

Article

Metallurgical Wastes as Resources for Sustainability of the Steel Industry

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Abstract: The industrial pollution caused by metallurgical waste accumulation has a negative impact on the three environmental factors: soil, air and water. Therefore, the correct management of these wastes would lead to: protection of the environmental factors, the saving of natural resources and sustainability of the steel industry. The purpose of this paper is to assess the chemical and mineralogical compositions of metallurgical wastes landfilled in the Păgida slag dump (Alba County, Romania), for sustainability of the steel industry and metal conservation. The chemical compositions of the two waste samples were analyzed by the XRF (X-ray fluorescence) technique. According to the chemical characterization, magnesium oxide (MgO) has potential to be used as an additional and raw material in the cement industry. The presence of oxides such as CaO, SiO₂, FeO and Al₂O₃ in the compositions of the metallurgical waste samples indicate that they have the potential for use as clinker materials in cement production. The iron and manganese contents from metallurgical wastes can be reused in the iron and steel industry. The presence of V₂O₅ and TiO₂ is connected with the making of stainless steel, and for this reason they have the potential to be reused in the stainless steel industry. The predominant chemical compounds are SiO₂, Fetotal, Cao and MgO. The mineralogical compositions were analyzed by the XRD (X-ray diffraction) technique. The mineralogical compounds presenting reuse potential in different domains are Fayalite, Magnetite, Magnesioferrite and Periclase. The mineralogical compounds from metallurgical wastes can be reused as: raw and/or additional materials in the process from which they originate (steelmaking); raw and/or additional materials in road construction and concrete production; pigments in paints; micronutrients in fertilizers; ore of iron, etc. Then, the theoretical assessments of the recovery potentials of the metals were estimated for slag dumps. Copper (Cu), vanadium (V), molybdenum (Mo) and nickel (Ni) have high recovery potential. The total economic value of the recovery potential of metals from slag dumps was assessed to be USD 1175.7440 million.

Keywords: conservation; metallurgical wastes; metals; mineralogical characterization; recovery potential; slag dump; steel industry; sustainability; X-ray diffraction



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1. Introduction

The metallurgical industry is one of the most significant sources of waste. In the metallurgical industry, the following types of wastes are generated: sintering dust and sludge from the sintering process; blast furnace dust and sludge from the blast furnace process; steelmaking dust and sludge from steel production in converters; steelmaking dust from steel production in electric arc furnaces; blast furnace and steelmaking slags; ceramic debris; sludges from wet dedusting of burned gases and melting losses [1–5]. A vast amount of metallurgical waste is discarded due to the rapid growth of several industrial sectors. Safe disposal of these metallurgical wastes is vital as they can cause severe threats to ecosystems and quality of life and deteriorate critical natural resources, predominantly

water and soil [6]. Knowledge about the characteristics of these wastes helps us to find a logical way for the recycling or landfilling of them.

Landfilling the metallurgical wastes in slag dumps involves the potential pollution of all environmental factors: air, water and soil; it also leads to removing land areas out of circuit; soil quality deterioration; monitoring of all environmental factors near the dump; adverse effects on human health; permanent loss of natural resources that exist in the composition of metallurgical wastes.

Due to the heavy metals content of metallurgical wastes, they may pose a risk of contamination for the environment and human health. Heavy metals are required in small quantities for maintaining good health, but in larger quantities they can become toxic or dangerous. Heavy metal toxicity can lower energy levels and damage the functioning of the brain, lungs, kidney, liver, blood composition and other important organs. Long-term exposure can lead to gradually progressing physical, muscular and neurological degenerative processes that imitate diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease and muscular dystrophy. Repeated long-term exposure of some metals and their compounds may even cause cancer [7,8].

Metallurgical wastes produced worldwide are estimated at 400 Mt/year [9]. The quantity of the metallurgical wastes generated by the metallurgical industry of Romania was 4.8 million tons, in one year. In Romania, about 33% of the total quantity of production waste was recovered, while the remaining 67% was disposed of (by landfilling or incineration) [10].

Metallurgical waste generated during steelmaking in electric arc furnaces is dependent on the production of steel. As the quantity of liquid steel produced increases, the amount of solid waste generated will increase, and as the quantity of liquid steel produced decreases, the quantity of solid waste will decrease. Between 2000 and 2010, Romania has generated on average about 281.702 thousand tons of dust and 2029.5 thousand tons of slag from steelmaking in electric arc furnaces. The largest quantities of dust and slag were generated during 2005–2008, and the lowest quantities were generated in 2009, 2002 and 2003. Metallurgical solid waste from steelmaking in electric arc furnaces, are stored in slag dumps near metallurgical plants, causing environmental pollution in all its components: soil, water and air [11].

The Environmental Report for Romania's Energy Strategy 2020–2030, with the perspective of 2050, estimates that industrial solid waste dumps affect 844 ha, of which 360 ha are excessively affected, most being in counties with mining, steel industry and non-ferrous metallurgy [12].

Metallurgical waste management options must be considered in the decreasing order of the following priorities [10]:

- waste prevention—by application of “clean technologies”;
- waste minimization—by implementing best practices in every waste generating activity;
- valorization—by reuse, material recycling and energy recovery;
- disposal—by incineration and landfill.

The main objective for waste treatment is promoting waste treatment in order to ensure rational environmental management and the subsidiary objective is encouraging waste treatment with a view to [10]:

- enhancing recovery;
- reducing the hazardous nature of waste;
- reducing the final disposal of waste in such a way as to safeguard human health and the environment.

