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## FRACTIONS OF HEAVY METALS IN RESIDUE AFTER INCINERATION OF SEWAGE SLUDGE

Comparative evaluation of metal occurrence was conducted for sludge originating from three wastewater treatment plants, which differ in wastewater treatment methods, processing and drying of sludge. It was demonstrated that metals (Zn, Cu, Ni, Pb, Cd, Cr) in sludge are mainly bound to organic-sulfide fraction. Zinc was also present in significant amounts in hydrated iron and manganese oxide fraction, nickel and cadmium in exchangeable-carbonate fraction, whereas lead in residue fraction. In ash obtained after calcination at 600 °C occurred mainly metal enriched nearly insoluble compound fraction (residual fraction). Metal accumulation in such non-mobile fraction is advantageous with respect to soil-water environment protection.

### 1. INTRODUCTION

Two main routes of sewage sludge utilization exist; one is its land application as soil conditioner or fertilizer while the other is thermal conversion for heat recovery. During thermal conversion processes, e.g. pyrolysis and combustion, volume and weight of the waste are diminished. During combustion, heavy metals can be found in slag, bottom ash, fly ash, and flue gas. The volatility of heavy metals depends on their form of occurrence, properties of sludge, and the conditions of combustion [1–3].

Combustion of sewage sludge results in an increase of concentrations of heavy metals in the combustion products. However, during the conversion, metals can form less mobile compounds (metals associated with the fraction of almost entirely insoluble compounds). Sequential extraction is a method used to determine the content of mobile and immobile forms of heavy metals in sludge and ash. The method allows defining the chemical forms of metals and the release of heavy metals into the solution

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under various environmental conditions. For this reason, the sequential extraction comprises several steps in which increasingly aggressive solvents are used. For each step, an appropriate solvent is chosen to extract a defined form of metal with well-known chemical properties [4, 5]. The aim of the method is not to identify individual forms of metals but the fraction as a whole.

Short, three-step extraction method was developed in the frame of Standards, Measurements and Testing Programme of European Union Commission and commonly known as BCR (Community Bureau of Reference) [6, 7]. The BCR procedure allows extracting metals from the following fraction of sludge: exchangeable-carbonate, iron and manganese oxides, organic-sulfide, and residual. The residual fraction comprises mainly metals associated with silicates and aluminum silicates, but also metals, which were not extracted in the previous steps of sequential extraction. In natural environment, these metals can be considered as permanently immobilized, which means that they are not mobile and their compounds are chemically passive and biologically unavailable.

The aim of this study was to investigate the influence of combustion of sewage sludge at 600 °C (removal of organic matter) on formation of immobile chemical forms of heavy metals (Zn, Cu, Ni, Pb, Cd, Cr) in ash.

## 2. EXPERIMENTAL

Dried sewage sludge samples were collected at three different mechanical-biological wastewater treatment plants in: Częstochowa (C), Myszków (M), and Łężyca – 7 km distant from Zielona Góra (Z). The average flow capacity of the plants was 48000, 9000, and 51000 m<sup>3</sup> per day, respectively. Activated sludge was used for the treatment of the sewage at the plants by the following processes: nitrification, denitrification, biological and chemical defosfatation. Stabilization of sludge at plant C was carried out by means of mesophilic methane digestion. The stabilized sludge was mechanically dewatered on a belt press, and then dried at 260 °C in a drying column. At plants Z and M, on the other hand, sludge was not stabilized. It underwent gravity thickening, and dewatering in a chamber filter press. Then the sludge was dried. For this purpose, at plant Z sludge was kept at 80–90 °C for 5 min with the use of a turbo-dryer, whereas, at plant M solar dryer was used.

The analyses of sludge from each wastewater treatment plant were performed in triplicates. In addition, ash samples collected after 1 hour combustion of dried sewage sludge at 600 °C in a muffle furnace were analyzed.

Total concentrations of heavy metals (Zn, Cu, Ni, Pb, Cd, Cr) in sludge and ash samples were determined by mineralization at 120 °C with the use of aqua regia (2 cm<sup>3</sup> 65% HNO<sub>3</sub> + 6 cm<sup>3</sup> 37% HCl). The mineralization time was 2 h.

In order to quantitatively determine the forms of heavy metals in the sludge and ash samples, sequential extraction was carried out according to BCR procedure [5, 8]. The procedure is presented in Table 1.

