

Piotr CELARY, Jolanta SOBIK-SZOŁTYSEK, Adrianna TAJCHMAN

Częstochowa University of Technology, Faculty of Infrastructure and Environment
Institute of Environmental Engineering
ul. Brzeźnicka 60a, 42-200 Częstochowa
e-mail: pcelary@is.pcz.czyst.pl, jszoltyssek@is.pcz.czyst.pl

Heavy Metal Volatilization during Vitrification of Tannery Sewage Sludge with Mineral Waste

Wolatylizacja metali ciężkich podczas witrifikacji garbarskich osadów ściekowych z odpadami mineralnymi

The study investigated the volatilization of heavy metals during vitrification of tannery sludge with mineral waste such as fly ash from brown coal combustion, foundry sands and carbonate flotation waste generated during ore enrichment process from the zinc-lead industry. The experiment focused on 6 metals Cr, Cd, Ni, Pb, Zn, Fe and how different waste additives affected their volatilization. In the study mixtures containing 35% w/w sewage sludge and 65% w/w mineral waste were vitrified. The 65% share consisted of either only fly ash, waste foundry sands or a mix of the previous with carbonate flotation waste at the following ratios 1:1, 1.5:1, 2:1 and 3:1. It was found that vitrification of tannery sewage sludge with certain mineral waste can be accompanied by reasonably low emission levels of chromium (as low as $22.4 \pm 1.4\%$) similar to those during incineration. The lowest chromium emission levels were noted for mixtures of sewage sludge with fly ash and a combination of fly ash and carbonate flotation waste at a ratio of 3:1. Very low nickel (as low as $9.5 \pm 6.5\%$) and iron (lowest being $1.2 \pm 0.6\%$) volatilization were also noted for the above mentioned mixtures although for one type of used sewage sludge the lowest amount of volatilized nickel was noted for the combination with foundry sands alone. However regardless of the used waste high degrees of volatilization were observed for cadmium ($\geq 73.4\%$), lead ($\geq 79.1\%$) and zinc ($\geq 87.8\%$).

Keywords: chromium, fly ash, heavy metal volatilization, sewage sludge, tannery industry, vitrification

Introduction

Sludge originating from the tannery industry contains significant amounts of chromium, high enough to classify it as hazardous waste [1]. This is due to the fact that almost 90% of tanneries in the world use chromium(III) salts as tanning agents [2], in the process of wastewater treatment compounds of this metal end up in the generated sludge. This results in the leather industry being responsible for about 40% of total chromium pollution in the world [3].

Landfilling remains the most common practice in management of this waste even though numerous studies investigating the fate of tannery sewage sludge in the soil showed it as being a potential threat to adjacent sites and aquifers by negatively affecting nitrogen and carbon mineralization, dehydrogenase activity, seed germination enhancing soil erosion as well as creating a risk of chromium contamination [3-7].

Vitrification is currently being investigated as a means of dealing with this waste in order to address the upcoming changes in the Polish law which will prohibit it from being landfilled after the year 2016 based on the Act on Waste of 27 April 2001, the Ordinance of the Minister of Economy and labor of 7 September 2005 on the criteria and procedures of storage of particular type of waste in landfills amended by the Ordinance of the Minister of Economy of 12 June 2007 and the Ordinance of the Minister of Environment of 13 July 2011 on municipal sewage sludge which implement the Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, the Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 on waste, Council Directive 99/31/EC of 26 April 1999 on the landfill of waste [8-13].

Vitrification has already been successfully used in treatment of various hazardous and industrial wastes containing large amounts of heavy metals because of low chemical reactivity and high resistance of the final product obtained in the process to environmental agents [14-21]. However while the safety and mechanical properties of the final vitrification products have been studied in great depth heavy metal volatilization accompanying the process seems to be often overlooked even though this aspect has become a great environmental concern with the increasing numbers of incineration plants [22-25].

The aim of this study was to present observations on the volatilization tendencies of heavy metals during vitrification of tannery sludge depending on the kinds and amounts of mineral waste added. The experiment focused on 6 metals Cr, Cd, Ni, Pb, Zn, Fe and on mineral waste typical for the industry of southern and central Poland.

1. Materials and methods

The study investigated the volatilization of heavy metals during vitrification of tannery sewage sludge with mineral waste. Each step was executed as illustrated in Figure 1.

