

Comparative Assessment of the Content of Heavy Metals in the Ash of Solid Fuel Pellets and Different Types of Sorted and Unsorted Solid Domestic Waste

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ABSTRACT

The research was aimed at evaluating the content of heavy metals in the ash of solid fuel pellets and various types of sorted and unsorted solid household waste. It highlighted the growing challenge of solid waste disposal and the potential of waste-to-energy technologies, and emphasized the importance of understanding the composition of fly ash due to its potential hazards. The research method involved the analysis of urban waste samples and their comparison with solid fuel pellets. The main findings revealed differences in chemical composition, with special emphasis on the presence and concentration of heavy metals. The highest concentrations of metal ions such as copper, strontium and lead were recorded in rubber, unsorted garbage and plastic. In the mixture of household waste of the Rybny landfill, such elements as: copper (Cu) – 0.141%, strontium (Sr) – 0.061%, and lead (Pb) – 0.016%. Studies show that Zn, Cu, Sr, Pb are the main threats in solid waste ash. Given the potential danger of these elements, the ash generated after incineration of solid household waste requires special handling and disposal (Retrieved, 2018, Perfect Publishing, 2015).

Keywords: heavy metals, ash, solid household waste, waste to energy.

INTRODUCTION

The problem of disposal of solid household waste (SHW) is relevant not only in Ukraine, but also in many other countries, as the volumes of this waste are constantly growing (Hitachi Zosen Inova 2017). This leads to the formation of significant landfills near cities. To regulate waste management, the European Union established the “EU Waste Framework Directive”, which establishes the rules for the collection, disposal and processing of all types of waste.

In Ukraine, between 11 and 13 million tons of municipal solid waste (MSW) are produced annually. The per capita waste production averages around 300 kg, with notable discrepancies between urban and rural settings. An increase in

waste production correlates with societal wealth improvements, as evidenced by the relationship between GDP per capita growth and per capita waste production rates (Barinov 2021). Recycling rates for MSW in Ukraine are reported to range between 3% and 8%, compared to up to 60 percent in European Union countries. Consequently, over 90% of MSW ends up in landfills and unauthorized dumping sites. Official data suggests that around 10,000 hectares of land accommodate close to 6,700 landfills and dumps, with actual figures potentially exceeding these estimates (Nowak 2013). The Ministry of Regional Development, Construction, Housing, and Utilities of Ukraine has identified a need for at least 626 additional landfills to manage the country’s waste disposal demands effectively.

In recent years, there has been a growing awareness of the environmental and health implications of improper waste disposal, leading to an increased emphasis on sustainable waste management practices. Waste-to-energy (WtE) technologies have emerged as promising solutions, offering the dual benefits of waste disposal and energy generation (Sharma and Basu 2020). The utilization of solid fuel pellets in this context adds another layer of complexity, warranting a detailed examination of the resultant ash composition.

WtE technologies (Brunner and Rechberger 2015) are developing as various methods of cleaning waste with the aim of converting it into electricity, heat, fuel and other useful materials. The WtE process (Ram et al., 2021) leaves behind secondary wastes, such as ash, sludge, slag, boiler ash, wastewater and emissions. Significant amounts of heavy metals can be observed in this ash, so understanding the exact chemical composition of the ash is critical. This work is devoted to the study of the chemical composition (and especially the amount of heavy metals) of ash in various types of sorted and unsorted solid household waste, pellets, and various types of wood and energy crops (Lopushniak and Hrytsuliak, 2023). All these materials can serve as fuel in solid fuel boilers, so understanding the level of danger and the possibilities of ash disposal after burning them is an urgent task. In Europe, it is forbidden to burn waste in equipment that is not adapted to it (Directive on waste incineration, 2000). When burning waste, not only toxic gases are produced, but also a large amount of ash, which, depending on its composition, requires special handling and disposal (Zhipeng and Bingru 2015). However, taking into account the potential energy benefit from burning household waste, there is a need for a detailed study of its chemical composition.

Today, the environmentally hazardous situation in various regions of Ukraine is significantly influenced by the imperfect domestic waste (DW) collection and transportation system. This system requires enhancements and continuous adaptation to manage the increasing quantity and diversity of household waste. This increase is attributed to urban population growth, changes in housing stock volumes, and the specifics of retail trade and production (Rehionalnyi plan. 2023).

A key factor in assessing the effectiveness of the waste management system is analyzing the morphological composition of waste, along with the infrastructure for collecting and managing

recyclable materials from DW. The analysis of the morphological composition of waste is pursued through two main approaches:

- 1) identifying the component composition of DW, focusing on qualitative characteristics;
- 2) establishing general standards for waste accumulation and evaluating the energy characteristics of waste to facilitate the adoption of energy-saving technologies (Holik and Yu 2023).