The main objective for the disposal of waste is disposing of waste according to the requirements of the waste management legislation in order to protect human health and the environment. Subsidiary objectives for disposal are [10]:

- securing the necessary waste disposal capacities by giving priority to waste disposal installations at area level;

- closing down waste disposal sites failing to meet EU requirements.

A part of the metallurgical solid wastes is reduced, reused, recycled or restored (4R), but another part is deposited in excavated land forming dumps [13].

Worldwide there is an intense activity to find solutions for the recovery of metallurgical wastes. Their use is driven by both economic and environmental considerations, aiming at the abolition of metallurgical slag dumps. The ideal target is to develop a sustainable system loop that can convert all the valuable resources that are landfilled as waste materials into useful products. Due to the large metallurgical waste quantities and the stricter environmental regulations, recycling and utilization of these wastes are an attractive alternative in order to: minimize and eventually eliminate the disposal cost; minimize the soil, air and water pollution; save the natural resources.

Sustainable development was introduced in a widespread way by the Brundtland Commission, which defined it as development that “meets the needs of the present without compromising the ability of future generations to meet their own needs” [1–5,14]. Sustainability has been applied to many fields, including engineering, manufacturing and design. Manufacturers are becoming increasingly concerned about the issue of sustainability. For instance, recognition of the relationship between manufacturing operations and the natural environment has become an important factor in decision making among industrial societies [2,3,15,16].

According to the paper [17], the metals from waste could be recycled by conventional methods: mechanical, hydrometallurgical, pyrometallurgical and bio/hydrometallurgical processes or a combination of these methods. In addition, the detection and assessment of valuable metals from metallurgical wastes landfilled in the slag dump are crucial for increasing the recycling rate of them. In the specialized literature there is no standardized method for quantification of the metal contents from metallurgical wastes. Consequently, information about the critical metal content of metallurgical wastes landfilled in slag dumps and standardization methods for their determination are limited in the literature.

The compositions of metallurgical wastes and their mineral constituents play an important role in their potential utilization. The most economic and efficient option for reducing metallurgical waste generation is through recycling. Metallurgical waste recycling has been successful in the ironmaking and steelmaking industries. These wastes are also being used in domains such as road construction, fertilizers, soil conditioners and for metal recovery [1].

For the analysis of environmental solid samples, XRF (X-ray fluorescence) has the advantage of being a rapid and inexpensive method, with a simple sample preparation. By using this technique, the chemical composition of wastes can be determined in a short time. XRF is characterized by good selectivity and a low detectability limit of ppm–ppb. According to the previous studies about XRF characterization, the main chemical compounds of metallurgical wastes can vary widely. Their main oxide chemical composition consists of: FeO, CaO, SiO₂, Al₂O₃ and MgO [5,11,18–22].

Mineralogical composition is the most important factor that influences the usability of metallurgical solid wastes [20–22] and the conservation of natural resources. In order to use these metallurgical wastes, one must first know their chemical and mineralogical properties. The chemical and mineralogical characterization of metallurgical wastes could effectively serve as a basis for identifying their potential utilization. X-ray powder diffraction is widely used in geology, environmental science, material science and engineering to rapidly identify unknown crystalline substances.

Studies on the phase composition of metallurgical wastes are very important in order to recover metals from wastes or to return them to the metallurgical process [23,24].

The interest in the characterization of metallurgical wastes is due to the need for: the identification of constituents that have potential for reuse in the field from which they come or in different fields; minimizing/eliminating the negative environmental impact of slag dumps; improving the management of these wastes; conservation of natural mineral resources; sustainability in the steel industry. The objective of our paper was to add to

information regarding the potential applications of metallurgical wastes landfilled in slag dumps in the field from which they come or in different fields.

The purpose of this paper is to improve the management of metallurgical wastes, by identifying the existing compounds in these wastes, which present reuse potential in different domains. Improving metallurgical waste management contributes to both metal conservation and a sustainable steel industry. Additionally, this paper aims to chemically and mineralogically characterize the metallurgical wastes from the Păgida slag dump, in order to identify their potential applications. The characterization and recycling of metallurgical wastes play a key role in their utilization and in establishing the opportunities for minimizing the amount of waste disposed. After the characterization of the metallurgical wastes, the theoretical recovery potentials of metals from metallurgical wastes landfilled in the Păgida slag dump were assessed.

The lack of previous studies refers to: the absence of an assessment methodology of the recovery potential of metals from slag dumps; the lack of the assessment of the economic value of the valuable metals from the metallurgical wastes from slag dumps; the need to improve the management of metallurgical wastes specific to the steel industry, through their characterization; the incomplete characterizations of metallurgical wastes; the detection and assessment of valuable metals from metallurgical wastes landfilled in the slag dump are crucial for minimizing the quantity of waste that is landfilled; in the specialized literature there is no standardized method for quantification of the valuable metal contents from metallurgical wastes from slag dumps; the lack of information about the critical metal content of metallurgical wastes landfilled in slag dumps and the standardization methods for their determination; the incomplete characterization of metallurgical wastes from slag dumps.

The novelty of this study consists in the: establishing of an assessment methodology of the recovery potential of metals from slag dumps; assessment of the economic value of the valuable metals from the metallurgical wastes in slag dumps; characterization of the metallurgical wastes from the Păgida slag dump; identification of the new mineralogical compounds: (Fe–Ringwoodite; Calcium iron oxide; Hedenbergite; Andradite (calcium iron silicate); Magnesioferrite; Fayalite magnesian manganoan); identification of valuable metals existing in metallurgical wastes from the Păgida slag dump; identification of the opportunities for minimizing the amount of metallurgical waste disposed; identification of potential applications of use for the metallurgical wastes from the slag dump in Păgida; improvement of the management of metallurgical wastes.