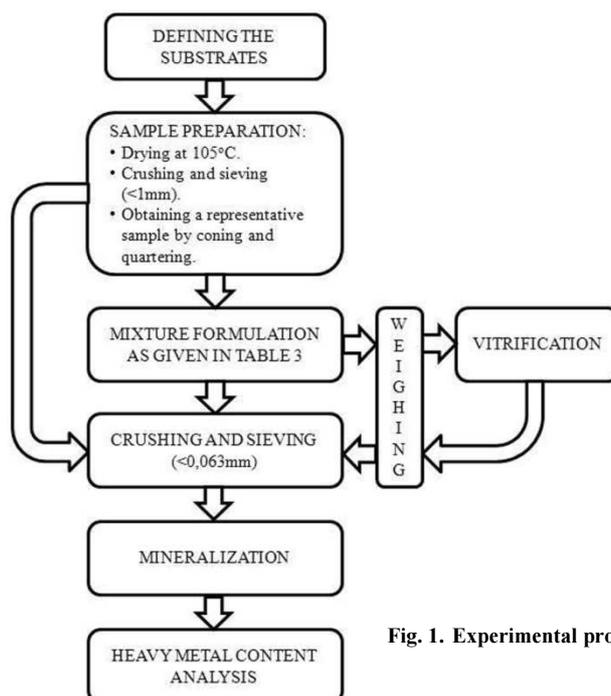


Fig. 1. Experimental procedures scheme

1.1. Substrates

The sewage sludge used in the study was collected from two tanneries located in Silesia, southern Poland:

- tannery A where two types of sewage sludge from different wastewater treatment processes were obtained: one of mineral (non-organic) character, from chemical precipitation (SS1P), and organic sewage sludge, obtained from wastewater flotation treatment (SS1F);
- tannery B where sewage from all production stages undergoes the same treatment resulting in one sewage sludge (SS2).

In order to achieve a vitreous product and incorporate heavy metals in a silica matrix in the vitrification process, sewage sludge needs to be vitrified with an addition of materials with high content of SiO_2 [26-28].

In the study, waste foundry sands (FS) obtained from the Małapanew ironworks located in southern Poland in the city of Ozimek (Opole Voivodeship) and fly ash (FA) from brown coal combustion at the Bełchatów power plant (Łódzkie Voivodeship, central Poland) served this purpose.

An addition of flux can be essential in order to decrease the melting point. For this reason, carbonate flotation waste generated during ore enrichment process from the zinc-lead industry (FW) obtained from inactive post-flotation material settlers in the Bytom region (Silesia) was used.

Heavy metal concentrations in the raw materials were analysed (Table 1), additionally a chemical characteristic of used sludge was also performed (Table 2).

Table 1. Content of chromium and other heavy metals in raw materials

Material	Heavy metal content, mg/kg db					
	Cr	Cd	Ni	Pb	Zn	Fe
SS1F	7317±129.3	0.2±0.1	10.9±0.1	4.6±0.1	115.5±2.5	63620.8±561.3
SS1P	168200±654.7	0.3±0.1	54.9±0.2	< 0.1	103.1±0.2	2432.3±84.2
SS2	28280±23.1	0.2±0.1	15.2±0.1	< 0.1	113.5±0.2	60525.9±296.0
FS	297.3±0.3	0.2±0.1	25.1±0.1	11.4±1.1	44.2±2.9	17919.8±54.8
FA	97.8±0.1	0.6±0.1	29.5±0.1	12.1±0.1	27.2±0.4	20817.5±205.4
FW	1.2±0.1	101.7±0.9	5.9±0.4	3201±36.4	2239±17.5	49919.8±104.4

db - dry basis

Table 2. Ultimate analysis of sewage sludge used in the study

Material	Ultimate analysis, %, w/w db				HHV MJ/kg
	C	H	N	S	
SS1F	30.0	5.5	6.7	6.5	14.3
SS1P	6.4	3.5	0.7	5.6	no ignition
SS2	25.4	5.9	2.7	1.3	11.6

db - dry basis

1.2. Mixture formulations

Before formulation, the substrates were dried to an air-dry state, crushed and sieved to obtain a fraction of < 1 mm. The amount of sewage sludge in the mixtures undergoing vitrification was constant at 35% w/w. The remaining 65% share consisted of either only fly ash, waste foundry sands or a mix of the previous with carbonate flotation waste at the following ratios 1:1, 1.5:1, 2:1 and 3:1.

