1. Introduction

Vitrification is an effective method of disposing hazardous waste containing heavy metal compounds. Waste for vitrification may be toxic and have very complex chemical composition, as well as unfavourable physical properties. It is usually difficult to dispose by-products from industrial processes, such as radioactive waste, fly ash, slag, medical waste, asbestos [2, 4, 7, 9]. Sanitation of polluted soils is a significant problem. Due to high contents of silicon, aluminium and other elements that soils contains, they are good materials for vitrification [3]. More and more frequently sewage sludge waste is subjected to vitrification [1, 6].

Vitrification process involves melting the material in high temperature heating furnace, and then quick cooling in cold water to convert the resulting liquid phase into a glassy structure. The energy expenditure depends on the type of material and furnace used. The resulting homogeneous glassy substance is characterized by high mechanical strength, low chemical reactivity and non-toxicity. Using waste vitrification of certain substances having characteristic traits of the products enables their recycling, mainly in construction industries [8, 13].

The process involves the formation of an impermeable and durable glass structure. Hazardous substances are disposed of in the following processes:
1) liquefaction of particles and incorporation into a crystalline structure of glass,
2) encapsulation of infusible compounds.
Liquefaction can permanently bind such elements as phosphorus, boron and silicon. During heating to the liquid phase and cooling, the elements become an integral part of the crystal lattice of the glass. They encapsulate the waste components involved, such as cobalt, lead, sodium, magnesium, lithium and caesium. These ingredients penetrate into the crystal lattice of glass acting as intrusive and infusible accessories. Encapsulation can occur both during the heating of shredded waste sludge with glass, as well as during cooling [11].

The organic compounds found in the waste are disposed during heating. This requires special heating crucibles in the heating system where the material is melted by an inductive current flow at high intensity. The dried deposit in these crucibles is to be provided and it is heated to the temperature of 1300–1450°C [12]. Partial liquefaction of waste occurs there, and then it continues to soak until the component migration process is completed. In this installation the crushed waste glass must be added as a flux and it will facilitate bringing the mixture to the form of a semi-fluid, or often, to the form of a paste. Liquid phase of the waste goes to the vats in which the cooling of the vitrified blocks takes place [5].

To modify the process of vitrification, granulation of waste materials is performed in a compact body of uniform shape and size. Granules are heated in rotary kilns or grate furnaces. After the phase of surface transitions the bodies are cooled in water, which makes them produce glossy and tight coat. Thus, the original shape of nuggets is retained, in contrast to melting of blocks in the vats.

Heating granules containing waste is usually carried out in a rotary kiln at the temperature range of 1100–1200°C, resulting in lower energy expenditure compared to the conventional process. This requires the preparation of mixtures for granulation and agglomeration process parameter selection [13].

The paper presents the processing of sludge waste with the use of briquetting method. The obtained bodies were directed to a ceramic kiln chamber and the vitrification of their surfaces followed. After cooling they were studied in terms of resistance to mechanical damage and chemical reactivity of the deposited environment. The most important effects of vitrification sludge process was waste volume reduction and the possibility of using it as a useful raw material in construction.
2. Material characterization and methodology

The research material was sludge from the municipal wastewater treatment plant "Hajdów" in Lublin. These deposits are fermented in separate digesters and mechanically dehydrated on belt and filter press. Then they were thermally dried in the fluidized bed in the pneumatic dryer, where the hydration level from of about 80% is reduced to a level of 10% of dry matter. The properties of the sediment are shown in Table 1.

**Table 1. Properties of sewage sludge from “Hajdów” plant**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water content</td>
<td>%</td>
<td>82–86</td>
</tr>
<tr>
<td>Flammable substances</td>
<td>% d.m.</td>
<td>64–72</td>
</tr>
<tr>
<td>Heavy metals:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>mg/kg d.m.</td>
<td>200–500</td>
</tr>
<tr>
<td>Cadmium</td>
<td>mg/kg d.m.</td>
<td>10–20</td>
</tr>
<tr>
<td>Zinc</td>
<td>mg/kg d.m.</td>
<td>3000–4000</td>
</tr>
<tr>
<td>Copper</td>
<td>mg/kg d.m.</td>
<td>200–500</td>
</tr>
<tr>
<td>Nickel</td>
<td>mg/kg d.m.</td>
<td>200–300</td>
</tr>
<tr>
<td>Chromium</td>
<td>mg/kg d.m.</td>
<td>300–500</td>
</tr>
<tr>
<td>Calorific value</td>
<td>kcal/kg</td>
<td>3600–4000</td>
</tr>
<tr>
<td>Melting point</td>
<td>ºC</td>
<td>1300–1320</td>
</tr>
<tr>
<td>Graining</td>
<td>mm</td>
<td>0,1–2,0</td>
</tr>
</tbody>
</table>

The homogenized mixture contains dried sewage sludge in the amount of about 42% by weight, crushed waste glass (about 50% by weight) and cement (about 8% by weight). Glass waste from used lamps and industrial glass were added in the form of dust by up to 0.2 mm fraction. Their use is preferred due to lower thermal reactivity to temperature.

