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INFLUENCE OF TEMPERATURE AND TIME OF SEWAGE SLUDGE INCINERATION ON THE MOBILITY OF HEAVY METALS

Sewage sludge ashes in comparison to sewage sludge are characterized by higher concentrations of heavy metals. The mobility of heavy metals in sewage sludge ashes determines their impact on the soil-water environment in the aspect of toxicology. This research statistically evaluates the influence of temperature and duration of SS incineration on the mobility of HM from SSA. For the incineration temperatures 600-980 °C and 2-20 min of incineration, the experiment domain was defined in accordance with the Box's two-factor experimental design. It was proved that it was not the time but the temperature of SS incineration that had the statistically relevant influence on the mobility of nickel and copper.

1. INTRODUCTION

The environmental usage of sewage sludge (SS) and its deposit in landfills are limited [1, 2]. Despite the limitations, the accumulation of sewage sludge contamination [3–5] and the increasing ecological awareness among citizens contribute to the growth of the quantity of sewage sludge utilized by thermal methods.

The incineration of sewage sludge is not a waste-free method because its product is ash containing heavy metals. Although during the incineration, some heavy metals are vaporized but later they condense on the surface of the sewage sludge particles [6, 7]. Van de Velden et al. [8] in a study on an industrial scale lasting over a year stated that 20% of Hg, 93% of As and almost 100% of Cd and Pb remained in the sewage sludge ash.

Heavy metals which enter the environment accumulate in both soil and living organisms [9]. The range of influence of the metal which enters living organisms depends

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on the chemical and the physical form of the metal itself. The most toxic metals are the ones which occur in the dissolved form, the least toxic on the other hand are the ones in the form of precipitated sludge [10]. Heavy metals can be divided into mobile ones, occurring in ion-exchange complexes which have a tendency to migrate, and immobile ones having no significant meaning as far as the toxicological aspect is concerned [11].

The sequential extraction is used in order to define the metal occurrence form, their means of bonding with matrix components and their potential reactivity under various physicochemical environmental conditions [12]. One of the sequential extraction procedures used is the one developed by the European Community Bureau Reference (BCR). The sequential analysis leads to obtaining four fractions of metals, which differ from each other in the mobility of heavy metals they contain [13, 14]:

- exchangeable (mobile) fraction associated with carbonates,
- reducible (mobile) fraction associated with Fe and Mn oxides,
- oxidizable (temporarily immobile) fraction bound to organic matter and sulfides,
- residual (immobile) fraction bound to crystalline structures.

No study has been conducted so far concerning the statistical evaluation of the influence of sewage sludge incineration parameters on the forms of occurrence of heavy metals in ashes. The aim of the study was to define the influence of temperature and time of sewage sludge incineration on the mobility of heavy metals from ashes. From the perspective of a potential risk connected with the environmental exposure to heavy metals, this can be important when the work parameters of the installation are not monitored, especially in the case of using sewage sludge ashes for forming embankments [15] and stabilizing terrain [16].

2. MATERIALS AND METHODS

After the anaerobic stabilisation, drainage and drying in a disc dryer, the sewage sludge was obtained from a municipal wastewater treatment plant in Sitkówka-Nowiny, which treats sewage from Kielce agglomeration, located in the central part of Poland. Its chemical composition was defined by the X-ray fluorescence spectrometry.

The sewage sludge was dried in a laboratory drier at 105 °C. Then it was crushed in a mortar to fraction <125 μ m which was incinerated in a laboratory furnace Naberthem in the range of 600–980 °C and during 2–20 min (most often sewage sludge is reported to be incinerated at 850–900 °C [17, 18]). After the combustion, the samples remained in the furnace until they cooled down to 20 °C.

Experimental design. The research was conducted in accordance with the Box two-factor experimental design [19, 20] created by adding symmetrically positioned star points and a central point to the two-level design type 2^2 . Each of the two independent

variables (incineration temperature and time) was described with five values. The experiment domain is shown in Table 1. The experiment involved five independent repetitions in each point of the design (Table 2).

