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EFFECT OF ADDITIVES ON HEAVY METAL IMMOBILIZATION DURING VITRIFICATION OF TANNERY SEWAGE SLUDGE

The aim of this study was to evaluate the effect of additives such as waste moulding sands (WMS) and dolomite flotation waste (F) on heavy metal immobilization during vitrification of tannery sewage sludge. Sewage sludge with addition of waste moulding sands of 25–45 vol. % and flotation waste of 5-25 vol. % was used in the vitrification process. The study demonstrated a direct correlation between the WMS fraction in the vitrified formulations and heavy metal immobilization in the obtained vitrificates. Vitrification of sewage sludge with these additives resulted in obtaining vitreous products with reduced heavy metal leaching properties; the lowest content of heavy metals in the leachates was found in the vitrificates with the highest content of waste moulding sands.

1. INTRODUCTION

Leather production in the leather industry generates significant amounts of industrial sewage and solid waste. A total of approximately 700 kg of waste is generated from 1 Mg of processed raw hides after completion of all the stages of manufacturing [1, 2]. Large amounts of water and chemical compounds are used during the leather tanning process, mainly chromium salts used as tanning agents, which remain present in sewage and sludge.

Therefore, tanneries are reported to be responsible for about 40% of global environmental pollution with chromium. High content of this metal in tannery sewage sludge causes that the biological treatment typical of this type of waste is significantly limited. Application of compost obtained from the sewage sludge generated by the leather industry is restricted because of the risk of heavy metals migration into the soil and their bioaccumulation in plants [3–5]. Szymański argues that [6] such sewage

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sludge may be used only as an addition to the composting mass. Therefore landfilling has become a common practice in managing this waste [7–9]. The law enforces a reduction in the levels of landfilled biodegradable waste which requires the development of alternative methods of waste treatment. One of these methods is vitrification, with its volumetric reduction of ca. 95% achieved by addition of inorganic components into the glass matrix [10, 11]. The final product obtained in this process is resistant to environmental agents, nontoxic and it exhibits low chemical reactivity, allowing its safe storage [12].

Thermal waste treatment methods (such as vitrification) have been successfully used in treatment of various hazardous materials such as asbestos, nuclear and medical waste [13–19].

2. EXPERIMENTAL

Raw materials. The sewage sludge used in the study was collected from the Szczakowa tannery located in Jaworzno. Two kinds of sewage sludge from different wastewater treatment processes were obtained: one of mineral (non-organic) character, from chemical precipitation (PSS), and organic sewage sludge, obtained after wastewater flotation treatment (FSS). The sludge samples differed in their organic mass and contents of heavy metals (mostly chromium, see Table 1). The difference resulted from the different methods of wastewater treatment used in the tannery.

Table 1

Content of chromium and other heavy metals in raw materials [mg/dm^3]

Material	Cr	Cd	Ni	Zn	Pb
PSS	1682±6.54	0.0034±0.0003	0.5499±0.002	1.031±0.002	<0.001
FSS	73.17±0.1	0.0019±0.0002	0.1091±0.001	1.155±0.025	0.0456±0.0001
F	0.0124±0.001	1.017±0.009	0.0598±0.0004	22.39±0.17	32.01±0.364
WMS	2.973±0.003	0.0015±0.0002	0.2514±0.0001	0.4419±0.0288	0.1139±0.0106

Vitrification of materials with low contents of SiO_2 requires using particular additives. Therefore, the authors used an addition of waste moulding sands with 0–10 mm fraction obtained from the Mała Panew ironworks located in Ozimek, Poland.

An addition of flux is essential in decreasing the melting point. In the present study, dolomite flotation waste (F) from the zinc-lead industry obtained from inactive post-flotation material settlers in the Bytom region was used as flux.

Composition of the vitrified mixtures. Before formulation, the substrates used for the compositions were dried to an air-dry state and sieved to obtain a fraction of <1 mm. Formulations with varied contents of substrates were prepared (Table 2).

