

# Leaching of APC residues from secondary Pb metallurgy using single extraction tests: the mineralogical and the geochemical approach

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## Abstract

Two air-pollution-control (APC) residues – one from flue gas cooling with alkaline water and one from deionised water cooling – from secondary lead metallurgy were submitted to two different standardized short-term leaching protocols: US EPA toxicity characteristic leaching procedure (TCLP) and static leaching according to Czech/European norm EN 12457-2. The experimental procedure was coupled with detailed mineralogical investigation of the solid material (SEM, XRPD) and speciation-solubility calculations using the PHREEQC-2 geochemical code. Both types of residues were considered as hazardous materials exhibiting substantial leaching of Pb (up to 7130 mg/l) and other inorganic contaminants. However, the APC residue produced by flue gas cooling with alkaline water (sample B) exhibits more favourable leaching and environmental characteristics than that produced by simple deionised water cooling (sample A). At pH < 5, primary caracolite ( $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$ ) and potassium lead chloride ( $\text{KCl}\cdot 2\text{PbCl}_2$ ) are completely or partially dissolved and transformed to residual anglesite ( $\text{PbSO}_4$ ), cotunnite ( $\text{PbCl}_2$ ) and laurionite ( $\text{Pb}(\text{OH})\text{Cl}$ ). At pH 5–6, anglesite is still the principal residual product, whereas at pH > 6, phosgenite ( $\text{PbCl}_2\cdot\text{PbCO}_3$ ) became the dominant secondary phase. The results are consistent with the mineralogical and geochemical studies focused on acidic forest soils highly polluted by smelter emissions, where anglesite, as a unique Pb-bearing phase, has been detected. From the technological point of view, the mixing of APC residue with alkaline water, followed by an increase in the suspension pH and equilibration with atmospheric  $\text{CO}_2$ , may be used to ensure the precipitation of less soluble Pb carbonates, which are more easily recycled in the Pb recovery process in the metallurgical plant.

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## 1. Introduction

Air-pollution-control (APC) residues and fly ash collected by flue gas cleaning facilities in metallurgical plants are classified amongst hazardous materials by both the European and the American legislation (European Waste Catalogue [1,2], US EPA regulations [3]). Smelters commonly re-process fly ashes and APC residues in rotary furnaces in order to recover more metals. If the flue gas treatment is inefficient, these APC residues may be emitted by smelter stacks and settle into the environment (soils, sediments, surface waters). As a result, high contamination of soils caused by long-term

smelter emissions has been observed at numerous smelting sites [4,5]. The degree of smelter-related contamination of soils seems to be directly linked to the mineralogy of primary particulate emissions. The works of Sobanska et al. [6] and Ohmsen [7] focused on primary Pb smelter dusts and emissions, and showed that the chemistry and mineralogy of emissions can be extremely complex, depending on (i) the temperature of the flue gas cleaning process, (ii) the nature of the cooling media (water and air) during the dust collection and (iii) the chemistry of the blast-furnace charge. The APC residues from primary Pb smelting derived from Pb–Ag–Zn ore processing are mainly composed of anglesite ( $\text{PbSO}_4$ ) and sulphides (galena  $\text{PbS}$ , sphalerite  $\text{ZnS}$  and greenockite  $\text{CdS}$ ) [6]. In contrast, APC residues from secondary Pb smelting, derived from scrap (mainly car batteries) processing,

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are composed of Pb chlorides (caracolite  $\text{Na}_3\text{Pb}_2(\text{SO}_4)_3\text{Cl}$ , potassium lead chloride  $\text{KCl}\cdot 2\text{PbCl}_2$ , cotunnite  $\text{PbCl}_2$  and laurionite  $\text{Pb}(\text{OH})\text{Cl}$ ) (Ettler et al., unpublished data). These Pb chlorides are commonly more soluble than Pb sulphides and sulphates [8].

So far, only few works have been published on the leachability of APC residues from base-metal smelters [9,10]. Taking into account the extreme compositional complexity of APC residues from Pb smelting, their leaching behaviour is poorly understood even under simple conditions and could be extremely important for environmental/technological strategies. This article is a continuation of the works on mineralogical and leaching characterisation of other mineral waste materials from Pb smelting, such as silicate slags [11,12]. In this study, we performed simple extraction experiments according to standardized short-term leaching protocols (toxicity characteristic leaching procedure (TCLP) [13], European norm EN 12457-2 [14]) on two different APC residues from a secondary Pb smelter. The intent of this paper is not only to assess their hazardous properties with respect to regulatory levels, but to couple these leaching tests with detailed mineralogical/geochemical investigation of fresh/leached solids and speciation-solubility thermodynamic modelling using the PHREEQC-2 geochemical code [15]. This approach helps to decipher the processes governing the leachability of hazardous compounds in the system of the APC residue and a chemically simple solution. Knowledge of these processes could also be important for (i) prediction of the solubility and metal release from APC residues deposited in the environment and (ii) technological pre-treatment of APC residues before further extraction of Pb and other metals/metalloids in the smelter factory.

