Original Research

Researching the Hazardous Potential of Metallurgical Solid Wastes

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Abstract

The purpose of our paper is to assess the hazardous potential of metallurgical solid wastes stored in a slag dump. We present the experimental procedures for determining chemical composition and for the leaching test of the 10 waste samples taken from the slag dump. According to the data obtained, in the composition of metallurgical solid wastes we identified the following compounds: manganese oxide (MnO), titanium dioxide (TiO₂), silica (SiO₂), total iron (Fe₉₀), alumina (Al₂O₃), lime (CaO), magnesia (MgO), lead oxide (PbO), zinc oxide (ZnO), chromium trioxide (Cr₂O₃), vanadium pentoxide (V₂O₅), and phosphorus pentoxide (P₂O₅). According to the leaching test, metallurgical solid wastes contain several heavy metals that can potentially be hazardous for all environmental factors (soil, water, and air). The content of hazardous heavy metals in the metallurgical wastes varies within the following limits: As (0.311-0.614 mg/L), Cr (0.192-2.514 mg/L), Mo (0.113-0.624 mg/L), Cd (0.104-0.479 mg/L), Pb (0.112-0.869 mg/L), Ni (0.112-3.212 mg/L), Zn (0.173-3.313 mg/L), and Hg (0.037-0.079 mg/L). From the point of view of the arsenic and mercury concentrations, the 10 samples of solid metallurgical wastes exceed the limit values for hazardous wastes.

Keywords: metallurgical wastes, waste characterization, pollution, slag dump, heavy metals

Introduction

According to the U.S. Environmental Protection Agency [4] and Council Directive 91/689/EEC [5], hazardous waste is a solid waste, or combination of solid wastes, which due to its quantity, concentration, or physical, chemical, or infectious characteristics may either cause or significantly contribute to an increase in mortality or an increase in serious irreversible or incapacitating reversible illness; or pose a substantial actual or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

The metallurgical industry produces significant amounts of waste, and this entails a constant risk for the environment and people. The types of metallurgical solid waste are: metallurgical slag and dust, sludge from the wet
detruding of burned gases, and melting loss. Metallurgical wastes contain various hazardous compounds that can be harmful to people and their environment [6-10].

The total quantity of metallurgical solid wastes continues to grow. The storage of these wastes involves occupying large areas of land, the contamination potential of all environmental factors (air, water, and soil), expenses related to land storage, monitoring of all environmental factors near the dump, and adverse effects on human health [11-20].

The environmental hazardous potential of metallurgical wastes is commonly assessed with laboratory leach tests [21] such as the “toxicity characteristic leaching procedure” devised by the U.S. EPA [22]. Chemical measurements are needed to compare the concentrations of hazardous substances present in metallurgical solid wastes with the limit values imposed by the Romanian legislation complying with that in the European Union. In order to be categorized as inert/non-hazardous/hazardous, the metallurgical solid wastes are subject to leaching testing. Romanian legislation establishes criteria and preliminary procedures for waste acceptance in different landfill classes [23].

For the analysis of environmental solid samples, x-ray fluorescence (XRF) has the advantage of being a rapid and inexpensive method with a simple sample preparation. Using this technique, the chemical composition of wastes can be determined in a short time. XRF is characterized by good selectivity and low detectability limit of ppm-pb [24, 25].

Atomic absorption spectroscopy (AAS) is ideally suited for the analysis of trace and ultra-trace elements. The technique is characterized by high sensitivity and selectivity, low detectability limit, and high precision [24, 26]. The cold vapour atomic absorption spectroscopy (CV-AAS) method for determining mercury in environmental samples is characterized by good recovery and reproducibility [24, 27].

The research conducted in this paper is focused on evaluating the hazardous potential of metallurgical solid wastes, stored in the slag dump, through their chemical characterization and determination of the constituents that can be released from these (leaching behavior). The objective of our paper was to add to information regarding the hazardous potential of metallurgical wastes.