Table 2

Formulations of the vitrified compositions [vol. %]

Formulation	Flotation sewage sludge	Precipitation sewage sludge	Waste moulding sands	Flux
PSS70 + WMS25 + F5	–	70	25	5
PSS50 + WMS45 + F5	–	50	45	5
PSS50 + WMS40 + F10	–	50	40	10
FSS50 + WMS30 + F20	50	–	30	20
FSS35 + WMS45 + F20	35	–	45	20
FSS35 + WMS40 + F25	35	–	40	25

Before vitrification, the formulations were dried to the analytical state at 105 °C.

Vitrification. 150 cm^3 of each formulation was prepared and placed in graphite pots with volume of 350 cm^3. The vitrification process was carried out in a plasma-arc furnace with argon as the plasma gas, at the constant gas flow of 20 dm^3/min. The processed substrate mixtures were treated for 10 min. After cooling, the obtained vitrificates were analysed.

Leaching tests. Sewage sludge used in the study and the obtained vitrificates underwent leaching tests performed according to PN-EN 12457-2 [20]. Due to the characteristics of the analysed material, as required by the Polish Norm, the tests were performed as one-stage batch tests at a liquid-to-solid ratio of 10 dm^3/kg.

Analysis of the content of chromium and other heavy metals. The content of chromium and other heavy metals (lead, cadmium, zinc, nickel) in the leachates from leaching tests, sewage sludge and formulations for vitrification were analysed by means of the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

With respect for Polish regulations [21], the results obtained from the leachates were converted from [mg/dm^3] to [mg/kg d.b.] (d.b. is dry basis). Before the analysis, solids were converted to water solutions by means of mineralization in a microwave digester with 7 cm^3 of HNO_3 (65%). The leachates before analysis were acidified (pH 2) with HNO_3 (65%).

3. RESULTS AND DISCUSSION

Heavy metal content in the formulations undergoing vitrification (Table 3) was correlated with the share size of particular substrates. The data show that the content of each metal in the vitrified formulation depended on the content of raw substrate (Table 1). The dolomite flotation waste was the main source of zinc, lead and cadmium. With the increased addition of this component, an increased content of the metals was found in the formulations.

Table 3

Content of chromium and other heavy metals in the compositions undergoing vitrification [mg/dm^3]

Formulation	Cr	Cd	Ni	Zn	Pb
PSS70 + WMS25 + F5	419.1±0.79	0.11±0.001	0.297±0.004	17.33±0.12	3.61±0.214
PSS50 + WMS45 + F5	282.9±0.08	0.099±0.001	0.268±0.001	15.4±0.04	3.37±0.107
PSS50 + WMS40 + F10	212.5±0.12	0.17±0.001	0.266±0.001	25.22±0.05	6.427±0.047
FSS50 + WMS30 + F20	23.96±0.02	0.38±0.001	0.135±0.005	49.64±0.08	12.61±0.132
FSS35 + WMS45 + F20	15.5±0.05	0.38±0.001	0.184±0.02	54.03±0.09	13.33±0.384
FSS35 + WMS40 + F25	13.15±0.01	0.40±0.002	0.142±0.001	58.84±0.28	15.05±0.005

The specific origins of the sewage sludge used in the study (leather industry) causes they were the main source of chromium in the formulations. The highest content of nickel was observed for PSS, followed by WMS. The quality of the obtained vitrificates differed significantly and depended on the composition of the vitrified formulation. The vitrificates obtained from the formulations with PSS had the hardness rating of 6 on the Mohs scale and differed in vitreosity. An increase in the content dolomite flotation waste caused that the vitrificates were more vitreous (Fig. 1).

Fig. 1. Products of plasma treatment: PSS50 + WMS45 + F5 (left), b) PSS50 + WMS40 + F10 (right)

Similar findings were observed for vitreosity of the vitrificates obtained from formulations with FSS. However, in these formulations, an addition of flux also affected the hardness of the products, which ranged from 4 to 6 on the Mohs scale. The glassiest vitrificates were obtained from formulations with similar content of WMS and F (Fig. 2). This confirms that the addition of flux reduces the melting point of silica present in the waste moulding sands.

