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ASSESSMENT OF LEACHABILITY OF HARMFUL COMPONENTS FROM ALTERNATIVE FUELS PREPARED WITH THE USE OF SEWAGE SLUDGE

OCENA WYMYWALNOŚCI SZKODLIWYCH SKŁADNIKÓW Z PALIW ALTERNATYWNYCH WYTWORZONYCH Z OSADÓW ŚCIEKOWYCH

Abstract: Fuels, inclusive of those produced with the use of wastes, must usually be stored before their combustion or co-combustion in industrial processes. When stored outside, the fuels are exposed to adverse atmospheric impacts. The fuel quality may get worse then and fuel components which may be environmentally harmful may be leached out as well. The paper presents the assessment of potential environmental threads which result from the storage of fuels which have been produced with the use of municipal sewage sludge and other components, *ie* fuel made of the sewage sludge and coal slurry (PBS fuel), fuel made of the sewage sludge and meat-and-bone meal (PBM fuel), and that obtained with the use of the sewage sludge and sawdust (PBT fuel). Leachability of environmentally harmful components was studied, with special attention paid to heavy metals. Four methods were employed to evaluate the pollutant leachability levels; different environmental conditions were simulated in those methods. The studies and analyses demonstrated that the temporary surface dumping of PBS, PBM and PBT fuels was safe from the viewpoint of leaching of the harmful component to soil and/or water courses.

Keywords: fuel from waste, storing of fuels, leaching of pollutants, heavy metals

Thermal processes make one of waste utilisation methods which are increasingly employed nowadays. The wastes may be subjected to combustion in typical waste incineration plants, or they may be used for co-combustion with conventional fuels in industrial processes like in the production of cement clinker, in power plants and in heat and power plants, etc. The available range of wastes is extensive, and some of those materials offer the properties which make them directly applicable as alternative fuels, with no need to modify their properties and/or their form. Physical treatment is required, on the other hand, for other wastes, *eg* size reduction or mixing with other components and possibly forming to facilitate the fuel handling procedures (granulate, pellets, briquettes), and first of all to provide stable physical-chemical properties of the fuels.

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The production of fuels with the use of the municipal sewage sludge makes an example of that outlet for waste materials. The author developed the process for the manufacture of granulated fuels in which the sludge and other components can be utilised, *ie* fuel made of the sewage sludge and coal slurry (PBS fuel), fuel made of the sewage sludge and meat and bone meal (PBM fuel), and fuel made of the sewage sludge and sawdust (PBT fuel) [1, 2]. Those fuels offer the properties which make them applicable as substitutes of hard coal in the cement clinker production process.

Calorific values of wastes are essential for utilisation of those materials as energy carriers. Which is equally important, however, is their contents of trace elements. In case of alternative fuels applicable in the cement industry, particular attention is paid to the contents of such heavy metals as: Cu, Cr, Co, Cu, Zn, Sb and Ni, as these may adversely affect the clinker quality, and to the contents of Cd, Hg and Tl, since they may be released as hazardous pollutants. The heavy metal contents for selected alternative fuels and for hard coal were presented in Table 1.

Table 1

Contents of trace elements for selected alternative fuels and for hard coal [3]

| Metal | Type of alternative fuel | | | Hard coal |
|-------|--------------------------|------------------------------|-----------|-----------|
| | Municipal wastes | Impregnated municipal wastes | Tyres | |
| | Contents [mg/kg] | | | |
| Cr | 8÷612 | 13÷1.406 | 5÷640 | 1÷260 |
| Zn | 245÷2.875 | 80÷1.059 | 14÷20.500 | 4.5÷405 |
| Cd | 1÷19 | 2÷8 | 0,1÷20 | 0.01÷10 |
| Pb | 3÷152 | 13÷443 | 3÷760 | 5÷270 |
| Co | 3÷22 | 3÷11 | 5÷207 | 0.5÷43 |
| Ni | 1÷240 | 9÷291 | 17÷380 | 1÷110 |
| Mn | 23÷505 | 91÷331 | 6÷890 | 5÷356 |
| V | 1÷23 | 5÷147 | 1÷60 | 10÷250 |
| Cu | 22÷3.906 | 132÷534 | 10÷300 | 0.3÷60 |
| Sr | 12÷94 | 25÷214 | NA* | NA* |
| Ba | 24÷357 | 69÷358 | NA* | NA* |

* NA - no data available

As regards the sewage sludge derived fuels, majority of heavy metals which are present in those materials comes from the municipal sewage sludge. Heavy metals make the biggest and most numerous group of micropollutants in the sludge since they are transferred to and accumulated in the sludge in the sewage treatment process [4-6]. The heavy metal contents in the sewage sludge utilised for the production of fuels were presented in Table 2.

