Single-Stage Extraction to Assess Metals Bioavailability from Smelting Dust

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Abstract

This paper examines the amount of bioavailable Zn, Cd, and Pb in dust samples derived from a zinc-lead smelter by means of single-stage extraction analysis. The efficiency of three extractants (NH_4OAc, $CaCl_2$, and H_2O) was compared with respect to their efficiency toward bioaccessible (exchangeable) metals fraction. The highest amount of metals was NH_4OAc extractable, indicating that the acetate-soluble fraction was a prevailing form in the analyzed dust and probably associated with the presence of metals in conjunction with soluble sulfates ($ZnSO_4$, $PbSO_4$). The largest amount of bioavailable Zn, Pb, and Cd was extracted from the finest dust particles, considered most dangerous for human health.

Introduction

The imperial smelting process (ISP) is a pyrometallurgical technology that smelts zinc and lead simultaneously in a single unit, called a blast furnace. The only Polish producer of zinc and lead using this method is a smelter located in a highly industrial area of Silesia. Non-ferrous zinc and lead smelting has been identified as one of the most polluting mineral industries [1, 2]. Flotation sludges, melting losses, slags, and other hazardous wastes are generated in every stage of ore processing. ISP also contributes to significant dust emission, originating from the actual sintering process, mechanical sinter crushing, and transportation [3, 4]. Most studies concerning metals emission from smelting processes focus on soil pollution [5-7], but there is a lack of

research characterizing the source of this pollution – dust [8, 9]. Exposure to airborne pollutants from metal processing and smelting can lead to various acute and chronic diseases, including birth defects [10], kidney and liver problems [11], metal fume fever [12], nervous system damage [13], and more. In fact, the factor that is largely responsible for those specific health outcomes is metals bioavailability [14]. It is the proportion of total metals that are available for incorporation into human organisms. Total metal concentrations do not necessarily correspond with metal bioavailability. Metals can be, for example, encapsulated in chemically inert phases, and therefore not readily available for the environment or humans.

Generally, the ISP dust consists mainly of zinc and lead oxides, sulfides, sulfates, carbonates, and silicates. Depending on various operations occurring in the smelter, the share of those compounds changes, influencing metal

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existence in particular available or non-available fractions [5, 8, 15]. For example, metals bound to sulfide compounds such as ZnS or PbS are immobile, in contrast to sulfates $ZnSO_4$ or $PbSO_4$, which are highly soluble [16] and, therefore, indirectly or directly bioavailable.

The method most popularly used for assessing metals bioavailability from solid environmental samples is single-stage extraction procedure. This enables a rapid and cost-effective extraction of metals bound with the defined dust fraction [17, 18]. Single-stage extraction, however, suffers from several drawbacks. One of these is the lack of suitable extractant, selective toward targeted metal fraction [8, 19]. Dust in fact does not contain chemically or physically distinct phases, thus it is difficult to associate a given extractant reagent with a particular physicochemical phase. A reasonable solution to this problem is the application of multiple extraction solutions, characterized by similar leaching capacity and chemical affinity [20]. Such an experimental scheme allows us to compare reagent selectivity with respect to a defined fraction, and as a result, a more accurate determination of the amount of metals associated with a particular fraction.

Our work attempts to:
(a) Check the influence of dust phase composition and its fractionation on the bioavailability of Zn, Cd and Pb
(b) Compare extractant efficiency toward bioavailable metals fraction

For this purpose three extraction solutions were used: H_2O, $CaCl_2$, and NH_4OAc.

Experimental Procedures

The Characteristic of the Process of Pyrometallurgical Production of Zinc and Lead

The smelter that is the object of the research comprises a metallurgical complex of a blast furnace, including [21]:
1. Sinter plant (sintering Zn-Pb concentrates) with sulfuric acid and cadmium plants
2. Blast furnace (separation of zinc and lead)
3. Zinc rectification plant and lead refinery (pyrometallurgical removal of impurities from products generated in the blast furnace).

