



The pH-dependent leaching of inorganic contaminants from secondary lead smelter fly ash

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ABSTRACT

The leaching behaviour of fly ash (FA) from a secondary Pb smelter was assessed using the pH-static leaching experiment according to prEN 14997 (pH range 3–11) coupled with mineralogical investigation of the leached FA by XRD and Rietveld analyses and thermodynamic modelling using PHREEQC-2. The procedure was performed on fresh FA and FA washed at a cumulative L/S ratio of 60 l/kg to remove readily soluble salts. For both fresh and washed FA, high amounts of inorganic contaminants were released under acidic conditions, exhibiting L-shaped leaching patterns: up to 300 g Pb/kg, 4.5 g Cd/kg, 4 g Zn/kg, 1.05 g As/kg and 70 mg Sb/kg. The washing of soluble salts significantly decreased the leachability of Cd, Zn, As and Sb and increased the release of Pb, especially under acidic conditions. The leaching of fresh FA removed part of primary caracolite and all the KPb_2Cl_5 and NaCl. The Pb release was controlled by the precipitation of anglesite and PbSO_3 under acidic conditions and of laurionite and carbonates (hydrocerussite and phosgenite) under alkaline conditions. In contrast, the washed FA was composed mainly of anglesite and PbSO_3 , both phases being the main solubility-controlling phases for Pb over the whole studied pH range.

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1. Introduction

The leaching behaviour of fly ash (FA) from secondary Pb metallurgy is important for assessment of contamination in specific scenarios. Fly ash from Pb metallurgy contains high amounts of metals and other inorganic contaminants and is classified as a hazardous material. The efficiency of the filtering systems in smelters is very high (99.85%); however, a certain amount of the residues can be emitted and may settle into the environment [1]. As a result, increased concentrations of metals may be released into soils in the vicinity of the smelters [2,3]. Understanding the leaching characteristics is important for both environmental and toxicological assessment. Using different leaching tests, information on the contaminant leachability and solubility-controlling phases can be obtained and the pH is one of the key parameters controlling the leaching process [4–7]. The release of metals is primarily controlled by the solubility of various solid phases directly affected by changes in the pH [5,8]. So far, numerous studies have investigated the leaching of metals as a function of the pH from mineral wastes from municipal solid waste incineration (MSWI) [4,5,9] or from contaminated soils and sediments [6,8]. General leaching trends

of metals (Cd, Zn, Cu, etc.) from MSWI residues exhibit a typical U- or V-shaped curve with higher concentrations in the acidic and alkaline pH regions as a result of precipitation/dissolution or sorption/desorption processes [10,11].

This paper is a continuation of previous works on the chemical and mineralogical characterisation of fly ash from secondary Pb metallurgy and leaching experiments using standardised simple extractions [1,2]. Here, we present the first results on the pH-dependent leaching behaviour of smelter fly ash using pH-static experiments according to the European standard prEN 14997 [12], performed on fresh and washed residue samples. The main objectives of this study were to investigate: (i) the pH-dependent leaching and identification of the solubility-controlling phases using pH-static leaching experiments and (ii) the effect of washout of soluble salts, to assess the leaching behaviour of the fly ash under real-life conditions. The leaching tests were coupled with mineralogical/geochemical investigation of fly ash and speciation-solubility thermodynamic modelling.

2. Materials and methods

2.1. Fly ash

The fly ash was collected at the secondary Pb smelter in Příbram (Kovohutě Příbram), Czech Republic, mainly processing used car

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batteries. The FA consists of a fine-grained solid material trapped by bag-type filters after flue gas cooling by alkaline water, which is collected as a leachate from the alkaline metallurgical slag disposal. The details of the smelter processing technology are given elsewhere [1]. In addition to fresh FA, a washed FA sample was also studied. To remove highly soluble salts, an aliquot part of the fresh FA was washed according to Hyks et al. [11] in a sequence of six steps to a cumulative L/S (liquid/solid) ratio of 60 l/kg (details see below).

The bulk chemical composition of both fresh and washed FA was determined after the dissolution/decomposition of FA residues in teflon beakers (Saville[®], Minnetonka, USA) in a mixture of HNO₃ and HF (1:5). The concentrations of the elements were determined by atomic absorption spectrometry (AAS; Varian SpectrAA 280 FS, Australia). The analyses were run in triplicate and the standard reference materials NIST SRM 1633b (Coal fly ash) and BCR-038 (Fly ash from pulverised coal) were used for quality control of chemical analyses. The contents of total inorganic carbon (TIC) and total sulfur (S) in the solid residues were determined by Eltra CS500 and Eltra CS530 C/S analysers (Germany). The content of Cl in the residue digests was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Spectro, Germany).

