

Original Research

**TRANSFORMATION OF WASTE FROM HAZARDOUS TO NON-HAZARDOUS:
STABILIZATION OF SOLID RESIDUE OBTAINED AFTER TWO-STEP
HYDROMETALLURGICAL TREATMENT OF EAF DUST**

DOI: 10.5937/EcoTER26568T

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Abstract

The paper investigated the stabilization process of the solid residue obtained after the hydrometallurgical treatment of EAF dust, which, due to elevated concentrations of heavy metals, shows toxic properties and does not meet the requirements for safe disposal. Stabilization was carried out by adding lime (5–10 wt.%) with the aim of immobilizing heavy metals. The results of the LP and TCLP tests showed that the efficiency of the stabilization process depends on the pH value of the environment and the amount of added lime. Under optimal stabilization conditions, specifically with the addition of 6 wt.% lime, effective immobilization of metals was achieved and the waste was classified as non-hazardous, enabling its safe disposal in a non-hazardous waste landfill.

Keywords: EAF dust, stabilization, TCLP and LP tests.

INTRODUCTION

The melting of scrap iron in an electric arc furnace is one of the most commonly applied processes in steel production, during which a significant amount of intermediate product of the process – electric arc furnace dust (EAF dust) is generated [1–3]. Due to the high content of heavy metals such as zinc, lead, cadmium, and others, as well as their possibility of self-leaching, the electric arc furnace dust is classified as hazardous waste in many countries worldwide [4–6]. For this reason, EAF dust represents a serious environmental issue, but at the same time a potential secondary resource for the recovery of zinc and other valuable components, which makes it a subject of interest for a large number of researchers [7–10]. The application of hydrometallurgical processes for the treatment of EAF dust enables the recovery of high-purity metals. Compared to pyrometallurgical processes, hydrometallurgical processes often have lower emissions of gases and dust, which contributes to reducing the

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negative impact of these processes on the environment [5,11–14]. However, after the application of hydrometallurgical treatment of EAF dust, a solid residue is obtained whose characteristics sometimes do not meet regulatory requirements for safe disposal (it may contain toxic components). Therefore, in order to meet the prescribed limit values, additional treatment of this solid residue is necessary [15–19].

In this paper, the possibility of stabilizing the solid residue obtained after the applied hydrometallurgical treatment of EAF dust was investigated. The treatment includes a two-step leaching process: EAF dust leaching with distilled water (pretreatment), followed by leaching of the obtained solid residue with a sulfuric acid solution. The stabilization process is aimed at reducing the mobility of the present heavy metals and transferring the solid residue from the category of hazardous to the category of non-hazardous waste, thus enabling its safe disposal. The investigation of the stabilization process in this paper was carried out in order to define the optimal amount of added lime required to ensure satisfactory characteristics of the stabilized material in terms of environmental acceptability. The efficiency of the stabilization process was evaluated using standard tests: the Leaching Procedure (LP test) and the Toxicity Characteristic Leaching Procedure (TCLP test), which are widely used for assessing the environmental and human health impact of waste after disposal, as well as for waste classification in accordance with current regulations.

MATERIALS AND METHODS

Characterization of the solid residue obtained after the applied two-step hydrometallurgical treatment of EAF dust

A physicochemical characterization of the solid residue obtained after the applied two-step hydrometallurgical treatment of EAF dust was carried out. As part of the physical characterization, the moisture content of the sample was determined. The pH value of the solid residue was measured according to method 9045D, which is used for measuring the pH value of soils and wastes. For the determination of the chemical composition of the solid residue, the following methods were used: Atomic Absorption Spectrophotometry (AAS), Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Volumetry (V), Carbon and Sulfur Analyzer (CSA), Spectrophotometry (SF), and X-ray Fluorescence Spectrometry (XRF). To determine the concentration of fluoride ions, a ion-selective electrode (ISE) and a ion meter were used.

Environmental impact assessment and stabilization of the solid residue

The solid residue obtained after the applied two-step hydrometallurgical process, i.e., water leaching followed by acid leaching, was investigated in order to assess its potential impact on the environment and human health after disposal. For this purpose, Leaching Procedure (LP test) and the Toxicity Characteristic Leaching Procedure (TCLP test) were applied in accordance with the Regulation on Categories, Testing, and Classification of Waste (Official Gazette of RS 56/2010, 93/2019, 39/2021, 65/2024).