The Sinter Plant comprises three technological units: the feedstock preparation station, where the stock mixture is prepared and passed to the sinter strand; the Dwight-Lloyd (DL) sintering machine station, where the roast sintering of the feedstock in the presence of air and at temperature of 1,200ºC takes place; the crushing station in which zinc-lead sinter is crushed and separated into fractions of various sizes: the granules of required size are transported to the blast furnace while the rest of the material is returned to the sintering machine.

The Blast Furnace Unit consists of two technological lines: the feedstock preparation unit and the blast furnace hall, in which the reduction and distillation of zinc and lead compounds at temperature of 1,000ºC occur. The vaporized zinc and liquid lead are obtained during the process.

The Lead Refining Plant comprises several technological units, in which drossing, copper removal, softening, silver and bismuth removal, and final refining of lead are carried out. The technology is suitable to perform total lead refining during which the complete removal of impurities like Cu, Sn, As, Sb, Ag, Bi occur. Recycled materials containing lead are remelted in a shaft rotary furnace (SRF).

Sample Collection

Dust was collected from the bag filters located in the particular divisions of the smelter:
1. Sinter Plant crushing center (12-chamber-filter servicing the sinter crushing and transfer)
2. Sinter Plant (12-chamber-filter operating in the area of the overflow of the collecting conveyor of the fit mix, mix discharge on to the sintering machine, and the first-stage roll crusher)
3. Blast furnace (14-chamber-filter covering the area of the slag and lead tapping, zinc vapor condenser, and zinc refinement)
4. Sinter plant (24-chamber-filter operating in the area of the hot sinter discharge from the sintering machine and the sinter pre-crushing)
5. Lead refining plant (10-chamber-filter, servicing all the technological sources, i.e. refining boilers, SRF, distillation furnace, and muffle furnace)
6. Sinter plant storage yard, technological process products returned to the sintering process (dust, sludge, melting loss, slickers)

For the purposes of the phase composition analysis, the feed from Primary Raw Material Warehouse and dust from the storage yard of the Secondary Raw Material Warehouse (a mixture of all recycled material directed to the sintering process) were additionally sampled.

Sample Preparation

Dust samples (5 kg each) were taken according to the standard [22] and dried at 105ºC. In order to remove larger particles, samples were sifted through the sieve of mesh equivalent diameter 250 μm. Particles with aerodynamic diameter equal to 10-63 μm were separated using an Air-Jet Laboratory Sifter 200 (Alpine), and smaller particles were fractionated using an A100 MZR pneumatic separator (Alpine).

Reagents and Solutions

Solutions for the extraction purposes were prepared from the reagents of analytical-grade quality (Merck, Germany). All laboratory glassware was rinsed in 10% (v/v) nitric acid during the night and three times with distilled water. For calibration curve preparation, single element standard solutions were used (Merck, Germany). The calibration solutions were prepared by diluting corresponding stock standards solutions (1 g/L^{-1}) by high purity deionized water (Millipore) with HNO_3 (Merck Suprapur) addition.

Extraction Analysis

Zn, Pb, and Cd contents were determined by means of atomic absorption spectrometry in AAS 3 flame spectrometer (Carl Zeiss Jena) following a microwave mineralization. System for mineralization consisted of two single, modular UniClever pressure mineralizers (Plazmatronika) equipped with a water cooling circuit. About 50 mg of sample was treated by spectrally pure acid mixture $HCl:HNO_3$ (4.5:2 cm³ volume ratio) and digested using the following program:

I step: 5 minutes heating time, 65% of the heating power (total heating power of 350 W)

II step: 5 minutes heating time, 85% of heating power

III step: 20 minutes heating time, heating power of 100%, cooling time 10 min.

Temperature in the reaction vessel of 200-250ºC provided complete digestion of the samples. After digestion samples were evaporated to a small volume (about 1 cm³) using an MCR-6-E rotor and the module for acid concentration FAM 40 using 750 W power for 5 minutes, and after that 450 W for 6 minutes, followed by the addition of 0.5 cm³ of nitric acid. Finally, samples were transferred quantitatively to flasks and filled to volume with distilled water.