Table 1

Factor	Code symbol	Central value	Variability unit	Measurement unit
Incineration temperature, T	X_1	790	190	°C
Incineration time, t	X_2	11	9	min

The experiment domain (ranges of independent variables)

Table 2

No.	X_1	X_2	Incineration temperature, T	Incinerationtime, t
1	-1	0	600	11
2	1	0	980	11
3	-0.707	-0.707	655.6	4.6
4	0	1	790	20
5	-0.707	0.707	655.6	17.4
6	0.707	0.707	924.4	17.4
7	0	0	790	11
7 ^{bis}	0	0	790	11
8	0	-1	790	2
9	0.707	-0.707	924.4	4.6

Experimental design

Mobility of heavy metals from sewage sludge ash. The BCR tests were applied to determine the heavy metal fraction in the sewage sludge and sewage sludge ashes. The tests were conducted in accordance with the four-step BCR sequential extraction procedure [17, 21, 22]. Heavy metals in the extracts were determined using an optical spectrometer with inductively coupled plasma ICP Perkin-Elmer Optima 8000.

Statistical evaluation of test results. The regression function analysis was performed based on the formula [19, 20]:

$$f(x) = \beta_0 + \beta_1 X_1 + \dots + \beta_m X_m + \beta_{11} X_1^2 + \beta_{12} X_1 X_2 + \dots + \beta_{mm} X_m^2$$
(1)

where: f(x) – the expected value of the dependent variable, $X_1, X_2, ..., X_m$ – independent variables, $\beta_0, \beta_1, ..., \beta_m, \beta_{11}, \beta_{12}, ..., \beta_{mm}$ – unknown regression function coefficients.

The coefficients of the regression function were obtained by the method of least squares. The significance of the coefficients of regression function was verified based

on the Student's *t*-distribution test for significance level of 0.05. Another important indicator is the coefficient of determination R^2 , which not only indicates the precision of fit, but can also be interpreted as the amount of variation of the dependent variable explained by the regression equation. The SAS version 9.3 was used for statistical calculations.

3. RESULTS AND DISCUSSION

The main compounds of studied sewage sludge were (in wt. %): $SiO_2 8.8$, $P_2O_5 7.1$, CaO 5.7, $Fe_2O_3 3.7$, $Al_2O_3 2.1$, and MgO 1.4 . Sewage sludge was characterized by moisture 72.6% and pH 7.5. It contained 33.69 wt. % d.m. of total organic carbon.

The basic form of studied heavy metals in sewage sludge is the residual fraction FIV. The exception is Cd, for which the dominant form is fraction FIII (39.71%). The contribution of fraction FIV in the total contents of metals in sewage sludge equals from 60.24% for zinc up to 99.23% for lead (Fig. 1, Table 3).



Fig. 1. Contribution of heavy metals in fractions of the sewage sludge

The average values of particular fractions of heavy metals in sewage sludge ashes are presented in Tables 4–10.

Table 3

Speciacion BCR	Cu	Cr	Cd	Ni	Pb	Zn
Fraction I	2.20±0.15	$0.42{\pm}0.06$	0.33 ± 0.02	2.66 ± 0.03	0.22±0.01	6.85±0.12
Fraction II	1.42 ± 0.04	0.16 ± 0.04	$0.49{\pm}0.01$	$1.09{\pm}0.03$	$0.20{\pm}0.04$	13.65 ± 0.05
Fraction III	6.84±0.16	$0.78{\pm}0.06$	$0.54{\pm}0.01$	3.23 ± 0.05	$0.59{\pm}0.07$	116.54 ± 0.82
Fraction IV	211.95±1.23	60.64±1.18	$0.00{\pm}0.00$	19.29±0.11	129.50±0.93	207.64±2.58
Sum of FI-FIV	222.42	61.98	1.36	26.27	130.51	344.68

The content of heavy metals in sewage sludge [mg/kg d.m.]

The total contents of zinc in the sewage sludge ashes was from 1398.53 up to 3019.00 mg/kg d.m. Its highest value was found for the ash obtained at 655.6 °C within 17.4 min, whereas the lowest one for that obtained at 924.4 °C within 4.5 min (Table 4). The difference in zinc contents in particular samples of the ashes indicates the transition of zinc compounds from solid phase into gas phase depends on the temperature of incineration. Vogel et al. [23] reported similar observations for zinc in the process of incineration of sewage sludge ashes.

The total content of zinc in the sewage sludge ashes is on a similar level to that in sewage sludge ashes reported by Dąbrowska [14], obtained by the incineration of three different sewage sludge samples at 600 °C.