2.2. Leaching procedure

2.2.1. Washing steps

To obtain the washed FA sample, readily soluble compounds were removed in a sequence of six washing steps at a fixed L/S ratio of 10 in each step according to Hyks et al. [11] until a cumulative L/S ratio of 60 l/kg was reached. The fresh FA sample was mixed with deionised water (MilliQ+) at L/S = 10 and agitated for about 10 min. The suspension was left to settle and thereafter the liquid was carefully removed and replaced with fresh water. An aliquot part of the leachate was filtered (Millipore 0.45 μm) and the physico-chemical parameters (pH, E_h and specific conductivity) were measured (Schott multimeters). This washing procedure was repeated six times. The leachate of each washing step was prepared for cation analysis (acidified with HNO₃ to prevent the precipitation of secondary phases) and anion analysis and for alkalinity measurements (for analytical details, see below).

2.2.2. pH-static leaching experiment

Both fresh FA and washed FA were subjected to the pH-static experiment according to European standard prEN 14997 [12]. All the experiments were performed in duplicate and with procedural blanks. Preliminary determination of the acid and base consumptions (ANC—acid neutralisation capacity; BNC—base neutralisation capacity) was performed before the pH-static leaching.

The pH-static experiments were carried out at 20 ± 4 °C for 48 h. A mass of 5 g of solid was placed in a 100-ml PE bottle and 45 ml of MilliQ+ deionised water was added to maintain an L/S ratio of 9 with a final ratio of about 10 after the addition of acid/base. The values were selected in the pH range of 3–11 (3, 4, 5, 6, 7, 8, 9, 10 and 11) to cover the conditions in the smelter area (pH_{soil} ~ 3.5) and other possible scenarios. Acid (14 M, 1 M HNO₃) or base (1 M, 2 M and 5 M NaOH) was added to adjust the pH values. During the initial period (4 h), acid (14 M HNO₃) and base (1 M NaOH) were added to obtain the predefined pH values. Continuous pH control and acid/base titration using primarily 1 M HNO₃ or 1 M NaOH followed. The reactors were continuously agitated (except for the time of pH control and titration). After 48 h, the reactors were centrifuged to settle residue particles and the leachate was filtered (Millipore 0.45 μm). The physico-chemical parameters (pH, E_h and specific conductivity) were measured immediately in the leachate (Schott multimeters). The leachate was prepared for cation and anion analyses and for alkalinity measurements.

2.3. Analytical procedure and geochemical modelling

Leachate samples from each experiment were analysed for Na, K, Ca, Mg, Fe, Mn, Ni, Cd, Pb and Zn by AAS (Varian SpectrAA 280 FS), Al, Si, Cr, Co, Ni, Cu, As, Se, Sr, Mo, Sn, Sb and Ba by ICP-MS (VG Elemental PlasmaQuad 3), total S by ICP-OES (Thermo IRIS Intrepid II XSP) and for the anions Cl⁻, SO₄²⁻ and NO₃⁻ by HPLC (Dionex ICS-2000). The accuracy of the determinations was controlled using a Merck IV solution (ICP multielement standard IV, Merck, Germany), CRM CZ9102 (Analytika, Czech Republic) and NIST SRM 1943d (Trace elements in water, NIST, USA). The alkalinity of the samples with pH > 4.5 was measured by back titration (0.05 M HCl) using a Schott TitroLine Easy automatic titrator. The analytical results were coupled with geochemical modelling using the PHREEQC-2 code [13] to determine the speciation of the contaminants in the leachates and the degree of leachate saturation with respect to the solubility-controlling phases as a function of the pH. The minteq.v4.dat database supplied with the PHREEQC-2 code was used for all the calculations.

2.4. Solid-phase analysis

Both fresh and leached FA were dried at 40 °C and finally ground to analytical fineness and subjected to X-ray diffraction (XRD) analysis (PANalytical X'Pert Pro diffractometer with X'Celerator detector; Cu Kα radiation, 40 kV, 30 mA, range 5–80° 2θ, step 0.02°, counting time 300 s per step). Qualitative analysis was performed with the X'Pert HighScore software 1.0 equipped with the ICDD PDF-2 database [14]. The results exclude the possible presence of amorphous admixtures, which were suggested by Ettler et al. [15]. Quantitative determination of the phases (%) was performed by means of the Rietveld procedure using the Topas 3 software supplemented with the ICSD database [16]. Consequently, the results were normalised with respect to the original mass of the sample in order to quantify transformations of the phases as a function of the pH.

3. Results and discussion

3.1. Chemistry and mineralogy of fly ash and the effect of washing

The chemical and mineralogical compositions of fresh and washed fly ashes are given in Tables 1 and 2, respectively. The principle constituents of the fresh FA are Pb (32%), Na (27%), Cl (27%),

Table 1
Chemical compositions of fresh and washed fly ashes (FA).