Apart from determining the total metal contents in the dust, the chemical partitioning of metals was assessed using one-stage extraction procedure. Non-fractionated and fractionated dust samples with aerodynamic diameters 0÷2.5, 10÷20, and 40÷63 μm were subjected to extraction.

The following extraction solutions were used:

- H_2O – extraction of water-soluble form, based on physical phenomenon of solubility
- $CaCl_2$ (0.05 mol/dm³, pH=7) – extraction of specifically adsorbed bioavailable fraction
- NH_4OAc (1 mol/dm³, pH=7) – extraction of exchangeable form by changing the ionic composition of the aqueous solution during sorption/desorption processes in neutral pH, which gives information about the share of metals that occur as weakly adsorbed ions on dust particles (for example chlorides, hydroxides, some oxides, and sulfates).

A particular extraction reagent (15 cm³) was added to the 0.1 g of dust sample, shaken for 2 hrs on a laboratory shaker (Elpin PLUS), and centrifuged on the MPW 6 (2,500 rpm.) centrifuge for 0.5 hr. The supernatant solution was filtered into polypropylene vessels and subjected to AAS analysis.

The accuracy of the tested extraction procedure was fulfilled by the number of extraction replicates (n=4).

X-Ray Diffraction Analysis

Dust composition was identified using a JCXA 733 X-ray microanalyzer (Jeol) equipped with an ISIS 300 energy-dispersive spectrometer (Oxford Instruments). Both qualitative and quantitative analysis were performed. The focal beam of diameter range equal to 1-2 μm and accelerating voltage equal to 20 kV was applied. All analyses were done in series, including a dozen to several dozen measurements.

Statistical Analysis

The Kruskall Wallis one-way ANOVA variance analysis was used to search for differences among single extractions. Statistical analysis was performed using Statistica 9.1 PL Software (StatSoft).

Results

Dust Mineral Composition

Dust composition was influenced by the feed streams and strictly dependent on processes occurring in the smelter, including: sintering, smelting, lead electro-refining, and sulfuric acid production. To illustrate the differences in chemical composition between feedstock and dust, the analysis was performed separately for those materials. Information regarding feed and dust phase composition is presented in Table 1. Although qualitatively those samples were similar, their quantitative composition differed. Feed consisted of: zincite – ZnO (35%), minium – PbO (26%), sulfur – S_{tot} (18%), and wustite – FeO (14%), where Zn and Pb occurred mainly as the sulfates $ZnSO_4$ (zincosite) and $PbSO_4$ (anglesite). Dust was also characterized by zincite (35%), minium (42%), sulfur (8%), and wustite (4.5%) domination, with the highest stechiometric share of the $PbSO_4$ (anglesite). The main elements in the emitted particles were therefore Zn – 33% and Pb – 31%, whereas Cd was only 0.8% (Table 2). Dust from the Secondary RMW had similar composition, with 66% zincite – ZnO domination, although sulfur contents were rather low (3%), indicating a small share of metals as sulfide and sulfate compounds. In all analyzed dust samples, Cd did not create its own chemical phases and occurred only as an admixture.

Single-Stage Extraction Analysis

Metals bioavailability was assessed using a single-step extraction procedure and calculated as a percentage of soluble metal fraction with respect to its total content in the dust (Table 2). Significant differences (Kruskal Wallis ANOVA, p<0.05) in metals extractability were found among single reagents, indicating their differentiated leaching ability. Acetate-extractable metal fraction was found to be the major phase in analyzed dust. Much smaller amounts of metals were extracted by calcium chloride and water. Generally the exchangeability was strictly element-dependent and declined in the following order Cd > Zn > Pb. The most labile was therefore Cd (up to 36%), while Pb and Zn were less extractable (approximately 14%). The share of exchangeable Cd varied from 25% to 29% (dust samples 1 and 2) to over 80% (dust samples 5 and 6) with an increasing tendency toward fine fractions (Figs 5 and 6). The lowest share of this fraction was found in dust sampled at the sinter plant crushing center (FT-12R) about 8%, and in the secondary raw material warehouse (19%), while the highest percentage of easily mobilizable Cd fraction was extracted from sinter plant (FT24) dust (44%). The total share of