Table 4

No.	Zn_FI	Zn_FII	Zn_FIII	Zn_FIV	Sum of FI–FIV
1	30.57 ± 3.78	85.01±14.12	$1085.03{\pm}162.34$	1554.61 ± 588.32	2755.22
2	$238.54{\pm}67.73$	134.04±33.79	362.16±122.19	696.02±281.77	1430.76
3	84.38±12.99	480.44±72.71	739.39±209.66	1162.35±522.23	2466.56
4	277.80 ± 36.89	198.17±17.65	827.10±151.46	1427.71 ± 520.33	2730.78
5	109.25 ± 10.66	485.65±71.24	639.10±73.52	$1785.00{\pm}508.63$	3019.00
6	288.01 ± 64.77	162.27±30.19	317.21±79.63	852.53±367.50	1620.02
7	225.88±38.75	175.20 ± 31.88	763.17±188.67	1409.37 ± 529.57	2573.62
7 ^{bis}	232.17±44.27	176.86 ± 24.27	700.08±143.26	1507.85 ± 542.26	2616.96
8	$253.04{\pm}29.98$	356.51±57.56	696.50±87.18	1538.47±593.31	2844.52
9	214.33±80.16	138.47±44.43	337.04±100.04	708.69±325.35	1398.53

The content of Zn in sewage sludge ash [mg/kg d.m.]

In all samples of sewage sludge ashes, zinc was bound mostly with fraction FIV, thus it formed mainly organometallic and aluminosilicate bonds (Fig. 2). Zinc contribution ranges from 47.12% for sewage sludge incinerated at 655.6.4 °C within 4.6 min up to 59.13% for sewage sludge incinerated at 655.6 °C within 17.4 min. The high values of standard error, especially for fraction FIV may be potentially caused by non-homogeneity of the studied matrix.



Fig. 2. Contribution of Zn in fractions of sewage sludge ashes

The dependence of zinc mobility on the temperature (T) and time (t) of the sewage sludge incineration is described by the function:

Zn _{mobile} =
$$72.11 - 0.129T - 3.747t + 0.000009T^2 + 0.0019Tt + 0.0949t^2$$
 (2)

The determination coefficient of 0.679 indicates a satisfactory match of the model with experimental results. The whole model is not statistically relevant; p has the value of 0.3147.



Fig. 3. Estimated mobility of zinc and experimental results

The increase of the temperature of incineration causes a small increase of zinc mobility (Fig. 3), whereas the increase of time of incineration from 2 to 11 min is initially accompanied by the decrease of zinc mobility. A further increase of incineration time causes the increase of zinc mobility (Fig. 3). However, due to the lack of statistical relevance of the model, the conclusions should be interpreted with caution.

Table 5

No.	Ni_FI	Ni_FII	Ni_FIII	Ni_FIV	Sum of FI–FIV V		
1	0.08 ± 0.06	$0.19{\pm}0.11$	17.87 ± 5.40	35.61±14.19	53.75		
2	2.88 ± 0.52	2.03 ± 0.42	4.87±1.06	28.63±10.24	38.41		
3	0.15±0.13	2.81±0.51	14.61±4.23	24.78±12.55	42.35		
4	3.75 ± 0.54	2.08 ± 0.31	6.61±1.17	40.03±13.60	52.47		
5	0.55 ± 0.34	4.13±0.33	17.73 ± 2.87	34.86 ± 9.32	57.27		
6	$3.44{\pm}0.41$	2.17 ± 0.31	4.01 ± 1.17	36.97±13.57	46.59		
7	$3.82{\pm}0.50$	2.04 ± 0.37	$7.09{\pm}1.04$	$34.93{\pm}12.40$	47.88		
7 ^{bis}	3.71±0.65	$2.23{\pm}0.31$	$7.39{\pm}1.59$	37.71±13.02	51.04		
8	4.47 ± 0.84	4.73 ± 1.04	8.41±1.24	$36.61{\pm}14.69$	54.22		
9	4.31±0.68	2.81 ± 0.47	5.55 ± 1.11	27.59±12.67	40.26		
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9 4.31±0.08 2.81±0.47 5.33±1.11 27.39±12.67 40.26							

The content of Ni in sewage sludge ash [mg/kg d.m.]



