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Leaching of heavy metals from thermal treatment municipal sewage sludge fly ashes

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Abstract: An increasing number of municipal sewage treatment plants in Poland, desirable from an environmental perspective, raises the problem of managing the growing volume of sewage sludge. The thermal treatment of municipal sewage sludge (TTMSS) method, by greatly reducing the waste volume, increases the heavy metal concentration in fly ash (primary, end product of the treatment process), which may constitute a risk factor when attempting to utilize them economically. The research paper concentrates on determining the TTMSS fly ash heavy metal leaching level. For this purpose, ash samples were subjected to leaching with the batch and percolation tests, and the heavy metal content in eluates was determined by the FAAS method. The obtained results served as a base to determine the level of heavy metal immobilization in the ash, the element release mechanism (percolation test), and the impact of the L/S (liquid to solid) ratio and pH on the heavy metal leaching intensity (percolation test). The conducted research indicated high immobilization of heavy metals in TTMSS fly ash, regardless of the applied study method, which corresponds to the results of other researchers. Lead was the most intensively eluted metal.

Introduction

A change in the approach towards wastewater treatment has been observed in Poland over the last two decades. Methods oriented at the mechanical removal of pollutants are replaced by highly-effective treatment technologies with enhanced removal of nitrogen and phosphorous compounds, which is manifested by the increased share of municipal sewage subjected to treatment with enhanced biogene removal from 30% in 2000 to 84% in 2017 (Bochenek et al. 2018).

The gradual development of water and sewage management, desirable from the environmental perspective, entails an issue of managing a growing volume of wastewater – from 2000 to 2017 the volume of wastewater generated at municipal wastewater treatment plants increased by 63% (Bochenek et al. 2018). Sewage sludge treatment consumes approximately 50% operational costs of an entire treatment plant, despite the fact that the quantity of generated sludge is only about 1÷3% of the flowing sewage volume (Boruszko, 2001), which makes the issue important not only from the environmental but also economic perspective.

One of the methods of sewage sludge management, specified by the National Waste Management Plan 2022 (*National Waste Management Plan 2022*, 2016) is their thermal conversion. Municipal sewage sludge (MSS) with a hydration below 30% can be characterized by the combustion heat close to natural energy media, i.e., straw, wood, peat and lignite, and therefore, they enable achieving autothermal combustion conditions and a positive energy balance (Grobelak et al. 2019). The outcome of MSS thermal treatment is waste with the largest share of fly ash. At this moment, the increasingly more processed waste is shifted in the process chain until a moment it is utilized by another process as a product or it is subjected to definitive disposal. Due to the assumption of circular economy, we should aim for the first solution. For this purpose, it is necessary to thoroughly study the properties of generated waste, so that we are able to utilize them in a safe and cost-effective manner, because due to the changes they have been subjected to, they might have achieved negative properties affecting the human environment.

There have been attempts documented in the source literature to utilize thermal treatment municipal sewage sludge (TTMSS) ashes for phosphate fertilizer production (Franz, 2008; Hudziak et al. 2012; Łukawska, 2014), wastewater treatment (after subjecting it to granulation and vitrification) (Białowiec et al. 2009), as a component of mineral binders, (Lam et al. 2010; Lin and Lin, 2005), concrete (Cyr et al. 2007; Rutkowska et al. 2018), hardening slurries (Falacinski and Szarek, 2016; Szarek, 2019), ceramic materials, (Anderson, 2002; Lin et al. 2008) and light aggregate (Borowski, 2011; Wainwright and Cresswell, 2001). Due to their origin, TTMSS fly ashes are characterized by increased content of certain heavy metals, which can obstruct their further utilization, due to the possibility of metals released to the environment.

Heavy metal leaching primarily depends on the external properties of the material and the operating conditions of a given material. The material properties include composition and internal structure (porosity), as well as associated conductivity (hydraulic permeability). Such concepts as material form (monolithic or refined) and the operating environment (in the ground, water, contact with aggressive media, pH, temperature) are associated with external conditions. Two general processes (with their combination in practice) causing the leaching of components from a medium can be distinguished (Van der Sloot i Dijkstra 2004):

1. Physical transport processes.
2. Chemical processes.

Within the physical transport processes, which determine heavy metal leaching, we can distinguish:

a) Advection – a dynamic process of dissolved or precipitated chemicals transported by a flowing liquid. Due to the material being exposed to the action of new liquids, heavy metal release can be a long process. A particular case of advection is percolation, which occurs when the liquid flows through a porous material (e.g. groundwater flowing through a porous soil medium).

b) Diffusion – a process, which involves mass flow induced by a gradient of concentrations generated in an isothermal single-phase system. Dissolved substances (e.g. in water) move spontaneously from areas with their higher concentration to areas with lower concentration, aiming at reaching equilibrium in the absence of liquid flow. A molecular cause for the phenomenon of diffusion are thermal motions of particles.

c) Surface wash-off – this phenomenon occurs at the initial stage of monolithic material leaching (only if not bound substances are available on the surface), when the material is exposed to a “fresh” portion of liquid, similarly to the advection process. It often causes high concentrations of washed-off substances in the initial eluate fractions. After surface wash-off depletes, further leaching from monolithic forms is by way of diffusion (Van der Sloot and Dijkstra, 2004).

The chemical processes controlling leaching include:

a) Solubility control – it involves a disintegration of ionic lattices due to a solvent, e.g. water. An example can be the dissolution of metal oxides (e.g. Zinc oxide) or minerals (e.g. Malachite).

b) Adsorption processes – these are dynamic processes occurring at the phase interface, e.g. solid body-liquid. As a result of two phases in contact at the interface surface, a field of unsaturated intermolecular attractive forces appears, which leads to the formation of adsorbent concentrations differential between the equipartition surface and its average composition (Podsiadło, 2014). Certain cations (e.g. Cu^{2+}), the leaching of which is not controlled by mineral solubility, are often released in accordance with adsorption (Van der Sloot and Dijkstra, 2004).

c) Ion exchange (availability control, sometimes called – wash-out) – ion exchange process can occur in the case of readily soluble salts (e.g. NaCL), the release of which is not determined by the mineral solubility and adsorption processes. In such a case, as a result of contact with water, they are immediately dissolved in large volumes.