Table 1. Average chemical composition of the feedstock samples from primary raw material warehouse (n=7), dust samples from the filter bags of the sinter plant (n=6), and dust from the secondary raw material warehouse (n=9). Data is presented as mean wt% ±SD.

Chemical compound	Feedstock mixture from the primary RMW	Dust from the secondary RMW sampling point 6	Dust from the sinter plant sampling point 1-5
SiO_2	1.86±2.53	0.75±0.42	1.38±1.00
TiO_2	-	-	0.12±0.23
Al_2O_3	0.19±0.12	0.43±0.41	0.24±0.19
FeO	14.02±9.09	0.38±0.32	4.53±6.23
MnO	0.62±1.25	0.24±0.11	0.12±0.05
MgO	0.14±0.14	-	0.11±0.14
CaO	0.60±1.03	0.24±0.22	1.22±1.39
Na_2O	-	-	0.16±0.40
K_2O	0.12±0.08	0.43±0.33	0.33±0.32
PbO	25.96±11.77	23.85±8.85	42.45±20.79
ZnO	35.42±10.42	65.85±14.48	34.62±23.33
S_{tot}	18.45±9.65	3.16±2.48	7.92±4.44
Ag_2O	0.17±0.14	0.44±0.38	0.61±0.71
As_2O_3	0.26±0.09	1.41±1.09	1.79±2.33
CdO	0.40±0.44	0.66±0.78	2.89±2.50
CuO	0.74±1.11	0.66±0.87	0.38±0.54
SeO_2	0.15±0.06	0.33±0.25	0.01±0.16
Sb_2O_3	0.17±0.14	0.42±0.26	0.41±0.72
SnO_2	0.65±1.13	0.73±0.86	0.51±0.85
In_2O_3	-	-	0.08±0.19
Total	100	100	100
Mineral compound	The stoichiometric share of the mineral compound in the grain		
$PbSO_4$	30.50±29.11	49.21±27.92	33.33±33.90
$ZnSO_4$	52.02±27.89	16.41±27.09	9.57±21.53
$CaSO_4$		9.36±26.48	
CdS	4.36±8.75		
$FeSO_4$	7.82±9.9		15.66±21.96
ZnO	1.36±1.66	18.13±13.16	7.84±9.14
PbO			9.68±13.79
FeO			20.61±25.43
Glaze	1.55±0.99	0.97±0.47	
Other compounds	2.36±2.26	5.87±2.82	3.29±1.65
Total	100	100	100

$CaCl_2$-exchangeable Cd varied from 4.43% (dust sample 3) to 69.33% (dust sample 5) in finest particles. As in the case of Cd, the highest share of Zn was acetate-extractable (13.38-75.83%), with an increasing solubility in a fine 0-2.5 μm fractions. Figs. 1 and 2 clearly show that the highest quantity of Zn was leached from dust collected at the 3rd, 5th, and 6th sampling points. Regardless of dust origin and its granulation, the proportion of H_2O-extractable and $CaCl_2$-extractable Zn was similar in all dust samples and ranged from 0.1 to 4.66%, with mean value 1.32%. The highest average Pb contents, amounting to 41%, were observed in acetate-exchangeable dust fraction, probably due to Pb occurrence as $PbSO_4$ – one of the most common phases in ISP industrial emissions. This significant share of easily soluble lead was especially well marked at the lead refining
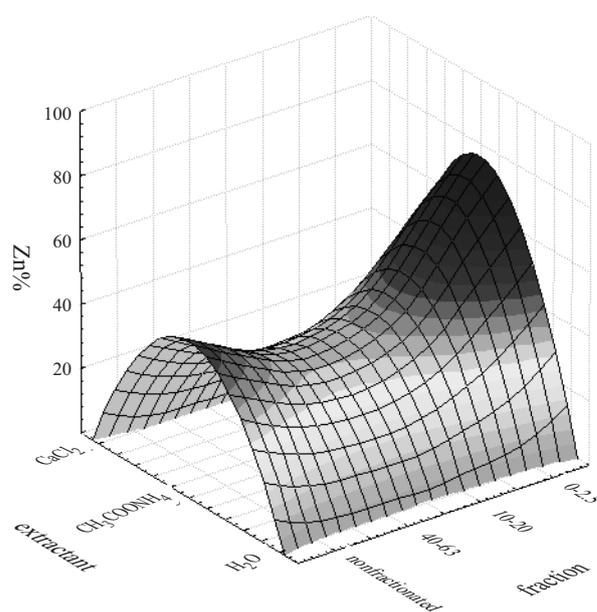