## 2. Materials and methods

### 2.1. APC residues

Two APC residue samples (3 kg) were collected with the courtesy of Mr. Zdeněk Kunický, Technical Director of the Secondary Pb Smelter in Příbram (Kovohutě Příbram), Czech Republic. They correspond to fine-grained solids trapped by bag-type filters after flue gas cooling in afterburning chambers to approximately 200 °C. The details on the operation of the smelter processing technology are given elsewhere [16]. Residue A corresponds to a solid sample trapped by a bag-type filter after flue gas cooling by pure water. Residue B is a sample from a bag-type filter trapped after flue gas cooling by alkaline water, which is a highly concentrated leachate from a controlled disposal site of alkaline metallurgical slag (approximate water composition: 30–40 g Cl/l, 60–80 g  $\text{SO}_4$ /l, 10 g Na/l, 10 g  $\text{CO}_3^{2-}$ /l, pH ~ 11). The bulk chemical composition of APC residues was determined after digestion in mineral acids and/or sintering and subsequent chemical analysis according to the procedures given by Šulček and Povondra [17] and Czech standard ČSN 720100 [18]. The solutions

were used for the determination of Na, K, Ca, Mg, Mn, Fe, Zn, Cd, Cu, As, Pb, Sb, Si and Al (Varian SpectraAA 200HT flame atomic absorption spectrophotometer, FAAS), Sn (VG Elemental PQ3 inductively-coupled plasma mass spectrometer, ICP-MS), S (Varian Vista Pro inductively-coupled plasma optical emission spectrometer, ICP-OES) and Cl (Beckman DU 62 UV–vis spectrometer). The content of total inorganic C (TIC) was determined by catalytic oxidation (1250 °C) using an Eltra Metalyt CS1000S elemental analyser (Neuss, Germany). The bulk chemical analyses were run in duplicate (maximum RSD was 12%, but generally < 5%) with procedural blanks. NIST-1633b (coal fly ash) and BCR-038 (fly ash from pulverised coal) standard reference materials were used for quality control of chemical analyses (RSD < 10%).

Mineralogical analysis was performed on both fresh and leached solid residues. X-ray powder diffraction (XRPD) was performed on a PANalytical X'Pert Pro diffractometer using  $\text{Cu K}\alpha$  radiation, at 40 kV and 30 mA, over the  $2\theta$  range 5–80°, in steps of 0.05° and with counting time 150 s (X'Celerator detector). Quantitative analysis was performed with the X'Pert HighScore software, version 1.0d (PANalytical, The Netherlands), equipped with a JCPDS PDF-2 database [19]. The residue samples were examined using a JEOL JSM 6400 scanning electron microscope equipped with a Kevex Delta energy-dispersion spectrometer (SEM/EDS). The granulometry of the APC residues was measured by the low-angle laser light scattering (LALLS) method using a Fritsch Analysette 22 Laser Particle Sizer equipped with a He–Ne laser ( $\lambda = 632.8$  nm). Both samples A and B are extremely fine-grained, with 83 and 71% of particles < 1.5  $\mu\text{m}$ , respectively. The specific surface was measured by three-point  $\text{N}_2$  BET surface measurement (Sorptomatic 1990, Carlo Erba Instruments, UK) yielding the values 3.80  $\text{m}^2/\text{g}$  (residue A) and 1.71  $\text{m}^2/\text{g}$  (residue B).

### 2.2. Leaching procedure

#### 2.2.1. Experimental protocol

The leaching experiments were conducted in 250 ml acid-washed HDPE bottles (Azlon®, UK), because the aspect of APC residues and the studied non-volatile contaminants did not require any special devices (such as zero headspace extraction (ZHE) vessels). All the experiments were performed in triplicate and with procedural blanks.

Leaching experiment 1 was conducted according to the experimental protocol of the static leaching test described in detail by European norm EN 12457-2 (EN) [14], recently also adopted in the Czech Republic. A mass of 20 g of solid was placed into the reactor and 200 ml of MilliQ+ deionised water (original pH 5.75) was added in order to maintain a L/S (liquid/solid) ratio of 10. The leaching test was performed at  $22 \pm 3$  °C for 24 h, and the reactors were gently agitated (10 rpm). After the experiments, the reactors were centrifuged to settle fine residue particles at the bottom before the filtration and measurements. Immediately after opening the reactor, the physico-chemical parameters (pH, Eh

and specific conductivity) were measured in the leachate. The values of pH and Eh were determined using a Schott Handylab 1 pH meter equipped with a Schott L 7137 A combined electrode and a Schott PT 737 A (Pt–Ag/AgCl) redox electrode, respectively. The temperature and specific conductivity were measured using an Schott Handylab LF 1 conductometer equipped with a LF 513 T measuring cell and a temperature detector. The supernatant was then filtered to 0.45  $\mu\text{m}$  (Millipore<sup>®</sup>) and split into two aliquot parts, for cation and trace element analysis (diluted and acidified to pH <2 by HNO<sub>3</sub>/HCl), and for anion analysis and alkalinity measurements. The dilutions were made immediately after the filtration to prevent the precipitation of secondary phases, as we expected extremely high element concentration in the leachates.