The study focused on determining the leachability of selected heavy metals (Zn, Cu, Cr, Cd, Pb) from TTMSS subject to testing with the percolation test (basic characterization test) and batch test (compliance test). The analysis of the relationship between the pH of eluates, cumulative L/S (liquid to solid) ratio and the concentration of individual metals was conducted. Furthermore, the ash metal leaching mechanism was investigated and the differences between results obtained with percolation and batch tests were discussed.

Materials and methods

The research subject was TTMSS fly ash coming from the Czajka municipal wastewater treatment plant, which is equipped with the largest MSS mono-incineration system in Poland, where the TTMSS process takes place in a Pyrofluid™ technology fluidized bed boiler (MPWiK 2017).

The studied ash was characterized by irregular grains of various size (Fig. 1) – characteristic feature of fluidized bed ashes; high water demand and fineness (within the meaning of (*EN 450-1:2012 Fly ash for concrete. Definition, specifications and conformity criteria*, 2012)) and a relatively low content of chemical compounds desirable from the perspective of using it as a binder component (Szarek and Wojtkowska, 2018).

Figs 1 and 2 show images of fly ash in the SEM technique. Larger irregular grains, often porous, constitute clusters of numerous mineral components. Fig. 1 contains only a few spherical agglomerates characteristic for fly ash. Fig. 2 shows a magnified view of an irregular ash grain in the form of silica. Fig. 3 presents an EDS analysis of area 1, which confirms the presence of silicon and aluminium oxides in the ash, determining the pozzolanic potential of the material.

The content of heavy metals (Zn, Cu, Cr, Cd, Pb) in TTMSS fly ash was determined using the flame atomic absorption spectroscopy (FAAS) method in mineralisate obtained as a result of sample mineralization in a mixture of HNO_3 and $HClO_4$ acids. Heavy metal content in fly ash is shown in Table 1. The ash was characterized by heavy metal content at a level similar to TTMSS fly ashes discussed in the source literature, e.g. (Benassi et al. 2019; Cyr et al. 2012; Donatello et al. 2010; Lynn et al. 2018; Mattenberger et al. 2008; Nowak et al. 2013).

Eluates for the determination of heavy metal content were obtained with the percolation test according to (*CEN/TS 14405:2004)* and the batch test (*EN 12457-2:2002)*, with the L/S ratio equal to 10 dm^3/kg d.m.

Table 1. Content of selected heavy metals in TTMSS fly ash

Heavy metal	TTMSS fly ash [mg/kg d.m.*]	Literature data** [mg/kg d.m.]
Zinc	3290±83	570÷10000
Copper	808±24	90÷5400
Chromium	179±9	16÷2100
Lead	83.0±6.5	1.2÷2100
Cadmium	14.0±0.7	0.1÷94

* material dry matter
** based on (Benassi et al. 2019; Cyr et al. 2012; Donatello et al. 2010; Lynn et al. 2018; Mattenberger et al. 2008; Nowak et al. 2013)

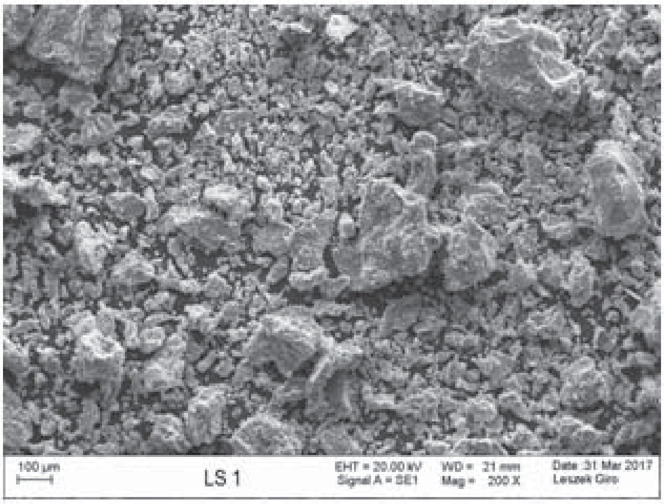

Fig. 1. Irregular ash grains from TTMSS, 200× magnification, BSD technique

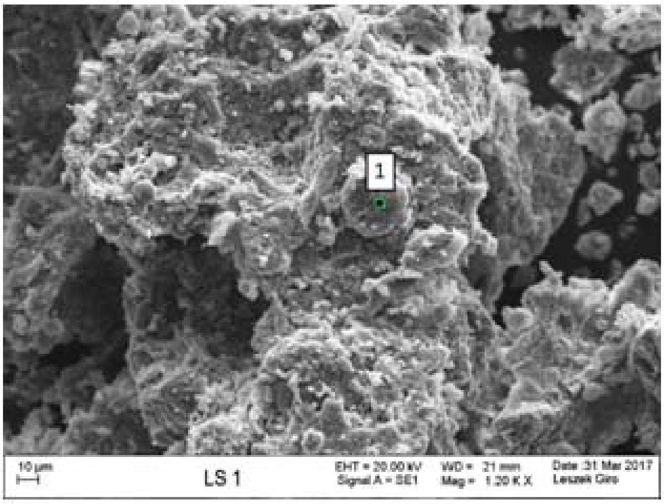

Fig. 2. Ash grains from TTMSS, 1200× magnification, SE technique

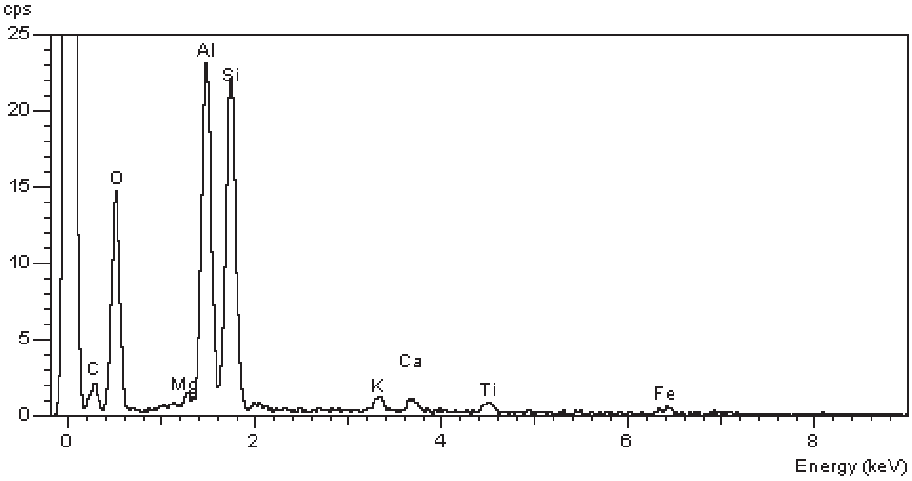

Fig. 3. EDS analysis of area 1

Table 2. Method's determination limits

Heavy metal	Determination limit [mg/dm^3]
Zinc	0.01
Copper	0.02
Chromium	0.03
Lead	0.03
Cadmium	0.01