The reference papers report that, the highest concentrations of heavy metals are observed for zinc and relatively high concentrations for copper, chromium and lead (in accordance with the series: $Cd < Ni < Pb \approx Cr \approx Cu < Zn$) [5]. Paulsrud and Nedland [7] quote the Lester's data [8] and they claim that such metals like cadmium, mercury and nickel are supplied by the industrial wastewater while copper and zinc are "delivered" predominantly by households. As regards lead, this may come both from the domestic sewage and from water which is drained from the ground surface.

Table 2

Contents of heavy metals in the sewage sludge used for the production of fuels from wastes [9]

| Metal | Range [mg/kg] | Median [mg/kg] | Coefficient of variation [%] |
|-------|---------------|----------------|------------------------------|
| Zn | 1.931÷3.503 | 2.418 | 54.06 |
| Fe | 1.264÷5.794 | 2.418 | 54.06 |
| Mn | 624.9÷826.8 | 713.1 | 8.40 |
| Cu | 104÷193.5 | 162.4 | 19.81 |
| Pb | 36.34÷64.89 | 48.34 | 12.93 |
| Ni | 1.96÷33.39 | 26.30 | 45.13 |
| As | 2.77÷6.73 | 4.95 | 26.38 |
| Sn | 0.06÷1.13 | 0.37 | 58.97 |
| Cd | 1.03÷3.09 | 2.30 | 27.65 |
| Cr | 28.60÷53.56 | 34.22 | 28.56 |
| Co | 2.88÷9.30 | 4.74 | 26.83 |
| Tl | 0.15÷0.64 | 0.30 | 41.90 |
| Hg | 0.91÷2.57 | 1.16 | 34.98 |
| V | 5.6÷10.79 | 10.06 | 58.97 |

Heavy metals are fixed in the sewage sludge both by the inorganic and organic matter [8]. Metals can be found in the sewage sludge in the dissolved form, they may be coprecipitated with metal oxides, and adsorbed or associated on particles of biological leftovers. They may be present as oxides, hydroxides, sulphides, sulfates, phosphates, silicates and/or organic compounds - humic complexes and compounds with complex saccharides [10, 11]. Fuentes et al [12] says that the mobility, bioavailability and ecotoxicity of the metals depend on the specific chemical forms or bindings in which the metals exist in the sludge.

Mobility of pollutants and their leachability from wastes attract the interest to a great degree when the waste materials are to be stored, and when they are to be discharged to the environment or utilised in farming. The waste-derived fuels need to be stored for some time before they can be utilised in industrial processes through their combustion or co-combustion.

When the fuels are stored inadequately, their quality parameters may decline: *eg* absorption of ambient humidity may impair their mechanical properties. Moreover, the organic substances contained in fuels may show biological activity. And last but not least, the environmentally harmful components may be leached out. Hence, when the fuels obtained from wastes are stored just in the open, under atmospheric conditions, attention should be paid to the fact that they will be exposed to atmospheric precipitation which may release pollutants contained in those fuels. The rate of that release may be affected by various climatic factors, *ie* rainfall, variable temperature, freezing-thawing cycles, and time over which the fuels are exposed to specific atmospheric conditions.

In order to verify mobility of the components which are present in the PBS, PBM and PBT fuels, leachability of pollutants, inclusive of heavy metals, under various environmental conditions were studied.

Materials and methods

Materials

Three types of fuels were investigated which had been produced with the use of the municipal sewage sludge obtained from the mechanical-biological sewage treatment plant, and with the use of other components. Enriched coal slurry from the "Rydultowy" Coal Mine, meat-and-bone meal from the animal waste utilisation plant, and beech sawdust from the wood processing plant had been used as additional fuel components.

