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Assessment of the chemical composition and mobility of selected heavy metals in sewage sludge from zinc and lead metallurgy

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ABSTRACT

Non-ferrous metallurgical wastes such as wastewater might be a source of metals transferred to the environment. Sewage sludge, formed in the process of neutralization of acidic wastewater, contains in its composition mainly lead (more than 64%) and a number of associated elements, often characterized by very high toxicity (e.g., Zn, Cd, Fe, Cu, Ca, K, Na and Mn). These elements can be present in the environment in stable or mobile form. The stability or mobility of elements is mainly determined by environmental conditions and their forms of occurrence. Based on studies such as scanning electron microscopy, X-ray with energy-dispersive spectroscopy, X-ray diffraction, a high inhomogeneity of the sample and a large number of forms of occurrence of metals (mainly lead compounds) were found. Sequential extraction using the BCR (Community Bureau of Reference) method revealed the existence of metals such as Pb, Zn, Fe, Cu and Cd in four fractions: ion-exchangeable, bound to iron and manganese oxides, bound to organic matter and residual fraction.

Keywords: Heavy metals; Post-neutralization sludge; Zinc and lead metallurgy; BCR sequential extraction

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1. Introduction

Sewage sludge is commonly studied for the removal of various elements, especially heavy metals, which are considered toxic to health and environment [1–4]. Municipal sludge is the most common type of sludge that is subjected to various metal separation processes such as chemical leaching [1,2], membrane processes [5] or electrokinetic processes [6]. While the recovery of heavy metals from municipal sewage sludge is a common and well-studied sector of environmental engineering, the recovery of metals from metallurgical waste still requires a lot of research. At the same time, it is not common practice to carry out qualitative and quantitative analysis of waste materials such as wastewater waste from non-ferrous metallurgy, as these materials do not often become the object of metal removal studies.

The post-industrial sector is full of products and wastes with varying metal content. Often, in addition to solid waste, contamination also affects the water that is turned in the plants during production.

In the production of lead and zinc carried out in the imperial smelting process, metallurgical wastewater can be a source of metals. These can include such products as condensates from roasting gases, wastewater from washing the halls and equipment of the Leaching Plant and Sulfuric Acid Plant. Their main ingredient is a mixture of liquefied gas condensates, which is the final result of the wet treatment of gases from the sintering of zinc-lead charges and the cooling waters from the cooling of the process node pumps. The remaining stream, which constitutes acidic wastewater, must be directed to the neutralization plant in order to neutralize and remove some of the metals present in larger quantities. These operations are necessary to remove unwanted metals thoroughly and then separate the precipitated metal compounds. Proper separation of heavy metal compounds, which are considered particularly hazardous

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to the environment and the health of living organisms [7,8], is an important economic as well as environmental aspect. Nevertheless, in the precipitated sludge, we can distinguish a large number of heavy metal compounds [9]. It is therefore very important to know the exact composition of such sludge, that is, to conduct a thorough qualitative, quantitative and fractional analysis to assess the mobility of metal compounds. Elements can exist in either stable form (bound in the crystal structures of minerals) or mobile form (present in ion-exchange positions in the structures or on the surface of grains). It should be noted that the stability or mobility of an element is mainly determined by environmental conditions, because even if an element is present in a stable form, the mineral component may decompose, which will result in the release of the element into the environment [10,11]. A sequential extraction analysis has been widely used to determine the forms of metals present in wastes such as sludges from lead and zinc metallurgy [2,12–14]. A wide range of procedures are used to proceed with the sequential extraction. The most popular method is BCR sequential extraction, and this procedure was used during research [15]. This technique is relatively simple and has been shown to be useful in assessing the mobility of metals in solid samples.

A key aspect in environmental engineering research on the removal of heavy metals from waste materials is accurate qualitative and quantitative analysis using available and inexpensive methods. Conducting such analyses facilitates further work on, for example, metal leachability studies, but also provides a lot of information about the sample itself, which can have a direct impact on the method of storage of waste materials or the possible recovery of valuable substances.