**Experimental Procedures**

The Păgida metallurgical slag dump is located near Păgida village, which belongs to the town of Aiud in Alba County, Romania. Păgida has an area of 22.45 ha and is located 6 km from the town of Aiud. Aiud is located in the depression corridor of the Mureș River at the confluence of the Transylvanian Plain to the northeast and of Târnăvelor Plateau to the southeast, and the Apuseni Mountains to the west. Aiud is crossed by the meridian 23°10 west latitude and by the parallel 46°10 north latitude.

The slag dump has a surface of 26,193 m² and a storage capacity of 240,000 m³. The types of wastes stored at the slag dump include metallurgical slag from steelmaking in the electric arc furnaces, refractory materials from the electric arc furnaces, acid and basic lining from the electric arc furnaces, foundry waste sands, casting cores, and molds.

The solid wastes landfilled to the dump are generated by the Steel Casting Division of the S.C. Metalurgica Transilvană metallurgical plant in Aiud, Romania. The metallurgical plant has the following divisions: Steel Casting with a total surface of 20,881 m² distributed in two buildings (one for casting, 14,164 m², and the other for cleaning, sanding, and storing parts and frames 6,717 m²); Heat Treatment at 4,651 m², with three horizontal furnaces for heat treatments, three vertical furnaces for heat treatments, and a high-frequency annealing machine; and Heavy Forge at 8,453 m², with five methane gas furnaces, forging presses, and pneumatic hammers.

The Steel Casting Division is used for the technological operations of liquid steelmaking, molding, and casting. It is equipped with three furnaces having capacities of 30, 10, and 3 tons (for stainless steelmaking). The types of steels made here are non-alloy casting steels, alloy steels, and carbon steels.

The raw materials used in the steelmaking process from which the solid wastes samples originate are old scrap and metallic wastes. The auxiliary materials used in this process are: oxidants (technical gaseous oxygen (O₂) and iron ore), fondants (lime (CaO)), fluidizing materials (fluorine (CaF₂), deoxidizer or ferroalloys (FeMn, FeCr, FeNi, FeMo, FeSi, FeV, FeAl, FeSi, SiCa), fuels (petrol coke, electrodes scraps), and alloying elements (Al, Mo, Cr, V, Ti).

The casts and ingots are made using pots fitted with argon bubbling devices.

The cleaning division is used for the cleansing and basic heat treatment operations. The debate operation is performed manually. The metal scraps are recovered and reintroduced into the technological process, and the remaining resulting waste (foundry waste sands) is transported and landfilled in a slag dump.

The analyzed waste samples were taken in 2013 from Păgida metallurgical slag dump. Fig. 1 shows the 10 sampling points of the metallurgical solid wastes. The waste samples were collected from 10 points close to the edge of the slag dump because the middle area was not very stable. The sampling points form a close curve around the slag dump. These sampling points were chosen so that the samples should be as representative as possible; they cover all types of wastes stored in this slag dump; they are approximately equally distributed around the slag dump and have samples from all the areas of the slag dump. The sampling points were recorded using GPS.

For a better representation, the samples consist of a mixture of solid wastes taken from a circle with a radius of 10 m around each of the 10 sampling points. Each sample consists of eight subsamples of solid wastes. Eight sub sampling points represent the north, northeast, east, southeast, south, southwest, west, and northwest directions.
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The selection of the research methods is based on the following considerations:

- XRF provides a rapid and non-destructive method for analyzing trace and major elements in environmental solid samples. The method is characterized by good selectivity and a low detectability limit of ppm-ppb [24, 25].
- Using AAS more than 50 metals and metalloids can be analyzed down to the trace and ultra-trace ranges. The significant advantages of AAS are its high selectivity and detection sensitivity, low detectability limit, and accurate and rapid determinations. AAS methods are suitable for monitoring the levels of heavy metals in environmental samples [24, 26].
- Cold vapour atomic absorption spectroscopy is extremely sensitive for mercury determination. CV AAS is used for mercury trace analysis because of its excellent detection limits and relative lack of interference [24, 27].

The instrumentation used for sample preparation included Kern Balances (Kern & Sohns, Germany), Retsch sieving shaker AS200 (Retsch GmbH, Germany) with mesh size of 4 mm, Sartorius vacuum filtration unit 0.45 μm pore size filters (Sartorius Stedim Biotech SA, Germany), and Hettich Universal 320 centrifuge (Hettich, Germany).