Fuels with the following compositions were studied:

PBS fuel - 60 wt. % of sewage sludge, 34 wt. % of coal slurry, and 6 wt. % of burnt lime,

PBM fuel - 75 wt. % of sewage sludge, 24 wt. % of meat-and-bone meal, and 1 wt. % of burnt lime,

PBT fuel - 80 wt. % of sewage sludge, 19 wt. % of sawdust, and 1 wt. % of burnt lime.

The fuel manufacturing process comprised the mixing step, forming operation, and drying in a special device which had been designed just for that purpose [13]. The tests involved granulated fuels with the grain size of 35 mm and humidity about 10%; the samples were subjected to seasoning over a few days before they were investigated.

Methods

Various environmental conditions were simulated to analyse the possible environmental hazards which would result from leaching pollutants of the PBS, PBM and PBT fuels during their temporary storage. Water extracts were prepared for that purpose with the use of various procedures, *ie*:

- a) fuel samples were placed in distilled water at pH 7 (**method I**) - method according to PN-EN 12457-4: 2006 [14],
- b) fuel samples were placed in distilled water which had been acidified to pH 4 (**method II**) - simulation of the impact of acid rains on leachability of fuel components,
- c) leachates obtained from the stored fuels, taken after 24 h and after 8 days (**method III**) - actual environmental conditions,
- d) extracts were prepared after freezing-thawing cycles (**method IV**) - simulation of winter conditions.

The methods applicable in preparing water extracts were presented below.

Method I - In accordance with the procedure provided in the Polish Standard PN-EN 12457-4: 2006 [14], the fuel samples were shaken with water during 24 hours at the liquid-to-solid (L/S) ratio equal to 10 (weight). Aqueous extracts were prepared at $20 \pm 5^\circ\text{C}$. When the shaking was finished, the containers were left to stand for about 15 minutes to let the solid particles settle down. Extracts were then filtered: the filter pore diameter was $0.45 \mu\text{m}$. After measuring the pH value, concentrated nitric acid(V) (HNO_3) was added to the extract to adjust that value to pH 1÷2 (for extract preservation). The aqueous extracts were then subjected to tests to find the content of the pollutants.

Method II - The procedure according to that method was also based on the standard PN-EN 12457-4: 2006 [14], but the fuels were flooded with distilled water which had been acidified with HNO_3 (V) to pH 4.

Method III - In that method, 100 g of fuel samples were placed in 1 dm^3 of distilled water and they were then subjected to freezing-thawing cycles (50 times). That number of

cycles was to simulate the average time for ambient temperatures below 0°C in winter. One cycle involved freezing a sample down to -18°C which was followed by thawing and bringing the temperature to +18°C [15]. Then, solids were filtered off and the level of impurities in water extracts was analysed.

Method IV - As opposite to the methods described above, which were conducted under laboratory conditions, that method was based on actual storage conditions: fuel samples (8 kg per each fuel) were exposed to direct rainfall. A special stands were prepared to collect the effluent, as shown in Figure 1.

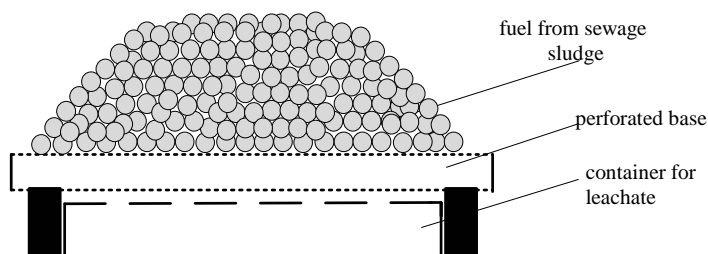


Fig. 1. Fuel leachate collection stand

A volume of each fuel was arranged on a perforated support and a container was placed below to collect the liquid effluent. The extracts were collected after 24 h and after 8 days of heavy rainfall. Basic pollution parameters were then analysed in the aqueous samples which were collected after respective exposure cycles and filtered to remove any possible solid matter.

Additionally, rainwater samples were also collected and analysed as blank samples.

The following parameters were analysed for all water extracts obtained as presented above:

- pH, according to PN-91/C-04540/05,
- specific conductivity, according to PN-EN 27888,
- leachability of chlorides, according to PN-ISO 9297,
- leachability of sulfates, according to PN-74/C-04566.09,
- ions of heavy metals were analysed with the use of an *inductively coupled plasma - atomic emission spectrometer* (ICP-AES), "Plasma 400" from Perkin-Elmer.