The acronyms referring to the particular mixtures are listed in Table 3.

Table 3. Formulation of mixtures undergoing vitrification

Sewage Sludge (35% w/w)	Waste foundry sands to carbonate flotation waste ratio				
	1:0	3:1	2:1	1.5:1	1:1
Tannery A (flotation)	SS1F-FS	SS1F-FS3	SS1F-FS2	SS1F-FS1.5	SS1F-FS1
Tannery A (precipitation)	SS1P-FS	SS1P-FS3	SS1P-FS2	SS1P-FS1.5	SS1P-FS1
Tannery B	SS2-FS	SS2-FS3	SS2-FS2	SS2-FS1.5	SS2-FS1
Sewage Sludge (35% w/w)	Fly ash to carbonate flotation waste ratio				
	1:0	3:1	2:1	1.5:1	1:1
Tannery A (flotation)	SS1F-FA	SS1F-FA3	SS1F-FA2	SS1F-FA1.5	SS1F-FA1
Tannery A (precipitation)	SS1P-FA	SS1P-FA3	SS1P-FA2	SS1P-FA1.5	SS1P-FA1
Tannery B	SS2-FA	SS2-FA3	SS2-FA2	SS2-FA1.5	SS2-FA1

1.3. Vitrification

Before vitrification, the mixtures were dried to an analytical state at 105°C. 50÷100 grams of each mixture was prepared and placed in graphite pots with a volume of 350 cm³. The vitrification process was carried out in a plasma-arc furnace with argon as the plasma gas, at a constant gas flow of 20 dm³ per minute. The processed substrate mixtures were treated for 10 minutes. After cooling, the obtained vitrificates were analysed.

1.4. Ultimate analysis

Elemental analysis of C, H, N and S for sewage sludge was performed with the use of Leco TruSpec CHNS analyser. The higher heating value was analysed using IKA C2000 in accordance with the polish norm PN-81/G-04513.

1.5. Analysis of heavy metal content

The content of chromium, cadmium, zinc, lead and nickel in the raw materials, mixtures and obtained vitrificates was analysed by means of the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The analysis was carried out with the use of an internal reference standard (Yttrium). Before the analysis, crushed and sieved (< 0.063 mm) solids were converted to a water solution by means of mineralization in a microwave digester.

1.6. Volatilization of heavy metals

Based on the concentrations of heavy metals in the mixtures and vitrificates obtained from their processing the degree of volatilization (V) (% , w/w) was calculated:

$$V = \frac{M_M - M_V}{M_M} \cdot 100\% \quad (1)$$

where M_M is the mass of metals in the mixture and M_V is the mass of metals in the vitrificate obtained by vitrifying that mixture.

1.7. Statistical analysis

In order to determine the potential impact of the kind of sewage sludge or/and mineral waste on the volatilization degree of the analysed heavy metals statistical analysis of the obtained results was carried out using ANOVA main effects. The analysis was performed using STATISTICA software (STATISTICA 8.0 StatSoft, Inc.).

2. Results and discussion

2.1. Chromium

In the study chromium volatilization (Fig. 2) varied greatly (22.4÷95.3%) and depended mostly on the composition of the mineral waste additives as well as their ratio. Volatilization ranged from 22.4 to 83.4% and 23.8 to 95.3% for the sewage sludge from tannery A from the flotation and precipitation treatment processes respectively. The emission of chromium for sewage sludge from tannery B also varied significantly, from as low as 25.2 up to 81.6%.

The lowest volatilization levels of chromium were similar and independent of the used sludge, similar results were noted for the highest emissions except for the SS1P which peaked up to 95.3% when vitrified with foundry sands alone (SS1P-FS).