The homogenization process involved mixing the ingredients in a mixer paddle and adding portions of water until the humidity content reached 5–8%. After homogenization the mixture was compacted by the stamp hydraulic press to be given cylindrical shape, and its volume was about 14 cm³. These compacts were sent to a laboratory chamber furnace with a capacity of 1400 W. Heating was performed at 1050ºC,
1100°C and 1150°C. Warm-up time was 30, 60 and 90 minutes. After
the warm-up the products were cooled in a bathtub filled with water,
and then they were tested. The studies identified:
- mechanical toughness,
- frost resistance and water absorption,
- leaching of hazardous substances.

Mechanical toughness of sinters acknowledged was based on the
measurement of compact breaking load, as well as resistance to gravity
drop. The value of the load force causing damage to the product was de-
termined experimentally by placing it horizontally between flat surfaces
of hydraulic testing machine and squeezing until the destruction of the
structure. The device’s resistance to gravity discharge was assessed by
the percent weight loss after three batches of samples dropped from the
height of 2.0 m onto a 20 mm thick steel plate.

Frost resistance was studied with the use of an indirect method
specified by the Polish standard PN-88/B-06250. The study involved
cyclic freezing and defrosting in air and in water. One cycle lasted
6 hours, and the sample was subjected to three such cycles. Then it was
tested for compressive strength of sintering. The degree of frost re-
stance was based on the ratio of strength to weight loss.

Absorbability study, i.e., the ability to absorb water through the
material at atmospheric pressure involved gradual immersion of the sam-
ples in water. Absorbability was defined as the ratio of mass of water
absorbed to the mass of dry sample material and was examined accord-
ing the Polish standard PN-EN 1097-6:2002.

Leaching studies were carried out by the Polish standard PN-EN
12457-4:2006. For the resolve of the fraction crushed 8-10 mm of the
sample taken, which were added to 500 mL of acidified (pH = 4) distilled
water. The leaching of ions from the dilution takes place in the process of
shaking for 5 hours. The suspension was then centrifuged and the clear
solution was separated to test substance contained in it. Ion concentra-
tion was determined using plasma emission spectrometry method by ICP-
AES and ICP-MS spectrometers.
3. Results and discussion

First, the influence of temperature and heating time on the state of the surface vitrification of briquettes were investigated. It was found that heating at 1050°C for 30 min does not ensure the creation of a consolidated glassy phase on the surface of the briquette. This surface was porous and cracked (Fig. 2.a). Increasing the temperature while maintaining the warm-up time did not solve the problem of creating a homogeneous glassy phase due to the rapid release of gases from the interior of the briquette, so the inside pores are visible (Fig. 2.b).

Extending the heating time to 90 min and using the temperature of 1150°C resulted in almost complete dissolution of a substantial change in the original shape of the briquette.

Homogeneous glassy surface layer of the sample was obtained at 1100°C and in the heating time of 60 min. The visual assessment of the briquette surface was uniformly vitrified with little pores filled with glass (Fig. 3a) as well as inside the solid (Fig. 3b).

These samples were sent for further studies to determine the basic physical and mechanical properties. The results of these tests are presented in Table 2.

Fig. 1. Photos of product heating at 1050°C, time 30 min: a – surface, b – sectional view

Rys. 1. Fotografie wyrobu nagrzewanego w temperaturze 1050°C, w czasie 30 min: a – powierzchnia, b – przekrój
Fig. 2. Photos of product heating at 1100°C, time 60 min: a – surface, b – sectional view
Rys. 2. Fotografie wyrobu nagrzanego w temperaturze 1100°C, w czasie 60 min: a – powierzchnia, b – przekrój

Table 2. Properties of vitrified products
Tabela 2. Właściwości zeszklonych produktów