Heavy metal contents were also analysed in the sludge-derived fuels.

Results and discussion

In order to be able to verify mobility of heavy metals to water extracts obtained from test fuels, heavy metal contents were also analysed in PBS, PBM and PBT fuels as in the initial materials. Those concentrations of trace elements were listed in Table 3 along with the levels established for the RDF (*Refused Derived Fuel*) fuel and for hard coal.

The highest concentrations were found for iron, manganese (PBM and PBT fuels), zinc (PBT fuel) and chromium (PBS fuel), which resulted from the highest concentrations of those elements in the sewage sludge utilised for the production of fuels. The analyses demonstrated that the heavy metals contents in the studied fuels were comparable with the

values reported by Genon et al [16] for the RDF fuel which had been produced with the use of municipal wastes. However, mobility of heavy metals from those fuels may be completely different, depending on the ways and forms the metals are fixed in the fuel.

Table 3

Heavy metals contents in fuels from sewage sludge, referred to contents in RDF fuel and in hard coal

| Heavy metal | Unit | PBS fuel | PBM fuel | PBT fuel | RDF fuel [16] | Hard coal [17] |
|-------------|-------|----------|----------|----------|---------------|----------------|
| Fe | mg/kg | 1150 | 2030 | 4305 | NA* | NA* |
| Mn | mg/kg | 165 | 350.9 | 319.3 | 28÷210 | 4÷1990 |
| Cr | mg/kg | < 181 | 22.08 | 93.68 | 11.3÷140 | 0÷60 |
| Zn | mg/kg | 250 | 446.1 | 881.2 | 225÷340 | 2÷3560 |
| Pb | mg/kg | 63.20 | 19.43 | 24.93 | 25÷157 | 2÷370 |
| Co | mg/kg | 14.12 | 3.89 | 6.27 | 0.6÷4 | 0÷140 |
| Ni | mg/kg | < 25 | 4.92 | 15.92 | 0.85÷21 | 0÷130 |
| V | mg/kg | 1.14 | 2.53 | 3.10 | 0.3÷7 | 2÷100 |
| Cu | mg/kg | 58.88 | 43.84 | 71.77 | 45÷266 | 0.5÷50 |
| As | mg/kg | 1.53 | 0.997 | 2.254 | 0.9÷8.8 | 0÷170 |
| Sn | mg/kg | 0.478 | 0.0304 | 0.0282 | 4÷500 | 0.02÷1 |
| Tl | mg/kg | 0.048 | 0.051 | 0.089 | 0.186÷1.282 | NA* |
| Cd | mg/kg | 1.25 | 0.434 | 1.690 | 0.02÷0.5 | 0.1÷3 |
| Hg | mg/kg | 0.987 | 0.421 | 0.859 | 0.1÷0.4 | 1÷10 |

* NA - no data available

Tables 4-6 provide specifications of pollutant leachability parameters for fuels produced with the use of sewage sludge; four methods were employed to measure those parameters. The findings were compared with the pollution levels which are permissible for the treated industrial wastewater (in accordance with the Regulation of the Minister of Environment, of 24 July 2006, Journal of Laws No. 137, item 984).

Specific conductivity makes one of essential parameters which provide information on the content of dissolved matter (ions) in water extracts. Higher conductivity is recognised as potentially indicative for impurities, especially biogenic substances and heavy metals [18]. Hence, that parameter was measured and its high values were found for the leachates from the fuels which had been stored for 8 days, and in water extracts which had been obtained with the use of dynamic methods. Extremely high electric conductivity (7.460 $\mu\text{S}/\text{cm}$) was found out for the acidic extract of the PBM fuel.

Such a high value may be accounted for by the fact that the fuel contained the meat-and-bone meal which released biogenic components. Gupta and Sinha demonstrated in their research [19] that conductivity of extracts obtained from fresh sewage sludge might reach 3.859 $\mu\text{S}/\text{cm}$. On the other hand, Merrington et al [20] reported that conductivity of the sludge which had been dried by evaporation could be higher than 12 S/m.

Rosik-Dulewska and Karwaczynska showed in their studies [21] that conductivity of water extracts from ash-sludge mixtures, modified with K_2SO_4 , might be as high as 44.800 $\mu\text{S}/\text{cm}$.