Element (mg/kg)	Fresh FA	Washed FA
Pb	240,300 ± 15,620 ^a	607,800 ± 10,810
Na	204,800 ± 2630	4190 ± 1301
K	32,770 ± 770	2550 ± 130
Ca	216 ± 50	256 ± 50
Mg	109 ± 12	92 ± 9
Si	2430 ± 570	2810 ± 70
Al	237 ± 90	303 ± 30
Mn	69 ± 2	104 ± 1
Fe	2980 ± 40	6170 ± 200
Zn	5020 ± 240	5880 ± 12
Cd	4490 ± 310	4760 ± 90
Cu	274 ± 9	616 ± 3
As	3900 ± 130	8750 ± 380
Sb	1630 ± 60	4810 ± 20
Sn	1780 ± 20	4610 ± 80
Cl	199,000 ± 3980	11,500 ± 230
TS ^b (%)	6.45 ± 0.014	6.64 ± 0.009
TIC ^b (%)	0.10 ± 0.010	0.31 ± 0.021

^a Mean value and standard deviation ($n = 3$).

^b TS, total sulphur; TIC, total inorganic carbon.

Table 2
Mineralogical compositions of crystalline portion of fresh and washed fly ashes (FA).

Phase	Formula	Fresh FA (%)	Washed FA (%)
Galena	PbS	1.5	2.5
PbSO ₃	PbSO ₃	3	38
Caracolite	Na ₃ Pb ₂ (SO ₄) ₃ Cl	38	–
Halite	NaCl	47	–
KPb ₂ Cl ₅	KPb ₂ Cl ₅	10.5	–
Anglesite	PbSO ₄	–	56.5
Leadhillite	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂	–	3

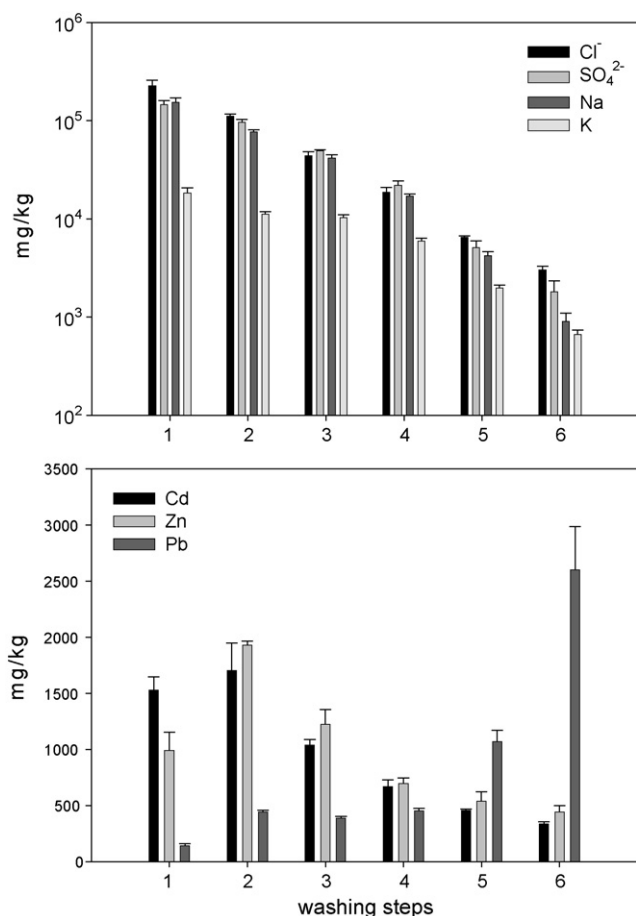


Fig. 1. Leaching of salts and metals from fresh FA as a function of washing steps.

S (7%) and K (4%), while Pb greatly predominates in the washed FA (85%) (Table 1). Halite (NaCl) and caracolite (Na₃Pb₂(SO₄)₃Cl) are the principal phases of the fresh FA, accounting for 47% and 38%, respectively, with minor K–Pb chloride (KPb₂Cl₅) (10%) and trace PbSO₃ and galena (PbS) (Table 2). The chemical and mineralogical compositions are in accordance with previous studies of this type of fly ash [2]. After complete washing out of the soluble salts, anglesite and PbSO₃ became the main phases (Table 2). The washing resulted in a significant decrease in the concentrations of Na, Cl⁻, SO₄²⁻ (two orders of magnitude) and K (one order of magnitude) (Fig. 1). These results are in accordance with other studies [4,5,11], indicating that some fly ash components are highly soluble. The concentrations of Zn and Cd also decreased during individual washing steps in contrast to Pb, exhibiting an increasing release (Fig. 1). However, the portions of Zn and Cd in both fly ashes were almost the same (Table 1). In contrast, there were significant differences between fresh and washed fly ashes in case of Fe, Cu, As, Sb and Sn (Table 1). The concentrations increased approximately two (Fe, Cu and As) or three times (Sb and Sn) in the washed FA due to

washing out of the salts, which increased their percentage of the bulk concentration.