■Ni_FI □Ni_FII □Ni_FIII □Ni_FIV

Fig. 4. Contribution of Ni in fractions of sewage sludge ashes

The total contents of nickel in the sewage sludge ashes equaled from 38.41 up to 57.27 mg/kg d.m. Its highest value was found for sewage sludge incinerated at 655.6 °C within 17.4 min (Table 5). It was found that nickel was bound with fraction FIV from 58.51 up

to 79.36% (Fig. 4). The total content of nickel in the ashes presented smaller values in comparison to the results obtained by Dąbrowska [14].

The dependence of nickel mobility on the temperature (T) and time (t) of incineration is described by:

$$Ni_{mobile} = -117.38 + 0.29T + 0.86t - 0.0002T^{2} - 0.0021Tt + 0.0243t^{2}$$
(3)

The determined coefficient R^2 equals 0.981, which indicates a very good match of the regression function with the experiment data. The whole model is statistically relevant; p equals 0.0015.

The influence of sewage sludge incineration temperature (p = 0.0010) is more statistically important for the mobility of nickel than the incineration time (p = 0.0199). The increase of the incineration temperature in the range of 600–980 °C causes an increase of nickel mobility. This relation occurs almost independently of the incineration time in the range of 2–20 min (Fig. 5).



Fig. 5. Estimated mobility of nickel and experimental results

The total contents of cadmium in the sewage sludge ashes equaled from 0.08 up to 26.32 mg/kg d.m. Its greatest value was found for sewage sludge incinerated at 980 °C within 11 min, the smallest one – for 790 °C within 20 min. The scope of conducted research was not to indicate the reasons of such a diversity in cadmium contents as far as the studied sewage sludge samples are concerned. Volatility of cadmium depends on its incinerated compound, e.g., cadmium chloride is volatile, while cadmium oxide

- non-volatile [24]. Eight out of ten samples of studied sewage sludge ashes are characterized by lower concentration of cadmium in comparison to the results obtained by Dąbrowska [14].

The analysis of fractions of cadmium showed that this metal is present in fractions FIII and FIV in most samples of sewage sludge ashes. The sewage sludge incinerated at 790 °C within 20 min and 924.4 °C within 17.4 min showed the greatest content of mobile fraction FI - 100% and 80.82%, respectively (Table 6, Fig. 6).

Table 6

No.	Cd_FI	Cd_FII	Cd_FIII	Cd_FIV	Sum of FI-FIV
1	$0.05{\pm}0.03$	$0.03{\pm}0.03$	$1.04{\pm}0.20$	$0.29{\pm}0.26$	1.41
2	4.04±3.09	0.41 ± 0.27	$0.50{\pm}0.38$	21.37±19.11	26.32
3	$0.03{\pm}0.02$	$0.04{\pm}0.02$	0.85 ± 0.42	$20.85{\pm}18.65$	21.77
4	$0.08{\pm}0.07$	$0.00{\pm}0.00$	$0.00{\pm}0.00$	$0.00{\pm}0.00$	0.08
5	0.13±0.12	0.15±0.13	$0.70{\pm}0.32$	$0.00{\pm}0.00$	0.98
6	$0.59{\pm}0.48$	0.06 ± 0.05	$0.08 {\pm} 0.07$	$0.00{\pm}0.00$	0.73
7	$0.07{\pm}0.04$	$0.03{\pm}0.02$	$0.09{\pm}0.04$	$0.00{\pm}0.00$	0.19
7 ^{bis}	0.05 ± 0.04	$0.01{\pm}0.01$	0.15 ± 0.08	$0.00{\pm}0,00$	0.21
8	$0.07{\pm}0.06$	$0.00{\pm}0.00$	0.08 ± 0.07	$0.00{\pm}0.00$	0.15
9	0.07 ± 0.06	0.08 ± 0.07	0.07 ± 0.06	2.63±2.36	2.85

The content of Cd in sewage sludge ash [mg/kg d.m.]



Fig. 6. Contribution of Cd in fractions of sewage sludge ashes

For the applied study design, the obtained results of cadmium mobility from sewage sludge ashes cannot serve as a base for the statistical description of cadmium mobility

on temperature and incineration time. The lack of a model for the cadmium mobility is caused by an insufficient variability of the obtained results.

The total contents of chromium in the sewage sludge ashes equaled from 53.98 up to 144.16 mg/kg d.m. Its greatest value was found for sewage sludge incinerated at 600 °C within 11 min, the smallest one for 924.4 °C within 4.6 min. The studied sewage sludge ashes were characterized by the total content of chromium from a relatively narrow range of values (53.98–144.16 mg/kg d.m) in contrast to sewage sludge ashes presented in [14] – 37.0–1112.0 mg/kg d.m. The analysis of fractions of chromium proved that for all sewage sludge ashes, the greatest contribution for chromium was in fraction FIV, from 94.02 up to 99.92% (Fig. 7, Table 7).