Table 4

Leachability factors for pollutants from PBS fuel

| Parameter | Unit | Method I | Method II | Method III | Method IV | | | Max permissible values* |
|------------------------|-----------------------------|----------------|-----------|------------|---------------|---------------------------|--------|-------------------------|
| | | | | | Precipitation | Leachate from stored fuel | | |
| | | | | | | 1 day | 8 days | |
| | | Water extracts | | | | | | |
| pH | - | 7.47 | 7.55 | 7.72 | 6.9 | 7.5 | 7.5 | 6.5-9 |
| Conductivity | $\mu\text{S/cm}$ | 1.520 | 1.510 | 599 | 43.61 | 950.5 | 1,588 | - |
| Sulfates | $\text{mgSO}_4/\text{dm}^3$ | 31.3 | 398 | 139 | 4.73 | 194 | 324 | 500 |
| Chlorides | mgCl/dm^3 | 265 | 41.6 | 23.8 | 15.83 | 165 | 149.3 | 1,000 |
| Chlorides and sulfates | mg/dm^3 | 296.3 | 439.6 | 162.84 | 110.56 | 359 | 473.3 | 1,500 |
| Zn | mgZn/dm^3 | 0.119 | 0.134 | 0.059 | 0.059 | 0.34 | 0.098 | 2 |
| Fe | mgFe/dm^3 | 3.73 | 4.21 | 0.152 | <0.01 | 0.15 | 3.1 | 10 |
| Mn | mgMn/dm^3 | 0.142 | 0.124 | <0.0004 | 0.005 | 0.04 | 0.18 | - |
| Cu | mgCu/dm^3 | 0.177 | 0.214 | 0.014 | 0.0029 | 0.14 | 0.04 | 0.5 |
| Pb | mgPb/dm^3 | 0.0093 | 0.011 | <0.010 | 0.00011 | <0.02 | <0.02 | 0.5 |
| Ni | mgNi/dm^3 | 0.147 | 0.116 | <0.043 | 0.00049 | 0.12 | 0.15 | 0.5 |
| As | mgAs/dm^3 | 0.026 | 0.087 | <0.050 | 0.0011 | <0.03 | <0.03 | 0.1 |
| Sn | mgSn/dm^3 | 0.0043 | 0.0044 | - | 0.00021 | <0.03 | 0.01 | 2 |
| Cd | mgCd/dm^3 | 0.0008 | 0.00092 | <0.001 | 0.00005 | 0.002 | <0.002 | 0.5 |
| Cr | mgCr/dm^3 | 0.017 | 0.025 | <0.001 | 0.00024 | <0.01 | <0.01 | 0.5 |
| Co | mgCo/dm^3 | 0.077 | 0.087 | <0.001 | 0.00036 | 0.029 | 0.036 | 1 |
| Tl | mgTl/dm^3 | 0.00015 | 0.00017 | <0.030 | <0.03 | <0.03 | <0.03 | 1 |

* - for treated industrial wastewater (in accordance with the Regulation of the Minister of Environment, of 24 July 2006, Journal of Laws No. 137, item 984)