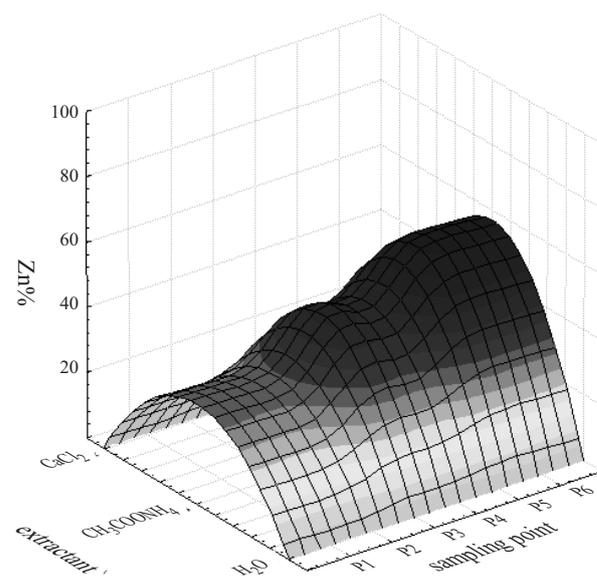Fig. 1. Zinc exchangeability in relation to dust fractionation (n=4).

Fig. 2. Zinc exchangeability in relation to dust origin (n=4).

Table 2. Total contents and the percentage share of Zn, Pb, and Cd exchangeable forms in non-fractionated dust samples. Data is presented as mean ±SD (n=3).

Metal fraction	wt%	Sampling position					
		1	2	3	4	5	6
Total	Zn	35.88±7.93	34.71±8.78	45.15±7.88	26.06±10.48	18.41±5.85	40.03±6.15
	Pb	29.10±6.61	28.05±7.62	27.56±5.68	36.87±12.09	38.71±6.29	29.25±4.57
	Cd	0.70±0.28	0.99±0.51	0.10±0.03	2.06±1.00	0.95±0.91	0.21±0.12
H_2O exchange-able	Zn	0.19±0.10	0.34±0.04	0.06±0.01	0.65±0.35	0.69±0.00	0.29±0.37
	Pb	0.17±0.07	0.22±0.08	0.68±0.21	0.39±0.13	0.32±0.17	0.15±0.04
	Cd	7.44±5.83	15.90±3.99	12.03±3.90	45.21±13.56	48.52±28.70	17.61±2.57
$CaCl_2$ exchangeable	Zn	0.59±0.12	1.33±0.56	1.31±0.39	2.74±0.72	2.56±0.00	0.99±0.12
	Pb	0.72±0.06	0.91±0.43	0.43±0.34	0.39±0.16	0.95±0.35	0.86±0.45
	Cd	9.28±2.45	16.13±3.19	25.09±7.01	50.16±6.27	61.25±3.63	32.70±12.23
CH_3COONH_4 exchangeable	Zn	16.93±4.80	20.48±1.09	57.75±2.09	29.10±2.74	70.01±20.72	62.36±5.96
	Pb	38.54±3.73	46.94±4.38	26.48±13.88	58.68±3.53	55.31±12.79	20.12±11.76
	Cd	20.53±6.28	29.71±5.10	54.36±13.65	64.35±2.87	77.40±4.56	63.89±5.76