The article presents the method and results of research on the mobility of heavy metals present in post-neutralization sewage sludge from the zinc and lead smelter using the ISP (Imperial Smelting Process) method in zinc and lead production. To determine the sludge mineralogy and speciation of elements of the samples, instrumental investigations of sludges were used by X-ray microanalysis with EDS, and scanning electron microscopy (SEM), which is a frequently used tool during sediment analysis giving a great deal of knowledge about the morphology or elemental content of the studied materials [16]. Moreover, to conduct fractional analysis X-ray diffraction (XRD) and sequential extraction using the BCR method were used. These methods are widely used in the literature to provide information of qualitative and quantitative analysis of the metallurgical sludges [16,17].

2. Materials and methods

2.1. Materials

The sludge samples were collected from an on-site treatment plant in Zinc and Lead Smelter in Poland. The sample comes from the acid wastewater neutralization plant, where it was subjected to thallium removal. The solution was filtered on a filter press and collected directly from production in the form of hard-compacted sediment with a high moisture content.

The following reagents were used in the work: hydrochloric acid (35%–38%, Merck), nitric acid (65%, Merck), hydroxylamine hydrochloride (0.5 M, Warchem), acetic acid (0.11 M, Merck), hydrogen peroxide (8.8 M, Chempur), ammonium acetate (1 M, Chempur).

2.2. Sludge sampling and preparation

Before subjecting the sample to testing, it had to be prepared using such techniques as drying, milling, and sieving. The total metal content (Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Zn) was analyzed after one-step mineralization of sludge in a mixture of concentrated acids according to the following procedure [18]. 0.1000 g (±0.0200 g) of sludge was digested with 6 mL of aqua regia. The digestion was carried out in a 100 mL Teflon vessels at room temperature for 3 h for three samples.

After digestion, the metals were analyzed by flame atomic absorption spectroscopy (AAS), using a Varian SpectrAA-880 spectrophotometer equipped with a SIPS system, which allowed precise dilution of the tested samples. Acetylene-air was used as the combustible gas for flame generation.

The calibration of spectrophotometer was performer using the appropriate standard solutions for each of the metals analyzed (1,000 mg/L, Merck, Poland).

In addition, to characterize the physical properties of the samples, the moisture content was also determined in air-dried and oven-dried (105°C) process of 20 g of the sample in triplicate.

Samples were dried to constant mass, ground in the mortar to particle size less than 2 mm and then in such form used to research.

2.3. Instrumental analysis of sludge chemical composition

JEOL JXA-8230 Electron Probe Microanalyzer with an accelerating voltage of 15 kV was used for sample characterization. It was availed to perform the scanning electron microscope (SEM) and X-ray microscope pictures. The tests were proceeded on the grained sample surface.

Electron images were taken, using secondary electrons (SEI – the contrast depended mainly on the surface topography) and backscattered electrons (COMPO – revealed differences in the chemical composition).

An X-ray microprobe with a sample sputtered with a conductive gold layer was used for the analysis. Quantitative analyses of selected grains were performed at various points using the wave-dispersion method (WDS). Several micro-areas were examined giving an average analysis for each grain. The visible contrast in these areas depended solely on the differences in chemical composition. Elemental distribution maps were produced using EDS, and qualitative and quantitative analyses of the chemical composition were also performed. The elemental distribution maps were obtained for each of the previously indicated micro-areas. Maps indicate concentrations of selected metals through the different colors from red – maximum concentration, through yellow, green, and blue, to black – minimum content. This article presents maps of the elemental distribution for a single micro-area.

To determine the mineralogical composition of the tested samples, XRD analysis was used. Phase identification and composition were examined by XRD according to

PN-EN 13925-1:2007, using a PANanalytical, X'PERT PRO diffractometer (Cu radiation at 30 kV and 40 mA).

2.4. Sequential extraction

Speciation analyses of selected metals were performed using a three-step sequential extraction procedure. The use of this analysis allowed the separation of four metal fractions: ion-exchangeable, associated with iron and manganese oxides, associated with organic matter, and residual.

The leaching of individual metal fractions in the 1st, 2nd, and 3rd steps took place in centrifuge tubes and was proceed using respectively: 40 mL of 0.11 M acetic acid in 1st stage, 40 mL of 0.1 M hydroxylamine hydrochloride in 2nd stage, 20 mL of 30% hydrogen peroxide and 50 mL of 8.8 M ammonium acetate in 3rd stage on an Ohaus Orbital Shaker (250 rpm, 16 h, RCF 1106). The fourth step involved carrying out the digestion of the sample residue with aqua regia. Separation of the sediment from the liquid took place using an MPW-380 centrifuge (3,000 rpm, 20 min). The rinsing of the sediments between individual steps was carried out by adding 20 mL of demineralized water, shaking the solution on a shaker (250 rpm, 20 min), and centrifuging (3,000 rpm, 20 min). A mass of 1 g (±0.027 g) of the sample was used for the test and it was carried out in 6 replications. The obtained solutions were analyzed for the presence of Zn, Pb, Cu, Fe and Cd using AAS.