3.2. Physico-chemical parameters and ANC/BNC

The pH value gradually decreased by about one unit as a result of washing. The natural pH of the fresh FA was 6.9, while the value of the washed FA was 5.7. Both samples had a very high buffering capacity, resulting in increasing consumption of acid/base during the pH-stat experiment (Fig. 2). The E_h values indicated oxidic conditions with values ranging from 475 mV (at low pH) to 250 mV. The specific conductivity of fresh FA leachates was relatively high during the pH-stat experiment (65–69 mS/cm), indicating a high content of total dissolved salts. The values were significantly lower (2–15 mS/cm) following washing.

3.3. pH-static leaching

Considering the relatively low concentrations of other toxic elements (e.g. Cu), only the most important inorganic contaminants are discussed in this study (Pb, Cd, Zn, As and Sb); their leaching behaviour as a function of pH can be derived from Fig. 3. Contaminant leaching showed a general trend with maximum concentrations at pH 3 and a more or less sharp decrease towards higher pH values in both variants of the test. The most significant decrease occurred in the pH range of 3–6. In some cases, the concentrations slightly increased at pH 11 (Pb and As in washed FA, Fig. 3), which is related to specific dissolution or sorption reactions. These results, exhibiting L-shaped leaching curves, are in contrast with experiments performed on fly ash from MSWI [9,10,17] showing generally V- or U-shaped leaching curves for metals, in particular Pb and Zn. The leachate concentrations of washed FA were significantly lower (even by several orders of magnitude) than in case of fresh FA for the majority of the analysed elements except for Pb.

Cadmium was released in relatively high concentrations with a significant decrease as the pH increased in both FA samples (fresh FA: 4500–2 mg/kg, washed FA: 2700–0.3 mg/kg, pH 3–11). The different leaching curves of Cd reflect the level of the chloride content. The leaching curve has a similar shape but is shifted towards higher pH due to larger amounts of Cl⁻ [9]. Based on speciation modelling, the formation of chloride complexes is probably responsible for the higher leaching of Cd. In the case of Zn, the leaching trend was mostly identical for both samples with a dramatic decrease in the neutral pH region (fresh FA: 4100–5 mg/kg, washed FA: 2500–1 mg/kg, pH 3–11). The influence of Cl⁻ on the Zn leaching was not as significant as for Cd [9]. The greatest concentrations of Pb released from the fresh FA ranged from 550 mg/kg to 650 mg/kg (pH 3–6). The decrease in the Pb concentration with the pH was not as dramatic as for Cd and Zn. At pH 7 the values lowered by about half and the decrease gradually followed to pH 11 (85 mg/kg). In contrast to other metals, increased mobility of Pb after washing was observed during the leaching experiment especially at low pH. The concentrations of Pb released from the washed samples were by three (pH 3) and two (pH 4 and 5) orders of magnitude higher, yielding concentrations of 300 g/kg, 70 g/kg and 10 g/kg, respectively. From neutral pH values, the Pb concentrations decreased slowly to 2–15 mg/kg (pH 10–11). Arsenic and antimony exhibited a similar trend as metallic contaminants. In the fresh FA, the concentrations of As and Sb ranged from 1050 mg/kg to 3.5 mg/kg and from 70 mg/kg to values below the detection limit, respectively. The maximum concentrations released from washed FA (pH 3) were 1 mg/kg for As and 4 mg/kg for Sb. The leaching of chlorides did not exhibit any specific pH dependence, while sulphates exhibited lower leachability under acidic conditions, probably due to the presence of solid sulphates (data not shown).

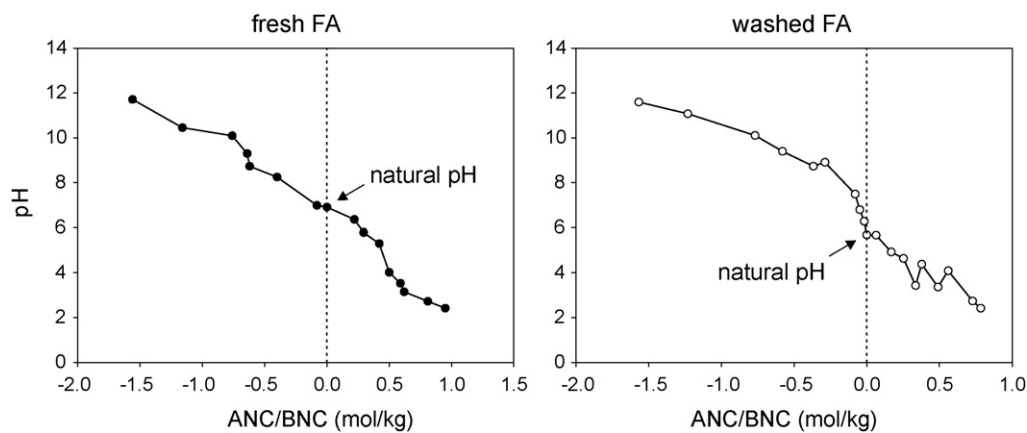


Fig. 2. ANC/BNC patterns for fresh and washed FA with indicated natural pH.