2. Materials and Methods

The Păgida metallurgical slag dump is located near Păgida village, which belongs to the town of Aiud, Alba County, Romania. The metallurgical wastes landfilled in the Păgida slag dump come from the metallurgical plant S.C. Metalurgica Transilvană S.A. Aiud, Romania. The types of wastes landfilled in the slag dump are: metallurgical slags (which are prevalent) from steelmaking in electric arc furnaces (EAFs), refractory materials from EAFs, acid and basic lining from EAFs, foundry waste sands, casting cores and molds, etc. A brief characterization of the metallurgical plant from which the landfilled wastes originate is presented in the reference [5].

Figure 1 shows the flow chart of the experiment.

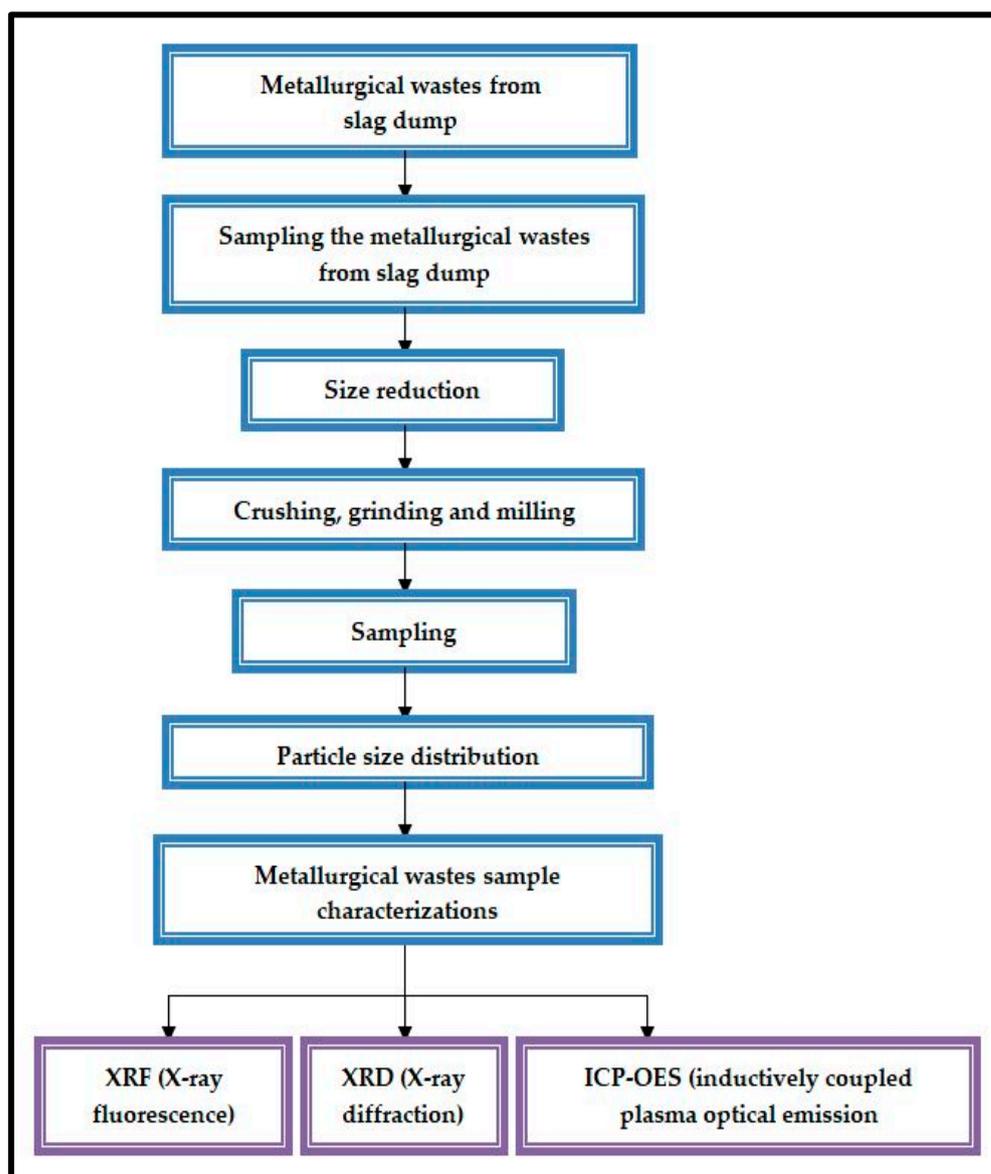
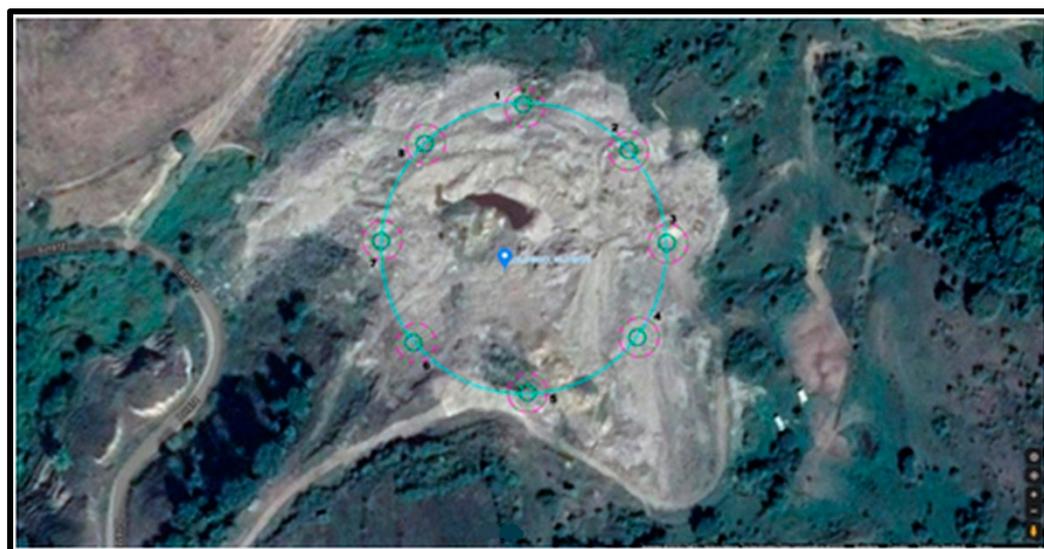


