PROSPECTS FOR METALLURGICAL PROCESSING OF ASH AND SLAG WASTE FROM COAL-FIRED POWER PLANTS UNDER ELECTROSLAG SMELTING CONDITIONS WITH METALS EXTRACTION

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https://doi.org/10.37904/metal.2025.5068

Abstract

Approximately 1 billion tons of ash and slag waste are produced annually from coal-fired power plants worldwide, including 6,8 million tones in Ukraine. The total amount of accumulated ash and slag waste in Ukraine exceeds 380 million tones. Their accumulation creates serious environmental risks and economic problems. Many methods based on physical, chemical and combined approaches are known for ash and slag waste disposal. Most often these wastes are used in the production of building and road construction materials. However, ash and slag wastes contain significant amount of metal oxides that can be extracted to form alloys. The total content of Fe, Al and Si oxides in ash and slag waste can reach 60%. However, the instability of the chemical composition is a serious problem in their metallurgical processing. Traditionally, the metallurgical methods for processing these wastes are based on carbon reduction, which involves significant CO_2 emissions to the environment. This approach is not in line with the current trend towards decarbonisation of industrial production. To find alternatives, the possibility of using the electrometallurgical smelting process with extraction of metals into an alloy in the recycling chain is being investigated using the ash and slag waste from Trypilska TPP. The aluminum waste is used as a metal oxide reducing agent. Laboratory experiments on the remelting of ash and slag waste by the method of reductive electroslag melting have shown the possibility of implementing a waste processing with the production of iron or aluminum-based alloys at the first stage of recycling.

Keywords: Ash and slag waste, electroslag smelting, aluminum reducing agent, ferrosilicoaluminum

1. INTRODUCTION

Ash and slag waste (ASW) from thermal power plants (TPPs), which currently amount to over 1.5 trillion tons worldwide, has an extremely negative impact on the environment. The main environmental problems are associated with their accumulation and storage [1]. Soils, water resources and air are polluted. Ash and slag contain heavy metals (mercury, lead, cadmium, arsenic, chromium) that penetrate the soil. The accumulation of waste leads to land degradation, making it impossible to use the territories for agriculture or other purposes. Up to 50% of ash and slag waste is stored in the form of ash dumps or slag reservoirs, which can infiltrate toxic substances into groundwater. Surface waters are polluted by runoff from ash and slag storage facilities, leading to eutrophication and poisoning of aquatic ecosystems. Ash and slag waste dust contains fine particles (< 0.1 mm), which can cause respiratory and cardiovascular diseases when carried by wind [2]. At the same time, impurities of heavy metals and radioactive elements in the products of coal combustion have a carcinogenic effect [3, 4]. As a result, the areas around ash dumps become unfit for human habitation.

In Ukraine, by 2022, about 6.8 million tons of ash and slag waste from thermal power plants were accumulated annually. Currently, more than 380 million tons of this waste have been accumulated in the ash dumps of Ukrainian thermal power plants. At the same time, the level of their utilization is 5-7%, which is significantly lower than in the USA (64%), India (67%), and China (70%) [5]. In EU countries, this figure is almost 94%, and in Germany, it is generally prohibited by law to accumulate ash and slag waste from thermal power plants. Moreover, the main direction of utilization of ash and slag waste from thermal power plants in these countries is their use in the production of cement, concrete, and other building materials [6, 7].

The presence of a large amount of iron oxides (up to 20%) and other components in the composition of ASW limits their use in the production of building materials and requires additional processing to remove harmful impurities. One of the main reasons for the low level of ASW utilization in Ukraine is the unstable composition of TPPs ash, and, accordingly, the impossibility of implementing large-scale industrial processing of ASW. Thus, the problem of utilization of TPPs ash and slag waste is very relevant for Ukraine [8].