Each test was used to test 3 samples from the same batch of TTMSS fly ash. Demineralized water was used as the leaching fluid in each test. Directly after collecting the obtained eluates, the process involved determining the pH and specific conductance, and after they were preserved with 65% nitric acid (V), the heavy metal content was determined with the flame atomic absorption spectroscopy (FAAS). Table 2 shows the determination limits of metals, whose leachability was studied.

Percolation test

The percolation test is used to evaluate the leachability of inorganic components from particulate waste and is a practical tool for assessing the leachability in conditions similar to the ones in a natural environment (Naka et al. 2016). Material is subjected to percolation with an assumed L/S ratio. A preset leaching flow directed from bottom to top of a vertical percolation column is used. Eluate is collected so as to obtain several independent fractions. The released quantity of heavy metals is calculated from Formula 1.

$$U_i = \frac{(V_i \cdot c_i)}{m_0} \tag{1}$$

where:

U_i – released quantity of the component in eluate fraction i, converted to material dry matter [mg/kg d.m.];
V_i – eluate i fraction volume [dm^3];
c_i – concentration of the considered component in eluate i fraction [mg/dm^3];
m_0 – sample dry matter in column [kg];
i – eluate fraction index ($i = 1,2,\ldots,7$) [–].

The ash metal leaching mechanism was analyzed as per the method described, i.a., in the papers (Van der Sloot and Dijkstra, 2004), (Van der Sloot et al. 2011). Heavy metal leaching graphs (component release, cumulative component release and component concentration relative to cumulated L/S ratio) were developed for this purpose. In the case of samples where individual eluates were characterized by a concentration below the determination limit, the determination limit value was adopted as the concentration. Thus, the obtained graphs were compared with reference data from the literature. This was used as a base to determine the processes controlling the heavy metal leaching in the studied materials.

Batch test

Batch test is a short-term one-stage dynamic test. The material (particle size below 4 mm) is subjected to dynamic mixing in contact with a leaching liquid (for 24 h), with the L/S ratio = 10 dm^3/kg dry matter (kg d.m.), which results in the extraction of its certain components. The main assumption of this method is the thesis that a state of equilibrium or a state close to a state of equilibrium between the phases is achieved in the course of this test. The released quantity of heavy metals is calculated from Formula 2.

$$A = C \cdot \left[\left(\frac{L}{M_D} \right) + \left(\frac{MC}{100} \right) \right] \tag{6}$$

where:

A – released component quantity with L/S = 10 dm^3/kg d.m. [mg/kg d.m.];
C – component concentration in eluate [mg/dm^3];
L – leaching liquid volume [dm^3];
M_D – test sample dry mass [kg];
MC – humidity ratio [%].

Statistical analysis

Uncertainties regarding the released quantities of the component were determined using a total differential. The analysis of the relationship between the pH of eluates, test duration or cumulative L/S ratio and the concentration of individual metals (only fractions of eluates with concentrations above the determination limit were adopted for the calculations) was conducted on the grounds of the partial correlation factor, taking into account the Spearman's rank correlation ρ_c, (due to the abnormal form of the distribution of obtained result, number of cases and often visible non-linear relationships).

Immobilization level

The level of immobilization of heavy metals in TTMSS fly ash was determined using Formula 3.where:

$$I_i = 100 - \frac{m_{i,e}}{m_{i,m}} \cdot 100\% \tag{3}$$

where:

I_i – immobilization level [%];
$m_{i,e}$ – mass of *i* heavy metal in eluate [mg];
$m_{i,m}$ – mass of *i* heavy metal in the material subjected to leaching [mg].

Results and discussion

Table 3 contains the test results for eluates collected with the percolation test, while Table 4 contains the test results for eluates collected with the batch test. Table 5 shows the level of metal immobilization in ash samples.

The analysis of the obtained results was based on a hypothesis that the mechanism of heavy metal leaching from TTMSS fly ash was analogous to metal leaching from construction materials.

The analysis of the impact of eluate sampling time using the percolation test on their pH, specific conductance and the concentration of individual metals did not indicate a significant partial correlation between the variables. This can be explained by the behavior of the leaching liquid flow range required in standard (*CEN/TS 14405:2004*), which probably eliminates the impact of the time variable on the test results.

Eluate reaction and specific conductance analysis

Figures 4 and 5 show a change of pH and specific conductance, respectively, of eluates collected with the percolation test.

Initial fraction of eluate sampled from a liquid percolating through ash deposits was characterized by a significant pH variability (Fig. 4). The subsequent fraction reached similar values. No significant correlation between the eluate pH (percolation test) and the cumulative L/S ratio was observed. The pH value in eluates obtained with the batch test was characterized by a small spread (standard deviation for 3 samples was 0.1), and the eluate collection method did not significantly affect the pH of the collected sample, however, each of the percolation test fractions was characterized by a slightly lower pH than eluates from the batch test. The reaction of aqueous extracts from ash samples for both tests was similar to pH, in which the solubility of most cations (e.g. Zn, Cu, Cr(III), Pb, Cd, Al., Fe, Ni) is the lowest – pH in the range between 8 and 10 (Bourg and Loch, 1995).