Table 1

Operating conditions required in the BCR sequential extraction method

Step	Sequential extraction procedure per 1g of dry matter material	Nominal target phase(s)	Fraction
1	40 cm <sup>3</sup> 0.11 M CH <sub>3</sub> COOH, 22 °C, shaking for 16 h	Soil solution, exchangeable cations, carbonates	exchangeable, acid soluble
2	40 cm <sup>3</sup> 0.5 M NH <sub>2</sub> OH·HCl (pH = 2), 22 °C, shaking for 16 h	iron and manganese oxyhydroxides	reducible
3	10 cm <sup>3</sup> 8.8 M H <sub>2</sub> O <sub>2</sub> (pH = 2–3), 22 °C, shaking for 1 h 10 cm <sup>3</sup> 8.8 M H <sub>2</sub> O <sub>2</sub> , 85 °C, 2 h 50 cm <sup>3</sup> 1 M CH <sub>3</sub> COONH <sub>4</sub> (pH = 2 with HNO <sub>3</sub> ), 22 °C, 16 h	organic matter and sulfides	oxidisable
4	2 cm <sup>3</sup> 65% HNO <sub>3</sub> + 6 cm <sup>3</sup> 37% HCl, 120 °C, 2 h	non-silicate minerals	residual

The produced extracts were quantitatively analyzed by means of atomic absorption spectrometry (using a spectrometer novAA 400, Analytic Jena) with quadruple repetition in order to determine concentrations of heavy metals.

### 3. RESULTS AND DISCUSSION

Sewage sludge collected at the plants C, Z, and M contained 61%, 64%, and 70% of organic matter, respectively. The total concentrations were at the level of 2980, 302, 131, 132, 7.8, 431 mg·kg<sup>-1</sup> in sludge C, 1042, 214, 46.3, 92.1, 2.8, 22.5 mg·kg<sup>-1</sup> in sludge Z, and 1350, 65.3, 32.5, 46.1, 3.8, 12.5 mg·kg<sup>-1</sup> in sludge M for zinc, copper, nickel, lead, cadmium, and chromium, respectively. The total content of heavy metals in the ash samples was 2.3–3.3 times higher than in the sludge samples. It can be explained with the reduced mass of the sludge after combustion leading to consequent increase of concentrations. The concentrations of heavy metals in the chemical fractions of the sludge and ash samples (in mg·kg<sup>-1</sup>) are given in Table 2, while the percentage content in Figs. 1–3.

Zinc was mainly present in the organic-sulfide fraction (1825 mg·kg<sup>-1</sup>) in sludge C, in exchangeable-carbonate fraction (467 mg·kg<sup>-1</sup>) in sludge Z, in iron and manga-

nese oxides fraction ( $584 \text{ mg}\cdot\text{kg}^{-1}$ ) in sludge M. These values correspond to the following percentage content of the total zinc in the sludge samples: 58%, 50%, and 46%, respectively.

Table 2

Chemical fractionation of heavy metals in sewage sludge and ash (means  $\pm$  standard deviation,  $n = 3$ )