The chemical compositions of the 10 waste samples were analyzed by the XRF technique using XRF-Spectro X-LAB 2000 equipment.

The metallurgical solid waste was sieved with a grain size below 4 mm.

The work procedure for the leaching test was made according to the standard SR EN 12457-1/2003 [28]. The leaching test standard refers to a liquid / dry solid ratio of 2 l/kg dry solid. Distilled water was used throughout the experiment. For implementing this test we took the following steps: preparation of the solid waste samples for testing; contact between the solid wastes samples and the aqueous solution (the optimum contact time is about 24 hours at 20ºC; the capped bottle was agitated at about 10 rpm for 24 h at 20ºC); the separation of the solid material from aqueous solution (leachate; the decantation time was 15 min and the mixture was centrifuged and filtered through 0.45 μm); and the chemical characterization of the leachate in order to identify the heavy metals.

The work procedure was made according to SR EN 16192:2012 [29]. The chemical composition of the leachate was established with the help of atomic absorption spectrometry, using an atomic absorption spectrometer SOLLAR S4. The mercury was determined by cold vapor atomic absorption using the EPA method [30]. The concentrations of metals obtained through the leaching test were compared with those mentioned in the reference [23].

Results and Discussion

Table 1 summarizes the chemical compositions of the 10 samples taken from the waste slag dump and analyzed by XRF. By analyzing the chemical composition of the 10 samples we found in all samples the presence of the following compounds: manganese oxide (MnO), silica dioxide (SiO₂), total iron (Fe₉₀₅), alumina (Al₂O₃), and calcium oxide (CaO); titanium dioxide (TiO₂) was identified in waste samples 1, 7, 8, and 9, having percentages between 0.1 and 0.41%; magnesia (MgO)
Iluțiu-Varvara D.-A. was identified in waste samples 1, 3, 4, 5, 7, and 9, having percentages between 2.5 and 15.5%; lead oxide (PbO) was identified in waste samples 1, 2, 4, 6, 7, and 10, having percentages between 0.6-2.1%; zinc oxide (ZnO) was identified in waste samples 1, 2, 5, 6, 7, 9, and 10, having percentages between 0.6-7.1%; chromium trioxide (Cr2O3) was identified in waste samples 2, 3, 4, 5, 7, 8, and 9, having percentages between 0.6-3.3%; vanadium pentoxide (V2O5) was identified in waste samples 3 and 9, having percentages between 0.4-0.54%; phosphorus pentoxide (P2O5) was identified in waste samples 1, 2, 3, and 9, having percentages between 0.23-0.42%.

The chemical composition of the wastes varies from sample to sample. The predominant chemical compounds in the composition of the analyzed wastes are: SiO2, CaO, and Fe_total. In the analyzed solid waste composition there are oxides of heavy metals, which have a negative impact on the environment and human health.

Table 2 presents the concentration of metals obtained through the leaching test and the permissible concentrations according to environmental legislation in force [23]. Analysis of the data presented in Table 2 shows:

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Concentration of elements [mg/L]</th>
<th>Limit values for inert wastes [mg/L]</th>
<th>Limit values for hazardous wastes [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
<td>Cr</td>
<td>Mo</td>
</tr>
<tr>
<td>1</td>
<td>0.314xx</td>
<td>0.218x</td>
<td>0.113</td>
</tr>
<tr>
<td>2</td>
<td>0.367xx</td>
<td>0.926x</td>
<td>0.434x</td>
</tr>
<tr>
<td>3</td>
<td>0.498xx</td>
<td>0.414x</td>
<td>0.127</td>
</tr>
<tr>
<td>4</td>
<td>0.359xx</td>
<td>2.514xx</td>
<td>0.129</td>
</tr>
<tr>
<td>5</td>
<td>0.614xx</td>
<td>1.432x</td>
<td>0.151</td>
</tr>
<tr>
<td>6</td>
<td>0.587xx</td>
<td>0.254x</td>
<td>0.624x</td>
</tr>
<tr>
<td>7</td>
<td>0.489xx</td>
<td>0.313x</td>
<td>0.134</td>
</tr>
<tr>
<td>8</td>
<td>0.419xx</td>
<td>0.697x</td>
<td>0.125</td>
</tr>
<tr>
<td>9</td>
<td>0.327xx</td>
<td>0.324x</td>
<td>0.279x</td>
</tr>
<tr>
<td>10</td>
<td>0.311xx</td>
<td>0.192x</td>
<td>0.315x</td>
</tr>
</tbody>
</table>