The obtained results indicate a significant negative correlation between the specific conductance of eluates obtained with the percolation test and the cumulative L/S ratio (ρ = -0.991). The plot of this indicator (percolation test) shows an initially strong leaching and dissolution of salts contained in the ash, which rapidly weakened along with an increased cumulative L/S ratio (Fig. 5), in the final fraction reaching values close to aqueous extracts obtained with the batch test. Gradual stabilization of the properties of eluates sampled with the percolation test indicates the possibility of the material reaching local equilibrium conditions in an actual operating environment and hence, enables attempting to predict the quantity of leached heavy metals over a longer period. It is believed that for certain application scenarios, adopting a cumulative L/S = 10 dm^3/kg d.m. for the tests may stimulate leaching over a period of even one hundred years of material operation (Van der Sloot and Mulder, 2002). For example, during the field lysimeter tests of soil, the L/S ratio achieved after 400 days of the experiment amounted to 0.6 dm^3/kg d.m. (Delay et al. 2007).

Heavy metal release analysis

Figures 6 to 10 present the total released quantities of heavy metals for TTMSS samples studies with the batch test (BA)

Table 3. Test results for eluates obtained with the percolation test

Name	Eluate	Cumulative L/S	pH	Specific conductance	Released quantity of a component [mg/kg d.m.]				
					Zinc	Copper	Chromium	Lead	Cadmium
	[–]	$[dm^3/kg_{d.m.}]$	[–]	[mS/cm]					
PA1	1	0.12	8.0	6.200	<0.001*	<0.002	0.009±0.001	0.012±0.002	0.002±0.001
	2	0.22	7.8	5.720	<0.001	<0.002	0.008±0.002	0.016±0.004	<0.001
	3	0.51	8.2	4.380	<0.003	<0.006	0.019±0.003	0.039±0.005	<0.003
	4	1.01	8.1	3.510	<0.005	<0.010	0.034±0.003	0.058±0.007	<0.005
	5	2.02	8.3	2.700	<0.010	<0.020	0.041±0.003	0.141±0.017	<0.010
	6	4.94	8.4	2.230	0.067±0.009	<0.058	0.102±0.031	0.251±0.039	0.070±0.003
	7	10.00	8.6	1.651	0.354±0.040	<0.101	<0.152	0.446±0.077	0.086±0.037
	Cumulative released quantity of component ΣU				0.421÷0.441	0.000÷0.199	0.213÷0.365	0.963±0.089	0.158÷0.177
	Uncertainty of range ΣU				0.380÷0.482	–	0.181÷0.397	–	0.121÷0.214
PA2	1	0.10	8.5	8.230	0.007±0.001	0.005±0.001	0.009±0.002	0.016±0.003	0.001±0.001
	2	0.47	8.6	5.710	0.016±0.003	0.015±0.001	0.021±0.002	0.054±0.012	0.005±0.001
	3	0.66	8.4	3.920	0.013±0.001	0.008±0.001	0.009±0.005	0.020±0.007	<0.002
	4	1.07	8.0	3.190	0.015±0.002	0.016±0.002	<0.012	0.033±0.011	<0.004
	5	2.11	8.0	2.540	0.043±0.008	0.044±0.002	0.037±0.002	0.088±0.018	<0.010
	6	5.69	8.1	2.190	0.125±0.02	0.129±0.007	0.115±0.021	0.215±0.022	<0.036
	7	10.00	8.2	1.781	0.140±0.01	0.158±0.020	<0.133	0.252±0.057	<0.045
	Cumulative released quantity of component ΣU				0.359±0.024	0.375±0.021	0.191÷0.336	0.678±0.066	0.006÷0.103
	Uncertainty of range ΣU				–	–	0.169÷0.358	–	0.005÷0.104
PA3	1	0.06	7.4	5.770	0.013±0.001	0.004±0.001	0.003±0.001	0.013±0.006	<0.001
	2	0.40	8.0	4.950	0.037±0.002	0.019±0.002	0.021±0.003	0.046±0.009	<0.003
	3	0.58	8.0	4.040	0.009±0.001	0.010±0.001	0.008±0.003	0.025±0.007	0.002±0.001
	4	1.07	8.1	3.300	0.021±0.001	0.014±0.003	0.015±0.003	0.037±0.004	<0.005
	5	2.01	8.1	2.600	<0.009	0.020±0.004	0.037±0.004	0.080±0.016	<0.009
	6	5.35	8.3	2.190	<0.033	0.073±0.020	<0.100	0.233±0.078	<0.033
	7	10.00	8.2	1.809	<0.047	0.098±0.011	0.172±0.034	0.312±0.128	<0.047
	Cumulative released quantity of component ΣU				0.080÷0.169	0.238±0.023	0.256÷0.356	0.746±0.151	0.002÷0.100
	Uncertainty of range ΣU				0.077÷0.172	–	0.221÷0.391	–	0.001÷0.101

* Calculated from determination limit (Formula 1)

Table 4. Test results for eluates obtained with the batch test

Sample	pH	Specific conductance	Released quantity of component *A* [mg/kg d.m.]				
	[–]	[mS/cm]	Zinc	Copper	Chromium	Lead	Cadmium
BA4	8.7	1.443	2.97±0.12	<0.20*	<0.30	1.87±0.22	<0.10
BA5	8.9	1.569	2.39±0.19	<0.20	<0.30	2.40±0.31	0.12±0.07
BA6	8.7	1.600	2.54±0.12	<0.20	<0.30	2.47±0.26	<0.10

* Calculated from determination limit (Formula 2)

Table 5. Immobilization level of heavy metals in TTMSS fly ash

Test	Sample name	Zinc [%]	Copper [%]	Chromium [%]	Lead [%]	Cadmium [%]
Percolation test	PA1	>99.99	>99.98	>99.80	98.84	>98.74
	PA2	99.99	99.95	>99.81	99.18	>99.26
	PA3	>99.99	99.97	>99.80	99.10	>99.29
Batch test	BA4	99.91	>99.98	>99.83	97.75	>99.29
	BA5	99.93	>99.98	>99.83	97.11	99.14
	BA6	99.92	>99.98	>99.83	97.03	>99.29