Metal	Fraction	Concentration [ $\text{mg}\cdot\text{kg}^{-1}$ ]					
		Sewage sludge			Ash		
		C	Z	M	C	Z	M
Zn	I	227.0 $\pm$ 7	467.0 $\pm$ 6	136.0 $\pm$ 4	510.0 $\pm$ 7	578.0 $\pm$ 4	360.0 $\pm$ 4
	II	930.0 $\pm$ 5	282.0 $\pm$ 4	584.0 $\pm$ 8	1107.0 $\pm$ 10	293.0 $\pm$ 5	406.0 $\pm$ 3
	III	1825.0 $\pm$ 11	145.0 $\pm$ 3	514.0 $\pm$ 5	1619.0 $\pm$ 12	159.0 $\pm$ 3	1408.0 $\pm$ 9
	IV	165.0 $\pm$ 5	44.0 $\pm$ 2	36.0 $\pm$ 3	5280.0 $\pm$ 18	1690.0 $\pm$ 8	2016.0 $\pm$ 13
	Sum	3147.0	938.0	1270.0	8516.0	2720.0	4190.0
Cu	I	1.3 $\pm$ 0.2	12.8 $\pm$ 1.1	1.5 $\pm$ 0.3	26.4 $\pm$ 2.4	21.0 $\pm$ 1.4	12.3 $\pm$ 0.7
	II	2.2 $\pm$ 0.2	6.2 $\pm$ 0.6	2.1 $\pm$ 0.2	65.6 $\pm$ 1.7	63.5 $\pm$ 2.1	8.5 $\pm$ 0.5
	III	257.0 $\pm$ 1.8	151.4 $\pm$ 2.3	56.3 $\pm$ 0.9	133.0 $\pm$ 2.2	106.3 $\pm$ 1.3	87.2 $\pm$ 0.8
	IV	25.1 $\pm$ 0.5	28.8 $\pm$ 1.3	9.2 $\pm$ 0.5	478.0 $\pm$ 3.8	347.0 $\pm$ 3.2	108.0 $\pm$ 1.9
	Sum	285.6	199.2	69.1	703.0	537.8	216.0
Ni	I	36.0 $\pm$ 0.9	9.0 $\pm$ 0.7	10.6 $\pm$ 1.1	7.4 $\pm$ 0.3	7.9 $\pm$ 0.5	8.2 $\pm$ 0.2
	II	21.4 $\pm$ 0.6	6.6 $\pm$ 0.5	7.9 $\pm$ 0.8	8.4 $\pm$ 0.4	3.4 $\pm$ 0.3	9.2 $\pm$ 0.4
	III	53.6 $\pm$ 1.3	7.8 $\pm$ 0.4	6.2 $\pm$ 0.4	12.3 $\pm$ 0.3	2.7 $\pm$ 0.2	14.4 $\pm$ 0.4
	IV	24.2 $\pm$ 0.8	17.0 $\pm$ 1.2	3.1 $\pm$ 0.2	322.0 $\pm$ 4.4	95.1 $\pm$ 1.8	52.1 $\pm$ 2.1
	Sum	135.2	40.4	27.8	350.1	109.1	83.9
Pb	I	8.6 $\pm$ 0.5	1.6 $\pm$ 0.2	2.0 $\pm$ 0.2	8.7 $\pm$ 0.4	8.8 $\pm$ 0.3	5.6 $\pm$ 0.2
	II	6.4 $\pm$ 0.5	1.7 $\pm$ 0.2	2.1 $\pm$ 0.3	3.9 $\pm$ 0.3	6.5 $\pm$ 0.4	1.6 $\pm$ 0.2
	III	31.5 $\pm$ 0.7	9.1 $\pm$ 1.1	31.0 $\pm$ 0.5	4.9 $\pm$ 0.2	18.3 $\pm$ 1.3	8.8 $\pm$ 0.4
	IV	90.5 $\pm$ 0.9	75.0 $\pm$ 1.5	7.8 $\pm$ 0.3	333.0 $\pm$ 3.8	207.0 $\pm$ 1.8	117.0 $\pm$ 2.2
	Sum	137.0	87.4	42.9	350.5	240.6	133.0
Cd	I	0.2 $\pm$ 0.1	0.7 $\pm$ 0.1	1.0 $\pm$ 0.2	2.7 $\pm$ 0.2	2.4 $\pm$ 0.3	1.9 $\pm$ 0.2
	II	1.1 $\pm$ 0.3	0.9 $\pm$ 0.1	0.5 $\pm$ 0.1	4.4 $\pm$ 0.3	1.4 $\pm$ 0.2	1.4 $\pm$ 0.3
	III	6.0 $\pm$ 0.4	0.9 $\pm$ 0.2	1.6 $\pm$ 0.3	4.1 $\pm$ 0.1	1.5 $\pm$ 0.3	1.7 $\pm$ 0.2
	IV	0.8 $\pm$ 0.2	0.6 $\pm$ 0.1	0.3 $\pm$ 0.1	7.4 $\pm$ 0.4	2.3 $\pm$ 0.2	4.7 $\pm$ 0.4
	Sum	8.1	3.1	3.4	18.6	7.6	9.7
Cr	I	2.5 $\pm$ 0.2	0.9 $\pm$ 0.2	<0.1	11.6 $\pm$ 3.1	7.3 $\pm$ 0.7	<0.1
	II	3.1 $\pm$ 0.1	0.5 $\pm$ 0.1	0.4 $\pm$ 0.1	5.1 $\pm$ 0.9	3.5 $\pm$ 0.4	0.3 $\pm$ 0.1
	III	345.0 $\pm$ 3.8	11.0 $\pm$ 0.8	7.4 $\pm$ 0.3	5.3 $\pm$ 0.3	1.5 $\pm$ 0.2	0.7 $\pm$ 0.2
	IV	90.4 $\pm$ 2.2	11.7 $\pm$ 1.1	3.5 $\pm$ 0.4	1090.0 $\pm$ 11	55.2 $\pm$ 3.2	36.0 $\pm$ 1.5
	Sum	441.0	24.1	11.3	1112.0	67.5	37.0

Fraction: I – exchangeable/carbonates, II – reducible, III – oxidisable, IV – residual.