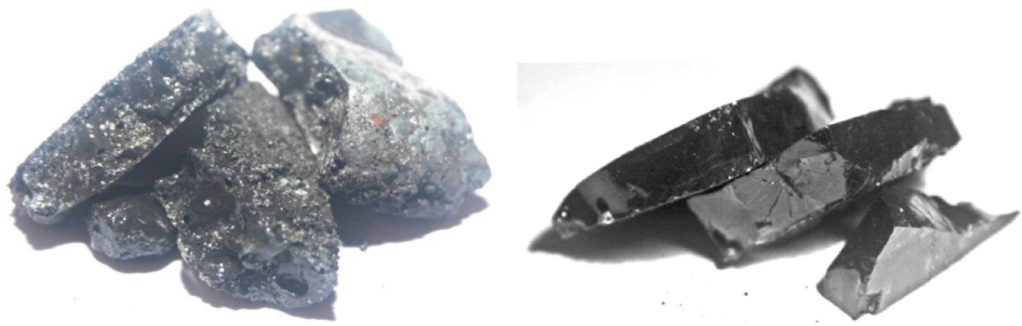

Fig. 2. Products of plasma treatment: FSS35 + WMS45 + F20 (left), SS50 + WMS30 + F20 (right)

Assessment of the possibility of storage of tannery sewage sludge in the landfills of inert waste and landfills of other than hazardous and inert waste was made based on the content of heavy metals in leachates (Table 4) and the limits defined in the Ordinance of the Minister of Economy and Labour as of 7 September 2005 [21] on the criteria and procedures for storage of waste in landfills (Fig. 3).

Table 4

Content of chromium and other heavy metals in leachates from sewage sludge [mg/kg db]

Leachate	Cr	Cd	Ni	Zn	Pb
PSS	7.664±0.065	0.0065±0.001	0.0783±0.0024	0.3635±0.002	<0.01
FSS	0.3555±0.002	0.0074±0.001	0.4377±0.0013	0.5053±0.006	0.0211±0.005

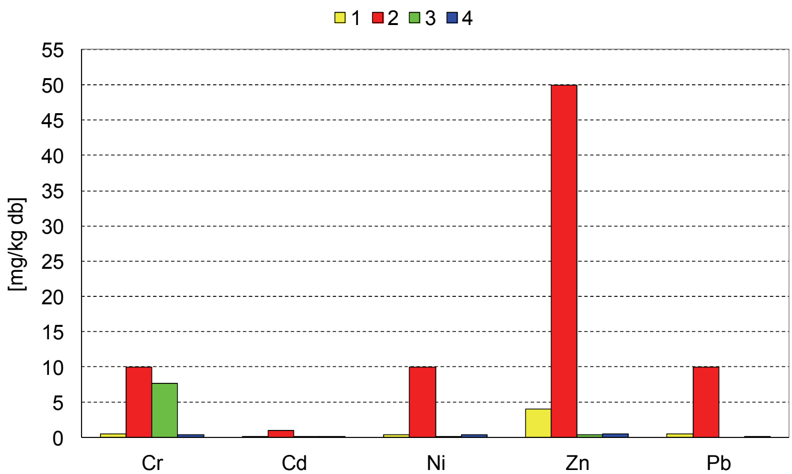

Fig. 3. Content of heavy metals in the leachate from sewage sludge and the limiting values present in the ordinance regarding waste storage in Poland [21]: 1 – limit value for storage in inert waste landfills, 2 – limit value for storage in other than hazardous and inert waste landfills, 3 – PSS, 4 – FSS

The sludge used in the study did not meet the requirements for storage in inert waste landfills. The content of chromium in the leachate from sewage sludge obtained from chemical precipitation exceeds the limits defined for storage in inert waste landfills by over 15 times. On the other hand, the sludge from flotation wastewater treatment meets the requirements for storage in inert waste landfills for chromium, although the content of the leached metal is close to the limits. However, the sludge cannot be stored in inert waste landfills as it exceeded the content of nickel in the leachate.