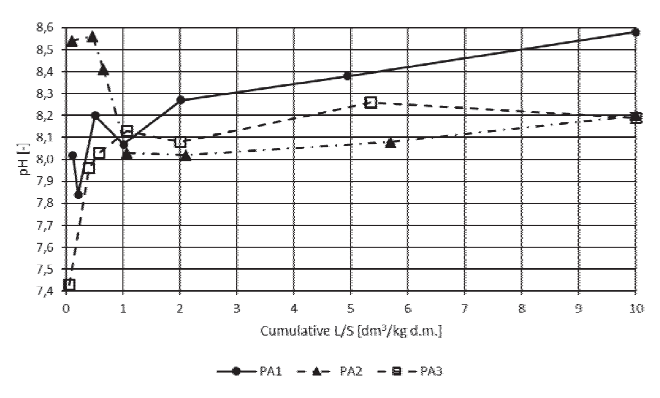

Fig. 4. Change of eluate pH depending on cumulative L/S ratio – percolation test

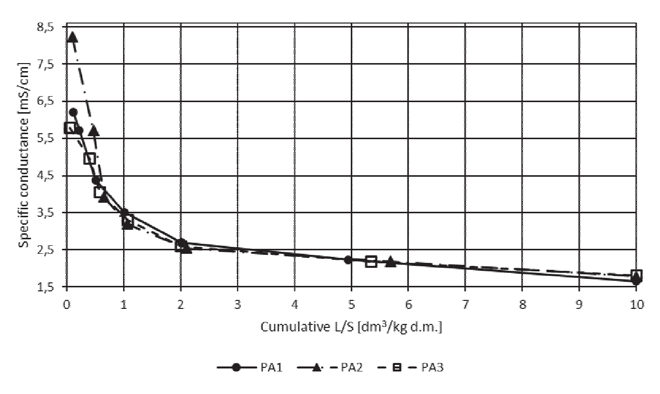

Fig. 5. Change of eluate specific conductance depending on cumulative L/S ratio – percolation test

and percolation test (PA), along with an uncertainty range (in the form of vertical "runners").

Zinc concentration in the eluates obtained using the percolation test indicated a significant, negative partial correlation with the cumulative L/S ratio (ρ_c = -0.661), however, no significant partial correlation was observed between the element concentration and eluate pH. Due to the low metal concentration in the eluates, leaching mechanism analysis was hindered. It can be conjectured that the mechanism was complex, however, given the waveform of the graphs showing the quantity of released Zinc depending on the L/S ratio it can be assumed that solubility was the leading release controlling mechanism (Figs 11 and 12). Zinc was more strongly released in the batch test (Fig. 6). The difference in leaching intensity between the methods absolutely surpassed the obtained uncertainty ranges, which proves the statistical significance of such a difference.

Comparing the obtained results with the source literature data it should be concluded that in the course of the conducted study (batch test), Zinc was leached more intensively than in the papers (Chen et al. 2013; Cyr et al. 2012), however, the element immobilization level (Table 5) should still be deemed as high (min. 99.91%). A high immobilization level can result from a significant share of the residual fraction (Tessier et al. 1979) in the total metal content in ash (Li et al. 2017).

Copper concentration in the eluates obtained using the percolation test indicated a significant, negative partial correlation with the cumulative L/S ratio (ρ_c = -0.797) and solubility, with a probable share of washing-out, was probably the release controlling mechanism (Figs 13 and 14). Two of the three eluates obtained using the percolation test contained more Copper than the eluates of the batch test (significant difference), in which none of the metal concentrations in the eluate reached the determination limit (Fig. 9). Copper compounds in ash are probably in a form which is characterized by low mobility (element immobilization at a level of min. 99.95% – Table 5) what is confirmed by the results of other researchers (Chen et al. 2013; Cyr et al. 2012; Donatello et al. 2010; Li et al. 2017), which is why they should not pose a threat to the environment.

A significant, negative relationship between the concentration in eluates collected with the percolation test and cumulative L/S ratio was observed in the case of chromium (ρ_c = -0.808). It can be assumed that chromium leaching from ash is a complex process. The probable mechanisms controlling this phenomenon were solubility and washing-out (Fig. 15–17). In all eluates collected with the batch test, the chromium concentration was below the determination limit (immobilization >99.83%), with similar, low concentrations of this element obtained by the researchers (Chen et al. 2013; Cyr et al. 2012). Overlapping of cumulative quantity ranges of released element proves the absence of a significant difference in the intensity of metal release between two used research methods (Fig. 8).

Lead concentration in eluates obtained with the percolation test decreased with increasing cumulative L/S ratio (significant relationship ρ_c = -0.856). It can be concluded that the mechanism controlling leaching of Pb from ash samples is solubility, whereas in the case of low L/S values washing-out is also possible

(Figs 18–20). As in the case of zinc, lead was significantly more intensively leached during the batch test. The difference in leaching intensity between the methods absolutely surpassed the obtained uncertainty ranges, which proves the statistical significance of such a difference (Fig. 9).

The released lead quantity was higher than the values in available literature sources (Cyr et al. 2012), however, the high element immobilization level (Table 5) may prove a high content of the residual fraction in the total metal content in ash (Li et al. 2017).

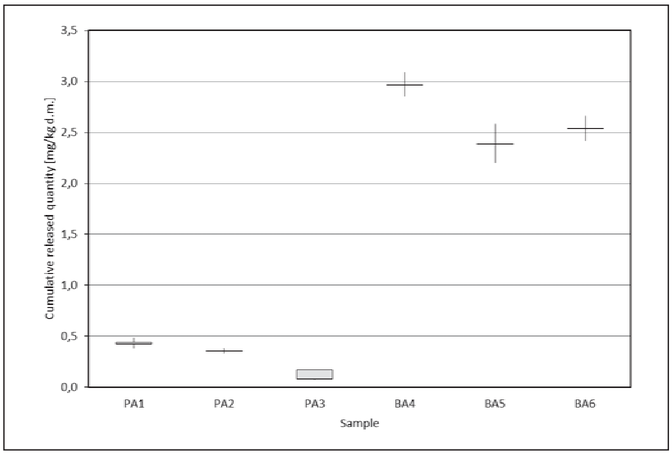

Fig. 6. Cumulative released quantity of zinc from TTMSS fly ash, samples examined by batch test (BA1-3) and percolation test (PA1-3), with marked uncertainty