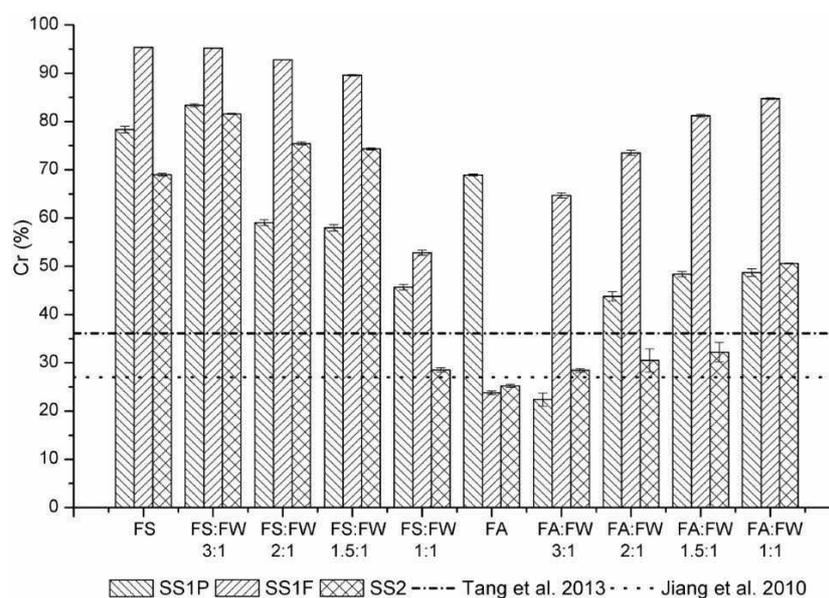


Fig. 2. Chromium volatilization

The addition of carbonate flotation waste to the waste foundry sands at a ratio of 1:1 resulted in the lowest emission levels of chromium independently of the used sewage sludge when waste foundry sands were the source of silica. As shown in Figure 3, the effects increased with the share of the carbonate flotation waste in the mixtures though the emission levels for ratios other than 1:1 weren't always lower than those from the processing of sewage sludge with foundry sands alone.

The exact opposite was found for mixtures with fly ash (Fig. 4). With the exception of post flotation sewage sludge from tannery A the lowest volatilization levels were noted when carbonate flotation waste was not present in the mixtures. Chromium emission levels increased directly with the increasing share of the carbonate

flotation waste though for SS1F the amount of released chromium was still lower than the one noted for fly ash alone.

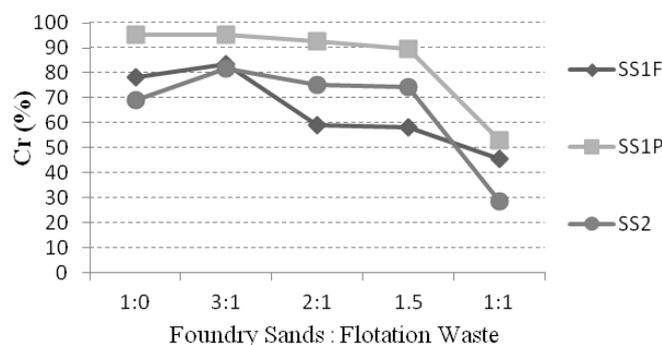


Fig. 3. Chromium volatilization trends for mixtures with foundry sands

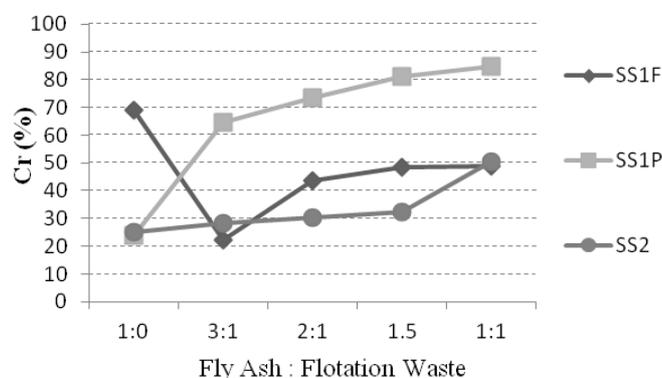


Fig. 4. Chromium volatilization trends for mixtures with fly ash

The lowest emissions overall for sludge SS1P and SS2 were observed for mixtures containing only fly ash which was not the case for SS1F. Vitrification of the post flotation sewage sludge (SS1F) with fly ash resulted in a chromium emission of $68.9 \pm 0.2\%$ being the third of the highest noted for this sludge. Best result ($22.4 \pm 1.4\%$) achieved for this sludge was for the combination of fly ash and carbonate flotation waste at a ratio of 3:1.

As shown in Figure 2 by using specific mineral waste additives it is possible to achieve similar or lower levels of chromium emissions than the ones reported during tannery sewage sludge incineration [1, 29].