2. MATERIALS AND METHODS

The composition of ash and slag waste differs for different Ukrainian TPPs, since these plants use different solid fuels and different combustion technologies. The fuel differs not only in the degree of metamorphism, the yield of volatile substances, the sulfur content, the composition of the organic part of coal, the content of mineral components, but also in the composition of the mineral non-fuel part of coal. Accordingly, ash and slag products of coal combustion have different chemical compositions [9]. According to information on the chemical composition of ASW from some Ukrainian coal-fired TPPs, the main part of ash and slag consists of aluminum, iron and silicon oxides. Moreover, the fluctuation of Al_2O_3 content is from 19.8% to 40.6%, Fe_2O_3 – from 8% to 23%, SiO_2 - from 16.7% to 57.8%. The total content of Al_2O_3, Fe_2O_3 and SiO_2 components in some ASW reaches 90%. In terms of pure substance, the average content of aluminum is 13%, iron – 15%, silicon – 25%. Thus, in the composition of ASW, three chemical components – Al, Fe and Si - make up at least 50%. Therefore, ASW of coal-fired TPPs can be considered as a complex raw material in technological processes of metals and silicon extraction.

Today, the extraction of metals from coal ash is a promising direction in the processing of TPPs waste [10, 11]. Methods for extracting metals from ASW of TPPs are multi-stage and can combine physical, chemical and biological approaches [12, 13]. Combined methods are the most effective for use on an industrial scale [14, 15]. The development of these methods will allow not only to reduce the amount of waste, but also to obtain metals for further use in industry [16, 17]. The main disadvantage of all known technologies for extracting metals from ASW of TPPs is the need for constant adjustment of technological parameters and operating modes of technological equipment in accordance with changes in the chemical composition of the waste heat. Over the years of operation of TPPs, constant changes of raw materials occur. The coal used has not only different technological properties, but also a different composition of the mineral part. At the same time, there is no differential storage of ASW at the TPPs according to its composition. Therefore, the elemental and material composition of ASW may change unpredictably during their sequential transportation from ASW collector to the industrial ASW processing plant. This situation will negatively affect the technical and economic performance of the plant. This article is devoted to the results of the development of a new method for extracting metals Al, Fe and the metalloid Si from ASW of TPPs to obtain ferrosilicoaluminum of satisfactory quality as the final product.

As raw materials for the research, samples of ASW from the ash-slag accumulator of the Trypilskaya TPP JSC "Centrenergo", Ukrainka, Kyiv region, Ukraine, were used. The TPP operated since 1977 and suspended its activity in 2024 due to destruction during missile attacks by the russian federation. The TPP consisted of 4 coal-fired power units with a total capacity of 1225 MW. Anthracite was the project raw material for combustion. Later, technical solutions were implemented at the TPP that allowed burning high-ash low-grade coal with a calorific value of about 12,500 kJ/kg. One of the power units was upgraded to use low-metamorphosed coal with a high volatile. As at 2024, about 30 million tons of MSW had accumulated in the ash dump, which almost corresponds to its design capacity. Previous studies have established the possibility of using ASW of the Trypilska TPP for the production of building materials and road construction [7].

3. RESULTS AND DISSCUSION

To determine the chemical composition of ASW, the X-ray fluorescence method (XRF express-analyzer INAM EXPERT 4I) was used. To determine the carbon content, infrared absorption (HORIBA EMIA-Pro) was used. The content of main components (wt%) and microcomponent oxides (ppm) in ASW from the Trypilska TPP is given in **Tables 1** and **2**.