Figure 1. Flow chart for the experiment.

The two analyzed metallurgical waste samples were taken from the Păgida slag dump, Alba County, Romania. For a better representation and variability, the two samples consist of a mixture of 128 subsamples of metallurgical wastes (sample 1 is composed of 64 subsamples, sample 2 is composed of 64 subsamples), taken from eight sampling points representing the north, north-east, east, south-east, south, south-west, west and north-west directions. A metallurgical waste sample is composed of 64 subsamples. The first sample consists of a mixture of metallurgical solid wastes, taken from a circle with a radius of 5 m around each of the eight sampling points. The second sample consists of a mixture of metallurgical solid wastes, taken from a circle with a radius of 15 m around each of the eight sampling points. The sampling points were recorded using GPS (Table 1). In order to evaluate the homogeneity of the metallurgical wastes from the slag dump, eight sampling points were established (Figure 2), which correspond to the center of the concentric circles (the circles represented in black have a radius of 5 m and the circles represented in pink have a radius of 15 m). Eight subsamples were taken from each sampling point. The 64 subsampling points, corresponding to a sample, are shown in green.

Table 1. GPS values for the sampling points.

No.	GPS Values
1	46°34'06.12" N, 23°74'95.83" E
2	46°34'05.21" N, 23°75'01.30" E
3	46°34'01.70" N, 23°75'03.79" E
4	46°33'98.33" N, 23°75'00.67" E
5	46°33'95.89" N, 23°74'96.17" E
6	46°33'97.48" N, 23°74'89.95" E
7	46°34'02.48" N, 23°74'87.32" E
8	46°34'05.37" N, 23°74'89.73" E

**Figure 2.** Sampling representation.

Metallurgical waste samples were taken from the surface of the slag dump or from a maximum depth of 0.6 m. Sampling from greater depths and from the middle of the slag dump was not possible due to its instability. The total amount of metallurgical waste taken was about 64 kg. Each sample weighed 32 kg, and each subsample weighed 0.5 kg. The dimensions of the subsamples varied in size: less than 20 mm, 20–40 mm and 40–60 mm. Each sample/subsample contained metallurgical wastes with the three dimensions mentioned above.

Initially, the waste samples were separated by size using different sieves. The metallurgical wastes were crushed, manually in the first stage, because they could not be used directly for further analysis. Then, the waste samples were subjected to MiniMill 2, in order to achieve the desired size (5 μm). The grinding procedure lasted 10 min and rotational speed was 300 rpm. MiniMill 2 uses the planetary ball mill principle with a single grinding bowl holder. The constituents of the metallurgical waste samples, after reducing the size, were analyzed using XRD.

A comparison between the particle size distributions before and after the grinding procedure is presented in Table 2. Particle size distribution before grinding, for the two samples, was as follows: $d < 0.005$ mm (sample 1: 3%; sample 2: 6%); 0.005 mm $< d < 10$ mm (sample 1: 76%; sample 2: 86%) and $d > 10$ mm (sample 1: 21%; sample 2: 8%). Particle size distribution after grinding, for the two waste samples, was as follows: $d < 0.005$ mm (sample 1: 7%; sample 2: 9%); 0.005 mm $< d < 10$ mm (sample 1: 74%; sample 2: 83%) and $d > 10$ mm (sample 1: 19%; sample 2: 8%). The particle size distribution plays a key role in the utilization of these wastes in different domains.

Table 2. Particle size distribution before and after the grinding procedure.

Distribution before Grinding (%) Sample 1	Distribution after Grinding (%) Sample 1	Distribution before Grinding (%) Sample 2	Distribution after Grinding (%) Sample 2	Grain Size (mm)
3	7	6	9	$d < 0.005$
5	11	9	14	$0.005 < d < 0.05$
6	15	15	29	$0.05 < d < 2$
34	38	44	28	$2 < d < 5$
31	10	18	12	$5 < d < 10$
21	19	8	8	$d > 10$

For XRD analysis, the powdered samples with grain sizes around 5 μm are optimal. Fine grain size is essential to minimize microabsorption corrections, to give reproducible peak intensities and to minimize the preferred orientation [25]. The mixtures of metallurgical waste samples were milled to a 5 μm grain size with MiniMill 2.

The chemical compositions of the two waste samples were analyzed by the XRF (X-ray fluorescence) technique using XRF Spectro X-LAB 2000 equipment (SPECTRO Analytical Instruments Inc. Kleve, Germany). The sample preparation procedure was performed according to the reference [26]. The standard used is presented in the reference [27]. The mineralogical compositions were analyzed by XRD (X-ray diffraction) technique. The existing mineralogical phases in the two metallurgical waste samples were identified using a DRON 3 X-ray diffractometer (Joint Stock Company “BOUREVESTNIK”, Saint Petersburg, Russia). The investigation was carried out using $\text{CuK}\alpha$ monochrome radiation. The diffractograms were recorded with the following parameters: $2\theta = 30(\text{deg}) \div 110(\text{deg})$, voltage ($U = 25 \text{ kV}$), current ($I = 20 \text{ mA}$), wavelength ($\lambda = 1.54187 \text{ \AA}$), count time (5 s) and the angular step (1 deg). The mineralogical compounds were identified based on a minimum of 3 diffraction peaks.