3. Results

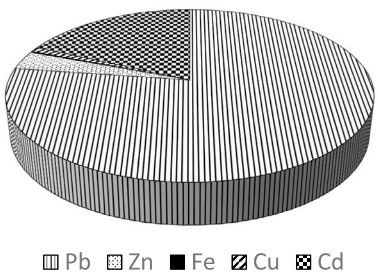
3.1. Moisture content

The total content of moisture in the tested sludge was determined. The moisture content depended on the drying method. Samples dried on air showed an average moisture content of 44.9% (±1.02%), while those dried in an oven at 105°C showed an average of 46.0% (±1.3%).

3.2. Total content of metals in the sample

Total content of metals in the tested sludge was determined. This value was calculated to the dry weight of the sample (105°C). Among the metals analyzed, Pb was found to be present in a significant amount. Other metals like Fe, Cu, Zn, Ca, K, Na, Cd, and Mn were present in a lower amount, and their average concentrations are summarized in Fig. 1.

Lead was found to be present in more than 69% of the total metal content determined in the sample. The remaining 31% are elements such as: cadmium (16%), calcium (9%), zinc (3%), sodium (1%), manganese (0.1%) iron and potassium (0.3%). The large difference between lead and zinc content may be due to the feedstock used in production, like lead ore.



Content of metal	mg/g
Pb	430.2 ± 22.6
Cd	100.9 ± 3.7
Ca	56.5 ± 4.2
Zn	19.5 ± 2.7
Na	6.4 ± 0.9
Cu	5.0 ± 1.3
K	1.8 ± 0.1
Fe	1.4 ± 0.4
Mn	0.4 ± 0.1

Fig. 1. Total metal concentration in the sludge.

3.3. Scanning electron microscopy

SEM proved to be a useful technique for examining the morphology of the samples. Fig. 2 shows the sample surfaces at four different magnifications – 50×, 300×, 500×, and 1,000×. SEM images show that the morphology of the analyzed material is complex. The dominant number of particles is irregularly shaped. The particle size of individual grains ranges from less than 10 µm to more than 100 µm. As can be seen in Fig. 2, irregular particles of various sizes adhere and aggregate to large particles. It is evident, that some amorphous fine particles are adsorbed on the surface of large irregular substances with solid shapes.

3.4. X-ray microanalysis

X-ray microanalysis of the tested samples showed considerable variability in the content of metals and other accompanying elements. Apart from the metals like Pb, Ca, Zn, Cu, Mg, Al, and Na, other elements, such as C, O, F, Si, and Cl, were found. The presence of Ca and Na in the sludge can come from neutralizing reagents. The main sources of S and Cl are probably neutralized sulfuric or hydrochloric acids, although they may also have been added in reducing or coagulating reagents [17]. Tested material is quite heterogeneous in composition, because the content of individual metals varied considerably depending on the measuring point. The presence of sulfur and oxygen possibly indicated the presence of metal oxide, sulfide or sulfate forms. The variation in the qualitative and quantitative results measured at different points in the material showed its great heterogeneity and the wide range of possible chemical compounds. Fig. 3 shows an example of photomicrograph along with EDS analysis for the tested samples.

3.5. XRD analysis

The XRD pattern of the tested material is presented in Fig. 4. The metal found in almost every identified chemical form is lead. It occurs in such compounds as PbO (Litharge), PbS (Galena), $PbSO_4$ (Anglazite), Ca_2Pb, $Pb_2Cl(O,OH)_{2-x}$ (Blixite) and $Pb[ClO_3]_2[H_2O]$. In addition, the presence of an amorphous and unidentified phase was identified in the material. Quantitative analyses were not performed in the sample due to uncertain identification, lack of identification data, and an incorrectly formed crystal structure.