The PHREEQC-2-calculated changes in speciation showed that metallic elements (Pb, Cd and Zn) predominantly formed chloro-complexes and/or sulphate complexes under acidic conditions in fresh FA leachates. As the pH increased, carbonates and a variety

of hydroxocomplexes were formed. In sharp contrast, free ionic forms of the metals predominated in the acidic and neutral region in washed FA. Sulphate complexes or hydroxocomplexes were mainly formed at high pH values. Arsenic and antimony were represented

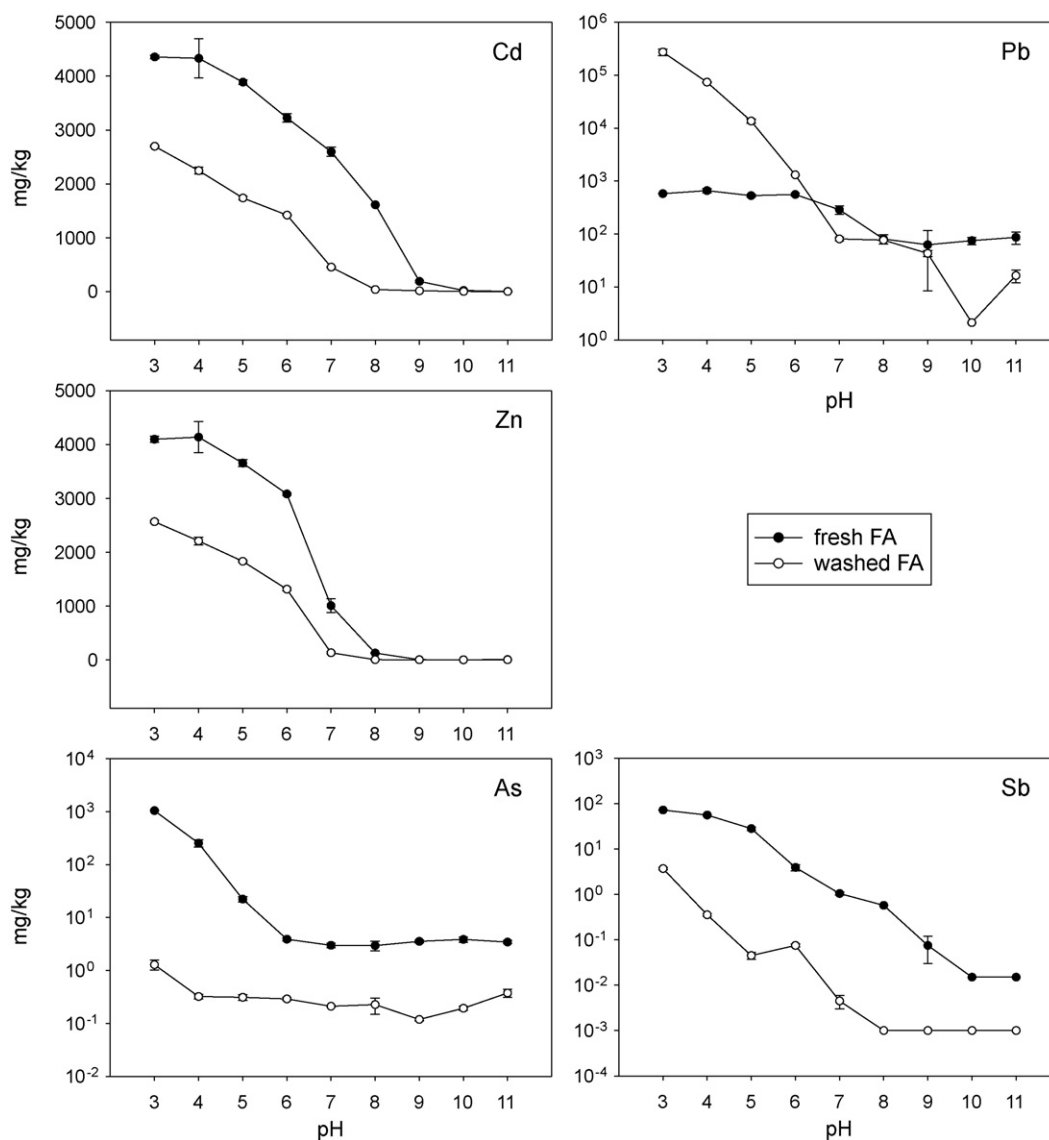


Fig. 3. Leaching of selected contaminants as a function of the pH.