Legend: x – concentration of the element that exceeds limit value for inert waste (accepted for inert waste landfills)  
xx – concentration of the element that exceeds limit value for hazardous waste (accepted for non-hazardous waste landfills)  
xxx – concentration of the element that exceeds limit value for hazardous waste (accepted for hazardous waste landfills)
The concentrations of the elements analyzed do not exceed the limit values for hazardous wastes (accepted for hazardous waste landfills).

From the point of view of the arsenic and mercury concentrations, the 10 samples of solid metallurgical wastes exceed the limit values for hazardous waste (accepted for non-hazardous waste landfills).

From the point of view of chromium (sample 4), cadmium (samples 6, 7, and 8) and nickel (samples 5 and 7) concentrations, the metallurgical wastes exceed the limit values for hazardous waste (accepted for non-hazardous waste landfills).

From the point of view of chromium (except sample 4), molybdenum (samples 2, 6, 9, and 10), cadmium (samples 1-5, 9, and 10), lead (samples 1, 2, 4, 6, 7, and 10), nickel (samples 1, 4, 8, and 10) and zinc (samples 2, 6, 7, and 9) concentrations, the metallurgical solid wastes exceed the limit values for inert waste (accepted for inert waste landfills).

From the point of view of the molybdenum (samples 1, 3, 4, 5, 7, and 8), lead (samples 3, 5, 8, and 9), nickel (2, 3, 6, and 9) and zinc (samples 1, 3, 4, 5, 8, and 10) concentrations, the metallurgical solid wastes are in the category of inert wastes.

Metallurgical solid waste contains several heavy metals (As, Cr, Mo, Cd, Pb, Ni, Zn, Hg), which can have a hazardous potential for all environmental factors (soil, air, and water) and human health. Because of the hazardous potential of the heavy metals identified in waste samples, it is necessary to investigate the contamination degree of soil, air, and water environmental factors on the slag dump and on its surrounding area.

Conclusions

This is the first published study regarding the hazardous potential of metallurgical solid wastes regarding the Păgida metallurgical slag dump in Romania. In the composition of metallurgical solid waste we identified the presence of the following compounds: MnO, TiO₂, SiO₂, total iron (Fe₅oal), Al₂O₃, CaO, MgO, PbO, ZnO, Cr₂O₃, V₂O₅, and P₂O₅.

According to the leaching test, the concentrations of the elements, identified in the metallurgical solid wastes, varies within the following limits: As (0.311-0.614 mg/L), Cr (0.192-2.514 mg/L), Mo (0.113-0.624 mg/L), Cd (0.104-0.479 mg/L), Pb (0.112-0.869 mg/L), Ni (0.112-3.212 mg/L), Zn (0.173-3.313 mg/L), and Hg (0.037-0.079 mg/L). The metallurgical solid wastes contains several heavy metals that can be potentially hazardous for all environmental factors (soil, water, and air).

The results can be extrapolated to the other metallurgical slag dumps if the wastes meet the following conditions: they originate from steelmaking in the electric arc furnaces; they come from the casting of steels; and they come from making the following types of steel: non-alloy casting steels, alloy steels, and carbon steels.

The metallurgical solid wastes contain amounts of: chromium, manganese, molybdenum, nickel, and vanadium. The presence of these elements is connected with the metallurgical process and the type of produced steel. These elements are the alloying elements that improve the properties of steel. The solid waste also contains zinc, lead, and arsenic. The presence of these elements is often associated with the composition of charge material, to which old scrap and metallic wastes is added.

Acknowledgements

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References


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