

NEUTRALIZATION OF WASTE FILTER DUST WITH CO₂ NEVTRALIZACIJA ODPADNEGA FILTRSKEGA PRAHU S CO₂

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In this paper we report on the possibility of neutralizing filter dust from Talum Livarna d.o.o. The filter dust that remains after cleaning flue gas with the classification number of waste 10 10 09* is alkaline and contains heavy metals, non-metals, organic pollutants, and, therefore, has the properties of hazardous waste. The possibility of neutralizing this dust with CO₂ was studied. The results showed that the treatment successfully lowered the pH value between the limits 6 and 9, which is within the legal constraints of pollution for strong acidic or alkaline waste. The contents of the hazardous substances were lowered, i.e., As, Cu, Ba, Zn, Cd, Cr, Ni, Pb, Sn, Mn and V, with percolation values that are below the level of the prescribed threshold-limit values for substances that allows their disposal in non-hazardous waste landfills. Only the percolation values of Sb, Cd, Mo and Se exceed the prescribed threshold limit values of substances that allow their disposal in inert waste landfills. The XRD analysis after the neutralization of the filter dust using CO₂ showed no presence of CaO. The neutralized filter dust can be land filled as a stabilized and unreactive waste in landfills for nonhazardous wastes. Their properties also offer the possibility for incorporating them into some other material or product, such as the production of new composite materials, their use in construction products and perhaps cements or usage in backfills.

Keywords: hazardous waste, filter dust, neutralization, stabilization, chemical properties

Raziskali smo možnost nevtralizacije filtrskega prahu iz podjetja Talum Livarna, d. o. o. Filtrski prah po čiščenju dimnih plinov s klasifikacijsko številko odpadka 10 10 09* je alkalen, vsebuje težke kovine, nekovine, organska onesnaževala, zato ima lastnosti nevarnega odpadka. Filtrski prah smo nevtralizirali s CO₂, da je nastal pretežno amorfen produkt. Po obdelavi smo uspešno znižali pH-vrednost v mejo med 6 in 9, kar je v dovoljenem območju za odpadke, onesnažene z močno kislino ali bazo. Prav tako je bila zmanjšana vsebnost nevarnih snovi, in sicer As, Cu, Ba, Zn, Cd, Cr, Ni, Pb, Sn, Mn in V, tako da so izluževalne vrednosti pod mejo predpisanih parametrov izlužka in je tako dovoljeno odlaganje na odlagališčih za nenevarne odpadke. Samo izluževalne vrednosti Sb, Cd, Mo in Se še prekoračujejo predpisane mejne vrednosti, ki so dovoljene za odlaganje na odlagališčih za inertne odpadke. XRD-analiza po nevtralizaciji filtrskega prahu s CO₂ ni pokazala prisotnosti CaO. Nevtraliziran filtrski prah se lahko odloži kot stabiliziran in nereaktiven odpadke na odlagališčih nenevarnih odpadkov. Glede na lastnosti obstaja možnost predelave in uporabe v koristne namene, npr. za proizvodnjo novih kompozitnih materialov, gradbenih izdelkov, morda cementa ali za zasipavanje.

Ključne besede: nevarni odpadki, filtrski prah, nevtralizacija, stabilizacija, kemijske lastnosti

1 INTRODUCTION

Hazardous wastes are a problem of modern civilization and therefore need to be handled in a prudent manner. A rapid increase in their amount, negative effects on the environment and a growing environmental awareness have led to changes in the field of waste management in recent decades. These factors have contributed to stricter regulations and the development of new technical and operational solutions.^{1,2} The strategy of waste management in Slovenia is directed towards actions that enable the overseeing, removal and reduction of the harmful effects of these wastes on the environment and humans, as well as their preparation for reuse, recycle and use as an energy source.²

The metallurgical industry is a major source of potentially hazardous waste materials, those by-products of the production of metals and alloys. These metallurgical wastes consist mainly of slags and dust sludges that result from flue-gas filtering. These so-called waste materials can be potentially utilized as resources, for

example, dust from the EAF process can be used as a source of Zn,^{3,4} metallurgical slags can be used in the production of building materials.⁵ A special aspect of the steel industry that requires particular attention is the production of stainless steel. During stainless-steel production, chromium oxidation occurs, which leads to the formation of CrO_x phases. They not only represent a loss from the production point of view,⁶⁻⁸ but also represent an environmental risk, because they can oxidize to dangerous hexavalent chromium (Cr⁶⁺).⁹ During the melting of secondary aluminium contaminated with oil, paint or plastic flue gases that contain dust contaminated with heavy metals, nonmetals, dioxins, furans and fluorides.¹⁰

Waste filter dust is formed inside the exhaust gas treatment apparatus of foundry furnaces during operation with help of an additive DESOMIX HK. The additive DESOMIX HK is a mixture of calcium hydroxide [Ca(OH)₂] and active chalk. Filter dust is classified as a hazardous waste with a classification number 10 10 09*, which puts it as far as regulation is concerned¹ amongst the group of dusts that contain dangerous substances.