In the case of the sludge samples C and Z, approximately 30% of zinc was present in the iron and manganese fraction. This can be correlated to the high amounts of iron

added during sewage treatment in the form of PIX (approximately 40%  $\text{Fe}_2(\text{SO}_4)_3$  solution) for precipitation of phosphates at which zinc sorption could occur. In the case of sludge M, significant amount of zinc (40%) was present in organic-sulfide fraction. A dominant role of this fraction in binding zinc is in agreement with previous studies by Alonso Alvarez [9], Fuentes [10], Stylianou [11], and Hanay [12]. Strong bonds between zinc, iron and manganese oxides in sewage sludge were reported by Walter [13], Chen [14], and Jamali [15], whereas, significant amounts of the metal in exchangeable-carbonate fraction of sludge were observed by Lasheen [16]. In the ash samples, zinc was mainly present in the residual fraction, being the fraction of compounds almost entirely insoluble: 5280  $\text{mg}\cdot\text{kg}^{-1}$  (62%) ash sample C, 1690  $\text{mg}\cdot\text{kg}^{-1}$  (62%) ash sample Z, and 2016  $\text{mg}\cdot\text{kg}^{-1}$  (48%) ash sample M.

Copper in the sludge samples was present in the organic-sulfide fraction at the concentrations of 257 (C), 151 (Z), and 56 (M)  $\text{mg}\cdot\text{kg}^{-1}$ . These values correspond to 90, 76, and 82% of the total concentration of the copper in the sludge samples, respectively. Copper shows strong affinity with organic compounds. This was underlined by Fuentes [10] and Lasheen [16]. In ash samples C, Z, and M, copper was mainly present in the fraction of compounds almost entirely insoluble: 478  $\text{mg}\cdot\text{kg}^{-1}$  (68%), 347  $\text{mg}\cdot\text{kg}^{-1}$  (65%), and 108  $\text{mg}\cdot\text{kg}^{-1}$  (50%), respectively. Significant amount of copper – 87  $\text{mg}\cdot\text{kg}^{-1}$  (40%) was also present in the oxidisable fraction of the ash sample M.

Nickel in the sludge sample C was present in the organic-sulfide fraction – 54  $\text{mg}\cdot\text{kg}^{-1}$  (40% of the total concentration of the metal in the sludge) and in exchangeable-carbonate fraction (27%). However, in the ash sample C it was associated with the fraction of compounds almost entirely insoluble – 322  $\text{mg}\cdot\text{kg}^{-1}$  (92%). In the case of both samples Z, sludge and ash, nickel was mainly present in the residual fraction – 17  $\text{mg}\cdot\text{kg}^{-1}$  (42%) and 95  $\text{mg}\cdot\text{kg}^{-1}$  (87%), respectively. In the sludge sample M, nickel was present in the exchangeable-carbonate fraction – 11  $\text{mg}\cdot\text{kg}^{-1}$  (38% of total concentration) and in iron and manganese oxides fraction - 8  $\text{mg}\cdot\text{kg}^{-1}$  (28%). On the other hand, in the ash sample M nickel was mainly present in the residual fraction – 52  $\text{mg}\cdot\text{kg}^{-1}$  (62%). A high concentration of nickel in exchangeable-carbonate fraction of sludge was reported by Hanay [12] and Jamali [15], however, Alonso Alvarez [9] and Chen [14] observed nickel mainly in organic-sulfide fraction.

In both samples, sludge and ash from wastewater treatment plants C and Z, lead was present in the fraction of compounds almost entirely insoluble, from 91 (C) and 75 (Z)  $\text{mg}\cdot\text{kg}^{-1}$  in the sludge samples, to 333 (C) and 207 (Z)  $\text{mg}\cdot\text{kg}^{-1}$  in the ash samples. These values correspond to 66% and 86% of its total concentration in the sludge and to 95% and 86% of its total concentration in the ash. The concentration of lead in sludge M was the highest in the organic-sulfide fraction – 31  $\text{mg}\cdot\text{kg}^{-1}$  (72%), and in ash M it was mainly present in the fraction of compounds almost entirely insoluble – 117  $\text{mg}\cdot\text{kg}^{-1}$  (88%). A dominant role of the residual fraction of sludge in binding lead was reported by Alonso Alvarez [9] and Fuentes [17].