Leaching experiment 2 was conducted according to the toxicity characteristic leaching procedure (TCLP) experimental protocol defined by US EPA [13]. With respect to the alkalinity and buffering capacity of both solid APC residues, measured according to the TCLP procedure, solution no. 1 with pH  $4.93 \pm 0.05$  was used. The leaching solution was prepared by addition of 5.7 ml of acetic acid (reagent grade, Merck, Germany) to 500 ml of deionised water (MilliQ+), supplementary addition of 64.3 ml of 1 M NaOH (reagent grade, Lachema, CZ) and dilution to 1 l. The final pH of the leaching solution was 4.90. An amount of 10 g was placed in the reactor and 200 ml of leaching solution were added in order to achieve an L/S ratio of 20. The experiment was conducted for 18 h at  $22 \pm 3$  °C, and the reactors were agitated at 30 rpm. The measurements of the physico-chemical parameters and leachate preparation for analyses were analogical to those of the previously described leaching test. In contrast to the defined TCLP protocol, the filtrations were carried out to 0.45  $\mu\text{m}$  (Millipore<sup>®</sup>) and not 0.6–0.8  $\mu\text{m}$  to ensure consistency with the EN leaching test. The solid residues of both leaching tests were dried at ambient temperature and prepared for analysis by SEM/EDS and XRPD.

### 2.2.2. Analytical procedure

The major cations and the majority of the trace elements in the leachates (Na, K, Ca, Mg, Si, Al, Fe, Mn, Cr, Co, Ni, Pb, Zn, Cu and Cd) were analysed by FAAS. The concentrations of As, Sn, Sb and Ba were determined by ICP–MS. The concentrations of dissolved organic carbon (DOC) and inorganic carbon (IC) were determined on a Skalar Formacs<sup>HT</sup> TOC analyser. In addition, the alkalinity of the samples with pH >4.5 was measured by back titration using the 0.05 M HCl (reagent grade Lachema, CZ) using a Schott TitroLine Easy automatic titrator. The concentration of sulphates (SO<sub>4</sub><sup>2-</sup>) in the leachate was determined by the gravimetric method with ignition of the residue (addition of BaCl<sub>2</sub> solution and precipitation of insoluble BaSO<sub>4</sub>) [20]. Chlorides (Cl<sup>-</sup>) in the leachate were determined by the argentometric method (titration by AgNO<sub>3</sub> solution using K<sub>2</sub>CrO<sub>4</sub> as an indicator) [20].

### 2.3. Speciation-solubility modelling

The PHREEQC-2 speciation-solubility code [15] was used to determine the speciation and the degree of saturation of leachates with respect to the mineral phases. The MINTEQ.dat database derived from MINTEQA2 [21] and containing the thermodynamic data of acetic complexes was used for model calculations. The PHREEQC-2 code can be used for ionic strengths up to 0.7 M (equivalent to sea water) and even higher [15]. The maximum specific conductivity of 62.4 mS/cm corresponded to a value of the ionic strength of approximately 0.39 M, as calculated by PHREEQC-2.

## 3. Results and discussion

### 3.1. Chemistry and mineralogy of APC residues

The chemical composition of the APC residues is given in Table 1. The principal chemical components are Pb, Cl, Na, S and K. Compared to residue B, sample A is enriched in Pb (30.5%), K (3.8%) and Cd (0.67%). In contrast, residue B is richer in S (9%), Na (2.6%), TIC (0.18%), As (0.14%) and Sb (0.05%) (Table 1). The enrichment of sample B in Na and S is closely related to the XRPD results, indicating the presence of thenardite (Na<sub>2</sub>SO<sub>4</sub>) and a more important relative abundance of caracolite (Na<sub>3</sub>Pb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl) than in residue A (Table 2). From the mineralogical point of view, the principal component of both residues is potassium lead chloride (KCl·2PbCl<sub>2</sub>) (Table 2). Observations by SEM/EDS showed that both residues are extremely fine-grained (<5  $\mu\text{m}$ ) and the individual phases could not be distinguished by EDS analyses (Fig. 1). The EDS X-ray mapping showed that other

Table 1  
Chemical composition of fresh APC residues from Pb metallurgy

Element (mg/kg)	APC residue	
	A	B
Pb	305175 ± 7075 <sup>a</sup>	235900 ± 11650
Cl	203150 ± 1050	202950 ± 1250
S	36205 ± 14	90415 ± 915
Na	25615 ± 2761	213770 ± 975
K	38534 ± 376	22993 ± 56
Si	2124 ± 39	1559 ± 97
Al	252 ± 4	230 ± 21
Fe	5010 ± 180	3753 ± 233
Mn	174 ± 0.2	77 ± 0.4
Ca	1702 ± 8	205 ± 11
Mg	97 ± 1	108 ± 0.3
Zn	4195 ± 85	4993 ± 93
Cu	141 ± 8	264 ± 1
Cd	6666 ± 304	4457 ± 168
Sn	1266 ± 7	1522 ± 109
As	274 ± 26	1382 ± 34
Sb	104 ± 6	487 ± 59
TIC <sup>b</sup>	<DL	1800

<sup>a</sup> Mean value and standard deviation for duplicates.

<sup>b</sup> TIC, total inorganic carbon; DL, detection limit is 500 mg/kg.