Fig. 7. Contribution of Cr in fractions of sewage sludge ashes

Table 7

No.	Cr_FI	Cr_FII	Cr_FIII	Cr_FIV	Sum of FI-FIV
1	$0.01 {\pm} 0.01$	$0.02{\pm}0.01$	1.83 ± 0.59	$142.30{\pm}27.98$	144.16
2	0.05 ± 0.03	0.05 ± 0.03	$0.20{\pm}0.11$	70.22±23.59	70.52
3	$0.003{\pm}0.003$	$0.01{\pm}0.01$	6.29±1.75	99.04±30.60	105.34
4	$0.00{\pm}0.00$	$0.00{\pm}0.00$	$0.08 {\pm} 0.10$	103.24±31.33	103.32
5	$0.01{\pm}0.01$	0.06 ± 0.05	4.92±2.23	$133.49{\pm}26.30$	138.48
6	0.25±0.17	$0.00{\pm}0.00$	$0.10{\pm}0.06$	95.84±31.13	96.19
7	0.21±0.18	$0.00{\pm}0.00$	$0.20{\pm}0.11$	97.76±30.35	98.17
7 ^{bis}	$0.01{\pm}0.01$	$0.01{\pm}0.01$	0.16 ± 0.09	106.17±31.54	106.35
8	0.01±0.01	0.07 ± 0.06	0.53±0.48	84.24±28.75	84.85
9	0.23±0.18	$0.04{\pm}0.04$	0.08 ± 0.07	53.63±21.33	53.98

The content of Cr in sewage sludge ash [mg/kg d.m.]

For the applied study design, the obtained results of chromium mobility from sewage sludge ashes did not allow for a statistical description of chromium mobility dependence on temperature and incineration time. The lack of a model for the chromium mobility is caused by an insufficient variability of obtained results (Fig. 7, Table 7).



Fig. 8. Contribution of Pb in fractions of sewage sludge ashes

Table 8

No.	Pb_FI	Pb_FII	Pb_FIII	Pb_FIV	Sum of FI–FIV
1	$0.00{\pm}0.00$	$0.00{\pm}0.00$	0.00 ± 0.00	139.98 ± 27.27	139.98
2	$0.00{\pm}0.00$	0.41 ± 0.37	$0.00{\pm}0.00$	$0.32{\pm}0.19$	0.73
3	$0.00{\pm}0.00$	$0.00{\pm}0.00$	$0.00{\pm}0.00$	108.82 ± 31.70	108.82
4	$0.00{\pm}0.00$	$0.00{\pm}0.00$	$0.10{\pm}0.09$	93.83±28.36	93.93
5	$0.03{\pm}0.03$	0.16±0.15	$0.00{\pm}0.00$	$128.47{\pm}24.80$	128.66
6	$0.00{\pm}0.00$	$0.04{\pm}0.04$	1.42±1.27	$6.30{\pm}5.41$	7.76
7	$0.00{\pm}0.00$	$0.00{\pm}0.00$	$0.00{\pm}0.00$	87.37±26.87	87.37
7 ^{bis}	$0.00{\pm}0.00$	1.13 ± 1.01	$0.00{\pm}0.00$	97.65 ± 28.91	98.78
8	0.002 ± 0.002	0.05 ± 0.05	$0.00 {\pm} 0.00$	75.55±27.65	75.60
9	0.00 ± 0.00	0.13±0.12	$0.03{\pm}0.03$	51.99 ± 46.50	52.15

The content of Pb in sewage sludge ash [mg/kg d.m.]

The total contents of lead in studied sewage sludge ashes equaled from 0.73 up to139.98 mg/kg d.m. (Table 8). Its greatest value was found for sewage sludge incinerated at 600 °C within 11 min, the smallest value was noted for 980 °C within 11 min. A very small content of lead in sewage sludge ash for 980 °C was caused by the volatility of this metal [24].

The analysis of fractions of lead proved that for most sewage sludge ashes the greatest contribution of lead was in fraction FIV, from 81.19 up to 100.00%. The exception was the sewage sludge incinerated at 980 °C within 11 min, then the largest contribution was the second fraction -56.16% (Fig. 8).