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Unit</th>
<th>Measured values</th>
<th>The limit values for road construction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Compressive strength</td>
<td>MPa</td>
<td>3.9</td>
<td>&gt;2.5</td>
</tr>
<tr>
<td>2</td>
<td>Resistance to gravitational drop</td>
<td>%</td>
<td>94.1</td>
<td>&gt;90.0</td>
</tr>
<tr>
<td>3</td>
<td>Bulk density</td>
<td>kg/m³</td>
<td>440.0</td>
<td>400.0 – 550.0</td>
</tr>
<tr>
<td>4</td>
<td>Freeze resistance</td>
<td>%</td>
<td>1.2</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td>5</td>
<td>Absorbability</td>
<td>%</td>
<td>14.4</td>
<td>&lt;37.0</td>
</tr>
<tr>
<td>6</td>
<td>Leaching metals in aqueous extracts</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cadmium</td>
<td>mg/dm³</td>
<td>0.005</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td></td>
<td>Mercury</td>
<td>mg/dm³</td>
<td>0.050</td>
<td>&lt;0.2</td>
</tr>
<tr>
<td></td>
<td>Chromium</td>
<td>mg/dm³</td>
<td>0.021</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>Lead</td>
<td>mg/dm³</td>
<td>0.051</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td></td>
<td>Copper</td>
<td>mg/dm³</td>
<td>0.162</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td></td>
<td>Zinc</td>
<td>mg/dm³</td>
<td>0.320</td>
<td>&lt;2.0</td>
</tr>
<tr>
<td></td>
<td>Ferrum</td>
<td>mg/dm³</td>
<td>0.350</td>
<td>&lt;10.0</td>
</tr>
</tbody>
</table>
The stress resulting in axial compression test of vitrified product averaged out at 3.9 MPa. It was higher than the limit for the compression of aggregates intended for road foundations of 2.5 MPa. Resistance to gravitational drop was also more than 4% higher than the limit. Thus, the mechanical properties of the products meet the criteria of strength for construction aggregates.

1.2% frost resistance and the absorption of 14.4% were obtained. These values are on average 50% lower than the permissible level for road constructions. So, the products are resistant to changing weather conditions. They can be stored for a longer period in the open air.

During deposition very small concentrations of heavy metals are leached from the briquettes. The observed concentrations of mercury ions in aqueous extracts are four times lower than the limit, lead concentration is 10-fold lower, cadmium is 20-fold lower, while chromium is 25-fold lower. This means that vitrified products are safe for the environment.

Using vitrification of granulated sewage sludge, other researchers received LECA-type products applied in construction as aggregates [13]. It was also confirmed that heavy metal compounds are built permanently into the structure of crystalline silicate and are not washed out. The presented results confirmed that the use of vitrification significantly reduced heavy metals leaching from the waste.

Similar results were obtained in the study of lightweight aggregates by vitrification of mining residues, heavy metal sludge, and incinerator fly ash [5]. The only drawback is the necessity of incurring significant energy expenditure per unit of mass of the product. Heating temperature grows up to 1300°C with complete melting of the waste in a powder form, which is then rapidly cooled to produce a glassy phase. Vitrification of waste in the form of a solid is a process of less intense energy due to the use of about 200°C lower heating temperature compared to the processing of waste in a powder form.
4. Conclusions

On the basis of the test results of the vitrified briquettes with sewage sludge the following conclusions were formulated:
1. No risk was noticed of dangerous substances migrating from briquettes as well as heavy metals leaching under external climatic factors.
2. Products containing sewage sludge after vitrification process are environmentally safe.
3. The products are suitable for widespread use as a replacement for aggregate-based course construction of paved roads, embankments and banks.

References

Zastosowanie metody zeszklenia do utylizacji komunalnych osadów ściekowych

Streszczenie

W publikacji przedstawiono wyniki badań dotyczące utylizacji odpadów z wykorzystaniem metody zeszklenia. Badana mieszanka odpadów składała się z dosuszonych i rozdrobnionych komunalnych osadów ściekowych w udziale masowym ok. 42%, a pozostałą część stanowiły popioły lotne ze spalania węgla, rozdrobniona stłuczka szkła oraz cement jako spoivo. Mieszankę aglomerowano w stempelowej prasie hydraulicznej uzyskując brykiety o walcowym kształcie, które następnie nagrzewano w piecu komorowym oraz schodził o wodzie. Uzyskane zeszkłone wyroby poddano testom badawczym wytrzymałości mechanicznej, mrozoodporności, nasiąkliwości oraz wmywalności związków metali ciężkich. Ich wytrzymałość była wystarczająca pod względem spełnienia wymagań stawianych materiałem przeznaczonym na podbudowy utwardzonych nawierzchni drogowych. Wyniki pomiarów mrozoodporności i nasiąkliwości potwierdziły dobrą odporność na zmienne warunki atmosferyczne. Nie stwierdzono zagrożenia migracji substancji niebezpiecznych zawartych w odpadach oraz wyląduwania metali ciężkich do środowiska. Zastosowanie zeszklenia brykietów zawierających osady ściekowe umożliwiło zatem uzyskanie produktów bezpiecznych dla środowiska, które mogą być stosowane jako materiał budowlany.