Table 2  
Mineralogical composition of fresh and leached APC residues

Phase	Composition	APC residue					
		A			B		
		Fresh	EN 12457	TCLP	Fresh	EN 12457	TCLP
K–Pb chloride	KCl·2PbCl <sub>2</sub>	***	**	**	***	–	–
Caracolite	Na <sub>3</sub> Pb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Cl	*	–	–	**	***	**
Thenardite	Na <sub>2</sub> SO <sub>4</sub>	–	–	–	*	–	–
Cotunnite	PbCl <sub>2</sub>	–	***	***	–	–	–
Anglesite	PbSO <sub>4</sub>	–	**	***	–	–	***
Phosgenite	PbCl <sub>2</sub> ·PbCO <sub>3</sub>	–	–	–	–	***	–
Laurionite	Pb(OH)Cl	–	*	*	–	*	*
Sylvite-halite	KCl–NaCl	–	–	–	–	*	*

Relative phase abundance: (\*\*\*) major; (\*\*) minor; (\*) trace; (–) not detected.

contaminant metals and metalloids (Cd, Cu, Zn, As and Sb) are homogeneously distributed within the fine-grained material. Thus, no specific phases concentrating these elements were determined by XRPD and SEM/EDS (Ettler et al., unpublished data).

### 3.2. Leaching

#### 3.2.1. Physico-chemical parameters

The value of the pH rose for both leachates only for residue B, reflecting the occurrence of H<sup>+</sup> consuming reactions commonly occurring at the solid–water interface (EN 5.75–6.40, TCLP 4.95–5.38) [11] and higher buffering capacity of this sample (TIC 0.18%, Table 1). Interestingly, the pH decreased to approximately 4.5 in both leachates from residue A. This phenomenon may be related to the presence of free acids resulting from the flue gas treatment without buffering capacity

(no alkaline water present in the cooling media; TIC < 0.05%, Table 1). The values of Eh indicated oxidising conditions throughout the experiment. The Eh values in leachates from sample A did not differ significantly from the initial leaching solutions, varying from 265 to 280 mV. In contrast, the Eh value for sample B decreased down to 170 and 147 mV for EN and TCLP leachates, respectively. The specific conductivities were relatively high, indicating a high level of total dissolved salts. Lower values were observed for leachates from sample A (27 mS/cm in EN and 21 mS/cm in TCLP leachate) and significantly higher values were obtained for sample B leachates (62 mS/cm in EN and 39 mS/cm in TCLP leachate).

#### 3.2.2. Contaminant leaching

The leached concentrations of the principal contaminant metals and metalloids are given and compared with the defined regulatory levels in Fig. 2. With the exception of Cu in sample B and As in sample A, all the contaminants exceeded both regulatory limits given by US EPA [13] and Czech Regulation No. 381/2001 [22]. However, the leaching results reflect a large number of parameters and processes controlling the contaminant leachability, in particular: (i) the solubility of the initial contaminant bearing phases, (ii) the physico-chemical parameters (mainly pH) and (iii) possible complexation by organic ligands (acetate in TCLP procedure) [12]. Lower contaminant concentrations were generally found in leachates from higher L/S ratios [10,23]. For the comparative reasons, the contaminant concentrations in leachates (mg/l) were recalculated according to the initial concentrations in the solids in order to obtain the leached amounts (in mg/kg and %) solubilised during the leaching test (Table 3).

Lead in all the leachates exceeded the regulatory levels (5 and 10 mg/l, Fig. 2). Lead is leached from both the principal constituents of APC residues (caracolite and potassium lead chloride). Significantly higher concentrations were observed in leachates from sample A, exhibiting 1487 and 6810 mg Pb/l (mean values) for the EN and TCLP tests, respectively. For sample B, the concentrations in the leachates were significantly lower, with values of 36 and 24 mg Pb/l, respectively. The higher reactivity of sample A is consistent with the ap-

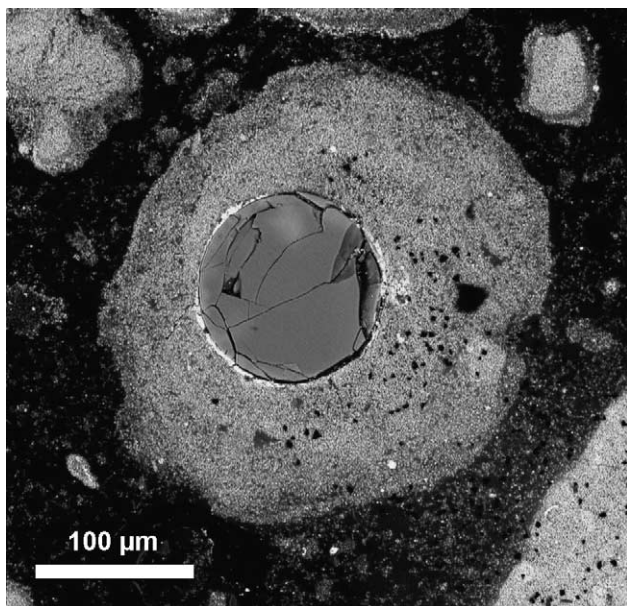


Fig. 1. SEM image of finely grained aggregates of A composed of potassium lead chloride (KCl·2PbCl<sub>2</sub>) and caracolite (Na<sub>3</sub>Pb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl) with silicate glass inclusion (in back-scattered electrons).