MATERIALS AND METHODS

The study used solid household waste samples provided by the Municipal Enterprise “Polygon SHW” of Ivano-Frankivsk. According to the data of the Municipal Enterprise “Polygon SHW” for 2020–2022, 68% of solid waste that ends up in the company landfills can be used as fuel and energy. On the other hand, 32% of solid waste is not suitable for use as an energy source, as it contains non-combustible components (such as glass, metal and unsorted residue).

In total, 21 samples were selected for analysis, namely 7 types of waste 1) paper and cardboard; 2) plastic; 3) a tree; 4) textiles; 5) rubber and leather; 6) biowaste; 7) unsorted combustible residue; each type of waste was sampled 3 times for the reliability of the analysis results (Ram, C., Kumar, A., Rani, P. (2021).

As a result, data were obtained on 7 different sorted components of solid household waste and the unsorted residue: 1) paper and cardboard; 2) plastic; 3) a tree; 4) textiles; 5) rubber and leather; 6) bio-waste; 7) unsorted combustible residue. A mixture of waste from the Rybna landfill was also selected, which simulates real components of solid household waste that can be used as fuel.

As a comparison, solid fuel pellets made from different types of trees and plants were used: 1) oak; 2) pine – 30% beech – 30% oak – 40%; 3) pine – 50% beech – 30% oak – 20%; 4) *Helianthus tuberosus*; 5) *aculil*; 6) *aculi2*; 7) beech. The research data included 21 samples, three groups of pellet samples with 7 samples in each group. The results were averaged for each group. To obtain ash, the samples were annealed in a SNOL 8.2 / 1100 muffle furnace at a temperature of 800 °C. To determine the amount of ash, the crucibles were weighed before and after the ashing process on analytical balances with an accuracy of 0.0002 g. In this way, samples of ash components of solid household waste and solid fuel pellets

were obtained, which were subsequently submitted for chemical analysis. Chemical analysis was carried out using an X-ray fluorescence analyzer EXPERT 3L. The research was carried out in a helium atmosphere with an accuracy of 10 ppm (Polutrenko, Fedorovich, 2022).

RESULTS AND DISCUSSION

Comparative studies of the chemical composition of the studied samples established that different types of solid household waste and pellets have varying chemical compositions and are mainly represented by a mixture of the corresponding oxides. Thus, the presence of the following chemical elements – calcium (Ca), oxygen (O), chlorine (Cl), potassium (K), iron (Fe), silicon (Si) – is typical for solid household waste at the Rybna landfill. In total, these elements make up 93.6% of the total ash mass of the Rybna landfill waste mixture (Fig. 1). As it can be seen from the graph, all other elements appear in much smaller quantities. nickel (Ni), zinc (Zn), chromium (Cr), copper (Cu) belong to heavy metals (Gjorgieva, 2018), and although their quantity is not large in comparison (Ni – 1.69%, Zn – 0.6%, Cr – 0.37%, Cu – 0.14%), during industrial incineration of household waste, their the amount will be potentially dangerous (Nowak et al., 2013). If the chemical composition of the ash of solid fuel

pellets and the ash of a mixture of solid household waste is compared (Fig. 1, 2), it can be seen that the same elements make up the bulk of the samples (Ca, O, K, Cl, Fe, Si). In total, these elements make up 92.1% of the total ash mass of the ash mixture of solid fuel pellets (Table 1). The only difference is observed in the amount of Cl manifestation, which is much greater in the solid waste mixture. This can indicate both the peculiarities of the accumulation of cholera in certain plants and the uneven distribution of chemical elements in the mixture of solid household waste (Poluszyńska 2020). The only representative of heavy metals that are present in a small amount in pellet ash is Zn – 0.35% (Fig. 2). Indicators in Tables 1 and 2 are listed in Figures 1–3 and depicted graphically for a better understanding of changes in indicators.

The results of the study of the content of chemical elements, the amount of which in TPE ash is insignificant, are presented in Figure 3. The content of individual elements in different types of ash from household waste was very diverse.