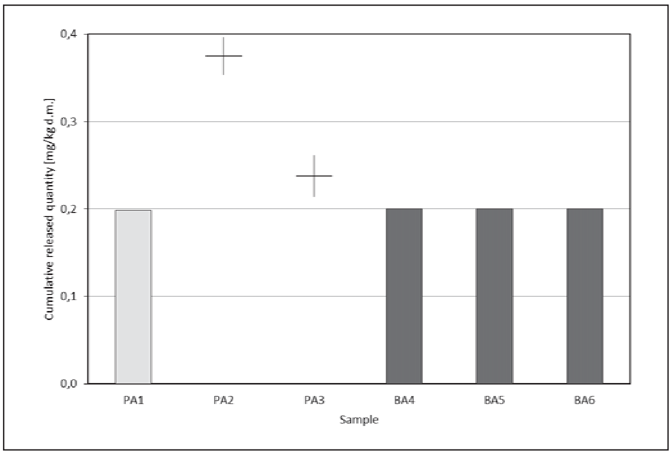

Fig. 7. Cumulative released quantity of copper from TTMSS fly ash, samples examined by batch test (BA1-3) and percolation test (PA1-3), with marked uncertainty

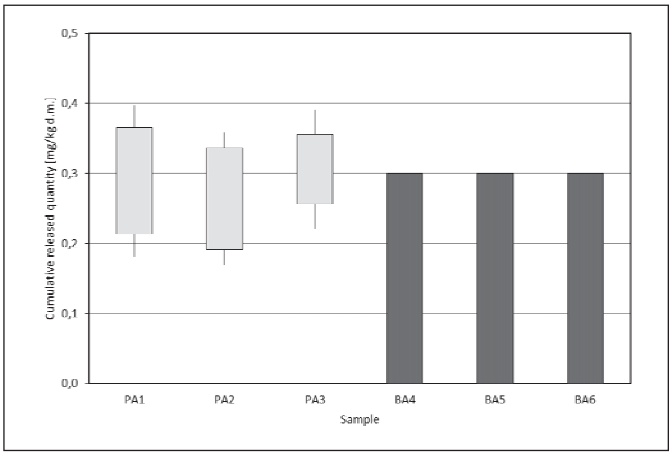

Fig. 8. Cumulative released quantity of chromium from TTMSS fly ash, samples examined by batch test (BA1-3) and percolation test (PA1-3), with marked uncertainty

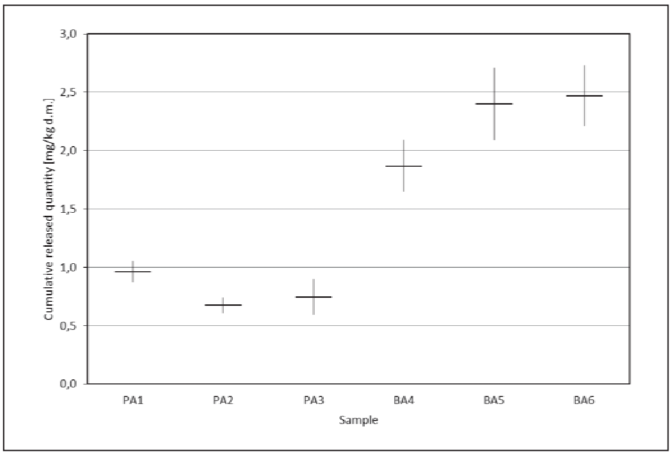

Fig. 9. Cumulative released quantity of lead from TTMSS fly ash, samples examined by batch test (BA1-3) and percolation test (PA1-3), with marked uncertainty

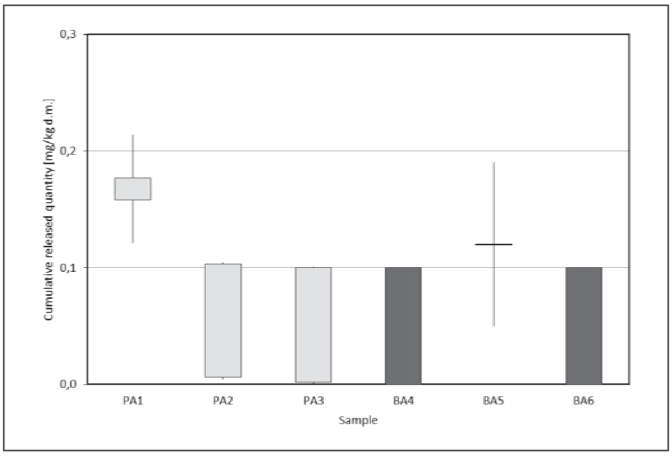

Fig. 10. Cumulative released quantity of cadmium from TTMSS fly ash, samples examined by batch test (BA1-3) and percolation test (PA1-3), with marked uncertainty

A relationship between cadmium concentration and the reaction (positive) or cumulative L/S ratio (negative) was observed in the case of eluates collected by percolating, however, due to the power of a non-parametric test, it is impossible to determine the partial correlation factors. Due to cadmium concentrations below the determination limit in eluates collected by percolating, it is also impossible to determine the element release controlling mechanism. In both tests cadmium was leached with a concentration oscillating around the determination limit, with similarly low element concentration obtained in the paper (Cyr et al. 2012). Overlapping of cumulative quantity ranges of released element quantities proves the absence of a significant difference in the intensity of metal release between the two used research methods (Fig. 10).

Based on the conducted research, it cannot be clearly stated, which test leads to releasing larger quantities of metals from TTMSS fly ash samples, which corresponds to the source literature data on the comparability of the batch test and percolation test, provided that the same L/S ratio and a similar eluate reaction are adopted (Van der Sloot and Mulder, 2002). This is why, if the experiment objective is to only determine the quantities of released heavy metal, the batch test is a more convenient method owing to it being less time-consuming.

Conclusions

The following conclusions can be drawn based on the conducted research:

1. A percolation test indicated a statistically significant correlation between the specific conductance of sampled eluates with the cumulative L/S ratio.
2. No correlation between heavy metal concentration and the pH value was identified in eluates collected by percolating. Most probably, this resulted from a similar reaction of the eluates and the impact of random uncertainty on the obtained results.
3. The concentration of heavy metals in eluates obtained with the percolation test was significantly correlated with the cumulative L/S ratio.
4. In the case of samples subjected to leaching with the percolation test, the dominating release controlling mechanism was probably solubility. The possibility of washing-out was also observed in the case of the initial eluate fractions (Cu, Cr, Pb).
5. Cr and Cd release in the case of both applied method of eluate sampling was at a similar level. Zn and Pb were released more intensively in the batch test, whereas Cu in