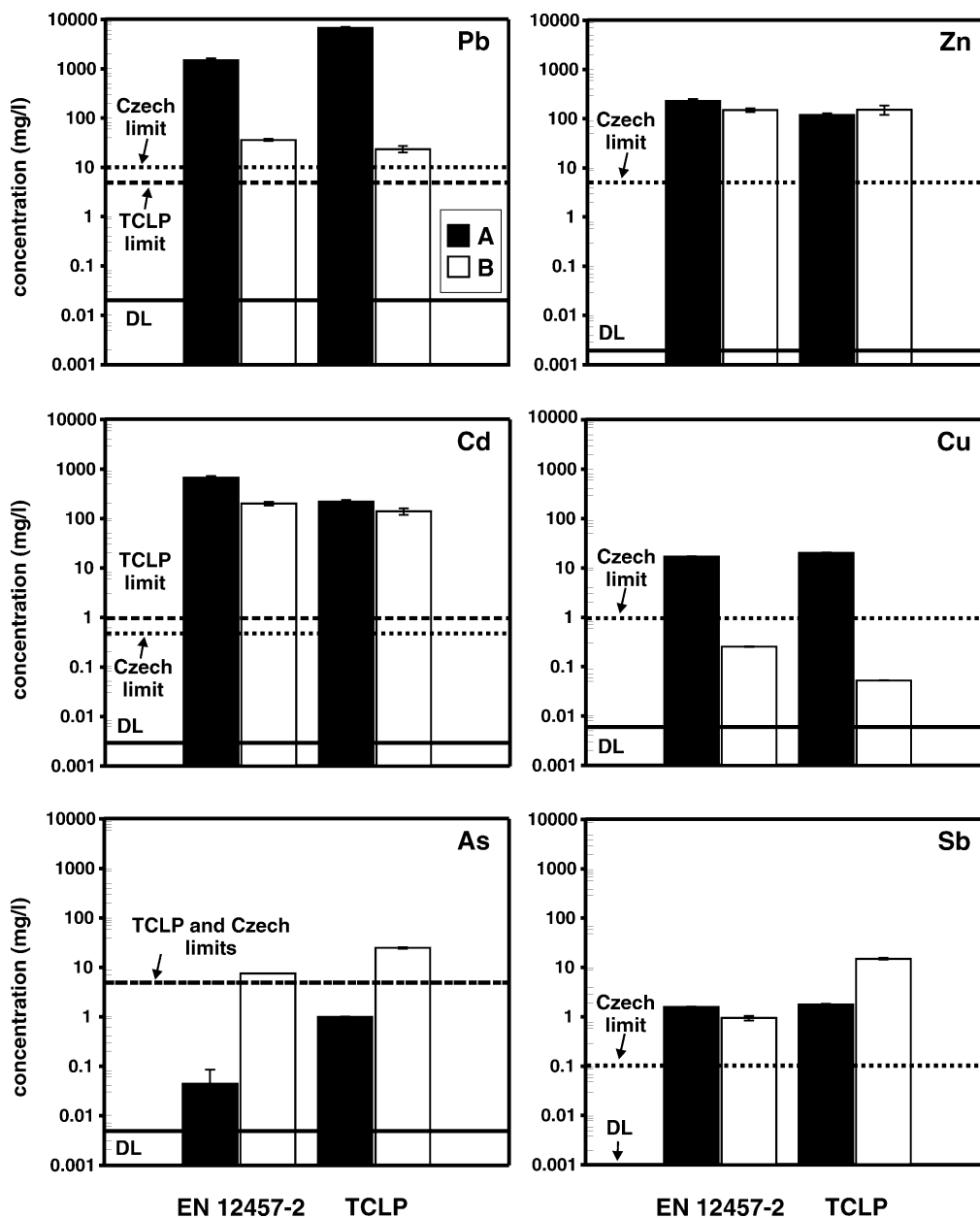


Fig. 2. Leaching results for Pb, Zn, Cd, Cu, As and Sb obtained by the European norm EN 12457-2 and TCLP leaching procedures. Standard deviations are indicated (based on triplicate analysis). The leachability regulation levels given by Czech Regulation No. 383/2001 [22] and TCLP [13] are indicated (if not, the regulatory level is not defined).

proximately double specific surface ( $3.8 \text{ m}^2/\text{g}$ ) compared to that of sample B. Nearly half of the Pb was solubilised by TCLP leaching of sample A, while the EN leaching test released only approximately 5% of the Pb (Table 3). In contrast, Pb solubilisation for sample B was significantly lower (0.15–0.20% of total amount) (Table 3).