The highest concentrations of metal ions such as copper, strontium and lead were recorded in rubber, unsorted garbage and plastic. In the mixture of household waste of the Rybna landfill, these elements are represented by copper (Cu) – 0.141%, strontium (Sr) – 0.061%, lead (Pb) – 0.016%, respectively. A significant amount of Antimony (Sb-0.081%) was also recorded in

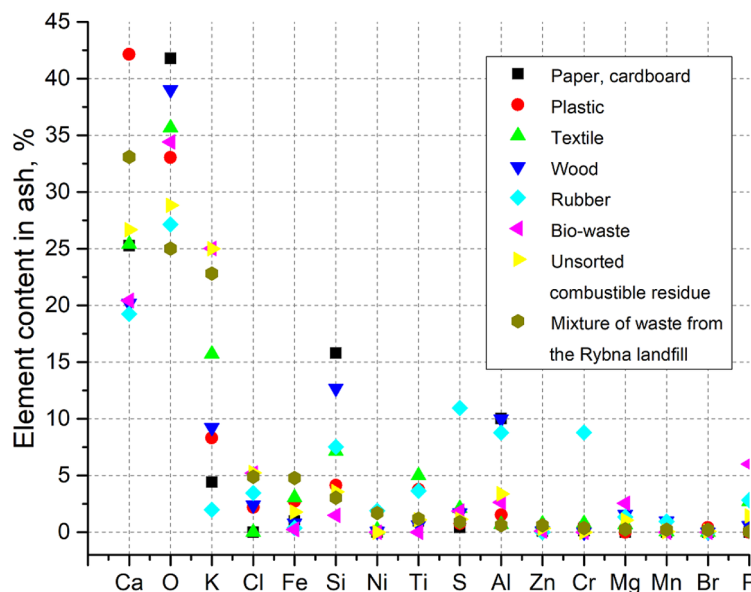


Fig. 1. The average chemical composition of ash of different types of solid household waste is calculated as a percentage by mass. (Chemical elements are shown, the amount of which is greater than 0.05% for the mixture of household waste at the Rybna landfill)

Table 1. The content of chemical elements in the ash of solid household waste at the at the Rybna landfill, %

Element	Paper. cardboard	Plastic	Textile	Wood	Rubber	Bio-waste	Unsorted combustible residue	Mixture of waste from the Rybna landfill
Ca	25.271	42.148	25.412	20.199	19.254	20.44	26.675	33.099
O	41.785	33.04	35.681	39.013	27.151	34.417	28.824	25.0132
K	4.42	8.326	15.726	9.239	1.978	25.027	24.999	22.8128
Cl	0	2.206	0	2.383	3.451	5.211	5.247	4.8842
Fe	0.997	2.727	3.056	0.797	0.385	0.246	1.779	4.7892
Si	15.79	4.126	7.158	12.687	7.542	1.481	3.569	3.0466
Ni	7.60E-04	3.65E	0.221	0.08513	1.901	3.70E	4.57E-04	1.6945
Ti	0.98	3.752	5.01	0.642	3.6472	3.21E	1.079	1.193
S	0.421	0.763	2.1	1.708	10.956	1.852	1.141	0.8942
Al	10.032	1.54	0.704	9.987	8.788	2.628	3.38	0.6234
Zn	0.109	0.127	0.74762	0.121	1.82E-04	0.1002	0.344	0.6084
Cr	0.123	0.53	0.762	0	8.788	0	4.57E-04	0.3718
Mg	0.00265	0	0.665	1.564	1.352	2.551	1.061	0.2626
Mn	4.45E-04	0.059	0.055	0.992	0.956	2.22E	0.056	0.219
Br	1.01E-04	0.416	0	4.44E	4.50E	3.06E	0.07	0.2128
P	0	0	2.702	0.582	2.841	6.02	1.434	0.0578
Cu	2.96E-04	0.088	3.83E	1.46E	0.468	1.05E	0.054	0.141
Sr	6.70E-04	1.32E	0	1.02E	2.80E	2.40E	1.31E-04	0.0609
Pb	0.065	0.06987	0	1.79E-04	0.54006	0.02443	0.28562	0.0164
Ag	0	0	0	0	0	0	0	8.10E-05
Nb	0	0	0	0	0	0	0	7.62E-05
Cd	0	0	0	0	0	0	0	3.94E-05
Ga	3.60E-04	0	0	0	4.10E	0	0	0
Rb	2.30E-04	0	0	0	8.70E-05	4.20E-04	5.70E-04	0
Zr	1.24E-04	0	0	0	2.40E-05	0	1.90E-04	0
Mo	0	6.30E-04	0	0	1.80E-04	0	4.30E-04	0
Sb	0	0.081	0	0	8.90E-05	0	0	0
Pd	0	0	0	0	6.20E-05	1.60E-04	1.40E-04	0
I	0	0	0	0	3.76E-04	2.28E-04	0	0
Re	9.10E-04	0	0	0	0	0	0	0
Ir	4.50E-04	0	0	0	0	0	0	0