The filter dusts are homogenous, alkaline, contain heavy metals, nonmetals, dioxins, furans and fluorides. Because the limit values of these toxic substances are exceeded during leaching, it is determined that these dusts have the properties of hazardous waste. Therefore, it has to be deposited in accordance with the relevant regulations.² Industrial wastes are deposited in subterranean depots, usually prepared in closed coal and ore mines.¹¹

There are many waste substances that react with carbon dioxide, for example, metallurgic slags, dusts from industrial thermal processes, combustion remains in which calcium oxide is a key component. The reaction between calcium hydroxide [Ca(OH)₂] and carbon dioxide (CO₂) is called carbonization. It is a natural reaction between an oxide or a base and CO₂.^{12,13} Direct binding between CO₂ and calcium hydroxide is slow. However, it can be accelerated with the addition of water. In such cases the CO₂ dissolves in water and dissociates and reacts with the dissolved and dissociated calcium hydroxide, therefore forming carbonate materials.^{12,13} During the formation of these carbonate materials the pH of the waste dust decreases, which results in the minimal solubility of the metals present in the waste dust.¹²⁻¹⁴ Complete carbonization can decrease the leaching of metals by 80%.¹⁴⁻¹⁶ Previous research¹⁴⁻²⁸ has shown that metal stabilization processes are more efficient if the treatment of the waste dust is conducted over an extended period of time and at high CO₂ concentrations.

The main goal of this research was to determine whether it is possible to obtain a chemically stable product from waste filter dust with the process of neutralization using CO₂. This would also enable this material to be reused in some other useful application or at least to process it enough so that long-term monitored deposition would be possible according to Slovenian regulations.² Should the treated waste powder leaching values be inside the legal constraints for nonhazardous waste there would be a possibility that this waste could be deposited as a cost-reducing measure in dumps for nonhazardous waste. If it could achieve the constraints for inert waste it could be reused for practical purposes, for example, the production of new composite materials, use in construction materials, perhaps in cements or use in landfills.

2 EXPERIMENTAL

Filter dust, a by-product of the treatment of exhaust gases, is classified as a hazardous waste with the classification number 10 10 09*. The analyzed sample comes from the release of a exhaust-gas treatment apparatus filter L9 in the company Talum Livarna, d. o. o.

The granulometric composition of the filter dust and the average particle size was determined with a device for laser-diffraction particle size analysis Cilas 1064. A qualitative analysis of the sample microstructure was facilitated using a high-resolution Scanning Electron

Microscope SIRION NC 400, equipped with NICA brand EDS detector. The X-ray analysis was conducted using a Philips XRD-analyzer W1800 hardware and X'pert High Score software.

2.1 Neutralization of the filter dust with CO₂

The first step in this research was the determination of the initial pH of the leachate of the filter dust sample originating from Talum Livarna, d. o. o. Three samples with different moisture contents were prepared:

- 11 % moisture content (sample label NFP1).
- 8 % moisture content (sample label NFP2)
- 14 % moisture content (sample label NFP3).

The moisturized samples were stirred using a glass rod, which helped to achieve a uniform water consistency of the sample. A Rushton mixer and a supply tube for the CO₂ were placed inside a glass beaker. The samples were exposed to a flow of 10 L/min of CO₂ for a period of 1 h.

The leaching and neutralization of the waste filter dust were carried out in accordance with the standard SIST EN 12457 – 4 (24 h leaching with water; ratio water/solid was 10/1). This was followed by a measurement of the pH and the leached inorganic parameters (metals) with help of the ICP-MS method. The ICP-MS device ionizes the sample with an inductively coupled plasma of argon gas. The ionized particles of the sample are then directed into a mass spectrometer. With the help of the ICP the presence of the following elements could be determined: Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Se, Sn, Sr, Zn, B, Be, Mo, Tl, V.