Table 5

Leachability factors for pollutants from PBM fuel

| Parameter | Unit | Method I | Method II | Method III | Method IV | | | Max permissible values* |
|------------------------|-----------------------------|----------------|-----------|------------|---------------|---------------------------|--------|-------------------------|
| | | | | | Precipitation | Leachate from stored fuel | | |
| | | | | | | 1 day | 8 days | |
| | | Water extracts | | | | | | |
| pH | - | 7.10 | 7.16 | 7.72 | 6.9 | 6.8 | 7.0 | 6.5-9 |
| Conductivity | $\mu\text{S/cm}$ | 7.250 | 7.460 | 782 | 43.61 | 950.5 | 2,954 | - |
| Sulfates | $\text{mgSO}_4/\text{dm}^3$ | 414 | 43.2 | 28.8 | 4.73 | 149 | 216 | 500 |
| Chlorides | mgCl/dm^3 | 48.1 | 251 | 76.9 | 15.83 | 280.3 | 274.4 | 1,000 |
| Chlorides and sulfates | mg/dm^3 | 462.1 | 294.2 | 105.7 | 110.56 | 429.3 | 490.4 | 1,500 |
| Zn | mgZn/dm^3 | 0.09 | 0.083 | 0.035 | 0.059 | 0.50 | 0.23 | 2 |
| Fe | mgFe/dm^3 | 0.508 | 0.77 | 2.345 | <0.01 | 3.00 | 9.95 | 10 |
| Mn | mgMn/dm^3 | 0.081 | 0.133 | 0.013 | 0.005 | 0.13 | 0.28 | - |
| Cu | mgCu/dm^3 | 0.018 | 0.019 | 0.014 | 0.0029 | 0.034 | 0.022 | 0.5 |
| Pb | mgPb/dm^3 | 0.0013 | 0.0013 | <0.010 | 0.00011 | <0.02 | <0.02 | 0.5 |
| Ni | mgNi/dm^3 | 0.225 | 0.209 | 0.044 | 0.00049 | 0.14 | 0.18 | 0.5 |
| As | mgAs/dm^3 | 0.04 | 0.0039 | <0.050 | 0.0011 | <0.03 | <0.05 | 0.1 |
| Sn | mgSn/dm^3 | 0.0026 | 0.0023 | <0.001 | 0.00021 | <0.003 | <0.003 | 2 |
| Cd | mgCd/dm^3 | 0.00014 | 0.00014 | <0.001 | 0.00005 | <0.002 | <0.002 | 0.5 |
| Cr | mgCr/dm^3 | 0.037 | 0.045 | <0.001 | 0.00024 | <0.01 | <0.02 | 0.5 |
| Co | mgCo/dm^3 | 0.038 | 0.036 | <0.001 | 0.00036 | 0.019 | 0.026 | 1 |
| Tl | mgTl/dm^3 | 0.00001 | 0.00001 | <0.03 | <0.03 | <0.03 | <0.03 | 1 |

* - for treated industrial wastewater (in accordance with the Regulation of the Minister of Environment, of 24 July 2006, Journal of Laws No. 137, item 984)

Table 6

Leachability factors for pollutants from PBT fuel

| Parameter | Unit | Method I | Method II | Method III | Method IV | | | Max permissible values* |
|------------------------|------------------------------------|----------------|-----------|------------|---------------|---------------------------|--------|-------------------------|
| | | | | | Precipitation | Leachate from stored fuel | | |
| | | | | | | 1 day | 8 days | |
| | | Water extracts | | | | | | |
| pH | - | 7.12 | 7.25 | 7.01 | 6.9 | 6.9 | 7.2 | 6.5÷9 |
| Conductivity | µS/cm | 2,700 | 2,550 | 1,178 | 43.61 | 784.8 | 2,014 | - |
| Sulfates | mgSO ₄ /dm ³ | 351 | 114 | 127 | 4.73 | 363 | 510 | 500 |
| Chlorides | mgCl/dm ³ | 45 | 40.2 | 11.2 | 15.83 | 36.98 | 38.01 | 1,000 |
| Chlorides and sulfates | mg/dm ³ | 396 | 154.2 | 138.2 | 110.56 | 400 | 548 | 1,500 |
| Zn | mgZn/dm ³ | 0.147 | 0.093 | 0.013 | 0.059 | 0.29 | 0.15 | 2 |
| Fe | mgFe/dm ³ | 1.599 | 0.499 | 0.243 | <0.01 | 0.42 | 14.5 | 10 |
| Mn | mgMn/dm ³ | 0.11 | 0.077 | 0.013 | 0.005 | 0.15 | 0.61 | - |
| Cu | mgCu/dm ³ | 0.017 | 0.023 | 0.012 | 0.0029 | <0.02 | <0.02 | 0.5 |
| Pb | mgPb/dm ³ | 0.0038 | 0.0036 | 0.021 | 0.00011 | <0.02 | <0.02 | 0.5 |
| Ni | mgNi/dm ³ | 0.197 | 0.232 | 0.029 | 0.00049 | 0.14 | 0.17 | 0.5 |
| As | mgAs/dm ³ | 0.022 | 0.035 | <0.050 | 0.0011 | <0.03 | <0.03 | 0.1 |
| Sn | mgSn/dm ³ | 0.0024 | 0.0015 | - | 0.00021 | <0.03 | 0.03 | 2 |
| Cd | mgCd/dm ³ | 0.00024 | 0.00031 | <0.001 | 0.00005 | <0.002 | <0.002 | 0.5 |
| Cr | mgCr/dm ³ | 0.014 | 0.071 | <0.001 | 0.00024 | <0.01 | <0.01 | 0.5 |
| Co | mgCo/dm ³ | 0.014 | 0.013 | <0.001 | 0.00036 | 0.019 | 0.03 | 1 |
| Tl | mgTl/dm ³ | 0.0004 | 0.00006 | <0.030 | <0.03 | <0.03 | <0.03 | 1 |