the sorted plastic waste. This may indicate that a plastic container in which dangerous chemicals were stored is entering the landfill, and accordingly, when using plastic from this landfill, attention should be paid to this. All other chemical elements (Ag, Nb, Cd, Ga, Rb, Zr, Mo, Sb, Pd, I, Re) are present in much lower concentrations (<0.0001%). Fig. 4 shows the results of chemical analysis of ash from solid fuel pellet products. Chemical elements the amount of which is less than 0.25% by mass are shown. As it can be seen from the graph, there is quite a significant difference in the manifestation of chemicals in

different products. Thus, Jerusalem artichoke has a significant amount of phosphorus (0.52%), chlorine (1.08%) and magnesium (0.61%) compared to other products. All test samples are characterized by a high occurrence of strontium (about 0.1%) and copper (about 0.1%). A high amount of phosphorus is characteristic of beech (0.79%) and conifers (0.44%). Considering the presence of heavy metals in the ash of the mixture of solid fuel pellets, a small amount of strontium and copper is observed. At the same time, their number is within acceptable limits. All other chemical elements are present in much lower concentrations (<0.01%).

Table 2. The content of chemical elements in the ash of solid fuel pellets, %

Element	Oak	Pine 30% Beech 30% Oak 40%	Pine 50% Beech 30% Oak 20%	Tuberosus	Pine (1)	Pine (2)	Beech	Average pellet mixture
Ca	33.964	35.208	36.538	35.825	33.182	37.891	20.043	33.23586
O	30.117	28.911	29.665	26.865	30.677	30.25	35.762	30.321
K	16.492	18.652	13.801	28.381	13.158	14.685	13.299	16.924
Fe	4.644	8.01	10.921	1.48	9.809	3.325	10.977	7.02371
Si	2.791	2.753	3.096	2.59	4.234	3.161	13.531	4.59371
Mn	5.588	2.688	3.123	0.224	4.892	7.444	1.643	3.65743
Al	2.025	1.613	1.499	1.606	1.645	1.645	1.884	1.70243
Ti	3.128	0.745	0.669	0.18	1.323	0.425	1.401	1.12443
Zn	0.357	0.569	0.176	0.152	0.632	0.374	0.201	0.35157
S	0.427	0.486	0.212	0.22	0.183	0.209	0.118	0.265
P	0	0	0	0.52	0	0.442	0.787	0.24986
Cl	0	0	0	1.089	0	0	0	0.15557
Sr	0.123	0.102	0.101	0.196	0.089	0.097	0.08	0.11257
Mg	0	0	0	0.617	0	0	0	0.08814
Cu	0.105	0.081	4.94E-04	1.85E-04	0.052	0.053	3.19E-04	0.04171
Sn	0	0.069	4.78E-04	0	0	0	0	0.00993
Cr	0	0	0	0	0.068	0	0	0.00971
Ru	0.065	3.06E-04	0	0	0	0	0	0.00933
Ni	4.68E-04	0.054	2.85E-04	4.60E-05	2.70E-04	0	0	0.00787
Zr	4.10E-04	0	0	7.30E-05	0	0	0.053	0.00764
Rb	4.91E-04	2.96E-04	3.69E-04	1.28E-04	2.86E-04	0	2.77E-04	2.64E-04
Pb	0	0	0	0	0	0	3.84E-04	5.49E-05
Mo	3.80E-04	0	0	0	0	0	0	5.43E-05
Ag	0	0	0	1.22E-04	0	0	0	1.74E-05
Ga	0	0	0	0	0	0	6.90E-05	9.86E-06

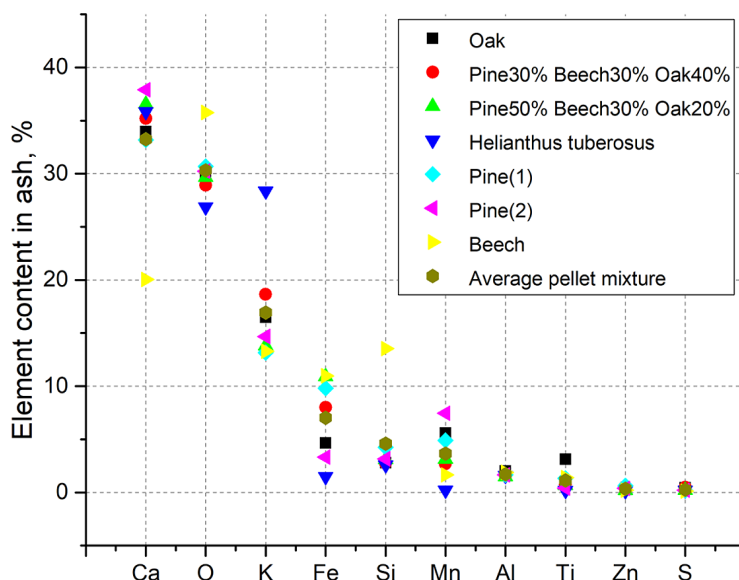


Fig. 2. The average chemical composition of ash of different types of products in solid fuel pellets is calculated as a percentage by mass. (The chemical elements the amount of which is greater than 0.25% for a mixture of solid fuel pellets are shown)

