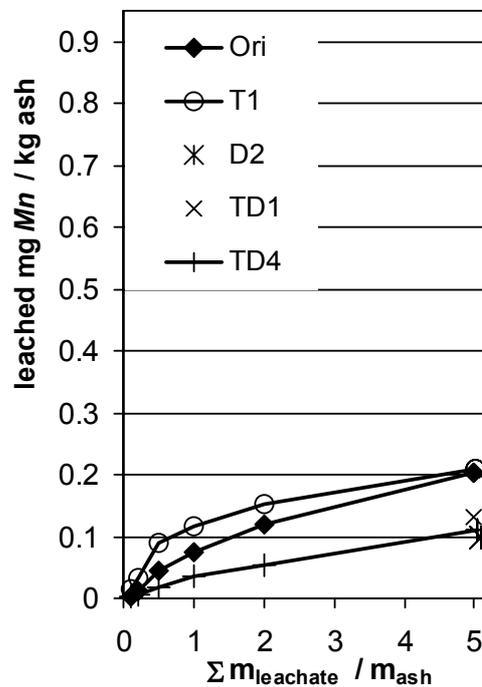


(b)

Figure 1. Pb-leaching curves after SFE with (a) Cyanex 302, (b) with TBP/D₂EHPA

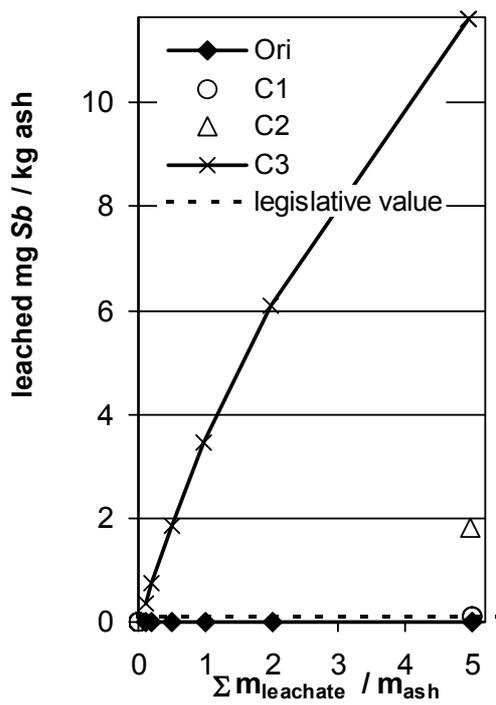


(a)

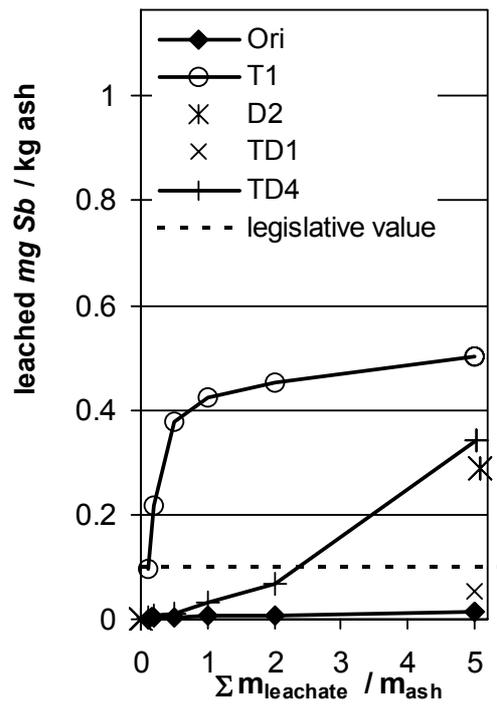


(b)

Figure 2. Mn-leaching curves after SFE with (a) Cyanex 302, (b) with TBP/D₂EHPA

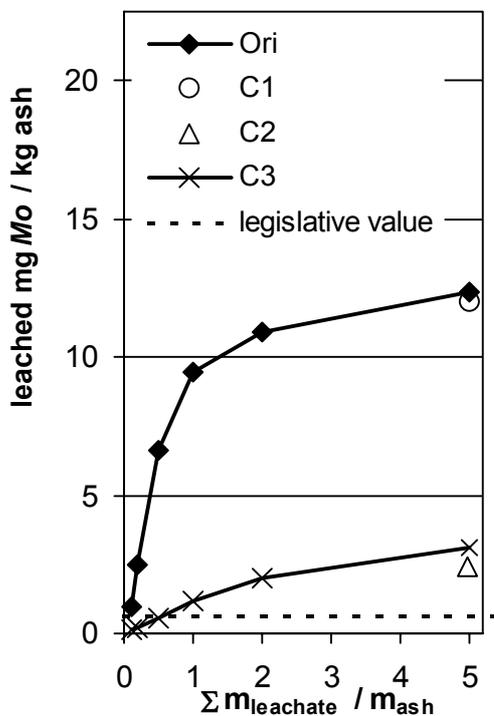


(a)

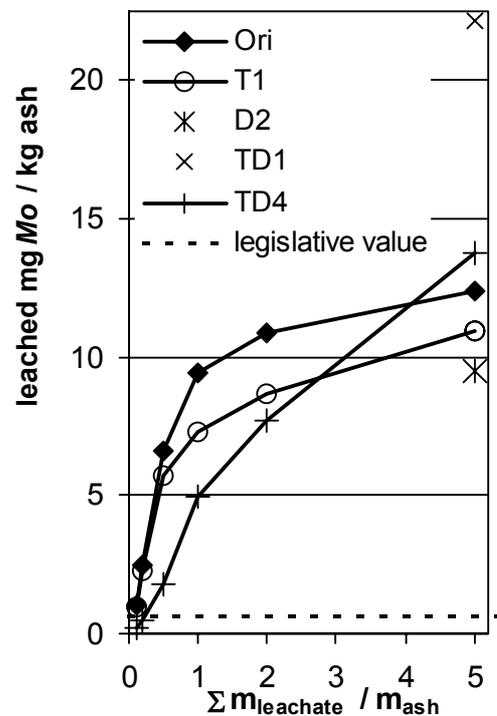


(b)

Figure 3. *Sb*-leaching curves after SFE with (a) *Cyanex 302*, (b) with *TBP/D₂EHPA*



(a)



(b)

Figure 4. *Mo*-leaching curves after SFE with (a) *Cyanex 302*, (b) with *TBP/D₂EHPA*

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