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Extraction of heavy metals from MSWI fly ash using hydrochloric acid and sodium chloride solution

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A B S T R A C T

Fly ash from municipal solid waste incineration contains a large potential for recyclable metals such as Zn, Pb, Cu and Cd. The Swiss Waste Ordinance prescribes the treatment of fly ash and recovery of metals to be implemented by 2021. More than 60% of the fly ash in Switzerland is acid leached according to the FLUWA process, which provides the basis for metal recovery. The investigation and optimization of the FLUWA process is of increasing interest and an industrial solution for direct metal recovery within Switzerland is in development. With this work, a detailed laboratory study on different filter cakes from fly ash leaching using HCl 5% (represents the FLUWA process) and concentrated sodium chloride solution (300 g/L) is described. This two-step leaching of fly ash is an efficient combination for the mobilization of a high percentage of heavy metals from fly ash (Pb, Cd $\geq$ 90% and Cu, Zn 70–80%). The depletion of these metals is mainly due to a combination of redox reaction and metal-chloride-complex formation. The results indicate a way forward for an improved metal depletion and recovery from fly ash that has potential for application at industrial scale.

Contents

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1. Introduction

Approximately 75,000 tons of fly ash (FA) are generated annually in Switzerland from 30 municipal solid waste incineration (MSWI) plants. Because of the contamination with organic and inorganic pollutants, treatment of fly ash is essential. Fly ash from Switzerland is currently exported untreated to underground storage, solidified with cement before deposition or acid leached according to the FLUWA process (Schlumberger et al., 2007; Bühler and Schlumberger, 2010). Nowadays, more than 60% of the fly ash in Switzerland is treated by the FLUWA process which represents the state-of-the-art. It provides a basis for extended methods such as the FLUREC process (Schlumberger et al., 2007), where metals from fly ash are directly recovered. MSWI fly ash comprises a large potential for recyclable metals such as Zn, Pb, Cu and Cd. Additionally, treatment of fly ash leads to a reduction of mass and heavy metals to be deposited. With the revised Swiss Waste Ordinance (Swiss Confederation, 2016), the treatment of fly ash and recovery of metals is prescribed from 2021 onwards. Therefore, the investigation and optimization of the FLUWA process is of increasing interest and an industrial solution for direct metal recovery within Switzerland is in development (ZAR, 2016).

The efficiency of heavy metal leaching is dependent on the binding environment of the metals and the leaching conditions (redox conditions, pH-value of ash slurry, liquid to solid ratio (LS), temperature, leaching time), as has been shown in a previous study (Weibel et al., 2017). Especially the redox conditions during the FLUWA process are of central importance for increasing the recovery of redox-sensitive metals (mainly Pb, Cu and Cd). Approximately 10% of the Swiss fly ash is presently acid leached with the addition of an oxidizing agent (e.g. hydrogen peroxide). Oxidizing conditions prevent the process of reductive cementation whereby mainly Cu and Pb are removed from the leaching solution (Weibel et al., 2017). Beside electrochemical processes, complexation of Pb and Cu by organic ligands (Johnson et al., 1996; Christensen et al., 1999; Hyks et al., 2009) or by inorganic ligands such as chloride (Byrne & Miller, 1984; Powell et al., 2007; Powell et al., 2009) significantly controls metal mobility. The use of concentrated sodium chloride solution (NaCl) for metal mobilization is well known from metallurgical processing where heavy metals are kept in solution by metal-chloride-complexes e.g. for Pb (Raghavan et al., 1998; Raghavan et al., 2000; Turan et al., 2004; Ruşen et al., 2008). The lead-sulphate residues react with Cl-ions, whereby the dissolved Pb forms up to four consecutive chloride-complexes in aqueous solution ($PbCl^+$, $PbCl_2$, $PbCl_3^-$, $PbCl_4^{2-}$). This formation of chloride-complexes significantly increases the solubility of Pb and other chloride-complex-forming metals such as Cu and Cd (Sinadinovic et al., 1997). Beside the addition of an oxidizing agent during fly ash leaching, a secondary leaching step of the residual filter cake from the FLUWA process using concentrated sodium chloride solution (NaCl) is therefore a promising option to enhance metal recovery from fly ash. The aim of this study is to investigate the mobilization of heavy metals from two different fly ashes by hydrochloric acid leaching (HCl, represents the FLUWA process) and subsequent NaCl-leaching with special attention to Pb and Cu mobilization. The factors influencing the metal mobility are investigated with emphasis on redox conditions and the role of the chlorine responsible for metal mobilization. This is achieved by chemical and structural characterization of the leached filter cakes and precipitates from the leaching solution, complemented with the determination of aqueous speciation of heavy metals in the leaching solutions using UV–VIS spectroscopy and thermodynamic modelling.

2. Materials and methods

2.1. Origin of fly ash and sample preparation

The leaching experiments were performed with fly ash from two MSWI plants in Switzerland (Table 1). Both plants are using the FLUWA process and in addition to their own fly ash they also treat fly ash from other MSWI plants. The first fly ash mix contains fly ash from two MSWI plants, both with an elevated portion of industrial waste input (fly ash A). The second mix contains fly ash from three MSWI plants with an elevated portion of household waste input (fly ash B). The primary bulk samples were generated from many sub-samples (2–3 samples of ca. 300 g per day) collected over a three-week sampling period. After being homogenized in a bucket, samples were split into 1 kg laboratory aliquots which were dried at 105 °C for further analyses. The dried fly ash samples (median grain size ca. 0.1 mm), were ground to a particle size <0.01 mm in a tungsten-carbide disk mill for chemical analysis. The original fly ash samples were used for the leaching experiments.

2.2. Leaching experiments

The leaching experiments were performed in two steps (Table 2). In a first step, the fly ashes were leached with HCl 5%

Table 1
Composition of fly ash mixes used in this study, determined by ED-XRF (mg/kg). The results by TD-ICP-OES revealed erroneous quantifications by ED-XRF for Al, Mg and Na due to matrix interferences (metallic Al^0) and low sensitivity of the ED-XRF at low energy (Mg, Na). The results of the TD-ICP-OES analyses were therefore preferred for these elements.

Element (mg/kg)	Fly ash A	Fly ash B
Al[a]	31,429	47,349
Ba	1881	1908
Br	3847	3211
Ca	152,700	185,500
Cd	370	275
Cl	103,300	109,900
Cr	468	465
Cu	2512	1776
Fe	20,510	20,010
K	46,900	46,750
Mg[a]	12,262	14,434
Mn	784	671
Ni	123	146
P	4497	4708
Na[a]	48,396	49,604
Pb	11,920	8114
S	55,430	54,580
Sb	2976	2396
Si	81,260	76,920
Ti	9308	10,660
Zn	65,420	40,510
Sn	1682	1,335

[a] Determined by TD-ICP-OES.