plant (about 55%) in the smallest dust grains (0-2.5 µm) (Fig. 3 and 4). The yield of $CaCl_2$ exchangeable Pb contents varied from 0.1 to 1.6% and was similar to the water extraction potential. Water-exchangeable Pb content was generally lower compared to Zn and Cd (Table 1).

Discussion of the Results

The average dust composition was found to be analogous to the dust samples collected before (Feedstock mixture from the Primary RMW) and after (Dust from the Secondary RMW) the bag filters. It was allocated among the main products of ISP processing – Zn, Pb and H_2SO_4 [23], mainly in the form of $ZnSO_4$ (zincosite) and $PbSO_4$ (anglesite). Generally the raw material for Zn-Pb smelting, contains 60-75% of lead (PbS), 3-10% of zinc (ZnS) and 0.5-1% of copper (CuS), while the remaining elements, including Cd, occur at a trace level (less than 0.3%) [24, 25]. This explains the small contents of cadmium in the dust. Among many factors controlling metal mobility, its origin and fractionation brings the greatest variability. Usually the share of bioavailable metal fraction in environmental samples is small – typically a few to several percent
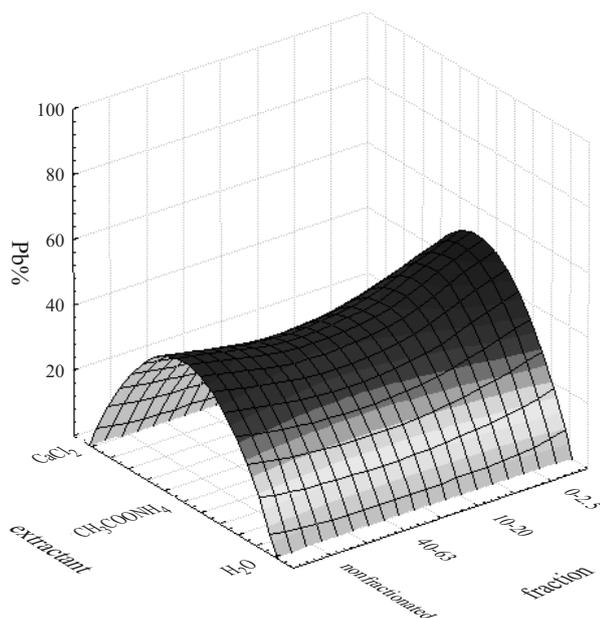

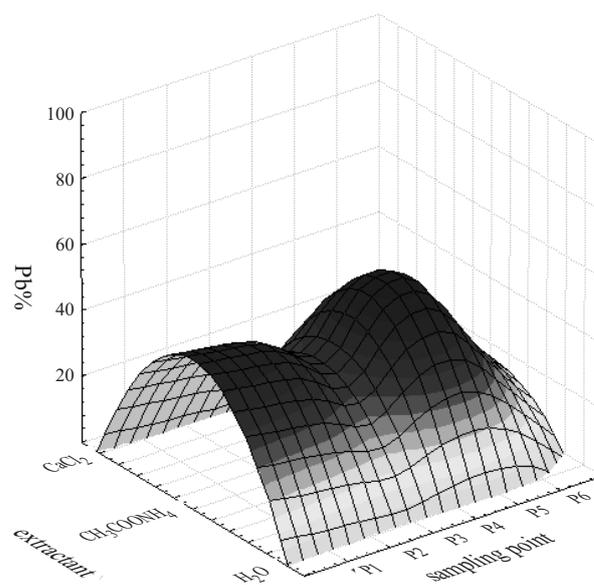Fig. 3. Lead exchangeability in relation to dust fractionation (n=4).