Table 3
Phase transformation as a function of the pH.

Phase	Formula	Fresh FA leaching (%)								
		FA	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	
Galena	PbS	1.3	0.5	0.5	0.5	0.6	0.8	0.7	1.1	
Caracolite	Na ₃ Pb ₂ (SO ₄) ₃ Cl	38	15.2	18.5	21.7	28.5	11.3	–	–	
PbSO ₃	PbSO ₃	3.2	1.7	2.2	2.6	4.5	8.8	11.6	7.9	
Anglesite	PbSO ₄	–	18.8	15.8	12.4	–	–	–	3.7	
Palmierite	PbK ₂ (SO ₄) ₂	–	2.7	3.5	2.6	–	–	–	–	
Phosgenite	PbCl ₂ ·PbCO ₃	–	–	–	–	3.2	1.6	0.2	0.2	
Laurionite	Pb(OH)Cl	–	–	–	–	–	11.3	16.1	16.9	
Hydrocerussite	Pb ₃ (CO ₃) ₂ (OH) ₂	–	–	–	–	–	0.7	5.4	4.5	
KPb ₂ Cl ₅	KPb ₂ Cl ₅	10.6	–	–	–	–	–	–	–	
Halite	NaCl	46.8	–	–	–	–	–	–	–	

Phase	Formula	Washed FA leaching (%)								
		FA	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	
Galena	PbS	2.5	1	1.5	1.7	1.9	2.2	2.3	2.3	
PbSO ₃	PbSO ₃	38	16.9	23.9	28.3	28.9	31.9	34.1	38.7	
Anglesite	PbSO ₄	56.5	49.2	65.5	65.3	65.1	61.1	57.6	49.9	
Leadhillite	Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂	3	–	–	2	2.9	3.5	3.6	4	

as oxidic species in the form of anions (H₂AsO₄[−], HAsO₄^{2−}, AsO₄^{3−} and SbO₃[−]) according to the pH value. At high pH, As is likely to form oxyanions (AsO₄^{3−}). This form is rather mobile since sorption reactions are limited under such alkaline conditions.

3.4. Phase transformation as a function of the pH

From a mineralogical point of view, the phase composition significantly changed depending on the pH and salt content (Table 3). The Pb leaching is controlled by only a few main Pb-bearing phases. Other contaminants (Cd, Zn, Sb and As) are assumed to be sorbed on trace phases (not detected by XRD) or Pb phases, or substitute other elements in their structures (such as Cd for Pb in caracolite [1]). X-ray diffraction showed a certain amount of amorphous/nanocrystalline matter (resulting in an increase in the background between 15° and 40° 2θ), probably formed by PbSO₃ [15]. The high content of these phases did not allow determination of the mineral composition in samples at pH 10 and 11. Galena (PbS) was found to be a stable minor phase in both FA samples in relatively stable fractions in the whole pH range.

Determination of the transformation processes is essential in the assessment of leaching behaviour of Pb since dissolution may result both in the formation of new phases and contaminant release into the solution. Soluble salts (halite and KPb₂Cl₅) were completely dissolved regardless of the pH, whereas caracolite (Na₃Pb₂(SO₄)₃Cl) was partly dissolved and partly converted to secondary phases: anglesite (PbSO₄) in the acidic region (pH 3–5) and laurionite (Pb(OH)Cl) in the alkaline region (pH 7–9). These transformations are in good agreement with preliminary data published by Ettler et al. [2]. At pH 6, caracolite exhibited the highest stability. However, at pH 7 the dissolution of caracolite was more effective in favour of the other phases followed by complete dissolution at pH 8 and 9 with laurionite and PbSO₃ as the main phases. Secondary phosgenite (PbCl₂·PbCO₃) occurred at pH 6 (3%) with decreasing percentage as the pH increased. Simultaneously, the portion of hydrocerussite (Pb₃(CO₃)₂(OH)₂) and laurionite increased in the pH range of 7–9. These results confirmed the PHREEQC-2 predictions of the presence of laurionite and phosgenite at pH > 7 (−0.5 > SI > 0) and pH 6–8 (−1 > SI > −0.5), respectively (Fig. 4). In contrast, the leachate was oversaturated with respect to hydrocerussite and undersaturated with respect to phosgenite at pH 8–11, indicating the presence of hydrocerussite and instability of phosgenite at high pH. According to Edwards et al. [18], Pb chlorides are readily soluble under circumneutral and alkaline conditions and the formation of lau-

rionite can be observed. A subsequent interaction with dissolved CO₂ leads to the formation of phosgenite. However, Phosgenite is, unstable in the alkaline region and is transformed to the final products, cerussite or hydrocerussite [18]. The PHREEQC-2 calculations predicted that cerussite (PbCO₃) should occur in the pH range of 6–11 with saturation indices near 0 in leachates from both fresh and washed FA. However, cerussite was never detected by XRD in leached FA.