Table 1 The content of main components in ASW from the Trypilska TPP (wt%)

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	MgO	P_2O_5	SO_3	MnO_2	TiO_2	V_2O_5	BaO
wt%	51.28	22.66	13.78	2.09	5.55	1.24	1.44	0.28	0.30	0.11	0.98	0.05	0.08

Table 2 The content of microcomponent oxides in ASW from the Trypilska TPP (ppm)

Oxides	MoO_3	Cr_2O_3	Ni_2O_3	CuO	ZnO	Ga_2O_3	As_2O_3	Rb_2O	SrO	Y_2O_3	ZrO_2	Nb_2O_5	PbO
ppm	31	134	139	132	114	30	105	120	389	46	273	22	30

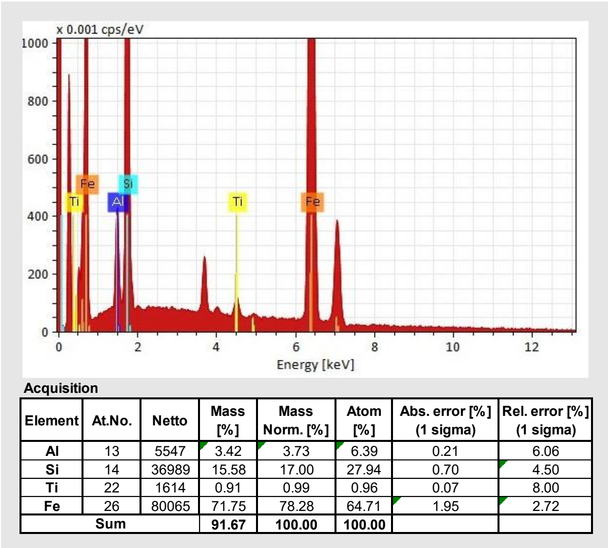
According to the results of the research, 28 metal and non-metal oxides were identified in the composition of ASW. The carbon content was 0.83%, sulfur – 0.07%. The elemental composition of ASW, taking into account oxides of chemical elements, the content of which exceeds 0.01%, is given in **Table 3**. Another fraction of microcomponent oxides, the total content of which is 0.16%, does not have a significant impact on the results of experiments on the extraction of metals from ASW. In the case of their transition to the final metal alloy, the proportion of these microcomponents does not exceed 0.001%.

Table 3 Elemental composition of ASW of the Trypilska TPP (wt%)

Element	Si	Al	Fe	Ca	K	Na	Mg	P	S	Mn	Ti	V	Ba	O
wt%	23.93	12.00	9.65	1.49	4.61	0.92	0.86	0.12	0.12	0.07	0.59	0.03	0.07	45.38

For experiments on obtaining ferrosilicoaluminum from ASW, an electrometallurgical process was chosen, which involves smelting metals by the electroslag melting (ESM) method. Carbon (carbothermy method) or aluminum (aluminothermy method) were used as reducing agents [18]. The extraction of metals to obtain ferroalloy is carried out in one stage at a melting temperature significantly higher than the melting temperature of slag and metal. The research was conducted on a laboratory installation for electroslag melting. The main elements of the installation were a crucible made of graphite (inner diameter of 75 mm, height of 180 mm), and a graphite electrode (diameter of 40 mm). At the first phase, the process took place in arc mode to melt the first portion of the charge containing 100 g of ASW. An electric current passes through the electrode and the molten ash, which creates a high resistance. At the same time, a large amount of thermal energy is released. As a result of heating, ASW melts, drops of molten metal separate from ASW and settle at the bottom of the mold. The molten metal, passing through the slag, is purified from non-metallic inclusions and gases. After the first portion of the charge is completely melted, the transition to a stable slag melting mode is carried out with the gradual addition of new portions of the charge in the amount of 50-70 g each. The purified metal gradually accumulates, forming a high-quality melt. After melting the entire charge, the resulting melt is maintained for 1 minute. Then it is poured into a mold, where the newly formed slag (in the upper layer) and metal (in the lower layer) are distributed by density along the height. After cooling and solidification of the metal and slag parts, they are separated and studied.