3 RESULTS AND DISCUSSION

3.1 Analysis of waste filter dust

With the aid of laser diffraction we determined that the sizes of the filter particles range from 0.47 μm to 47.30 μm. Some 20 % of the particles are in the size range between 0.47 μm and 10 μm, while the remaining

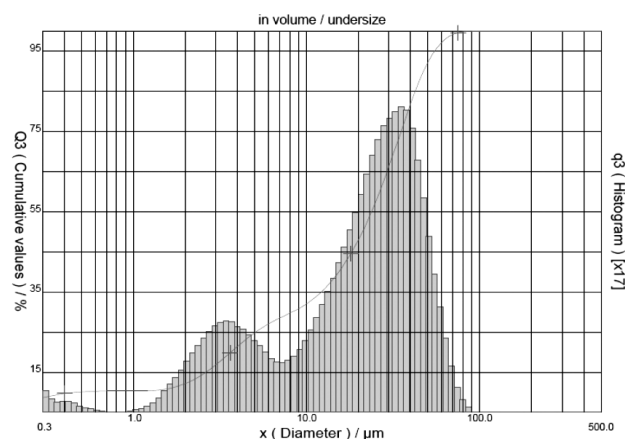


Figure 1: Size of the filter particulates
Slika 1: Velikost delcev filtrskega prahu

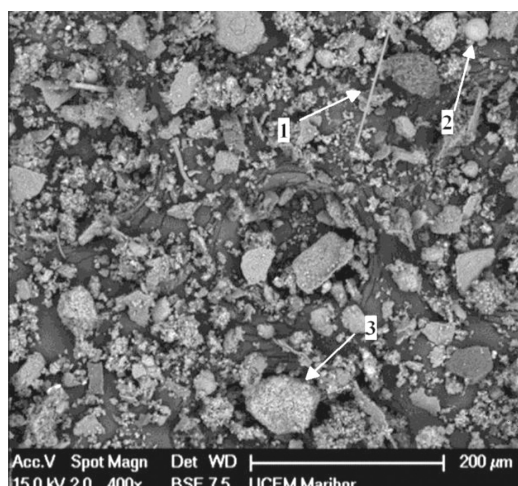


Figure 2: SEM analysis of filter dust: 1-rod-shaped particle, 2-spherical particle, 3-asymmetrical particle

Slika 2: SEM-analiza filtrskega prahu: 1-paličast delec, 2-sferičen delec, 3-asimetričen delec

80 % fall between 10 µm and 47.30 µm. **Figure 1** shows the size of filter particulates.

The SEM analysis of the sample dust showed that the morphology of the sample is not uniform. The particles were of different shapes, i.e., rod-shaped, spherical and asymmetrical (**Figure 2**). The particles also differed according to the chemical composition. The EDS analysis of the sample dust showed asymmetrical particles that had peaks for the elements: O, Al, Ca and Zn. The rod-shaped particles had peaks for the elements: O, Na, Mg, Al, Si, K and Ca. The spherical shaped had peaks for the elements: O, Si, Ti, Mg, Zn, Al, Si, Ca in K. Recurring elements with in all shapes were elements: O, Al and Ca.

The results of the chemical analysis of the waste filter dust are presented in **Table 1**.

Table 1: Levels of measured parameters in the filter dust

Tabela 1: Vsebnost izmerjenih parametrov v filtrskem prahu

Parameter	Amount in the s. s. sample, mg/kg
Al	2.1
Sb	45.1
As	10.0
Cu	540.2
Ba	3225.3
Zn	2501.6
Cd	24.7
Cr	154.7
Mo	15.4
Ni	128.0
Pb	282.3
Se	20.2
Co	2.1
Sn	130.9
Mn	130.3
Tl	0.6
V	15.4

The chemical analysis also revealed that the samples contained 3.5 % of moisture.

3.2 Filter-dust leachate analysis

The filter dust leachate contains high levels of heavy metals, such as: Sb, Cu, Ba, Cd, Mo, Ni, Se. It contains chlorides and fluorides. Present are also As, Zn, Cr, Pb, Co, Sn, Mn, Tl and V (**Table 2**). In the presence of water these chemical elements could leach into the soil and damage the environment, if the waste dust were to be deposited freely. It can be seen by observing **Table 2** that some quantities of leached heavy metals exceed the limiting values for dumping on sites equipped to handle inert waste. The leachate of filter dust has a highly alkaline pH value of 12.71. The data shows that the waste filter dust is of a heterogeneous composition and that it presents a hazard to the environment and it could have a great impact on the chemical and ecological balance, if not deposited correctly.

3.3 Analysis of filter-dust leachate neutralized with CO₂

The aim of the neutralization experiment with CO₂ was to evaluate the reduction of the pH values and the inorganic parameters and to attain, if it is possible, a chemically stable product that could be safely and harmlessly stored or deposited. The results show that the pH values could be reduced with this process, as shown in **Figure 3**.