2.2. Nickel

Similarly to chromium, nickel volatilization (Fig. 5) varied significantly ($9.5\div 86.6\%$) and differed depending on both the sewage sludge and mineral waste composition. Volatilization ranged from 13.2 to 86.6% and 13.4 to 49.8% for the sewage sludge from tannery A from the flotation and precipitation treatment

processes respectively. The emission of chromium for sewage sludge from tannery B varied from 9.5 up to 85.7%.

As in the case of chromium the lowest volatilization levels of nickel were similar and independent of the used sludge, similar results were also noted for the highest emissions except for SS1P which was noticeably lower ($49.8 \pm 2.6\%$ for SS1P-FS).

The addition of carbonate flotation waste affected the volatilization of nickel however with the exception of SS2 mixtures with fly ash no direct correlation has been observed.

The lowest emission levels of $9.5 \pm 6.5\%$ (SS2-FA), 13.2 ± 8.1 (SS1F-FA3) and $13.4 \pm 1.3\%$ (SS1P-FS) seem to be in line with Kuo et al. [28] who reported low volatilization of this metal when vitrifying MSW fly ash.

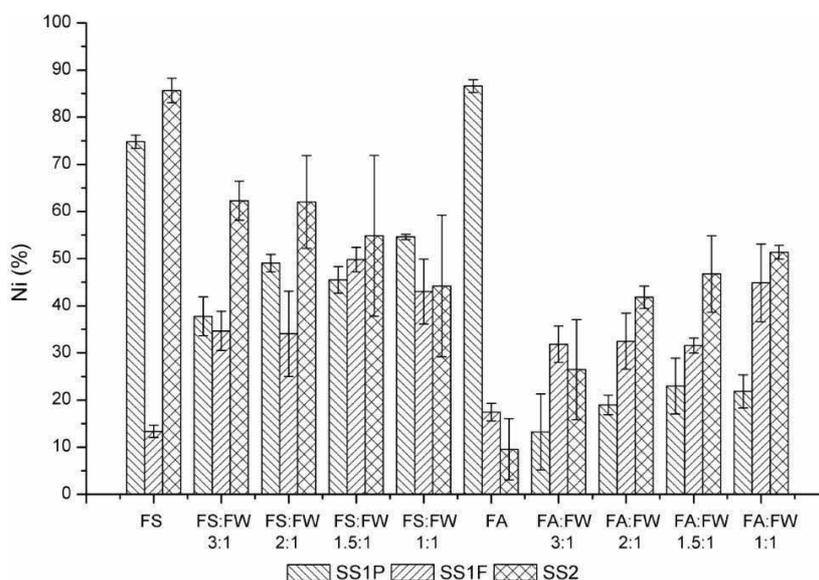


Fig. 5. Nickel volatilization

2.3. Iron

Iron behaviour was also very similar to that of the previously described chromium and nickel, starting from a big discrepancy in its volatilization depending on the combinations of used mineral wastes ($1.2 \div 87.7\%$). Moreover in most cases the same combinations of waste providing the lowest volatilization levels of Cr and Ni also resulted in the lowest emissions of iron thus for SS1P and SS2 the mixtures with fly ash alone proved to be most effective in reducing the amount of volatilized iron ($1.2 \pm 0.6\%$ and $3.9 \pm 0.2\%$ respectively) while for SS1F best effects were noted for a combination of fly ash and flotation waste at a ratio of 3:1 ($6.9 \pm 0.2\%$ emission). Even more so volatilization of this metal for formulations with fly ash increased with the addition of carbonate flotation waste just like in the case of Cr and Ni.

2.4. Cadmium, lead and zinc

The high degrees of volatilization observed for Cd ($\geq 73.4\%$), Pb ($\geq 79.1\%$) and Zn ($\geq 87.9\%$) shown in Tables 4-6 are in agreement with studies of other authors reporting high emissions of these metals even at lower temperatures [1, 28, 29]. Moreover attempts made by Tang et al. [29] to reduce the emission levels during incineration by using hydroxyapatite didn't provide the desired results for zinc.

These results should be taken into account when considering thermal treatment, especially vitrification, of waste with high content of the above mentioned heavy metals. However due to the fact that these metals were only abundant in the carbonate flotation waste even though their volatilization levels were high their initial content in the mixtures composed solely of sewage sludge with either waste foundry sands or fly ash were minimal to start with thus making the potential emissions negligible.