Fig. 4. Lead exchangeability in relation to dust origin (n=4).

of the total metal content. In our presented study the amounts of H_2O- and $CaCl_2$-extractable metals in fact do not exceed a few percent, but the amount of NH_4OAc-exchangeable fraction was high and accounted for as much as 77% (Table 1). The highest leaching efficiency of NH_4OAc was probably connected with its higher ionic strength compared to H_2O or $CaCl_2$, which generally yielded similar results. The complexing properties toward transition metals usually increase in the order: $H^+>Ca^{2+}>Mg^{2+}>NH_4^+$ [26]. Another possible explanation for CH_3OAc high exctractability is that among different aqueous solutions targeted for the exchangeable metals fraction, like for example $MgCl_2$, $CaCl_2$, KNO_3, $Mg(NO_3)_2$, $Ca(NO_3)_2$, NH_4OAc, $NaOAc$, NH_4NO_3, and NH_4Cl [8], ammonium acetate also shows a partial affinity toward oxidizable fractions. This is of particular importance considering that ZnO and PbO are the main components of ISP dust. The contents of exchangeable Zn, Pb, and Cd in sampled dust varied within a wide range, mainly due to the diverse solubility of compounds in which those elements occurred. Highest exchangeability was observed in dust sampled at the lead refining plant, containing large amounts of sulfate compounds like $Pb(SO_4)_2$, $PbS·SO_4$, and $PbO·SO_4$, formed during the final refining [24, 27]. This relatively high proportion of lead refining plant dust could also be due to the formation of certain amounts of easily soluble chlorine, as a result of recycled materials pollution during processing in the short rotary furnace. It should, however, be emphasized that lead in the ISP dust occurs mainly in residual fractions (PbS), extractable only under oxygen-rich or highly acidic conditions [28]. Lead inaccessibility was especially marked in dust from the blast furnace (only 26%), probably due to the formation of non-soluble PbS as a result of sulfates reduction in strongly reducing conditions (Table 1, Fig. 4). Among three studied metals, the largest share in the exchangeable fraction had Cd, accounting for 85% in
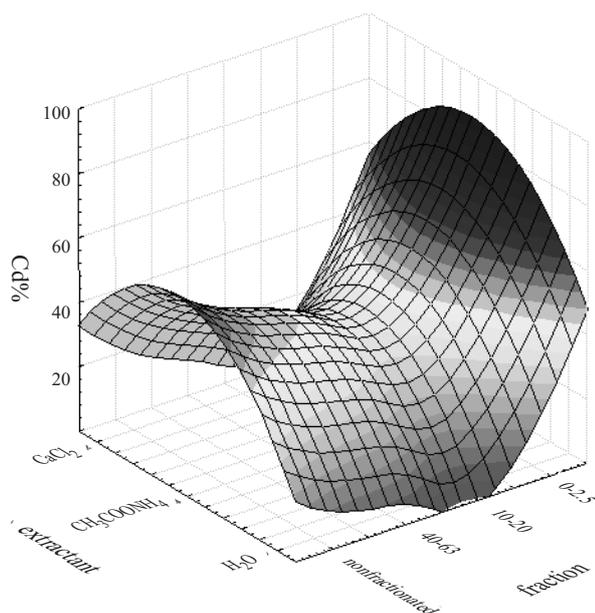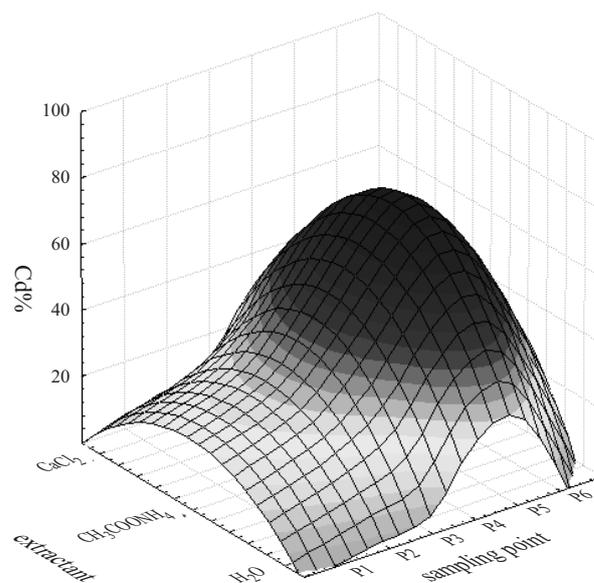

