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Chemical associations and mobilization of heavy metals in fly ash from municipal solid waste incineration

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ABSTRACT

This study focusses on chemical and mineralogical characterization of fly ash and leached filter cake and on the determination of parameters influencing metal mobilization by leaching. Three different leaching processes of fly ash from municipal solid waste incineration (MSWI) plants in Switzerland comprise neutral, acidic and optimized acidic (+ oxidizing agent) fly ash leaching have been investigated. Fly ash is characterized by refractory particles (Al-foil, unburnt carbon, quartz, feldspar) and newly formed high-temperature phases (glass, gehlenite, wollastonite) surrounded by characteristic dust rims. Metals are carried along with the flue gas (Fe-oxides, brass) and are enriched in mineral aggregates (quartz, feldspar, wollastonite, glass) or vaporized and condensed as chlorides or sulphates. Parameters controlling the mobilization of neutral and acidic fly ash leaching are pH and redox conditions, liquid to solid ratio, extraction time and temperature. Almost no depletion for Zn, Pb, Cu and Cd is achieved by performing neutral leaching. Acidic fly ash leaching results in depletion factors of 40% for Zn, 53% for Cd, 8% for Pb and 6% for Cu. The extraction of Pb and Cu are mainly limited due to a cementation process and the formation of a $PbCu^0$-alloy-phase and to a minor degree due to secondary precipitation ($PbCl_2$). The addition of hydrogen peroxide during acidic fly ash leaching (optimized acidic leaching) prevents this reduction through oxidation of metallic components and thus significantly higher depletion factors for Pb (57%), Cu (30%) and Cd (92%) are achieved. The elevated metal depletion using acidic leaching in combination with hydrogen peroxide justifies the extra effort not only by reduced metal loads to the environment but also by reduced deposition costs.

1. Introduction

The main objectives of thermal treatment of municipal solid waste are mass and volume reduction, destruction of organic contaminants, energy and metal recovery. Two main residues are produced after incineration on grates at 800–1000 °C: bottom ash (20 wt.% of the waste input) and fly ash (2 wt.%). The partition coefficient of metals among the residues during combustion has been studied by several authors (Brunner and Mönch, 1986; Verhulst and Buekens, 1996; Morf et al., 2000, 2013; Abanades et al., 2002; Funari et al., 2016). Heavy metal fractionation depends on the composition of municipal solid waste (MSW), the binding environment of the metals and the operating conditions of the incinerator. Metal transfer to the fly ash is favoured by higher furnace temperatures and thus increasing amounts of dust particles as well as elevated chlorine and sulphur concentration in the flue gas (Jakob et al., 1996; Belevi and Moench, 2000; Morf et al., 2000). Ash particles enriched in heavy metals, salts and organic pollutants are collected at the heat recovery section (boiler ash, coarse particles) or removed from the flue gas by fabric filters or electrostatic precipitators (ESP ash, fine particles). The mixture of boiler and ESP ash is usually combined and referred to as fly ash. Volatile components are removed from the flue gas in a subsequent dry or wet flue gas cleaning process. Water is injected directly into the flue gas in wet flue gas cleaning where mainly HCl, HF and NH_3 are removed (acidic scrub water). In a second step, NaOH is added to remove sulphur oxides (SO_2, SO_3) as sodium sulphate solution (neutral scrub water). These scrub waters can be further used to leach the fly ash in order to remove heavy metals, as first shown in the 3R process (Vehlow et al., 1990). In Switzerland, acidic fly ash leaching (FLUWA process) has been established since 1997 and offers an effective method for heavy metal separation and recovery (Schlumberger et al., 2007). Nowadays, 50% of the fly ashes in Switzerland are treated according to the FLUWA process which represents the state of the art. The other 50% are directly

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Table 1
Technical details of investigated MSWI plants.

Parameter	Plant A	Plant B	Plant C
Type of furnace	2× reciprocating grate	1× moving grate and 1× reciprocating grate	4× reciprocating grate
Produced fly ash (t/day)	6.5	7	8
Fly ash leaching type	Neutral leaching	Acidic leaching (FLUWA process)	Optimized acidic leaching (optimized FLUWA process)
Volumes	Fly ash: 0.35 t/h Process water: 4 m^3/h	Fly ash: 7 t/h Scrub water: 10 m^3/h Deion. water: 2.5 m^3/h (filtration)	Fly ash: 1 t/h Scrub water: 3.5 m^3/h H_2O_2 (35%): 40 L/t fly ash Deion. water: 0.7 m^3/h (filtration)
LS ratio	11.4	1.4	3.5
pH process-/scrub water	pH 7.9–9.5	pH <1	pH <1
Extraction time	60 min	20 min per tank	25 min per tank
Mass loss (wt.%)	5	13	32
pH of ash slurry	pH 10.8 (25 °C)	Tank 1: pH 2.5–3.2 (60 °C) Tank 2: pH 5.5 (55 °C)	Tank 1: pH 2.5–3.5 (60 °C) Tank 2: pH 4.2 (58 °C) Tank 3: pH 4.8 (55 °C)

deposited in underground storage abroad or extracted with water (neutral leaching) to remove water-soluble salts before stabilization/solidification with cement (Ferreira et al., 2003; Quina et al., 2008a). Neutral leaching shows low metal extraction efficiency (<5%), mainly dependent on the resulting pH-value of the ash suspension. Within the next five years, all fly ash produced in Switzerland has to be acid leached according to the state of the art as prescribed in the Swiss Waste Legislation (Swiss Confederation, 2016).