According to stoichiometric calculations, 170 g of pure carbon is required to carry out the reduction process of all oxides contained in 1000 g of ASW. Pure graphite powder with a purity of 99% and a particle size of ≤0.1 mm was used as the reducing agent. To lower the melting temperature, CaO was added to the charge, and to reduce the viscosity of the slag, CaF_2 was added. To increase the iron content in the metal alloy, metallic iron was added to the charge. As a result of the experiment, a metal alloy weighing 690 g was melted from 1 kg of ASW. The results of the analysis of the alloy composition using a scanning electron microscope (SEM Tescan Vega 3) are shown in **Figure 1a**.



Element	At.No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	Abs. error [%] (1 sigma)	Rel. error [%] (1 sigma)
Al	13	5547	3.42	3.73	6.39	0.21	6.06
Si	14	36989	15.58	17.00	27.94	0.70	4.50
Ti	22	1614	0.91	0.99	0.96	0.07	8.00
Fe	26	80065	71.75	78.28	64.71	1.95	2.72
Sum			91.67	100.00	100.00		

a) b)

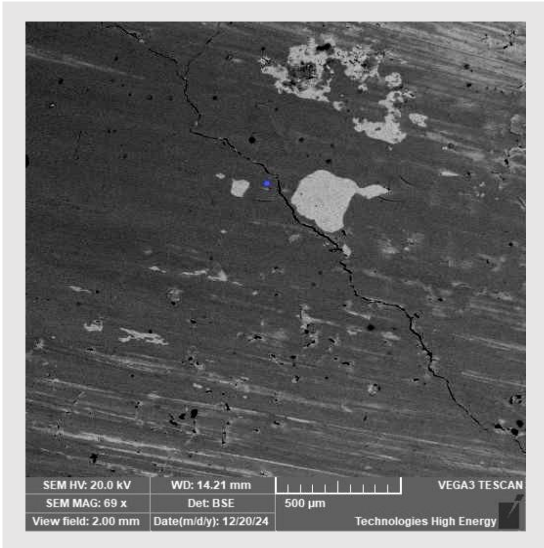


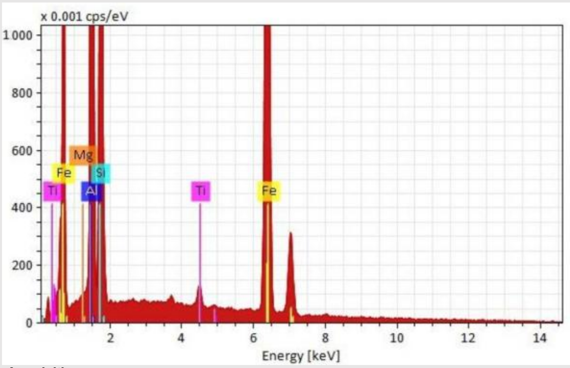
Figure 1 (a) Metal alloy composition; (b) SEM image of the ferrosilicon alloy cross-section obtained from ASW by the carbothermy methodthe

According to the results of the carbothermic process of smelting metals from ASW, ferrosilicon of the composition $Fe_{78}Si_{17}$ with impurities of 3.7% Al and 1.0% Ti was obtained. The reduction of metal oxides in the ESM process with carbon material as the reducing agent is very difficult. Unlike other metallurgical processes, where carbon is used as a reducing agent, in ESM only a direct chemical reduction reaction is possible upon direct contact of solid carbon with oxide molecules [19]. Under ESM conditions, it is practically impossible to ensure such contact throughout the entire volume of the reaction mixture. Therefore, on microscopic examination of the cross-section, many unreacted graphite particles were found in the metal alloy (**Figure 1b**). As a result, a low percentage of reduced metal oxides was obtained.