Fig. 6. Cadmium exchangeability in relation to dust origin (n=4).

acetate-exchangeable form. Similar results were obtained by Min et al. [29], who studied the environmental activity of metals in zinc leaching residue, and found that among Zn, Pb, and Cd, the most extractable was Cd. Is was directly related to its high solubility – the values of the first hydrolysis constant (pK_{1h}) of the bivalent cations (Me^{2+}) is 10.1-11.6, 8.7-8.96, and 7.1-7.7 for Cd, Zn, and Pb, respectively [29-31]. Since metals solubility (extractability) is combined with respiratory uptakes, it can be assumed that the presence of Cd in smelter dust is a serious health threat. Significant concentrations of extractable cadmium were observed in the dust collected at the sinter plant (Table 2, Fig. 6) due to high volatilization and evaporation of cadmium oxides and cadmium sulfides in the sintering temperatures (1,200ºC). Small amounts of extractable Zn in dust samples collected at the sinter plant crushing center compared to 3, 5, and 6 sampling points, was associated with a significant share of inaccessible ZnS (sphalerite). An important observation was made in respect to Cd-extractability. The sum of Cd extracted independently by H_2O, $CaCl_2$, and NH_4OAc from sample Nos. 4, 5, and 6 was higher than 100%. This is consistent with the literature data indicating a lack of ectractant selectivity toward exchangeable metals fraction [32].

Dust samples most highly loaded by metals and probably with highest environmental impact were collected at the blast furnace hall (with a major share of condensing, spherical particles originating from thermal transformations), from the lead refinery and the sinter plant divisions. Apart from the extraction solution type, the second factor that influenced metal release from dust was its fractionation. The dust samples collected in the bag filters show a large distribution of particle size between 0.1 and 63 µm. A detailed result regarding the granulometric composition of dust release from zinc and lead smelting are presented elsewhere [33]. In general, the metals exchangeability was inversely

Fig. 5. Cadmium exchangeability in relation to dust fractionation (n=4).

proportional to grain size. This phenomena was mostly noticeable in the case of dust samples collected at the blast furnace and lead refinery bag filters, rich in particles likely arising from metal evaporation and condensation at high temperatures, with a significant share of sulfate compounds [33, 34].

Conclusions

Metals bioavailability was correlated with the type of operations occurring in the smelter. An operation that provided the greatest source of bioavailable Zn, Pb, and Cd was lead refining. This means that people working in a lead smelter are probably mostly exposed to the harmful effects of metals. It is particularly important with respect to the neurotoxic properties of lead. The information concerning Zn, Pb, and Cd dust occurrence in a biologically available form is very important, since it provides the best available information on the major species present in air. The final information derived from elementary analyses and x-ray diffraction analysis indicate that $PbSO_4$ and $ZnSO_4$ particles smaller than 2.5 μm are mainly responsible for the health hazards caused by ISP emission. By comparing the relative affinity of NH_4OAc, $CaCl_2$, and H_2O reagents toward operationally defined bioavailable fraction, we also conclude that the estimation of metals bioavailability using single extraction procedure is not sufficient. To achieve comparability between operationally defined single-step extractions, few extractants targeted for specified fraction should be used. However, despite the limitations of the single extraction (poor reagent selectivity, difficulties in comparing results from different methods, etc.), this method is the simplest way to predict metals mobility from solid samples.

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