* - for treated industrial wastewater (in accordance with the Regulation of the Minister of Environment, of 24 July 2006, Journal of Laws No. 137, item 984)

Solubility of metal compounds is controlled principally by the reaction of the medium. The ion exchange sorption process (between metal ions and hydrogen ions) is limited under alkaline and neutral conditions, while it is much more extensive in the acidic environment. The reaction was similar for water extracts obtained with various methods for all fuels and it was within the range from 6.9 to 7.72. Wang [22] noted the pH scope of within 6.8÷7.4 in his studies on various types of sewage sludge. Similar results were also obtained by Polish researchers: Biernacka and Pawlowska measured pH 6.2÷7.6 for sewage sludge materials [11].

The tests indicated that leaching the fuels out with the use of rainwater with pH 6.9 over the period of 24 h resulted in extraction of sulfates at the levels of 194 mg/dm³ for PBS, 149 mg/dm³ for PBM and 363 mg/dm³ for PBT fuel. Those values were compared with concentrations analysed in water extracts after 8 days, and higher sulfate contents were found in the latter case: by 51% for PBS, by 40% for PBM, and by only 24.14% for PBT. The high and excessive sulfate content in the leachate from PBT after 8 days of storage (510 mg/dm³) resulted probably from the highest fraction of sewage sludge in that fuel in relation to fuels: PBS and PBM.

Extraction of chlorides, however, is more uniform (the values for leachates after 1 and after 8 days of storage are closer to each other).

Based on chloride and sulfate contents in water extracts one may declare that the freezing-thawing cycles (method III) had the lowest impact on chemical destabilisation of the fuels obtained from sewage sludge, while leachability of sulfates and chlorides was much more affected by the eluent reaction.

The tests showed the highest leachability levels for Fe from all investigated fuels. Especially high concentrations of that element were found in extracts obtained by method IV - in leachate after 8 days of storage, *ie* 3.1 mg/dm³ for PBS, 9.95 mg/dm³ for PBM, and as high as 14.5 mg/dm³ for PBT which was unacceptably excessive (the permissible value for treated industrial wastewater is 10 mg/dm³). That high Fe concentration in the leachate from PBT is connected with a very high Fe content in the fuel - the highest content among all tested fuels.

Despite relatively high contents of Cr, Pb and Co in fuels, those elements were present in leachates in trace elements. On the other hand, Zn, Mn and Cu (which were also present in fuels at high concentrations) were much easier to leach out; their levels were as follows: 0.035÷0.5 mg/dm³ for Zn, 0.0004÷0.61 mg/dm³ for Mn, and from 0.02 to 0.214 mg/dm³ for Cu. Those concentrations are much lower than the values allowed for Zn and for Cu (there is no permissible value for Mn).

As results from the data presented above, the levels of heavy metals in water extracts obtained after 1 and after 8 days of storage were different for individual elements. One may not declare generally that leachability of tested heavy metals increases or decreases for longer storage times. Such an assumption may be made in the analysis of a specific heavy metal. For example, the concentration of Zn after 1 day of storage is much higher for all the test fuels than after 8 days. The trend is opposite for Ni, Mn and Co. Additionally, concentrations of heavy metals in water extracts from fuels are known to be much higher than the heavy metals contents in atmospheric precipitation.

It was concluded from the research findings that atmospheric precipitation was not responsible for any considerable leaching pollutants out of the fuels, except for Fe. The concentrations of heavy metals in leachates (apart from one case) were very low, much below than the limit values as specified in Journal of Laws № 137, item 984 [23].

The effect of reaction on leachability of heavy metals was also verified in the study. The papers [18, 21, 24] report that strong acidification could induce extensive release of heavy metals which are present as oxides (Fe, Al, Mn) or in other minerals. Cd is considered the most mobile element; it undergoes leaching as early as at pH 6.5. Alloway and Ayres [25] declares the lowest solubility for Cr, Pb and Hg. Some metals like for example Zn, and to a lower degree Cu, show increased solubility also at the alkaline reaction. However, no essential differences were noted in our research in heavy metals concentrations which had been obtained at the acidic and neutral media. Some regular behaviour may be noticed only when the PBS fuel was treated with water acidified with HNO₃ to pH 4 (method II): leaching of heavy metals (except for Ni and Mn) was somewhat better when distilled water is used (method I).