The diffractograms were recorded and interpreted using Matmec software. The recording of the diffractograms was performed through a computer connected to the X-ray diffractometer. For the interpretation of the diffractograms, Match! software (Crystal Impact GbR, Bonn, Germany) was used, which employed data from the PDF-2 (Powder Diffraction File) database (ICDD, International Centre for Diffraction Data, Newtown Square, PA, USA). Depending on the intensity (I) of the peaks, the mineralogical compounds identified in the metallurgical waste samples were established as major, intermediate and minor. The interplanar distances (d) were determined with Bragg’s relationship [25]

$$2d \cdot \sin\theta = n\lambda \quad (1)$$

where: d is the interplanar distance; θ is the Bragg angle (the angle between the X-ray beam and the crystal lattice planes); n is the reflectivity degree; λ is the wavelength (\AA).

The selection of the research methods was based on the following considerations:

- XRF (X-ray fluorescence) provides a rapid and non-destructive method for the analysis of trace and major elements in environmental solid samples. The method is characterized by good selectivity and a low detectability limit of ppm–ppb [18,19];
- X-ray diffraction (XRD) is one of the most powerful and modern techniques for qualitative and quantitative analysis of crystalline compounds. The technique provides information that cannot be obtained in any other way. The identification of the mineralogical phases found in metallurgical wastes is a helpful technique for finding their potential applications. Therefore, the analysis of these spectra is usually performed after chemical analysis, which orientates the search of the pattern peaks and leads to the identification of the sample structures. The minerals’ investigation by X-ray diffraction can detect traces of crystalline phases up to 1% by mass [24,25,28,29].

The trace elements of the solid samples were determined by ICP-OES using a PerkinElmer instrument OptimaTM 5300DV (PerkinElmer, Inc. USA) after mineralization in aqua regia ($\text{HNO}_3 + 3\text{HCl}$).

After the characterization of the metallurgical wastes, recovery potentials of metals were estimated by using the methodology presented in the paper [30]. The approximate quantity of the metallurgical wastes landfilled in the slag dump is 840,000 tons. Recovery potential of metals was determined from experimental analyses. Price of metals was determined considering the prices reached at London Metal Exchange, Romanian Commodities Exchange, Shanghai Metals Market and Federal Institute for Geosciences and Natural Resources [31–35]. Economic value was determined by multiplying the price of metals and the recovery potential of metals from slag dump. This is a theoretical estimation of the recovery potential of metals from metallurgical wastes landfilled in the slag dump.

3. Results and Discussion

Table 3 summarizes the chemical compositions of the two samples, taken from the Păgida slag dump, analyzed by the XRF (X-ray fluorescence) technique.

Table 3. Chemical compositions of the metallurgical wastes and standard deviation (average \pm standard deviation) (%).

No.	MgO (%)	CaO (%)	Al ₂ O ₃ (%)	Fe _{total} (%)	SiO ₂ (%)	MnO (%)	P ₂ O ₅ (%)	V ₂ O ₅ (%)	TiO ₂ (%)
1	12.9 \pm 1.8	20.1 \pm 1.9	6.9 \pm 0.6	24.2 \pm 1.8	25.8 \pm 2.9	7.5 \pm 0.5	0.36 \pm 0.5	0.37 \pm 0.6	-
2	18.3 \pm 1.8	26.2 \pm 1.9	3.9 \pm 0.5	19.6 \pm 1.6	22.3 \pm 1.5	5.7 \pm 0.4	0.45 \pm 0.5	0.72 \pm 0.9	0.39 \pm 0.4

The chemical composition, as a percentage, of the compounds identified in the characterized metallurgical wastes varies between: 12.9 and 18.3% for MgO, 20.1 and 26.2% for CaO, 3.9 and 6.9% for Al₂O₃, 19.6 and 24.2% for Fe_{total}, 22.3 and 25.8% for SiO₂, 5.7 and 7.5% for MnO, 0.36 and 0.45% for P₂O₅ and 0.37 and 0.72% for V₂O₅. In sample 2, titanium dioxide (TiO₂) was identified.

An analysis of the chemical composition of the two metallurgical waste samples shows that:

- the chemical composition of the metallurgical wastes varies from sample to sample;
- the predominant chemical compounds in the composition of the analyzed wastes are: SiO₂, Fe_{total}, CaO and MgO;
- in their composition, no free CaO and no free MgO was identified;
- the waste samples have significant concentrations of total iron (Fe_{total});
- the most important content of total iron (Fe_{total}) was found in sample 1 (24.2%).

The presence of oxides such as CaO, SiO₂, FeO and Al₂O₃ makes metallurgical wastes useful as clinker materials in cement production [20,36]. The separation of metallic iron from metallurgical wastes and its use in various fields would save and conserve the existing natural resources [37]. The iron content from metallurgical wastes can be reused in the iron and steel industry.

Table 4 presents the content of trace elements in metallurgical wastes, determined by inductively coupled plasma optical emission spectrometry (ICP-OES).

Table 4. Content of trace elements in metallurgical wastes.