Due to insufficient variability of the obtained results, a statistical description of lead mobility in dependence on incineration time and temperature (Fig. 8).

The greatest content of cobalt was found in the sample after the incineration of sewage sludge at 790 °C within 2 min (10.60 mg/kg d.m.), whereas the smallest one in ash after incineration at 655.6 °C within 4.6 min (Table 9). Cobalt was found in sewage sludge ashes in all fractions (Fig. 9).



Fig. 9. Contribution of Co in fractions of sewage sludge ashes

Table 9

No.	Co_FI	Co_FII	Co_FIII	Co_FIV	Sum of FI–FIV
1	0.25 ± 0.03	$0.52{\pm}0.08$	5.51±1.12	$0.82{\pm}0.56$	7.10
2	1.70±0.25	1.14 ± 0.21	2.51±0.56	4.46±2.25	9.81
3	0.56 ± 0.09	2.11±0.38	3.28 ± 0.90	1.14 ± 0.63	7.09
4	2.04±0.25	1.10 ± 0.09	2.89±0.41	$3.79{\pm}1.88$	9.82
5	0.99±0.21	2.02 ± 0.58	$2.80{\pm}0.40$	$1.69{\pm}0.96$	7.50
6	2.06 ± 0.27	1.26±0.13	1.93 ± 0.49	$3.82{\pm}1.88$	9.07
7	2.06 ± 0.28	0.95±0.19	2.41±0.58	$3.48{\pm}1.74$	8.90
7 ^{bis}	1.98 ± 0.34	0.94±0.15	2.36 ± 0.47	4.15±2.11	9.43
8	2.68 ± 0.38	1.57 ± 0.20	2.48±0.16	3.87±2.32	10.60
9	2.19±0.34	1.52±0.21	2.42±0.54	2.15±1.04	8.28

The content of Co in sewage sludge ash [mg/kg d.m.]

The greatest contribution of cobalt in sewage sludge incinerated at given temperature and time constitutes the sum of fraction FIII and FIV.

The dependence of cobalt mobility on the temperature (T) and time (t) of sewage sludge incineration is described by the function:

$$Co_{mobile} = -104.772149 + 0.349113T - 1.168831t$$
$$-0.0000192T^{2} - 0.002106Tt + 0.110744t^{2}$$
(4)

The determination coefficient of 0.5086 indicates a poor match of the model with the experimental results. The whole model is not statistically relevant; *p* equals 0.5889.



Fig. 10. Estimated mobility of cobalt and experiment results

Based on the regression function response surface (Fig. 10) it has been found that the increase of incineration temperature causes a minor increase of cobalt mobility. Whereas the increase of the incineration time from 2 to 11 min is initially accompanied by an insufficient decrease of cobalt mobility. A further increase of incineration time causes a minor increase of cobalt mobility. Due to the lack of statistical relevance of the model, the conclusions for the mobility of cobalt should be applied with caution.

The total contents of copper in the sewage sludge ashes equals from 325.28 up to 553.51 mg/kg d.m. Its greatest value was found for sewage sludge incinerated at 600 °C within 11 min, the smallest one was noted for 924.4 °C within 17.4 min. The analysis of fractions of copper proves that the dominant form of copper for all studied sewage



sludge ashes are organometallic and aluminosilicate compounds, i.e. immobile forms (Fig. 11, Table 10).

Fig. 11. Contribution of Cu in fractions of sewage sludge ashes

Table 10

No.	Cu_FI	Cu_FII	Cu_FIII	Cu_FIV	Sum of FI–FIV
1	$0.00{\pm}0.00$	0.18 ± 0.10	144.59 ± 46.16	$408.74{\pm}106.60$	553.51
2	26.07±3.26	15.49 ± 4.41	84.17±20.69	226.07±79.92	351.80
3	$0.00{\pm}0.00$	$0.39{\pm}0.28$	141.73±53.79	241.96±131.37	384.08
4	3.29±1.66	0.46 ± 0.41	$115.04{\pm}16.30$	315.52±113.41	434.31
5	$0.05 {\pm} 0.05$	$0.49{\pm}0.44$	159.65±21.88	303.18±89.22	463.37
6	11.76 ± 6.70	6.75±3.32	78.47±10.71	228.30±90.74	325.28
7	2.86±1.19	$0.59{\pm}0.28$	106.95 ± 19.92	$278.53{\pm}101.86$	388.93
7 ^{bis}	$2.00{\pm}0.94$	$0.69{\pm}0.46$	85.01±15.66	$299.65{\pm}105.80$	387.35
8	$2.02{\pm}0.77$	$1.04{\pm}0.45$	136.27±17.90	261.80±98.63	401.13
9	11.02 ± 6.45	6.23 ± 3.37	$117.04{\pm}16.20$	192.08 ± 89.84	326.37

The content of Cu in sewage sludge ash [mg/kg d.m.]