Cadmium also exceeded the defined limits in leachates (0.5 and 1 mg/l) and the Cd leachability was significantly higher for sample A (Fig. 2). Both APC residues exhibit slightly lower leached concentrations for the TCLP procedure (Fig. 2). Recalculated leached amounts revealed that all the Cd from sample A was released into the solution in the

EN test (99%), while only 67% (mean value) was extracted in the TCLP leachate (Table 3). For sample B, the leached amounts attained 45 and 63% (mean values) for the EN and TCLP tests, respectively. These observations are related to the fact that the Cd leaching behaviour is strongly dependent on the pH and the composition of the leaching solution [24]. Higher amounts of Cd are generally released in the low-pH region [24], as was observed for sample A. Furthermore, strong leaching may occur even at higher pH values in solutions with high concentrations of  $\text{Cl}^-$ , due to formation of soluble Cd-chloro complexes [24]. This is in accordance with the observed higher concentrations of Cl in EN solu-

Table 3  
Comparison of the amount of leached metal and metalloid contaminants (in mg/kg and percent of total content) for different leaching methods

Element	APC residue							
	A				B			
	EN 12457		TCLP		EN 12457		TCLP	
	mg/kg <sup>a</sup>	% <sup>a</sup>	mg/kg	%	mg/kg	%	mg/kg	%
Pb	14867 ± 1470	4.9 ± 0.5	136200 ± 4668	45 ± 2	360 ± 18	0.15 ± 0.01	471 ± 70	0.20 ± 0.03
Zn	2315 ± 205	55 ± 5	2384 ± 165	57 ± 4	1497 ± 128	30 ± 3	3034 ± 639	61 ± 13
Cd	6570 ± 430	99 ± 8	4433 ± 316	67 ± 6	2008 ± 172	45 ± 4	2784 ± 408	63 ± 9
Cu	45.0 ± 0.82	32 ± 2	52.1 ± 1.41	37 ± 2	2.55 ± 0.03	0.97 ± 0.01	1.05 ± 0.01	0.40 ± 0.00
As	1.23 ± 0.04	0.45 ± 0.05	1.27 ± 0.03	0.47 ± 0.05	7.56 ± 0.04	0.55 ± 0.01	49.4 ± 2.00	3.6 ± 0.2
Sb	1.59 ± 0.03	1.54 ± 0.09	3.57 ± 0.08	3.4 ± 0.2	0.94 ± 0.10	0.20 ± 0.03	29.9 ± 1.33	6.2 ± 0.8

<sup>a</sup> Mean value and standard deviation for triplicates.

tions with respect to TCLP leachates (A: 1005 mg/l versus 715 mg/l; B: 1790 mg/l versus 956 mg/l) (see also Section 3.2.3).

The Zn concentrations in all the leachates exceeded the Czech Regulation limit (5 mg/l; the TCLP regulatory level is not defined) and are similar for both leaching methods (Fig. 2). However, slightly higher leached amounts (%) were always observed in TCLP leachates, as the acetate probably enhanced the residue dissolution (Table 3) [12]. The copper leachability was relatively low, exceeding the Czech regulatory limits (1 mg/l) only for sample A, where the leached amounts ranged from 32 to 37% of the total content (mean values) (Table 3). For sample B, the Cu leachability was less than 1% of the total content (Table 3). These observations are consistent with the significantly higher Cu solubility at low pH values [25].

Arsenic exceeded the regulatory levels (5 mg/l) only in leachates from sample B, probably due to the higher concentrations in the original solid (Table 1 and Fig. 2). The leached amount was, however, relatively low (<1% of the total content) with the exception of the TCLP leachate from sample B (Table 3). The leachability of As is strongly dependent on the pH, with higher amounts released under acidic conditions [26]; the obtained leaching data indicate that this phenomenon could be taken into account for the TCLP leachates exhibiting slightly higher As leachability (Fig. 2 and Table 3).

Antimony in the leachates exceeded the Czech regulatory level (0.1 mg/l) for both leaching experiments and samples. In contrast, the total leached amounts were relatively low with respect to the total content in the solid residue (<3.4%), with the exception of TCLP leaching of sample B, indicating that about 6% was solubilised (mean value). As for As, the leaching behaviour of Sb is probably dependent on the pH, with higher leachability at low pH (TCLP extracts).

Table 3 shows that Pb, Cd and Zn are the principal inorganic contaminants that are easily extracted from the initial solid APC residues even in the short-term extraction test (up to 99% of the total content). Copper may be classified amongst important contaminants only for sample A. In contrast, significantly lower amounts of As and Sb were solubilised from the residues; however, these contaminants are

also important because they are toxic at low concentrations [22].