No.	Elements	Sample 1 (ppm)	Sample 2 (ppm)
1	V	2983	3214
2	Cr	152	89
3	Ni	795	898
4	Cu	2841	3567
5	Zn	148	49
6	As	113	64
7	Mo	1398	1198
8	Sn	329	39
9	Sb	199	63
10	Pb	59	25
11	Cd	783	894
Total		9800	

The minor metal constituents were found as traces, with a concentration of less than 9800 ppm for sample 1 and a concentration of less than 10,100 ppm for sample 2. The trace elements determined in the two samples contained V, Cr, Ni, Cu, Zn, As, Mo, Sn, Sb, Pb and Cd.

Metallurgical waste samples contain vanadium and titanium. These are part of the category of critical raw materials, in 2020, according to the Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and The Committee of the Regions—Critical Raw Materials Resilience: Charting a Path towards greater Security and Sustainability. These wastes also contain chromium, molybdenum and nickel. The presence of these chemical elements is associated with the type of produced steel. They can be reused in steelmaking as chemical alloying elements.

Figures 3 and 4 present the diffractograms of the two metallurgical waste samples.

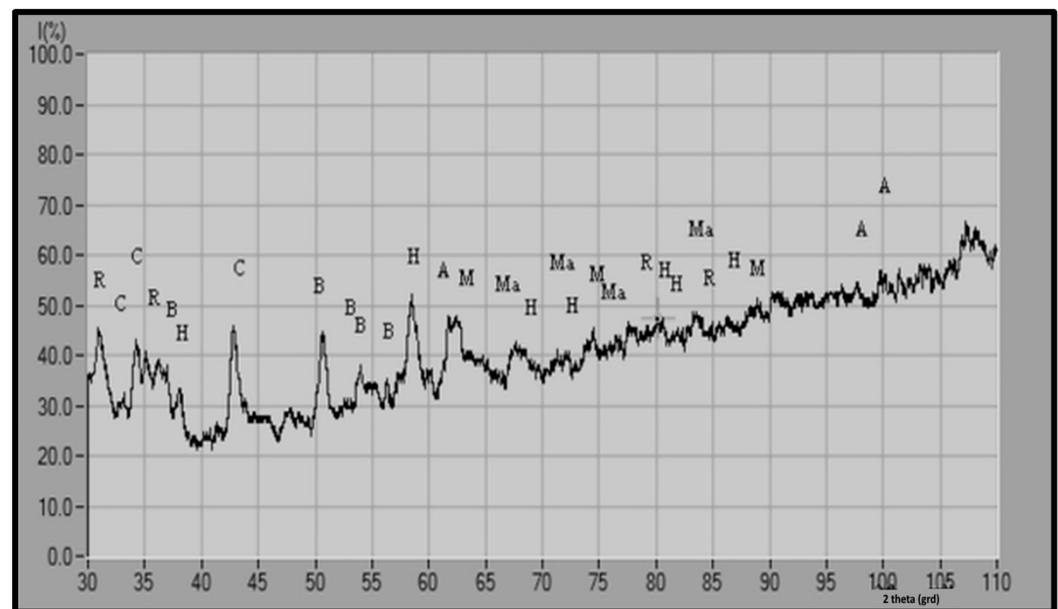


Figure 3. The diffractogram of metallurgical waste sample 1. Legend: R—(Fe—Ringwoodite ($\text{Fe}_2(\text{SiO}_4)$)); C—(Calcium iron oxide (CaFe_3O_5)); B—(Brownmillerite $\text{FeAlO}_3(\text{CaO})_2$); H—(Hedenbergite $\text{CaFe}(\text{Si}_2\text{O}_6)$); A—(Andradite (calcium iron silicate) ($\text{Ca}_3\text{Fe}_2 + 3(\text{SiO}_4)_3$)); M—(Magnesioferrite (MgFe_2O_4)); Ma—(Magnetite ($\text{Mg}_{0.04}\text{Fe}_{2.96}\text{O}_4$)).