3.6. Elemental distribution maps

Element distribution maps were defined for each photomicrographed area. Fig. 5 presents two examples of distribution maps in the defined micro areas for the sample. Elemental distribution maps showed the common areas for individual elements. Based on the maps shown below and the intensity of the color, we could assume that some

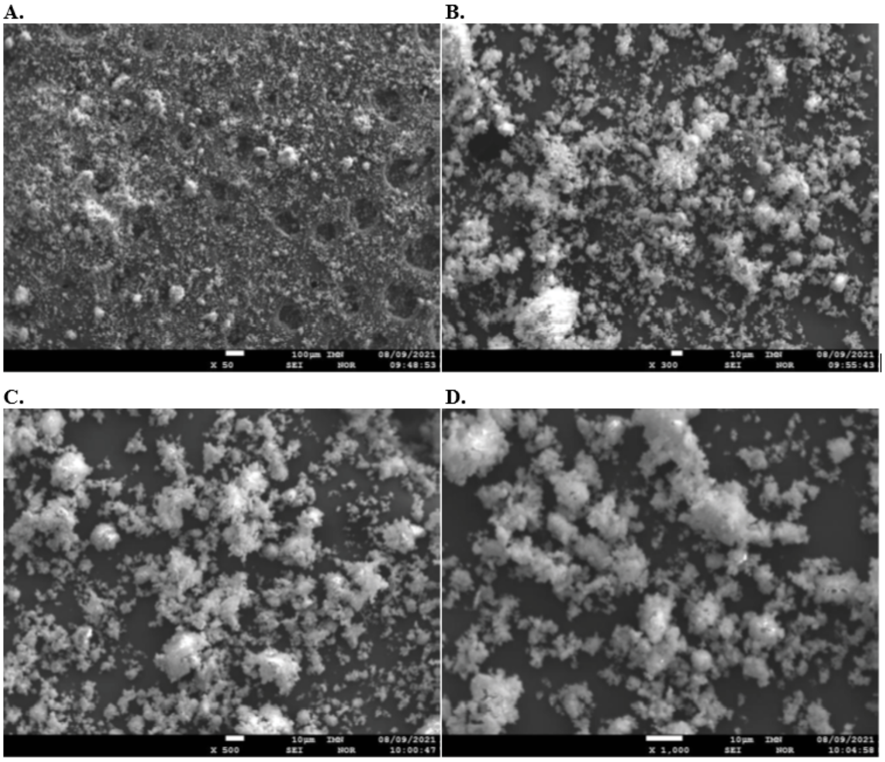
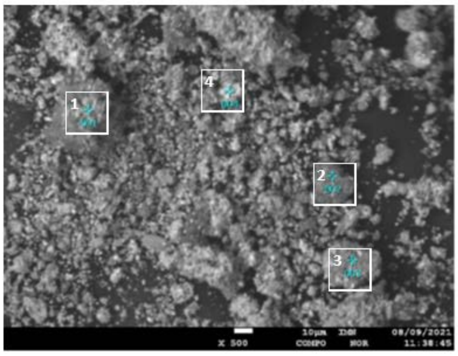
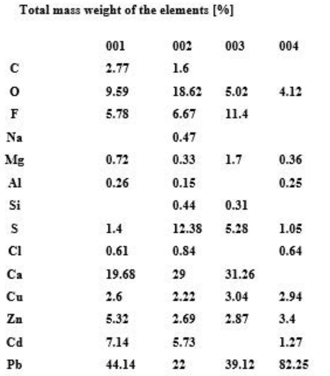


Fig. 2. Electron images of the sample taken in SEI modes: (A) 50× zoom, (B) 300× zoom, (C) 500× zoom and (D) 1,000× zoom.





Total mass weight of the elements [%]

	001	002	003	004
C	2.77	1.6		
O	9.59	18.62	5.02	4.12
F	5.78	6.67	11.4	
Na		0.47		
Mg	0.72	0.33	1.7	0.36
Al	0.26	0.15		0.25
Si		0.44	0.31	
S	1.4	12.38	5.28	1.05
Cl	0.61	0.84		0.64
Ca	19.68	29	31.26	
Cu	2.6	2.22	3.04	2.94
Zn	5.32	2.69	2.87	3.4
Cd	7.14	5.73		1.27
Pb	44.14	22	39.12	82.25