Aluminothermic reduction is a promising method for extracting metals from various wastes. Aluminum is a stronger reducing agent than carbon, so it reduces metal oxides more effectively [20]. Considering the conditions of ESM and the impossibility of reducing metal oxides with carbon by indirect methods, it was decided to use aluminum as a reducing agent. The objective of the study was to obtain ferrosilicoaluminum with the composition $Fe_{55}Si_{20}Al_{25}$ using ESM of ash and slag waste. According to the stoichiometric equations of interactions between aluminum with silicon oxide and iron oxide, the composition of the charge for the process was calculated: 1000 g of ASW, 100 g of CaO, 343 g of Al, 657 g of Fe. As a result of melting, 1170 g of metal alloy was obtained.

Studies with a scanning microscope showed that the obtained metal alloy has a composition of $Fe_{47}Si_{23}Al_{29}$ (**Figure 2a**). As impurities, there are titanium of 1.08% and magnesium of 0.276%. The obtained result is close to theoretical calculations. Almost all of the titanium has been converted into ferrosilicoaluminum. SEM image of the cross-section of the obtained ferrosilicoaluminum is presented in **Figure 2b**. As a result of this melting, a secondary slag was obtained, which consists of 70% Al_2O_3.

a)



Acquisition

Element	At.No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	Abs. error [%] (1 sigma)	Rel. error [%] (1 sigma)
Mg	12	369	0.27	0.27	0.41	0.06	23.49
Al	13	50578	28.37	28.71	38.71	1.39	4.91
Si	14	43237	22.24	22.50	29.15	0.99	4.44
Ti	22	1574	1.07	1.08	0.82	0.08	7.47
Fe	26	51980	46.87	47.33	30.90	1.29	2.76
Sum			98.82	100.00	100.00		

b)

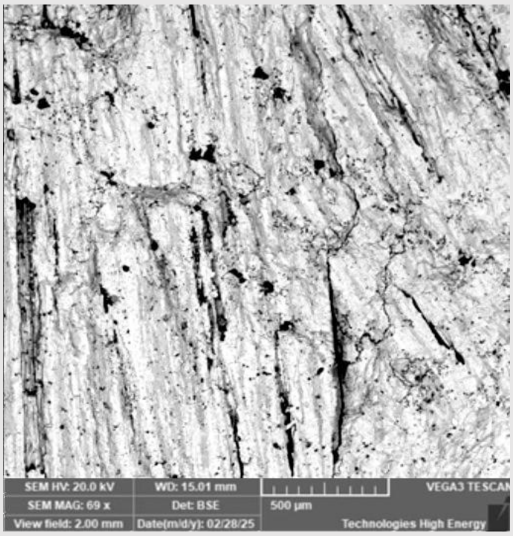


Figure 2 (a) Metal alloy composition; (b) SEM image of the cross-section of the ferrosilicoaluminum obtained from ASW by the aluminothermy method

4. CONCLUSION

In Ukraine, over 380 million tons of ASW have been accumulated in the ash dumps of Ukrainian TPPs. At the same time, the level of their utilization is 5-7%. The total content of Al_2O_3, Fe_2O_3 and SiO_2 components in some TPPs reaches 90%. Therefore, ASW of TPPs can be considered as a complex raw material for the extraction of metals and silicon.

The main disadvantage of all known technologies for extracting metals from ASW of TPPs is the need for constant adjustment of technological parameters and operating modes of technological equipment in accordance with changes in the chemical composition of ASW.

As raw material for the research, samples of ASW from ASW accumulator of Trypilska TPP, Ukraine were used. According to the research results, 28 metal and non-metal oxides were identified in the composition of ASW. The total content of Al_2O_3, Fe_2O_3 and SiO_2 components was 88%.

To conduct experiments on obtaining ferrosilicoaluminum from ASW, the electroslag melting method was chosen. Carbon and aluminum were tested as oxide reducing agents. The best result was obtained when the aluminothermy method was used to obtain ferrosilicoaluminum with the composition $Fe_{47}Si_{23}Al_{29}$.

ACKNOWLEDGEMENTS

This publication of research results was supported by the German Academic Exchange Service (DAAD) under the Program "Ukraine digital: Ensuring academic success in times of crisis" (2025).

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