To ensure the safe disposal of the solid residue, an additional treatment of the investigated solid residue was carried out using a stabilization process. Stabilization is a physicochemical procedure in which contaminated solid material is transformed so that hazardous components

are converted into less mobile, less soluble, or less toxic forms. The process involves mixing the waste with binders (cement, fly ash, cement kiln dust, lime, etc.), where, in the presence of water, a hydrated matrix is formed, the pH value increases, and metal precipitation is promoted, resulting in their immobilization [20,21]. In this paper, quicklime (CaO) was chosen as the stabilization agent due to its affordability and high efficiency. Calcium from the lime acts as a flocculant and a source of alkalinity, reduces moisture content upon contact with water, disinfects the material through an exothermic reaction, prevents unpleasant odors, neutralizes acidity, and immobilizes metals such as Pb, Zn, Fe, Ni, and Cr into insoluble forms. Additionally, the reaction of calcium with silicon and aluminum oxides forms stable compounds that additionally encapsulate pollutants [20].

Since the solid residue obtained by the two-step leaching process was characterized as waste that cannot be disposed of in a landfill without additional treatment, experimental investigations of the stabilization process were conducted. These experiments involved mixing the wet solid residue (with a moisture content of 17%) with 5, 6, 7.5, and 10 wt.% lime. To assess the impact of the stabilized solid residue on the environment and human health, LP and TCLP tests were performed after each conducted experiment.

RESULTS AND DISCUSSION

Characterization of the solid residue obtained after the applied two-step hydrometallurgical treatment of EAF dust

As part of the physical characterization, the moisture content of the solid residue obtained after the applied hydrometallurgical treatment of EAF dust was determined to be 17.0%, while the measured pH value of the solid residue was 3.54. The results of the chemical characterization of the solid residue obtained after the applied hydrometallurgical treatment of EAF dust are presented in Table 1.

Table 1 Chemical composition of the solid residue obtained after the applied two-step hydrometallurgical treatment of EAF dust

Element	Content, %	Method	Element	Content, %	Method
Zn	8.01	V	Sn	0.0817	ICP-AES
Fe	38.90	AAS	Cd	0.0350	ICP-AES
Pb	3.80	ICP-AES	K	0.1623	ICP-AES
Na	0.15	ICP-AES	Cu	0.0950	ICP-AES
Ca	4.32	ICP-AES	Ni	0.0187	ICP-AES
Mn	2.24	ICP-AES	Cl	0.0075	SF
Si	0.96	XRF	F	0.0001	ISE
S	3.50	CSA	Cr	0.4917	ICP-AES
C	9.60	CSA	As	0.0048	ICP-AES

Considering the content of components in the solid residue, shown in Table 1, it can be further treated for the recovery of other valuable metals, such as lead [7,22–24]. In addition, the solid residue obtained after zinc recovery can be used in other industries [3,7,17,25,26].

However, if the utilization of the resulting solid residue is not foreseen in further planned activities, it may be disposed of in an appropriate landfill, following prior waste classification in accordance with applicable regulations.

Environmental impact assessment and solid residue stabilization

The results of the leachability test of the solid residue obtained after two-step leaching (Table 2) indicate elevated concentrations of cadmium, lead, zinc and sulfates in the LP eluate and lower pH value, which exceed the permitted limit values for disposal at non-hazardous and hazardous waste landfills. These findings confirm that additional treatment of solid residue is necessary prior to final disposal.

Table 2 Leachability tests – LP tests of the solid residue before and after the stabilization process