The phase composition of washed FA samples was the same throughout the pH range except for leadhillite (Pb₄(SO₄)(CO₃)₂(OH)₂) (Table 3). Based on PHREEQC-2 calculations, the leachates were undersaturated with respect to laurionite and phosgenite throughout the pH range (Fig. 4). Taking into account the low stability of laurionite and phosgenite in washed residues, the principle phase was anglesite with various percentages as a function of the pH (50–70%). The greatest amounts of anglesite were formed in the pH range of 4–6. The second main phase was represented by orthorhombic PbSO₃. This phase exhibited increasing stability as the pH increased. The most effective dissolution of PbSO₃ occurred at pH 3, when almost half the original phase was dissolved. Increased leachability of Pb at pH 11 may have several reasons. Despite the missing information about the phase composition at pH 11, we suppose that PbSO₃ as dominating phase is less stable under such alkaline conditions and therefore partly dissolved. According to Hyks et al. [11], the leaching of Pb at high pH can be described by the solubility of Pb₂(OH)₃Cl. Following the PHREEQC-2 calculations, lanarkite (PbO·PbSO₄) and cerussite were oversaturated in the pH range of 7–9 with decrease at pH 10 and 11 (Fig. 4) indicating their potential dissolution. However, these phases were not detected by XRD.

Some general characteristics were exhibited by both fresh and washed FA based on PHREEQC-2 calculations. In the range up to pH 9, metallic phases with Mo were predicted, especially CdMoO₄ and PbMoO₄. According to the results of ICP–MS analyses, the Mo concentrations were relatively low for formation of significant amounts of molybdate phases detectable by conventional XRD. The presence of anglesite predicted by PHREEQC-2 was confirmed at pH < 9 in both FA samples, in good accordance with the mineralogical study. The leachates were undersaturated with respect to galena in both FA samples. In contrast, galena was a relatively stable phase, probably for kinetic reasons, and it was only slightly dissolved at lower pH values (Table 3). The presence of cotunnite (PbCl₂), which was previously detected in smelter fly ash of different chemical and mineralogical composition [1], and lanarkite, both predicted by

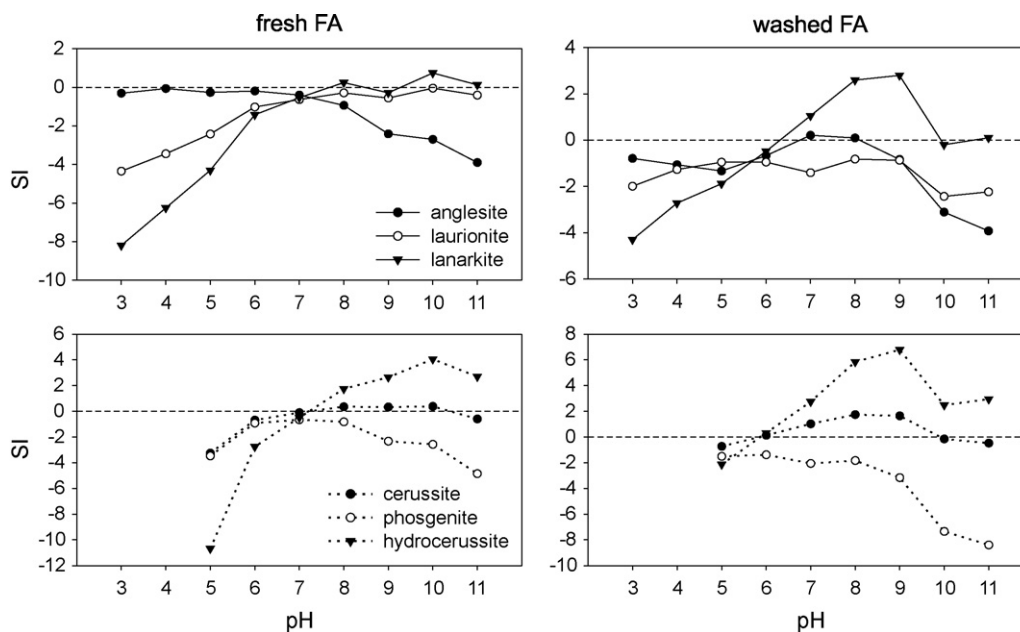


Fig. 4. Saturation indices of selected possible solubility-controlling phases according to the PHREEQC-2 calculations.