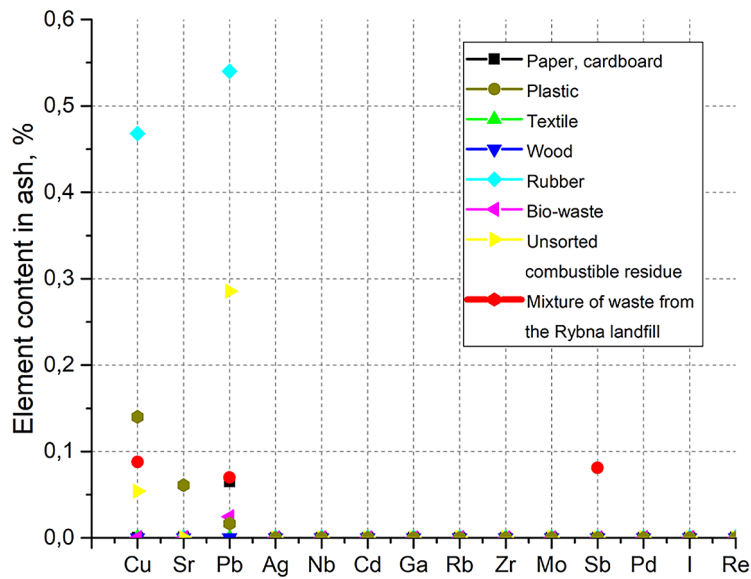


Fig. 3. The average chemical composition of ash of different types of solid household waste is calculated as a percentage by mass. (The chemical elements the amount of which is less than 0.05% for the mixture of household waste at the Rybna landfill are shown)

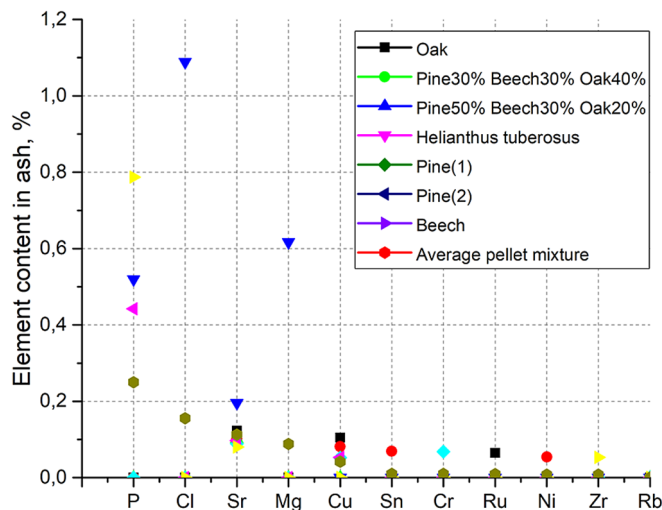


Fig. 4. The average chemical composition of ash of different types of products in solid fuel pellets is calculated as a percentage by mass. (The chemical elements the amount of which is less than 0.25% for a mixture of solid fuel pellets are shown)

CONCLUSIONS

The problem of disposal of solid household waste (SHW) is urgent because the volumes of this waste are constantly increasing. Incineration of household waste is an effective way of both disposal and obtaining energy. When MSW is burned, a large amount of ash rich in various chemical elements is formed. The main chemical substances and compounds encountered in the analysis of samples, namely toxic elements

and heavy metals, are characterized by low concentrations. The content of individual elements in different types of ash from household waste was very diverse. The highest concentrations of metal ions such as copper, strontium and lead were recorded in rubber, unsorted garbage and plastic. In the mixture of household waste of the Rybna landfill, these elements are represented by copper (Cu) – 0.141%, strontium (Sr) – 0.061%, lead (Pb) – 0.016%, respectively. In the conducted research such chemical elements as – Cu, Pb, Sr, Ni,

Zn, Cr, do not exceed permissible standards. The research shows that Zn, Cu, Sr, Pb are the main threat in solid waste ash. Given the potential danger of these elements, the ash formed after burning solid waste requires special handling and disposal.

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