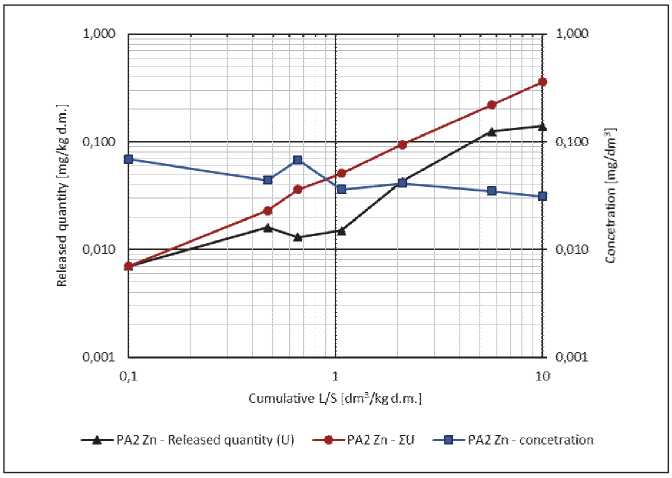

Fig. 11. Zinc leaching versus cumulative L/S ratio, PA2 sample – percolation test

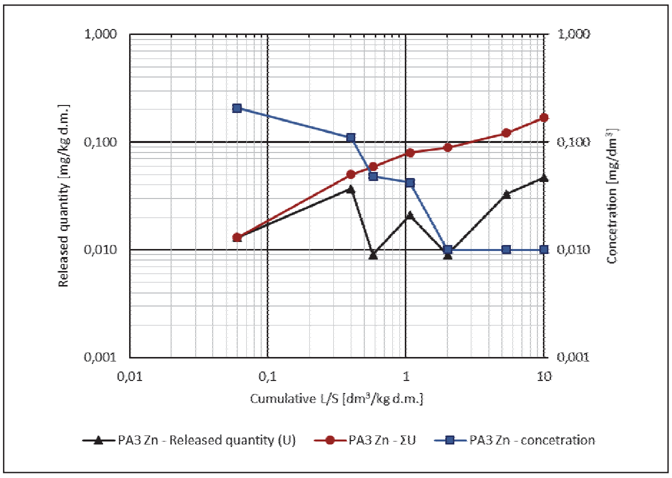

Fig. 12. Zinc leaching versus cumulative L/S ratio, PA3 sample – percolation test

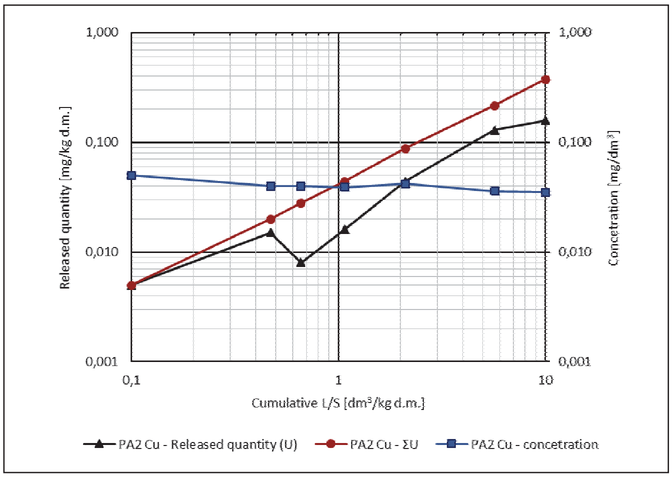

Fig. 13. Copper leaching versus cumulative L/S ratio, PA2 sample – percolation test

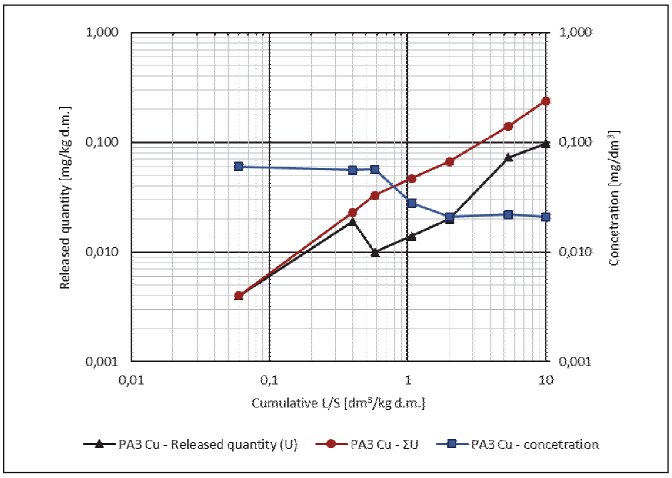

Fig. 14. Copper leaching versus cumulative L/S ratio, PA3 sample – percolation test

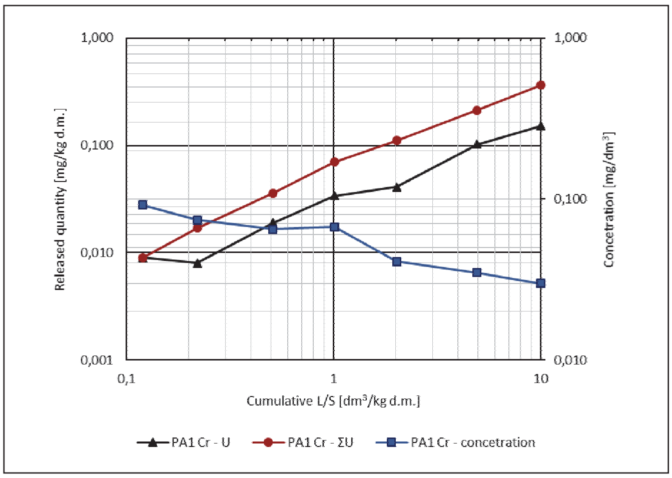

Fig. 15. Chromium leaching versus cumulative L/S ratio, PA1 sample – percolation test