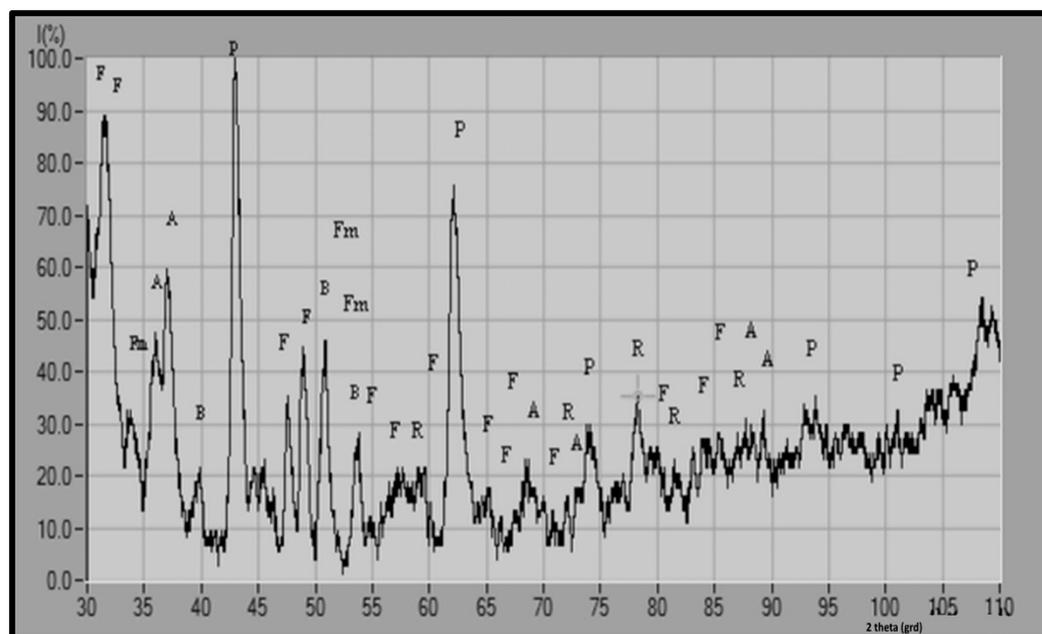


Figure 4. The diffractogram of metallurgical waste sample 2. Legend: F—(Fayalite magnesian manganooan ($Mg_{1.145}Fe_{1.742}Mn_{1.113}SiO_4$; $Mg_{0.347}Fe_{1.548}Mn_{1.105}SiO_4$)); Fm—(Fayalite manganooan ($(Fe,Mn)_2SiO_4$)); A—(Andradite (calcium iron silicate) ($Ca_3Fe_2 + 3(SiO_4)_3$)); B—(Brownmillerite ($Ca_4Al_2Fe_2 + 3O_{10}$)); P—(Periclase (MgO)); R—(Fe–Ringwoodite ($Fe_2(SiO_4)$)).

Appendices A and B show the mineralogical compounds identified in the metallurgical waste samples.

The weight percentage for each mineralogical phase was determined according to the relative peak intensities related to the mineral structure factor [25]. The percentages for the mineral compositions of the two metallurgical samples are shown in Table 5.

Table 5. Weight percentages of the identified mineralogical phases.

No.	Mineralogical Phase	Symbol	Sample 1 (%)	Sample 2 (%)
1	Fe–Ringwoodite	R	22 ± 0.6	5 ± 0.6
2	Calcium iron oxide	C	18 ± 0.5	-
3	Brownmillerite	B	16 ± 0.7	14 ± 1.0
4	Hedenbergite	H	26 ± 2.3	-
5	Andradite (calcium iron silicate)	A	3 ± 0.4	17 ± 0.5
6	Magnesioferrite	M	6 ± 0.5	-
7	Magnetite	Ma	9 ± 0.6	-
8	Fayalite magnesian manganooan	F	-	22 ± 0.8
9	Fayalite manganooan	Fm	-	3 ± 0.4
10	Periclase	P	-	39 ± 2.3

According to the mineralogical characterization, the following compounds were identified in the metallurgical waste samples: Magnesioferrite ($MgFe_2O_4$), (sample 1: 6 ± 0.5%; sample 2: not identified), Magnetite ($Mg_{0.04}Fe_{2.96}O_4$), (sample 1: 9 ± 0.6%; sample 2: not identified), Hedenbergite ($CaFe(Si_2O_6)$), (sample 1: 26 ± 2.3%; sample 2: not identified), Calcium iron oxide ($CaFe_3O_5$), (sample 1: 18 ± 0.5%; sample 2: not identified), Fe–Ringwoodite ($Fe_2(SiO_4)$), (sample 1: 22 ± 0.6%; sample 2: 5 ± 0.6%), Andradite ($Ca_3Fe_2 + 3(SiO_4)_3$), (sample 1: 3 ± 0.4%; sample 2: 17 ± 0.5%), Brownmillerite ($FeAlO_3(CaO)_2$, $Ca_4Al_2Fe_2 + 3O_{10}$), (sample 1: 16 ± 0.7%; sample 2: 14 ± 1.0%), Fayalite magnesian manganooan ($Mg_{1.145}Fe_{1.742}Mn_{1.113}SiO_4$, $Mg_{0.347}Fe_{1.548}Mn_{1.105}SiO_4$), (sample 1: not identified;

sample 2: $22 \pm 0.8\%$), Fayalite manganite ((Fe,Mn)₂SiO₄), (sample 1: not identified; sample 2: $3 \pm 0.4\%$) and Periclase (MgO) (sample 1: not identified; sample 2: $39 \pm 2.3\%$).

An analysis of the mineralogical composition of the two waste samples shows that:

- the mineralogical composition of the metallurgical wastes from the slag dump is complex;
- the mineralogical composition of wastes varies from sample to sample;
- the major mineralogical phases identified in the metallurgical waste sample 1 are: Hedenbergite and Fe–Ringwoodite; the major mineralogical phases identified in the metallurgical waste sample 2 are: Periclase and Fayalite magnesian manganite;
- the intermediate mineralogical phases identified in the metallurgical waste sample 1 are: Calcium iron oxide and Brownmillerite; the intermediate mineralogical phases identified in the metallurgical waste sample 2 are: Andradite and Brownmillerite;
- the minor mineralogical phases identified in the metallurgical waste sample 1 are: Magnetite, Magnesioferrite and Andradite; the minor mineralogical phases identified in the metallurgical waste sample 2 are: Fe–Ringwoodite and Fayalite manganite;
- in both waste samples, the following mineralogical phases were identified: Fe–Ringwoodite, Andradite and Brownmillerite;
- they contain valuable components that can be reused in various processes;
- the existing ferrous components in the waste samples can be reused (after mechanical pre-processing and magnetic separation) as raw materials in the process from which they originate or other processes;
- the existing mineral components in the waste samples can be used as raw materials for obtaining cement or in other industrial fields [38,39];
- from an economic point of view, the usage of mineralogical compounds from metallurgical wastes may reduce the cost of extracting and processing the natural resources;
- the identified mineralogical compounds have a great economic importance in terms of saving natural resources.