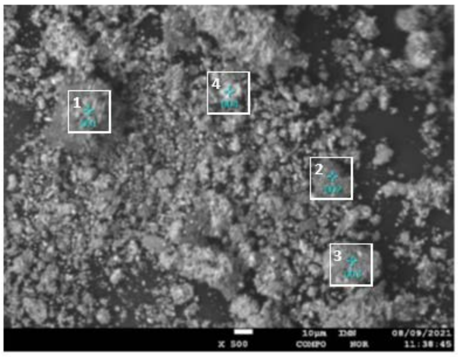
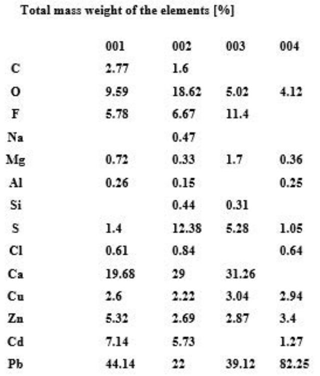


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Fig. 3. Electron image of a composition-type sample with marked areas of qualitative and quantitative analysis with total elements content.

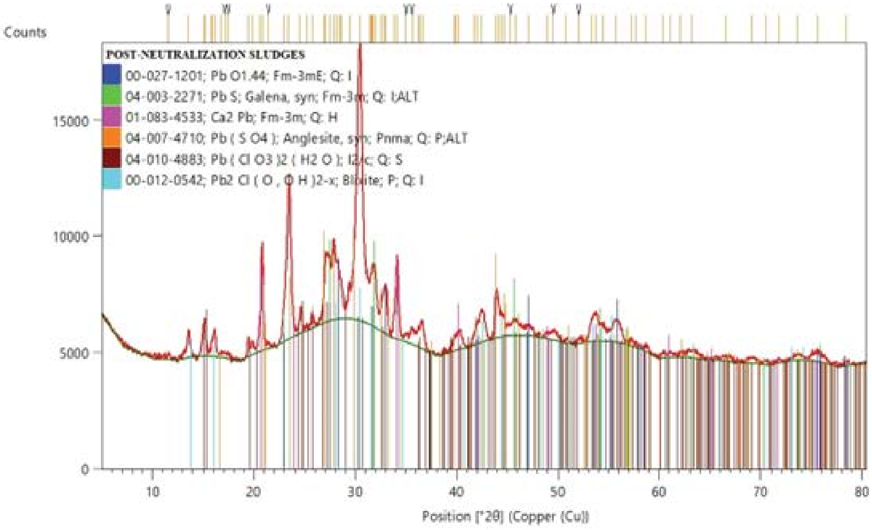

Fig. 4. X-ray diffraction pattern of metallurgical sludges.

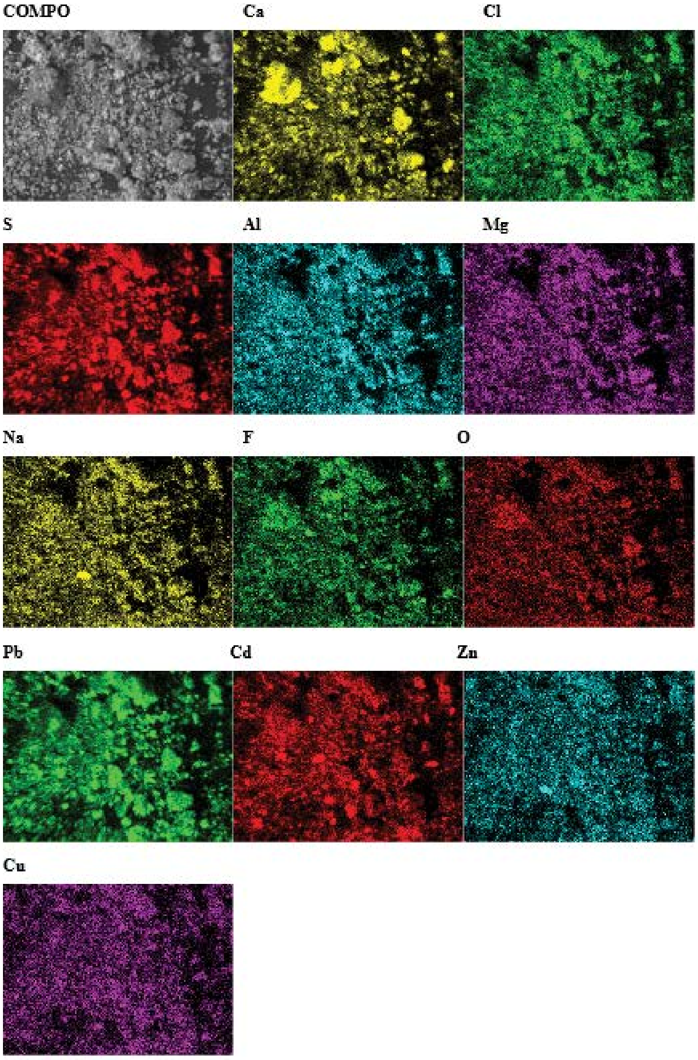

Fig. 5. Elemental distribution maps, magnification 500× zoom.