### 3.2.3. Contaminant speciation in solution

PHREEQC-2 thermodynamic calculations assisted in estimation of dissolved inorganic and organic species of contaminants in leachates. Lead speciation in EN leachates indicated predominance of the free ionic form  $\text{Pb}^{2+}$  (62–78% of total speciation) and of the  $\text{PbCl}^+$  complex (up to 32%). The neutral  $\text{PbCO}_3(\text{aq})$  complex was observed only in the EN leachate from sample B (pH 6.4) accounting for up to 5% of total speciation. In the TCLP leachates, acetic complexes were predominant ( $[\text{Pb-acetate}]^+$  and  $[\text{Pb-acetate}_2]^0$ ), along with only 10% of  $\text{Pb}^{2+}$  and  $\text{PbCl}^+$  complexes at pH 4.5 and 4% at pH 5.4. Comparison of the two leaching tests indicates higher leached concentrations within the TCLP leachates from both residues; this observation is consistent with the strong chelation effect of acetate, which accelerates the dissolution of the primary phases [12]. Cadmium in the EN leachate from sample A consisted in 55% of the free ionic form and 45% of chloride complexes ( $\text{CdCl}^+$  and  $\text{CdCl}_2$ ). At higher pH values (EN leachate from sample B with pH 6.4), the proportion of Cd complexes was similar with a low amount of the  $\text{CdHCO}_3^+$  complex accounting for 0.3% of the total speciation. In addition, significantly lower amounts of Cd leached from sample B during the EN test and PHREEQC-2 calculated speciation could suggest a possible solubility-controlling mechanism, such as nucleation of newly formed Cd carbonate (see Section 3.3). Cd acetates are predominant (47–73%) in TCLP leachates, but the free ionic form and chloride complexes are still important, accounting for 15–32 and 12–22%, respectively. Zinc was mainly present in the free ionic form in all the leachates (48–98%) with an increasing percentage of acetic complexes at higher pH (34–54%). The  $\text{ZnCl}^+$  complex accounted only for up to 4% in EN leachates. However, copper exhibited a much stronger tendency to form acetic complexes in TCLP leachates (70–87%), while EN leachates contained predominantly the free ionic form (96–98%) associated with minor  $\text{CuCl}^+$  and  $\text{Cu}(\text{OH})_2$  complexes appearing at higher pH values. The PHREEQC-2 calculations indicated that As is present in the oxidized

Table 4  
Saturation indices of selected Pb-bearing phases as calculated by PHREEQC-2 geochemical code

Phase	Composition	Leachate from APC residue			
		A		B	
		EN 12457	TCLP	EN 12457	TCLP
Anglesite	PbSO <sub>4</sub>	−3.307 <sup>a</sup>	−3.567	−2.613	−4.331
Cerussite	PbCO <sub>3</sub>	− <sup>b</sup>	−	0.827	−
Phosgenite	PbCl <sub>2</sub> ·PbCO <sub>3</sub>	−	−	0.014	−
Hydrocerussite	Pb <sub>3</sub> (CO <sub>3</sub> ) <sub>2</sub> (OH) <sub>2</sub>	−	−	1.119	−
Cotunnite	PbCl <sub>2</sub>	−1.467	−1.937	−2.722	−4.719
Laurionite	Pb(OH)Cl	−0.612	−1.018	−0.236	−3.005

<sup>a</sup> Mean value for triplicates.

<sup>b</sup> Not calculated.

As(V) form as the arsenate (H<sub>2</sub>AsO<sub>4</sub><sup>−</sup> and HAsO<sub>4</sub><sup>2−</sup>) in all the leachates. However, Sb was more sensitive to changes in the Eh potential and formed different redox species Sb(OH)<sub>3</sub>, HSbO<sub>2</sub> and SbO<sub>3</sub><sup>−</sup>. The SbO<sub>3</sub><sup>−</sup> complex was dominant in the EN leachate from sample B, while other leachates showed significant enrichment in Sb(III) species.

### 3.3. Phase transformation during the leaching process

The mineralogical study of the leached APC residues indicated significant changes in the phase composition occurring during the leaching process (Table 1). In sample A, potassium lead chloride was partially dissolved under acidic conditions (pH 4.5) of both leaching tests, yielding cotunnite (PbCl<sub>2</sub>) as a residual phase (Table 1). Caracolite was completely dissolved and transformed to residual anglesite (PbSO<sub>4</sub>) and laurionite (Pb(OH)Cl) was present only in trace amounts (Table 1). The PHREEQC-2 calculated saturation indices of the principal Pb-bearing phases are given in Table 4. In contrast to mineralogical evidence, the leachates were undersaturated with respect to anglesite, cotunnite and laurionite. This observation confirms that these phases were formed as residual products during the leaching (not newly formed by precipitation from solution) and would be further metastable in the system. The stabilisation of cotunnite requires highly acidic environments and higher Cl activities than those observed in our leachates (2–3 × 10<sup>−2</sup>) [27]. As a result, cotunnite breaks down to laurionite as the pH increases [27]. Consequently, anglesite will be the most stable residual product of APC residue dissolution in acidic environments, with its solubility product that is approximately three orders of magnitude lower than that of cotunnite (log *K*<sub>anglesite</sub> = −7.79, log *K*<sub>cotunnite</sub> = −4.77) [8,21].

Investigation of the phases in leached sample B showed that the pH and bicarbonate concentration in the leachate are the key parameters influencing the dissolution of the primary residue constituents (Table 2). A more acid TCLP extract (pH 5.4) favoured complete dissolution of the potassium lead chloride (Table 2) and partial dissolution of caracolite, resulting in the presence of residual phases: dominant anglesite and trace laurionite. However, caracolite dissolves more slowly in the EN leachate with pH 6.4, and was still present as the prin-