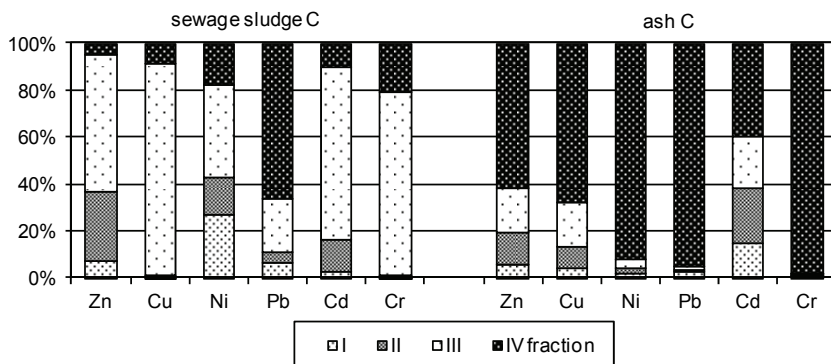


Fig. 1. Percentage distribution of heavy metals in fractions of sewage sludge C and ash C: I – exchangeable/carbonates, II – reducible, III – oxidisable, IV – residual

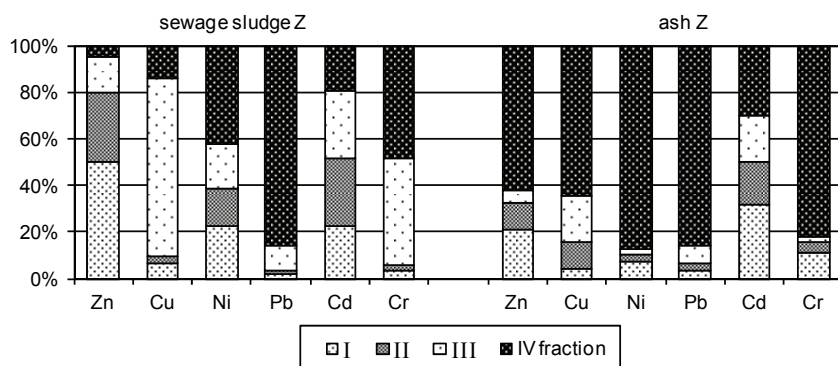


Fig. 2. Percentage distribution of heavy metals in fractions of sewage sludge Z and ash Z: I – exchangeable/carbonates, II – reducible, III – oxidisable, IV – residual

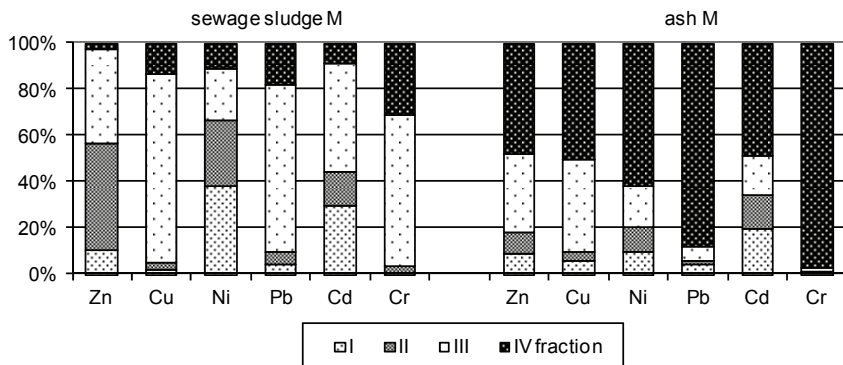


Fig. 3. Percentage distribution of heavy metals in fractions of sewage sludge M and ash M: I – exchangeable/carbonates, II – reducible, III – oxidisable, IV – residual