Parameter	Unit	Measured value					Reference value for inert waste ¹⁾	Reference value for non-hazardous waste ²⁾	Reference value for hazardous waste ³⁾
		Solid residue	Stabilized with 5 wt.% CaO	Stabilized with 6 wt.% CaO	Stabilized with 7.5 wt.% CaO	Stabilized with 10 wt.% CaO			
pH	-	4.89	8.07	10.22	10.98	11.67	-	6–13⁴⁾	-
Conductivity	μS/cm	3499	2482	2417	2821	3759	-	-	-
Antimony, Sb	mg/kg dm	0.07	0.07	<0.06	<0.06	<0.06	0.06	0.7	5
Arsenic, As	mg/kg dm	<0.20	<0.20	<0.20	<0.20	<0.20	0.5	2	25
Barium, Ba	mg/kg dm	0.28	1.9	1.4	1.90	0.44	20	100	300
Copper, Cu	mg/kg dm	12	<0.05	<0.05	<0.05	25	2	50	100
Cadmium, Cd	mg/kg dm	11	<0.04	0.04	<0.04	<0.04	0.04	1	5
Molybdenum, Mo	mg/kg dm	<0.07	1.1	1.5	1.9	3.5	0.5	10	30
Nickel, Ni	mg/kg dm	0.85	<0.07	<0.07	0.51	0.34	0.4	10	40
Lead, Pb	mg/kg dm	118	0.40	5.1	41	100	0.5	10	50
Selenium, Se	mg/kg dm	0.16	0.29	0.40	0.40	0.31	0.1	0.5	7
Chromium, Cr	mg/kg dm	0.13	<0.05	<0.05	0.05	0.14	0.5	10	70
Zinc, Zn	mg/kg dm	5578	7.8	22	2.8	21	4	50	200
Mercury, Hg	mg/kg dm	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.01	0.2	2
SO₄²⁻	mg/kg dm	28310	16210	19686.8	14420	13970	1000	20000	50000
Cl ⁻	mg/kg dm	125.9	66.5	75.7	94.9	110.5	800	15000	25000
F ⁻	mg/kg dm	14	19	34	36	35	10	150	500

^{1), 2), 3)} Annex 10 of the Regulation on Categories, Testing, and Classification of Waste (Official Gazette of RS 56/2010, 93/2019, 39/2021, 65/2024), Article 2, Parameters for testing waste and landfill leachates from inert¹⁾, non-hazardous²⁾, and hazardous³⁾ waste. Ambient temperature 21 °C, humidity 52%, pressure 970 hPa.

⁴⁾ Reference value for pH according to the Regulation 56/2010, 93/2019, 39/2021, 65/2024, Annex 7, H15 – Waste that has the property to generate, by any means after disposal, another substance, e.g., leachate exhibiting any of the listed characteristics (H1–H14), ranges from 6 to 13.

The increased concentrations of cadmium, zinc and sulfates are likely a consequence of insufficient washing of the solid residue with water after the two-step leaching process, resulting in a portion of the pregnant leaching solution remaining trapped within the material. Additional washing could contribute to reducing their concentrations. Furthermore, the

measured pH value is below the prescribed limit values, which could also be corrected by additional washing of the solid residue with water. Based on the results of the TCLP test (Table 3), the solid residue after the second step of leaching – acid leaching, is classified as waste that cannot be disposed of, as it exhibits toxic properties due to elevated concentrations of cadmium and zinc in the eluate.

Considering the potentially harmful impact on the environment and human health, as confirmed by the results of both tests, it is clear that appropriate treatment of the solid residue is necessary prior to its final disposal in a landfill. To this end, in this paper, investigations of its chemical stabilization with the addition of lime (5–10 wt.%) were carried out.

The results of testing the toxic characteristics of the solid residue intended for disposal, before and after the implemented stabilization processes with the addition of lime at 5, 6, 7.5, and 10 wt.%, are presented in Table 3.

Table 3 Toxic characteristics – TCLP tests of the solid residue before and after the stabilization process

Element	Unit	Measured value					Reference value for waste toxicity ¹⁾
		Solid residue	Stabilized with 5 wt.% CaO	Stabilized with 6 wt.% CaO	Stabilized with 7.5 wt.% CaO	Stabilized with 10 wt.% CaO	
Antimony, Sb	mg/l	<0.006	0.038	<0.006	0.032	0.033	15
Arsenic, As	mg/l	<0.020	<0.020	<0.020	<0.020	<0.020	5
Barium, Ba	mg/l	0.018	0.16	0.068	0.095	0.098	100
Copper, Cu	mg/l	2.5	0.007	0.011	0.040	0.044	25
Cadmium, Cd	mg/l	2.2	0.79	0.40	0.16	0.050	1
Molybdenum, Mo	mg/l	<0.007	0.014	0.007	0.068	0.093	350
Nickel, Ni	mg/l	0.17	0.061	0.077	<0.007	<0.007	20
Lead, Pb	mg/l	2.4	2.2	0.76	1.4	0.40	5
Selenium, Se	mg/l	0.015	0.018	0.005	0.010	0.008	1
Chromium, Cr	mg/l	<0.005	<0.005	<0.005	0.008	0.010	5
Zinc, Zn	mg/l	1141.7	306.1	228.8	107.7	38.7	250
Mercury, Hg	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.2
Vanadium, V	mg/l	<0.007	<0.007	<0.007	<0.007	<0.007	24
Silver, Ag	mg/l	<0.005	<0.005	0.005	<0.005	<0.005	5