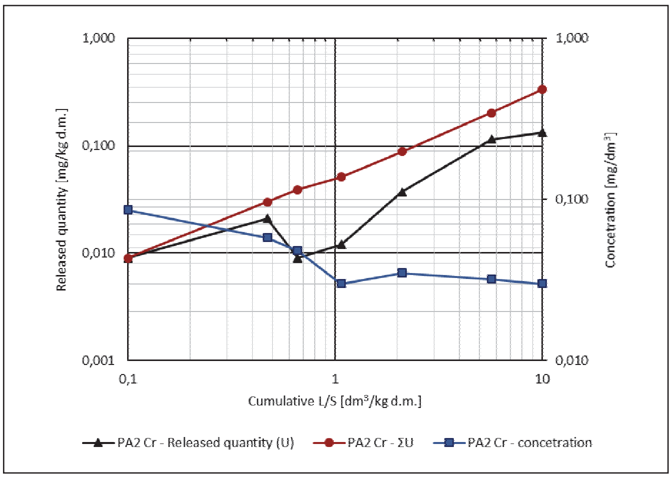

Fig. 16. Chromium leaching versus cumulative L/S ratio, PA2 sample – percolation test

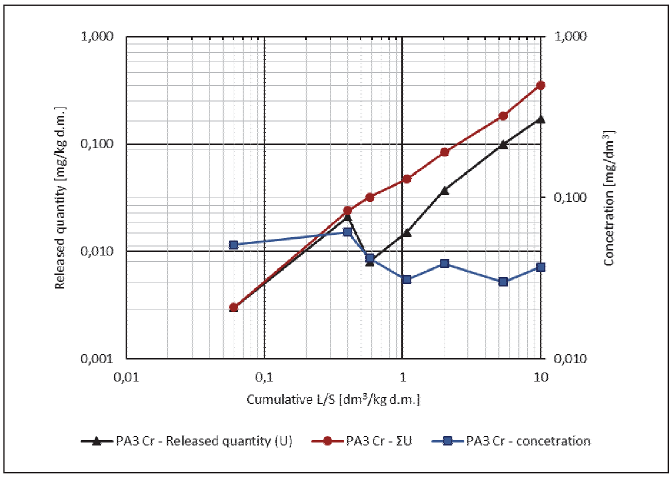

Fig. 17. Chromium leaching versus cumulative L/S ratio, PA3 sample – percolation test

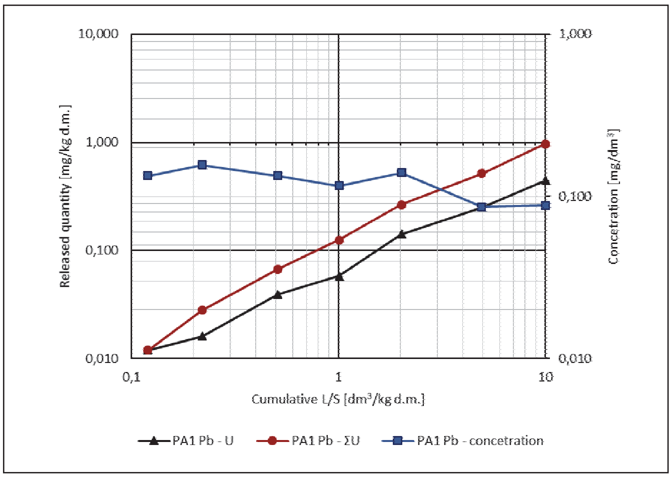

Fig. 18. Lead leaching versus cumulative L/S ratio, PA1 sample – percolation test

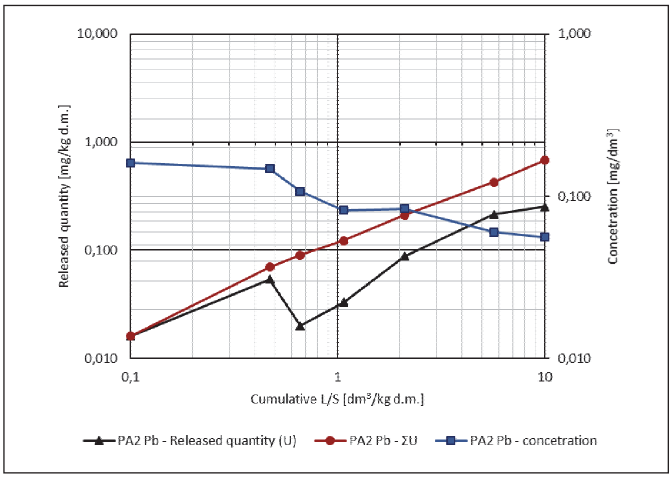

Fig. 19. Lead leaching versus cumulative L/S ratio, PA2 sample – percolation test

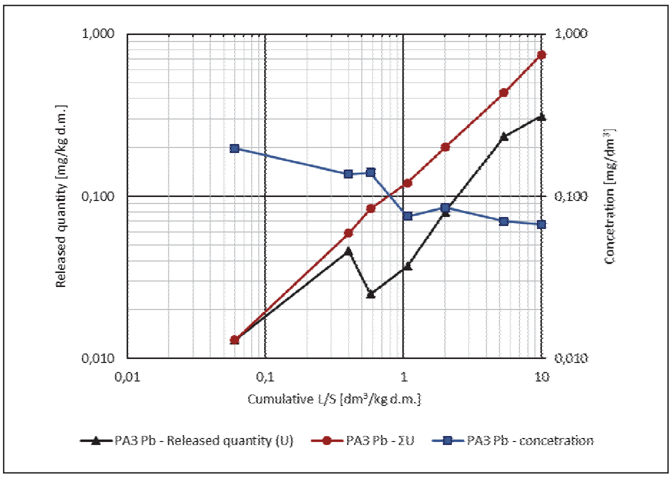

Fig. 20. Lead leaching versus cumulative L/S ratio, PA3 sample – percolation test

the percolation test (although not as significantly). Based on the conducted research, it cannot be clearly defined in which testing method heavy metals were released more intensively, which corresponds the source literature data on the comparability of the batch test and percolation test (provided the same L/S ratio and a similar eluate reaction) (Van der Sloot and Mulder, 2002).

6. Regardless of the applied eluate collection method, lead was the element most intensively leached from TTMSS fly ash, however, the high element immobilization level may

prove a high content of the residual fraction in the total metal content in ash (Li et al. 2017).

7. TTMSS fly ash immobilized heavy metals at a high level.
8. The observed intensity of heavy metal release from tested TTMSS fly ash was at a similar level to the results obtained by other researchers.
9. The batch test, owing to it being less time-consuming, is a method more convenient for studying leachability in cases in which the fundamental objective is to determine the quantity of released heavy metal.

Acknowledgements

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