Cadmium was present in sludge sample C mainly in the organic-sulfide fraction –  $6.0 \text{ mg}\cdot\text{kg}^{-1}$  (74%). In sludge sample M, it was present in both fractions organic-sulfide and exchangeable-carbonate –  $1.6 \text{ mg}\cdot\text{kg}^{-1}$  (47%) and  $1.0 \text{ mg}\cdot\text{kg}^{-1}$  (29%), respectively. In sludge sample Z, cadmium was present in all fractions: organic-sulfide, iron and manganese oxides, exchangeable-carbonate, and residual. The percentage of its total concentration in all four fractions was 29, 29, 23, and 19%, respectively. A dominant role of the organic-sulfide fraction of sludge in binding cadmium was indicated by Chen [14], Jamali [15], and Obarska-Pempkowiak [18]. In the ash sample M, cadmium was mainly present in the fraction of compounds almost entirely insoluble –  $4.7 \text{ mg}\cdot\text{kg}^{-1}$  (48%), whereas, in the other fractions: exchangeable-carbonate, iron and manganese oxides, and sulfide, its percentage content was: 20, 14, and 18%, respectively. In ash C cadmium was associated with the residual fraction –  $7.4 \text{ mg}\cdot\text{kg}^{-1}$  (40%) and in the fraction of iron and manganese oxides (24%). In ash Z, it was present in both fractions exchangeable-carbonate and residual and the concentrations were –  $2.4 \text{ mg}\cdot\text{kg}^{-1}$  (32%) and  $2.3 \text{ mg}\cdot\text{kg}^{-1}$  (30%), respectively.

Chromium in sludge samples was mainly present in the organic-sulfide fraction:  $345 \text{ mg}\cdot\text{kg}^{-1}$  (78%) in sludge C,  $7.4 \text{ mg}\cdot\text{kg}^{-1}$  (66%) in sludge M, whereas, in the ash samples it was mainly present in the residual fraction:  $1090 \text{ mg}\cdot\text{kg}^{-1}$  (98%) in ash sample C and  $36 \text{ mg}\cdot\text{kg}^{-1}$  (97%) in ash sample M. In the case of both samples Z, sludge and ash, chromium was mainly present in the fraction of compounds almost entirely insoluble –  $11.7 \text{ mg}\cdot\text{kg}^{-1}$  (49%) and  $55 \text{ mg}\cdot\text{kg}^{-1}$  (82%), respectively.

During the analysis of sewage sludge it was observed that copper, cadmium, and chromium were bound to the organic-sulfide fraction, and lead, except of sludge M, was present in the residual fraction. Nickel, depending on the sludge sample, was present mainly in the exchangeable-carbonate, the organic-sulfide, or the residual fraction. Zinc was found in the exchangeable-carbonate, the iron and manganese oxides or the organic-sulfide fraction.

The present study shows that after combustion of sewage sludge at  $600 \text{ }^\circ\text{C}$  from the three wastewater treatment plants, heavy metals in ash samples are mainly present in the residual fraction; this is the fraction of compounds almost entirely insoluble. The highest concentrations in these fractions were observed for lead (86–95%), chromium (82–98%), and nickel (62–92%) (Figs. 1–3).

The combustion of sewage sludge at  $600 \text{ }^\circ\text{C}$  favoured the formation of mineral structures in ash. Analysis of ash samples indicated the presence of following minerals: quartz, dolomite, illite, anhydrite, giniite ferric and albite calcian ordered.

Haustein [19] also reported enrichment of metals in the residual fraction of ash, obtained after combustion of sludge. Whereas, Chen [20] found that heavy metals were enriched in the residual fraction of slags. The highest increase of nickel and chromium contents was observed in the residual fraction of slags obtained at  $500 \text{ }^\circ\text{C}$ . For slags obtained at  $900 \text{ }^\circ\text{C}$  also a high increase of copper, cadmium, and zinc concentrations was observed in the residual fraction. The residual fraction is considered as

a fraction containing metals chemically stable and biologically inactive. This fraction contains mainly metals built into the crystal structure of primary and secondary minerals. Metals accumulated in this fraction of sludge are not to be considered dangerous to groundwater. Combustion of sewage sludge resulted in the formation of immobile forms of heavy metals. It is especially valid for chromium, nickel, and copper.

However, metals were still found in the mobile, exchangeable-carbonate, ash fraction. The following concentrations were detected: 6–21.3, 3.8–5.7, 2.1–9.8, 2.5–4.2, 14.5–31.6 and 1–10.8% of the total content of zinc, copper, nickel, lead, cadmium, and chromium, respectively.

In order to lower the concentration of metals in this fraction, combustion of sewage sludge at higher temperatures can be performed as indicated by Chen [20].

#### 4. CONCLUSIONS

In sewage sludge, heavy metals are mainly associated with the organic sulfide fraction. Significant amounts of zinc were also present in the fraction of iron and manganese oxides, of nickel and cadmium in the exchangeable-carbonate fraction, and of lead in the residual fraction. In ash samples obtained after combustion at 600 °C, heavy metals are mainly enriched in the residual fraction. The highest concentration in this fraction was observed for lead, chromium, and nickel. Metal accumulation in this non-mobile fraction is advantageous with respect to soil-water environment protection.

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