Within the FLUWA process, the fly ash is leached with hydrochloric acid (acidic scrub water) in a multistage cascade. The extractability of heavy metals is depending on the alkalinity of the fly ash, acidity of the scrub water, liquid to solid ratio (LS), temperature and extraction time. After ca. 60 min of extraction, the suspension is separated by vacuum belt filtration into a metal depleted filter cake and a metal enriched filtrate solution. The filter cake is deposited and the metalliferous filtrate is used for direct metal recovery (FLUREC; Schlumberger et al., 2007) or fed to a waste water treatment plant with metal hydroxide sludge precipitation and subsequent zinc recovery abroad. The extraction of heavy metals from fly ash is mainly dependent on the metal associations and their accessibility. The incorporation of metals in carbonates, oxides, silicates or glasses or its presence in metallic form affects the solubility and dissolution rates of the metals during fly ash leaching. This is evident from the concentrations in the remaining filter cakes (Johnson et al., 1999; Van Herck et al., 2000).

To increase the recoveries of mainly Zn, Pb, Cu and Cd from the fly ash and therefore minimize the metal load to the landfills, the knowledge of the binding forms of heavy metals and the enclosed phases (host particles) controlling the metal leaching in fly ash is essential. Numerous studies related to the characterisation of untreated fly ash are known (Eighmy et al., 1995; Sandell et al., 1996; Le Forestier and Libourel, 1998; Thipse et al., 2002; Li et al., 2004; Kutchko and Kim, 2006; Quina et al., 2008b; Mahieux et al., 2010) and a lot of data on the mineralogical composition of leached filter cake are obtained from laboratory experiments (Kirby and Rimstidt, 1994; Eighmy et al., 1995; Liu et al., 2009; Karlfeldt Fedje et al., 2010; Bayuseno and Schmahl, 2011).

The aim of this study is to investigate the industrial scale leaching process from fly ash to improve heavy metal separation and to estimate the limiting factors of depletion. The focus is on chemical and mineralogical characterisation of fly ash and the corresponding filter cake from three Swiss MSWI plants. Plant A is performing neutral leaching, plant B acidic leaching and plant C optimized acidic leaching with the addition of an oxidising agent. The detailed characterization of the fly ash contributes additionally to a better understanding of the ash formation processes.

2. Materials and methods

2.1. Origin of fly ash and filter cake

The three MSWI plants have similar flue gas cleaning systems built of boiler, electrostatic precipitator (ESP), flue gas scrubber, catalyst and chimney. Fly ash is only composed of boiler- and ESP ash and additional residuals from the flue gas cleaning process are removed separately (e.g. dioxin, mercury). Plant A produces 6.5 t/d fly ash that is neutrally leached using water from the last step of the water treatment process with an initial pH of 7.9–9.5 (process water). Neutral leaching is performed by mixing 0.35 t/h fly ash and 4 m^3/h process water with a pH of 10.8 after 1 h of extraction (Table 1). Plant B produces 7 t/d fly ash that is treated using the scrub water from the wet flue gas cleaning process. This acidic fly ash leaching (FLUWA process) is performed in a two-stage extraction cascade using 7 t/h fly ash and 10 m^3/h of a mix of acidic and neutral scrub water. The reaction of fly ash and scrub water in the first extraction tank result in a pH of 2.5–3.2 at 60 °C after 20 min. The second extraction tank is used for reaction stabilization and the pH value increases to 5.5 at 55 °C after 40 min. A pH >4 is required in the last extraction tank for smooth vacuum belt filtration. This is achieved by varying the fly ash/scrub water ratio or if necessary by the addition of lime or sodium hydroxide. Plant C produces 8 t/d fly ash and together with the fly ash from another Swiss plant, the mixture is treated by acidic leaching. The acidic fly ash leaching at plant C is performed with the addition of hydrogen peroxide 35% (40 L/t fly ash) in a three-stage extraction cascade (optimized FLUWA process). In a first extraction tank 1 t/h fly ash and 3.5 m^3/h of a mix of acidic and neutral scrub water are extracted and a pH of 4.2 is adjusted after 30 min of extraction. The ash slurry is further transferred into a second and third extraction tank to stabilize the reaction before filtration. The metalliferous filtrate is used for direct metal recovery by solvent extraction and zinc electrowinning (FLUREC).

2.2. Sampling and sample preparation

Heavy metal concentration in fly ash varies significantly, mainly depending on waste input and season. It has been shown that a sampling of fly ash and filter cake over three weeks (November/December 2013) is necessary for representative samples of each

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