cipal phase in the solid sample (Table 2). The complete absence of potassium lead chloride in leached sample B is in accordance with the finding of Edwards et al. [27] who showed that Pb chlorides are easily dissolved in circumneutral and alkaline conditions. The dissolution of Pb chloride will result in the formation of laurionite that in turn reacts with dissolved CO<sub>2</sub> yielding phosgenite, as described by Edwards et al. [27]. Phosgenite has been observed as the principal phase in EN-leached sample B (Table 2). The PHREEQC-2 calculations showed that lead carbonates (cerussite PbCO<sub>3</sub>, hydrocerussite Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> and phosgenite PbCl<sub>2</sub>·PbCO<sub>3</sub>) were supersaturated in EN leachates from sample B (Table 4). Edwards et al. [27] observed that phosgenite crystallises around pH 5, but cerussite requires higher pH values. In general, at pH above 4.5, a solution that is saturated with respect to phosgenite is also highly supersaturated with respect to cerussite, which means that phosgenite is unstable in this pH range [27,28]. The work of Pina et al. [28] also demonstrated that phosgenite is commonly transformed to cerussite (PbCO<sub>3</sub>) as the pH increases. In spite of the PHREEQC-2 predictions showing strongly positive saturation indices for otavite (CdCO<sub>3</sub>), this phase was not detected by XRPD. It may, however, be present (below the detection limit of XRPD) or could precipitate if the pH of the system increased [24].

### 3.4. General discussion and environmental/technological issues

APC residues from Pb metallurgy were found to release substantial amounts of metals and metalloids (Pb, Zn, Cd, Cu, As and Sb) during standardized leaching tests. Even these short-term leaching procedures performed with chemically simple solutions may be useful for understanding the dissolution processes in smelter emission-contaminated environments, especially soils. Ettler et al. [5] found that anglesite is often detected by XRPD in soil profiles heavily contaminated by Pb smelting activity (with up to 35,500 mg Pb/kg). In contrast, Pb chlorides or other Pb-bearing phases were not detected. This observation is probably closely related to the pH values of smelter-impacted soils from Příbram, ranging from 3.5 to 5.6 [5] and is supported by the present leaching data indicating that in this pH range anglesite is the prin-

principal residual product resulting from caracolite dissolution (Table 1). Furthermore, residual Pb chlorides with significantly higher solubility than anglesite were completely dissolved after a long-term residence in soil [5,21]. Lead released by this dissolution process could significantly migrate down in the soil profile, as revealed by the Pb isotopic study [4]. The results of simple leaching tests coupled with knowledge of the Pb speciation in real smelter-impacted soil [5] show that (i) the phase dissolution/transformation is strongly dependent on the pH and (ii) the kinetics of the dissolution of primary APC residues phases is relatively fast and their transformation is observed in experiments lasting 24 h.

According to the regulatory levels, both APC residues can be defined as hazardous waste materials. However, this study also shows that the APC residue produced by cooling of the flue gas by alkaline water (sample B) exhibits significantly better leaching characteristics (especially in Pb release) (Fig. 2, Table 3). In contrast, sample A, produced by cooling of the flue gas by distilled water, probably contains free acids adsorbed on the residue particles and the resulting leachates remain acidic (pH 4.5). Supplementary mixing of APC residues with alkaline water, followed by an additional increase in the pH and equilibration with atmospheric CO<sub>2</sub> might be used for dissolution of primary Cl-rich phases accompanied by simultaneous precipitation of carbonates (phosgenite > cerussite) (Tables 1 and 3) (see also [29]), which are more suitable for additional Pb recovery in the metallurgical plant. The cadmium concentration in the suspension could be controlled by the precipitation of otavite (CdCO<sub>3</sub>) [24]. This technology could also be combined with the Ferrox process proposed by Lundtorp et al. [30] and tested on APC residues from municipal waste incinerators. The Ferrox stabilisation process is based on residue mixing with a solution of Fe<sup>2+</sup> sulphate, followed by precipitation of newly formed Fe(III) oxyhydroxides which are good adsorbents for inorganic contaminants. This approach would be necessary to prevent the mobility of other metals and metalloids (Cu, Zn, As and Sb) released from this type of residue.

#### 4. Conclusions

Simple standardized leaching tests (EN 12457 and TCLP) performed on two types of APC residues from Pb metallurgy indicated a large number of dissolution and phase transformation processes occurring during residue/solution interaction. At pH ~ 4.5, caracolite (Na<sub>3</sub>Pb<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>Cl) was completely dissolved and potassium lead chloride (KCl·2PbCl<sub>2</sub>) was partly dissolved. Predominant anglesite (PbSO<sub>4</sub>), associated with minor cotunnite (PbCl<sub>2</sub>) and laurionite (Pb(OH)Cl), became the principal residual products. Similar conditions can be taken into account in smelter-polluted soils with acidic pH, where only less soluble anglesite has been detected by XRPD [5]. At higher pH values, potassium lead chlorides tend to be completely dissolved and caracolite to be partly dissolved. At pH 5.4, anglesite was still the principal residual product

while, at pH > 6, carbonates (e.g., phosgenite PbCl<sub>2</sub>·PbCO<sub>3</sub>) became the predominant secondary phases.

Comparison of the leaching data with the regulatory levels revealed that both types of APC residue may be considered to be hazardous materials. However, the cooling of flue gas by alkaline water with high concentrations of salts yields an APC residue (sample B) with more favourable leaching and environmental characteristics than the one trapped after preliminary cooling by deionised water (sample A). Mixing of the APC residue with alkaline water, followed by an increase in the pH of the suspension and equilibration with atmospheric CO<sub>2</sub> could be used for the precipitation of less soluble Pb carbonates (e.g., cerussite with log *K* = -13.13 [21]), which are readily recycled in Pb processing in the metallurgical factory.

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