Leachability of pollutants was lowest after the use of freezing-thawing cycles. The experimental findings demonstrated that the concentrations of heavy metals were much lower (except for iron from PBM) than the concentrations in water extracts obtained by methods I and II. The lowest leachability may be evidence of no effect from low temperatures on the pollutants leaching process from the stored fuels. However, it may also prove that the shaking process (in which the fuels lose their mechanical properties - they become soaked) employed in methods I and II adds to the increased concentrations of test elements in water extracts. The experiments suggest that mobility of pollutants which are present in the stored fuels may be lower in the winter season.

Conclusion

The fuels which are produced of wastes, before their utilisation in combustion processes for energy recovery, should be stored within a properly prepared storage place. Most waste materials which are utilised for the production of fuels have capillary structures and hygroscopic properties. Hence, fuels should preferably be stored under some roofing or in confined areas to maintain their good quality. Yet, fuels may also be stored in the open area, under atmospheric impacts, which may be environmentally harmful since harmful pollutants may be leached out from the fuels.

The studies presented in this paper covered the pollutants leaching process from the fuels obtained from sewage sludge, with consideration given to impacts from various environmental conditions, *ie* effect of atmospheric precipitation and time of exposure, and the effect of changing temperatures as well as freezing-thawing cycles.

Based on the conducted analyses, one may conclude that:

- the values for individual parameters in the conducted tests did not exceed the limit values as established for industrial wastewater to be discharged to the environment (except for two cases: sulfates and iron for PBT fuel),
- any longer time of exposure of the stored waste materials to atmospheric precipitation could apparently release more pollutants. Increased concentrations for most of test compounds in leachates were found after 8 days if extensive rainfall,
- the highest level of leaching within the heavy metals was noted for iron,
- no considerable differences were found in heavy metal concentrations versus changes in the reaction. However, the reaction was found to affect leachability of sulfates and chlorides,
- no negative influence was noticed for changing and low temperatures (below 0°C) - the pollution levels in water extract after freezing-thawing cycles were lower than those in fuel leachates,
- the fuels produced with the use of sludges, despite the fact that leachability of their harmful components is below the permissible limits (apart from two cases) should be stored under some roofing to maintain their physical properties and to avoid potential environmental hazards.

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OCENA WYMYWALNOŚCI SZKODLIWYCH SKŁADNIKÓW Z PALIW ALTERNATYWNYCH WYTWORZONYCH Z OSADÓW ŚCIEKOWYCH

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Abstrakt: Składowanie paliw, w tym także paliw wytworzonych z odpadów, jest jedną z operacji poprzedzających proces ich spalania lub współspalania w procesach przemysłowych. Czasowe magazynowanie paliw prowadzone na otwartej przestrzeni stwarza warunki do niekorzystnego oddziaływania czynników atmosferycznych na jakość paliw, ale może również prowadzić do wymywania składników, często szkodliwych dla środowiska. W artykule przedstawiono ocenę potencjalnych zagrożeń dla środowiska w trakcie składowania paliw wytworzonych z komunalnych osadów ściekowych i innych komponentów, tj. paliwo z osadów ściekowych i mułu węglowego (paliwo PBS), paliwo z osadów ściekowych i mączki mięsno-kostnej (paliwo PBM) oraz paliwo z osadów ściekowych i trocin (paliwo PBT). Zbadano wymywalność z paliw składników szkodliwych do otoczenia ze szczególnym uwzględnieniem metali ciężkich. Oceny poziomu wymywalności zanieczyszczeń dokonano, stosując cztery metody symulujące różne warunki środowiskowe. Na podstawie przeprowadzonych badań i analiz można stwierdzić, że czasowe składowanie paliw PBS, PBM i PBT w warunkach środowiska naturalnego jest bezpieczne pod względem wymywania składników szkodliwych do otaczającego środowiska glebowego czy wodnego.

Słowa kluczowe: paliwa z odpadów, osady ściekowe, składowanie paliw, wymywalność zanieczyszczeń, metale ciężkie