Table 4. Volatilization of heavy metals during vitrification of mixtures with sewage sludge from Tannery A obtained from the wastewater flotation treatment

Formulation	Volatilization, %			
	Zn	Pb	Cd	Fe
SS1F-FS	90.3 ± 1.1	79.1 ± 7.7	75.1 ± 20.0	83.8 ± 0.4
SS1F-FS3	98.6 ± 0.1	99.7 ± 0.4	97.6 ± 2.2	76.7 ± 0.1
SS1F-FS2	98.6 ± 0.1	99.7 ± 0.2	95.7 ± 0.2	64.9 ± 0.3
SS1F-FS1.5	99.2 ± 0.1	99.7 ± 0.3	96.7 ± 0.6	60.2 ± 0.9
SS1F-FS1	99.2 ± 0.0	99.7 ± 0.2	96.0 ± 0.3	41.1 ± 0.7
SS1F-FA	95.9 ± 0.3	100.0 ± 0.0	83.3 ± 13.4	87.7 ± 0.1
SS1F-FA3	97.6 ± 0.1	100.0 ± 0.0	93.5 ± 0.1	6.9 ± 0.2
SS1F-FA2	98.7 ± 0.0	100.0 ± 0.0	94.7 ± 0.2	15.5 ± 0.3
SS1F-FA1.5	99.1 ± 0.1	100.0 ± 0.0	93.5 ± 0.2	25.9 ± 0.6
SS1F-FA1	99.3 ± 0.0	100.0 ± 0.0	94.0 ± 0.2	37.3 ± 0.8

Table 5. Volatilization of heavy metals during vitrification of mixtures with sewage sludge from Tannery A obtained from the chemical precipitation treatment process

Formulation	Volatilization, %			
	Zn	Pb	Cd	Fe
SS1P-FS	88.1 ± 0.6	–	–	67.9 ± 0.2
SS1P-FS3	97.9 ± 0.1	100.0 ± 0.0	99.4 ± 0.3	81.3 ± 0.2
SS1P-FS2	99.0 ± 0.1	100.0 ± 0.0	98.9 ± 0.7	78.8 ± 0.1
SS1P-FS1.5	99.1 ± 0.1	100.0 ± 0.0	99.2 ± 0.2	64.5 ± 0.3
SS1P-FS1	99.1 ± 0.1	100.0 ± 0.0	98.6 ± 0.4	36.6 ± 1.0
SS1P-FA	93.8 ± 0.8	–	89.3 ± 9.4	1.2 ± 0.6
SS1P-FA3	97.4 ± 0.1	100.0 ± 0.0	99.6 ± 0.3	14.5 ± 0.7
SS1P-FA2	99.4 ± 0.0	100.0 ± 0.0	99.7 ± 0.3	32.1 ± 1.1
SS1P-FA1.5	99.3 ± 0.1	100.0 ± 0.0	99.7 ± 0.2	59.0 ± 0.6
SS1P-FA1	99.5 ± 0.1	100.0 ± 0.0	99.5 ± 0.1	70.7 ± 0.2

– indicating heavy metal content below detection limit in the mixture undergoing vitrification

Table 6. Volatilization of heavy metals during vitrification of mixtures with sewage sludge originating from Tannery B

Formulation	Volatilization, %			
	Zn	Pb	Cd	Fe
SS2-FS	87.8±1.1	100.0±0.0	73.4±30.7	31.7±0.6
SS2-FS3	98.2±0.2	99.8±0.1	94.4±2.4	44.5±0.3
SS2-FS2	97.9±0.4	99.6±0.5	97.3±0.7	44.3±0.4
SS2-FS1.5	98.3±0.1	99.8±0.0	98.0±0.3	37.1±1.0
SS2-FS1	98.4±0.1	99.8±0.0	95.5±0.6	31.9±0.8
SS2-FA	90.4±0.5	100.0±0.0	84.9±14.2	3.9±0.2
SS2-FA3	98.6±0.1	100.0±0.0	90.0±1.6	30.8±0.9
SS2-FA2	98.8±0.0	100.0±0.0	95.8±0.1	36.0±1.9
SS2-FA1.5	99.1±0.1	100.0±0.0	94.3±0.5	36.6±1.8
SS2-FA1	99.2±0.0	100.0±0.0	94.0±0.3	62.9±0.6

2.5. Statistical analysis

The carried out statistical analysis clearly showed that both the origin of the sewage sludge as well as the kind of mineral waste used have a statistically significant impact on the volatilization of the heavy metals analysed in this study, the latter having greater importance.