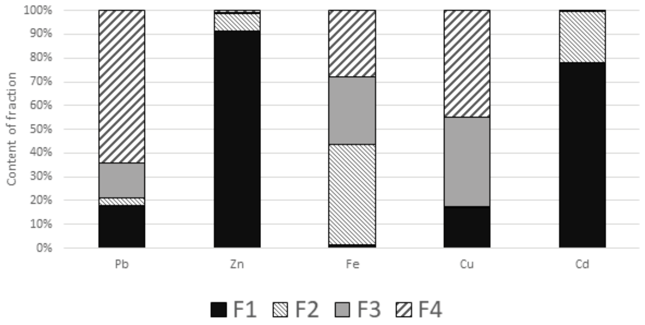

Fig. 6. Concentration of metals in the individual fractions of sludge sample. F1 – ion-exchangeable fraction associated with carbonates, F2 – fraction associated with iron and manganese oxides, F3 – fraction associated with organic matter, F4 – residual fraction.

elements coexisted in a chemical compound. Almost identical areas with similar element content were observed for aluminum, chlorine, magnesium, and sodium. The pattern, indicating the maximum concentration of the element for sulfur (red), was identified in similar areas for calcium (yellow) and lead (green), possibly indicating the common presence of such forms as PbS (lead sulfide) or CaS (calcium sulfide). The map of the distribution of lead and sulfur showed very similar patterns, with a higher concentration of sulfur (red) in comparison to lead(green), possibly indicating the occurrence of the PbS compound.

3.7. Sequential extraction analysis

The results of the speciation analysis performed on selected samples for the five predominant heavy metals, Pb, Cd, Zn, Cu and Fe are shown in Fig. 6. The total sum of all analyzed forms of each metal was adjusted 100%, based on which, the relative fractions for each speciation form were calculated.

The results of the sequential extraction showed a wide variation in the fractions of Pb, Cd, Zn, Cu, and Fe present in the sludge. It showed that lead was associated mainly with a residual fraction (F4) with about 45%, but also presented in significant proportions (about 15%) in the ion-exchangeable fraction (F1) and the fraction associated with organic matter (F3). Cadmium and zinc associated with fraction F1 were primarily presented and reached over 78% and 90% of the total content of these metals in the material, respectively. Zinc bound to fraction associated with iron and manganese oxides (F2) took 7%, cadmium 22% and fractions F3 and F4 were presented in the very small amount (less than 1%) for both metals. Iron associated with F3 and F4 reached similar content (28%), where fraction F2 of this metal took 42%. The amount of iron associated with F1 is negligible (2%). The content of copper bound in the fraction F1 reached nearly 50%, whereas fractions F3 and F4 show similar content of 25%.

4. Conclusions

Analyzed sludge samples derived from zinc and lead metallurgy wastewater treatment plants showed a variety of metals present, occurring in various forms. One metal was found to be present in higher concentrations and that was Pb. Other metals, occurring at lower concentrations, were found in the order Cd > Ca > Zn > Na > Cu > K > Fe > Mn. Tested material exhibited a wide variety of metal compositions and forms, while possessing a high degree of complexity, as confirmed by X-ray microanalysis and XRD analysis. Elemental distribution maps for selected micro-areas were also determined, allowing accurate observation of the distribution areas of individual elements and preliminary phase analysis of the material. Sequential extraction analysis showed the presence of metals, in various amounts, in four identified fractions: ion exchangeable, bound to iron and manganese oxides, organic, and residual. The five selected metals (Pb, Zn, Cu, Fe and Cd) were evaluated for their association to varying degrees with the different leachable fractions. Lead was largely associated with F4 (residual fraction), zinc, cadmium and copper with F1 (ion-exchangeable fraction) while iron was mainly associated with F2 (fraction associated with iron and manganese oxides). The tested materials did show a high moisture content, which was close to 45%.

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