The sludge meets the criteria for storage in other than hazardous and inert waste landfills. Leaching tests performed for the obtained vitrificates (Table 5) confirmed reduced heavy metal leaching for all the metals, with the exception of zinc, observed in the formulations with the highest content of sewage sludge.

Table 5

Content of chromium and other heavy metals in leachates from the vitrificates obtained in the study [mg/kg d.b.]

<table>
<tr><th>Leachate</th><th>Cr</th><th>Cd</th><th>Ni</th><th>Zn</th><th>Pb</th></tr>
<tr><td>PSS70 + WMS25 + F5</td><td>1.968±0.007</td><td rowspan="6"><0.005</td><td rowspan="6"><0.05</td><td>0.4723±0.008</td><td rowspan="6"><0.01</td></tr>
<tr><td>PSS50 + WMS45 + F5</td><td>0.27±0.002</td><td>0.0798±0.006</td></tr>
<tr><td>PSS50 + WMS40 + F10</td><td>0.48±0.003</td><td>0.0983±0.002</td></tr>
<tr><td>FSS50 + WMS30 + F20</td><td>0.156±0.008</td><td>1.803±0.012</td></tr>
<tr><td>FSS35 + WMS45 + F20</td><td rowspan="2"><0.05</td><td>0.0534±0.002</td></tr>
<tr><td>FSS35 + WMS40 + F25</td><td>0.0889±0.001</td></tr>
</table>

The contents of cadmium, nickel and lead were below the detection threshold of the apparatus. The reduced content of chromium in the leachates from vitrificates was correlated with the content of PSS in the formulations undergoing vitrification. For the formulation with 70 vol. % content of PSS, a fourfold reduction was observed while this value for the 50 vol. % content was 28 times greater. The increased amount of WMS in the formulations resulted in reduced metal leaching.

Higher Zn leaching found for PSS70 + WMS25 + F5 and FSS50 + WMS30 + F20 is caused by the addition of zinc-rich flux combined with the smallest content of WMS in the vitrified formulations, which, providing a larger addition would be present, is likely to have absorbed the metal during vitrification, thus reducing its leaching capability. Among other formulations with higher content of WMS, the amount of the leached zinc decreased compared to the sewage sludge used in the study. Except for the PSS70 + WMS25 + F5 formulation, all of the obtained vitrificates meet the criteria defined by the Ordinance [21] for storage of waste in the inert waste landfills. The vitrificate obtained from processing of the PSS70 + WMS25 + F5 formulation did not meet the required criteria for chrome leaching.

4. CONCLUSIONS

• Tannery sewage sludge vitrification with the use of certain additives can provide an effective method of treatment used for this type of waste.

• An increase in the content of waste moulding sands in the composition is likely to cause higher immobilization of heavy metals through incorporation of these elements in the silica matrix.

• The results obtained in the present study show no indications of any effect of addition of dolomite flotation waste on immobilization of heavy metals.

• Due to high concentration of zinc, cadmium and lead compared to other substrates, the substrate used as the flux in the process was the main source of these metals in the formulations.

• A correlation between the ratio of flux to WMS influencing the vitreosity of the obtained products has been observed.

• The highest level of heavy metal immobilization was found for the formulations with the highest content of waste moulding sands, i.e. PSS50 + WMS45 + F5 and FSS35 + WMS45 + F20, which confirms the heavy-metal binding properties of WMS.

• Proper contents in the formulations for vitrification is essential in obtaining a material which can be stored in inert waste landfills, which seems to be an optimal solution in the aspect of the environmental safety and economical balance achieved by a reduction in the costs of building and operation of inert waste landfills.

• An important advantage of the formulations used for vitrification in this study is that all of the raw materials used were of waste character. This allows the correlated management of various types of waste within one process.

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