¹⁾Annex 10 of the Rulebook on Categories, Testing and Classification of Waste (Official Gazette RS 56/2010, 93/2019, 39/2021, 65/2024), Article 1, Parameters for testing the toxic characteristics of waste intended for disposal.

The results of the LP and TCLP tests indicate that the efficiency of the solid residue stabilization process significantly depends on the amount of added lime and the achieved pH value. With the addition of 5 wt.% lime, the LP test confirmed successful metal immobilization, as the concentrations of all elements were below the limit values for non-hazardous waste at a basic environment of pH≈8. However, the TCLP test revealed toxic characteristics due to an increased concentration of zinc, which can be explained by a

decrease in the pH value during the application of the extraction reagent and the subsequent dissolution of this metal.

With the addition of 7.5 wt.% lime, the TCLP test results did not indicate toxic characteristics of the stabilized solid residue, whereas the LP test results showed an increased concentration of lead above the permitted values for non-hazardous waste. The higher pH value (pH $\approx$ 10.98) favored the formation of soluble lead compounds and its transfer to the eluate. A similar trend was observed with the addition of 10 wt.% lime, where the TCLP test again showed no toxicity, but the LP test recorded even greater lead leaching (pH $\approx$ 11.67), even above the limits for hazardous waste disposal. These results confirm that a strongly basic environment increases the mobility of lead.

Remeteiová et al. [27] and Montenegro et al. [24] report in their studies that during the water leaching of EAF dust at pH values in the range of 6.5–11.0, approximately 53% of calcium is leached. The authors further note that at pH values above 11, leached calcium precipitates as hydroxide; however, under these conditions, the dissolution of lead compounds also occurs, resulting in the transition of lead into the solution. Considering that in this paper the LP tests were conducted using water as a reagent, and the use of lime for stabilization achieved a pH of the leaching solution of almost 11 (10.98 when stabilized with 7.5 wt.% lime) and above 11 (11.67 when stabilized with 10 wt.% lime), lead concentrations in the eluates exceeding the permissible limit for waste disposal can be attributed to those conditions.

The optimal results were achieved with the addition of 6 wt.% lime, where both the LP and TCLP tests showed that the concentrations of all elements were below the prescribed limit values, without showing any toxic characteristics. This confirms that the addition of 6 wt.% lime provides effective metal immobilization and enables safe disposal of the stabilized solid residue at the non-hazardous waste landfill.

CONCLUSION

Based on the results obtained in this paper, it can be concluded that the solid residue obtained after the two-step hydrometallurgical treatment of EAF dust, and due to elevated concentrations of heavy metals as determined by LP and TCLP tests, is classified as hazardous waste and does not meet the conditions for safe disposal, and therefore requires additional treatment.

The application of the stabilization process with the addition of lime proved to be an effective method for reduce the mobility and toxicity of metals from the investigated solid residue, where it was determined that the effectiveness of the process significantly depends on the amount of added stabilization agent and the pH value. At both lower and higher lime contents, undesirable effects were observed, such as the remobilization of certain metals (zinc at lower pH and lead at higher pH values).

According to the results of the LP and TCLP tests, the optimal stabilization conditions in the paper were achieved with the addition of 6 wt.% lime, when the concentrations of all analyzed elements in the eluate were below the prescribed limit values, without exhibiting any toxic characteristics. This allows for effective metal immobilization and the classification of

the waste as non-hazardous, thereby creating conditions for its safe disposal in a non-hazardous waste landfill. The obtained results indicate that the application of the stabilization process represents a reliable and economically acceptable solution for managing the solid residue obtained after the two-step hydrometallurgical treatment of EAF dust.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Science, Technological Development and Innovation of the Republic of Serbia for financial support according to the contracts with registration No. 451-03-33/2026-03/200052 and 451-03-34/2026-03/200131.

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