The dependence of copper mobility on the temperature (T) and time (t) of the sewage sludge incineration is described by the function:

$$Cu_{mobile} = 65.30457 - 0.188672T - 0.04606t + 0.000135T^{2} + 0.000177Tt - 0.003741t^{2}$$
(5)

The determination coefficient of 0.967 indicates a very good match of the model with the experimental results. The whole model is statistically relevant; p is 0.0046.



Fig. 12. Estimated mobility of copper and experiment results



♦ Cd FI+FII \triangle Cr FI+FII ▲ Pb FI+FII \times Co FI+FII % Cu FI+FII \bigcirc NI FI+FII \Box Zn FI+FII Fig. 13. Contribution of the sum mobile fractions (FI + FII) of heavy metals in sewage sludge ashes, %

Copper mobility slightly increased after exceeding 750 °C. The temperature of sewage sludge incineration is statistically relevant for the influence on the mobility of copper from sewage sludge ashes, p equals 0.0023. The time of incineration does not have a statistically relevant influence on the copper mobility because p equals 0.9722 (Fig. 12).

Most studied sewage sludge ashes were characterized by the greatest contribution of cobalt in fractions FI and FII. Therefore cobalt was found to have the greatest mobility among all marked heavy metals (Fig. 13). The next metal in the sequence of the decreasing contribution of mobile forms was cadmium and zinc. The greatest mobility of cadmium was identified for the sewage sludge incinerated at 790 °C within 20 min. The maximum incineration temperature and the maximum incineration time did not guarantee lack of mobility of heavy metals. The contribution of mobile forms of heavy metals was similar in all samples.

Significant differences between total concentrations and contributions in fractions FI–FIV of particular heavy metals for various temperatures and time of incineration depended on forms of heavy metals present in sewage sludge, i.e. their melting and boiling temperatures. In sewage sludge, heavy metals occur in diversity of chemical compounds such as sulfates, carbonates or amorphous manganese and iron oxides, etc. The boiling points of pure metals are significantly higher than those of their salts, e.g., the boiling point of zinc equals 907 °C, and nickel – 2732 °C, whereas, that of NiSO₄ is 840 °C, and of ZnSO₄ – 740 °C. Therefore the mobilities of heavy metals depend on types of chemical compounds they occur [25–27].

Similarly to the results obtained by Dąbrowska [14], the studied sewage sludge ashes contained the greatest amount of zinc, nickel and chromium in fraction FIV, copper was also present in the fraction of compounds almost entirely insoluble (FIII) [14]. According to [14, 21] lead was mainly present in residual fraction (FIV) in contrast to studied sewage sludge ashes, in which apart from samples with dominant amount of lead in residual fraction, sewage sludge ash of more than 55% lead contribution was found in the reducible fraction.

According to Chen and Yan [21], the temperature of sewage sludge incineration presents a statistically significant influence on the contribution of cadmium and chromium in non-residual fraction, whereas the time of sewage sludge incineration presents a statistically significant influence on the contribution of copper in non residual fraction.

4. CONCLUSION

Due to the decrease of sewage sludge organic mass, the relative contents of heavy metals in sewage sludge ashes increased. The differences in heavy metals concentrations in sewage sludge ashes in comparison to sewage sludge were connected with their different volatilities during incineration. The results of the study on the dependence of mobility of heavy metals from sewage sludge ashes on incineration time and temperature did not allow to obtain statistical models which would describe the influence of the above mentioned incineration parameters on the mobility of cadmium, chromium and lead. As far as the mobility of zinc and cobalt is concerned, the obtained models were not statistically relevant. The models describing the dependence of mobility on the time and temperature of sewage sludge incineration were obtained for nickel and copper. It has been proved that the temperature, and not the sewage sludge incineration time, has a statistically important influence on the mobility of nickel and copper.

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