PHREEQC-2, was not confirmed in this study. The PHREEQC-2 calculations indicated the formation of possible Cd- or Zn-bearing phases (otavite CdCO_3 , $\text{Cd}(\text{OH})_2$, zincite ZnO and smithsonite ZnCO_3) in both fly ashes. The leaching behaviour of Cd could be described by precipitation of otavite in the range of pH 7–10. The formation of $\text{Cd}(\text{OH})_2$ could be responsible for the decreasing Cd concentrations above pH 10 [11]. The washed FA leachates were saturated with respect to $\text{Cd}_4(\text{OH})_6\text{SO}_4$ in the range of pH 9–11. Similar to Hyks et al. [11] the formation of zincite was predicted for pH values 9–11. Smithsonite represents another possible phase that may limit the release of contaminants mainly between pH 6 and 9. However, none of these phases was detected by XRD perhaps because of its low sensitivity (detection limit $\sim 1\%$) or because of the presence of these metals as isomorphous substitutions in major phases. The release of other contaminants is probably controlled by sorption processes or their incorporation into mineral phases [4,10]. The PHREEQC-2 calculations are in agreement with experimental data under acidic conditions; possible controlling phases are dissolved and the concentrations of contaminants increase. In MSWI waste residues, surface complexation processes and adsorption to hydrous ferric oxides (HFO), hydrous aluminium oxides (HAIO) and complexation with dissolved organic carbon (DOC) were found to partly control the leaching of metals (Cu, Pb and Zn) [10,11]. In contrast, the presence of these compounds was not confirmed in our smelting residues. Thus, these processes were not included in the modelling. Another difficulty in the model predictions is the missing thermodynamic data for some key solubility-controlling phases such as PbSO_3 and caracolite.

3.5. General discussion and environmental implications

The effect of the pH and salt level on the leaching behaviour of the main contaminants in the fly ash was demonstrated. In particular, inorganic contaminants, such as Pb, Cd, Zn, As and Sb, were more leached at low pH, which is in agreement with other studies (e.g. 4, 5, 7, 9, 11 and 17). However, in contrast to fly ash from MSWI, where U- or V-shaped leaching patterns were observed, we generally report L-shaped leaching behaviour (Fig. 3) related to the specific mineralogical composition of the smelter fly ash and the strongly pH-dependent phase transformations. Leaching charac-

teristics also showed the importance of the sulphate and chloride levels. During the washing steps, most readily soluble salts were removed, along with large amounts of metals. The intention of this experimental step was to approximate “real-life” conditions, including the effect of rain and initial rapid wash-out of readily soluble salts in a specific scenario, such as in soils in the vicinity of the smelter. In the long-term perspective, solutions with low salt content and thus low ionic strength (as in the soils in our case) would represent a specific disposal site more accurately [4]. As a result, the phase composition of FA significantly changed after washing to predominantly contain anglesite and PbSO_3 . The main environmental issue seems to be related to the dissolution of primary Pb chlorides (mainly caracolite) followed by release of Pb and mobilisation of contaminants under acidic conditions. Anglesite (PbSO_4), the principal newly formed phase during the pH-stat leaching, was also detected in soils in the vicinity of the smelter [3]. Previous studies showed that the pH values of the soils in the studied smelter area range from 3.5 to 5.6 [3] and these pH values in the pH-stat leaching will be the most relevant for the prediction of FA leaching behaviour under “real-life” conditions. The results of this study also confirm the relatively high stability of anglesite under different conditions when soluble salts are rapidly washed out. In addition, the mineralogical study indicates that the amorphous/nanocrystalline phase (probably PbSO_3) partly crystallises during the washing followed and is probably partly oxidised to secondary anglesite.

4. Conclusions

The contaminant (Pb, Cd, Zn, As and Sb) leaching from fly ash from secondary Pb metallurgy showed a strong dependence on the pH and salt content. The most effective release occurred at pH 3 and 4 with decreasing trend towards the neutral/alkaline region. The leaching was controlled by dissolution and transformation of several mineral phases, particularly Pb-bearing phases. Halite and KPb_2Cl_5 were completely dissolved throughout the pH range. Caracolite was partly dissolved and converted to newly formed anglesite (pH 3–5) and/or laurionite (pH 7–9). Transformation of PbSO_3 seems to have a significant influence on anglesite formation and leaching of Pb after washing out of soluble salts. During the washing steps, caracolite, halite and KPb_2Cl_5 were completely removed

from the fly ash. After washing, the fly ash was primarily formed by secondary anglesite, which was stable and predominant within the studied pH range. Another main phase was PbSO_3 , exhibiting increasing stability with increasing pH. At pH 3, the dissolution of PbSO_3 and other Pb-bearing phases resulted in release of 300 g Pb/kg. In contrast, the washing out of highly soluble salts decreased the leachability of Cd and Zn. The results show that pH-static experiments represent a powerful instrument for understanding the leaching behaviour of the smelter fly ash under different conditions. Moreover, this study has direct implications for contamination of acidic soils in the vicinity of the Pb smelters.

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