The kind of mineral waste used in the mixtures with sewage sludge had the greatest influence on the volatilization of chromium ($F = 59.47$, $p < 0.001$), and the least on the emissions of iron ($F = 30.55$, $p < 0.001$), nickel ($F = 28.08$, $p < 0.001$) and zinc ($F = 22.1$, $p < 0.001$).

A similar trend was found for the origin of the sewage sludge which as well had the greatest impact on the volatilization of chromium ($F = 26.17$, $p < 0.001$) and a noticeably smaller one on the other metals ($F = 6.01$ at $p < 0.001$, $F = 6.91$ at $p < 0.001$, $F = 7.45$ at $p < 0.001$ and $F = 5.8$ at $p < 0.001$, for Fe, Cd, Ni and Zn, respectively).

Conclusions

Considering the limitations of biological treatment of tannery sewage sludge as well as restrictions regarding the use of the final product given the observed in the study relatively low volatilization levels of chromium during vitrification, given right conditions, thermal treatment of tannery sewage sludge should be the preferred method of dealing with this waste.

By using specific amounts and kinds of mineral waste, like fly ash and its combination with flotation waste for which best results were achieved in this study (formulations SS1F-FA3, SS1P-FA and SS2-FA), it is possible to treat tannery sewage sludge via vitrification while keeping emission levels of chromium similar

to those during incineration and acceptable volatilization degrees of other metals such as nickel or iron.

Though high emission levels of Cd, Pb and Zn may also occur in lower temperatures during incineration especially in the presence of chlorine it should be noted that due to an almost complete volatilization of cadmium, lead and zinc the processed waste should ideally be free of these metals. This important aspect should be taken into account when considering vitrification as a treatment method for handling given waste.

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Streszczenie

Zbadano wolatyлизację metali ciężkich podczas witrifikacji garbarskich osadów ściekowych z odpadami mineralnymi, takimi jak popioły lotne ze spalania węgla brunatnego, piaski poformierskie oraz odpady poflotacyjne powstające podczas procesów wzbogacania rud w przemyśle cynkowo-olowiowym. Badania skupiły się na 6 metalach, tj.: chromie, kadmie, niklu, ołowiu, cynku i żelazie, oraz jak poszczególne dodatki w postaci odpadów mineralnych wpływały na ich wolatyлизację. Witrifikacji poddano mieszaniny składające się z 35% wagowych osadów ściekowych oraz 65% wagowych odpadów mineralnych. Udział w postaci 65% odpadów mineralnych składał się z popiołów lotnych, piasków poformierskich albo ich mieszaniny z odpadami poflotacyjnymi w stosunku 1:1; 1,5:1; 2:1 oraz 3:1. Badania wykazały, że witrifikacja garbarskich osadów ściekowych z określonymi dodatkami mineralnymi może być prowadzona przy stosunkowo niskiej emisji chromu (najniższa odno-

towana wynosząca $22,4 \pm 1,4\%$), zbliżonej do wartości podawanych dla procesu spalania. Najniższą emisję chromu odnotowano dla witrifikacji mieszanin osadów ściekowych z popiołami lotnymi oraz osadów ściekowych z kombinacją popiołów lotnych z odpadami poflotacyjnymi w stosunku 3:1. W przypadku dwóch osadów ściekowych niewielką emisję niklu (nie niższą niż $9,5 \pm 6,5\%$) oraz żelaza (najniższa odnotowana wynosząca $1,2 \pm 0,6\%$) również uzyskano dla wyżej wspomnianych mieszanin, wyjątek stanowił jeden z badanych osadów ściekowych, dla którego najniższą wolatylizację niklu osiągnięto, witryfikując go z samymi piaskami poformierskimi. Niezależnie od użytych odpadów mineralnych wysoki stopień wolatylizacji odnotowano dla kadmu ($\geq 73,4\%$), ołowiu ($\geq 79,1\%$) oraz cynku ($\geq 87,8\%$).

Słowa kluczowe: chrom, osady ściekowe, popioły lotne, przemysł garbarski, wolatylizacja metali ciężkich, witrifikacja