The leachate pH values for the samples NFP1, NFP2 and NFP3 were monitored for a period of 32 d. The chemical stability of the neutralized samples was satisfactory and the pH values were between 6 and 9. The attained pH values confirm that the waste is not contaminated with a strong acid or base. Because of the leachate exposure to CO₂ found in the surrounding air, metal

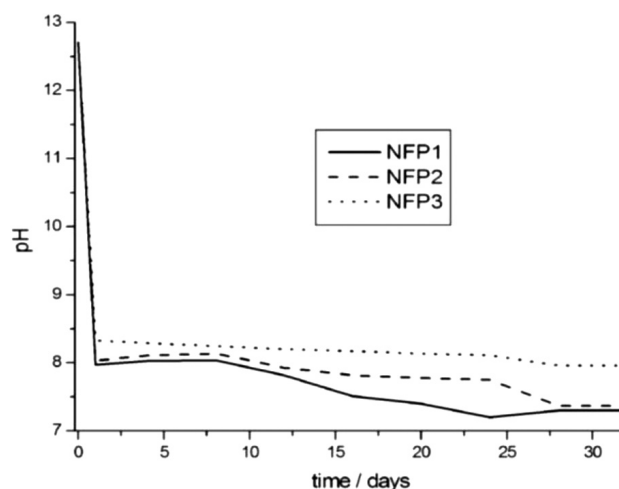


Figure 3: Filter dust leachate pH values of samples NFP1, NFP2, NFP3

Slika 3: pH-vrednosti izlučkov vzorcev NFP1, NFP2 in NFP3

Table 2: Leachate results for chosen parameters in the samples NFP1, NFP2, NFP3 and filter dust – compared to limiting legal constraints
Tabela 2: Vrednosti izluževanja nevarnih snovi vzorca NFP1, NFP2, NFP3 in filtrskega prahu - primerjava z zakonodajnimi vrednostmi

Parameter	Filter dust leachate result mg/kg	CO ₂ NFP1 neutralized filter dust leachate result mg/kg	CO ₂ NFP2 neutralized filter dust leachate result mg/kg	CO ₂ NFP3 neutralized filter dust leachate result mg/kg	Limiting legal constraint of a parameter L/S = 10 L/kg (mg/kg)		
					Inert waste	Hazardous waste	Non-hazardous waste
Sb	0.26	0.34	0.26	0.31	0.06	5	0.7
As	0.01	0.01	0.01	0.01	0.5	25	2
Cu	2.63	12.99	1.95	0.38	2	100	50
Ba	73.17	5.19	4.71	4.86	20	300	100
Zn	3.41	0.77	0.38	0.37	4	200	50
Cd	0.18	0.21	0.11	0.11	0.04	5	1
Cr	0.01	0	0	0	0.5	70	10
Mo	0.49	0.77	0.73	0.65	0.5	30	10
Ni	0.44	0.20	0.15	0.11	0.4	40	10
Pb	0	0.05	0.01	0.04	0.5	50	10
Se	0.19	0.36	0.28	0.28	0.1	7	0.5
Co	0	0.01	0	0			
Sn	0.05	0.01	0.01	0.01			
Mn	3.73	1.92	1.57	1.51			
Tl	0	0.04	0.03	0.02			
V	1.00	0.31	0.23	0.10			

oxides bound to CO₂ and there was an additional drop in the pH over a period of 32 d. In sample NFP1 the initial pH was 12.71, while after neutralization it dropped to 7.97, and after a period of 32 days it was measured at 7.30.

Table 2 presents the leaching results for the chosen leachate parameters of the samples NFP1, NFP2, NFP3 and the waste filter dust, compared to environmental legal constraints. The neutralization reduced the leachate values of the As, Cu, Ba, Zn, Cr, Ni, Pb, Sn, Mn and V to a level that could enable this waste to be deposited as non-hazardous waste. The leachate values for the Sb, Cd, Mo and Se remained too high for this waste to be deposited as inert waste. The highest heavy-metal reduction occurred in sample NFP3 with 14 % moisture. This proves that the reaction of the carbonization is the fastest and most successful when the moisture is high and there is a lot of water present. During the neutralization waste filter dust in samples NFP1, NFP2 and NFP3 CO₂ underwent a chemical reaction and bound to calcium hydroxide [Ca(OH)₂] in the presence of moisture. The carbonate CaCO₃ was formed. An XRD analysis showed no presence of CaO in any of the samples, which indicates that the carbonization was complete. The formed carbonates are less soluble and less alkaline than the oxides and hydroxides found in the filter dust.

4 CONCLUSIONS

Neutralization helped to transform a hazardous waste into a non-hazardous waste, which could be deposited on sites for non-hazardous waste. CO₂ neutralization presents a viable technological solution for the stabilization

of waste filter dust. The neutralized dust could be used as a bulk material.

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