The mineralogical compounds from metallurgical wastes could be reused for different applications. For example [1,40–50]:

- Fayalite can be used as refractory sands, abrasives and mineral specimens;
- Magnetite can be used as: ore of iron; a heavy medium (magnetite is often mixed with a liquid for use as a heavy medium for specific gravity separations); an abrasive (synthetic emery is produced by mixing magnetite with aluminum oxides); a toner in electrophotography; a micronutrient in fertilizers; a pigment in paints; an aggregate in high-density concrete;
- Magnesioferrite can be used: in heterogeneous catalysis, adsorption, sensors, magnetic technologies and also for the adsorption of SiO₂; for ferrite pigment production; it can be highly effective in cleaning water sources by degrading contaminants and removing other unwanted substances from the environment;
- Periclase is used as an additional material in the cement industry, at a site-batching plant, or by blending MgO clinker into the cement clinker before grinding them together. According to Walling [32], MgO-based cements provide a large-scale replacement for Portland cement in the production of steel-reinforced concretes for civil engineering applications.
- Periclase (MgO) is one of the raw materials used for making Portland cement. It has been found that adding MgO powder to concrete will influence mechanical properties, but will have very little effect on thermal properties. Long-term studies have demonstrated that because the hydration process is irreversible and Mg(OH)₂ is stable, the mechanical behavior of MgO concrete is stable [42,46–48].

Table 6 presents the potential applications of the mineralogical compounds, identified in the metallurgical waste samples, according to different references reported in the specialized literature.

Table 6. Potential applications of mineralogical compounds in different fields.

Mineralogical Phase	Applications	References
Brownmillerite	Material for energy and environmental applications (fuel cells, supercapacitors, batteries).	Vavilapalli et al. [51]
Magnesioferrite	Semiconductor material; Heterogeneous catalysis; Adsorption; Sensors; Magnetic Technologies	Willey et al. [52]; Swapan et al. [53]
Magnetite	Medicine; Technology; Bioremediation; Analytical analysis.	Katz, E. [54]; Wroblewski et al. [55]
Periclase	Concrete; Construction of dams; Agricultural fertilizers.	Du, C. [42]; Gao et al. [56]

According to reference [57], metallurgical wastes can be reutilized in various applications such as construction or agriculture. Additionally, they come as valuable secondary raw materials for their own sectors in integrated steel plants for internal recycling and for other users. The chemical composition and mineralogy determine the properties and the performance of recycling solutions. The removal of metallic iron from the slag by magnetic separation is necessary. Due to the high content of iron oxides, steelmaking slags must be exploited for an efficient recovery of their valuable iron units. In order to reach the granulation required for different applications, these metallurgical wastes must be crushed, sieved and then the magnetic fraction must be removed. The magnetic fraction may be utilized as a component for sintering mixture. Metallurgical wastes (including electric arc furnace slag) can be used as an aggregate or as a supplementary cementitious material in bound applications, such as concretes, mortars, alkali-activated materials and stabilized soils [58].

Metallurgical slag is a secondary raw material resource in metallurgical plants. It can be directly taken back to steelmaking and used as flux, from which the useful elements can be recovered [59].

Metallurgical waste, such as EAF slag, can be used as a construction material, asphalt aggregate, pavement material and engineering material. Another potential application of this waste is the production of fertilizers [60].

Table 7 presents a comparative analysis of mineralogical compounds identified in the metallurgical waste samples and mineralogical compounds reported in the specialized literature, in similar waste types. The new mineralogical compounds identified are: Fe–Ringwoodite; Calcium iron oxide; Hedenbergite; Andradite (calcium iron silicate); Magnesioferrite; Fayalite magnesian manganooan.

From the data analysis presented in Table 7, it results that the metallurgical wastes have complex mineralogical phases that vary from one steel mill to another and from one steel type to another. The list of minerals identified in the metallurgical wastes shows that mineralogical composition can vary with a wide range of major, minor or trace compounds. This aspect demonstrates the need for mineralogical characterization of these wastes.

The variations in the chemical and mineralogical compositions of the two metallurgical samples investigated could be attributed to one or a combination of the following reasons: the technology used; the specifics of each technological stage; the physical–chemical processes that take place during steelmaking in electric arc furnaces; the type of auxiliary materials used for steelmaking; the chemical compositions of the charge components; the type of produced steel; the type of refractory furnace linings; the type of fluxing agent used; the type of ferroalloys (FeMn, FeCr, FeNi, FeMo, FeTi, FeV, FeAl, FeSi, SiCa) used in the steelmaking process; the type of fuel (petrol coke, electrodes scraps); the type of alloying elements.

Table 7. Comparative analysis of mineralogical compounds identified in metallurgical wastes and those reported in various studies.

Types of Metallurgical Wastes	Mineralogical Compounds Identified	References
Metallurgical wastes from slag dump (slag from EAF is prevalent)	Fe–Ringwoodite; Calcium iron oxide; Brownmillerite; Hedenbergite; Andradite (calcium iron silicate); Magnesioferrite; Magnetite; Fayalite magnesian manganoan; Periclase.	This study
EAF slag from carbon steel	Spinel; Quartz; Calcite; Wustite; Hematite; Larnite; Gehlenite; Brownmillerite.	Horckmans et al. [61]
Stainless steel slag	Spinel; Quartz; Calcite; Periclase; Dicalcium silicate; Cuspidine; Larnite; Wollastonite; Akermanite; Merwinite; Bredigite.	Horckmans et al. [61]
Steel slag	Larnite; Wuestite; Mayenite; Srebrodolskite; Portlandite.	Chamling et al. [62]
EAF slag	Dicalcium silicate, Merwinite, Gehlenite, Wüstite, Hematite and Magnetite, Mayenite, Brownmillerite; Periclase.	Brand et al. [63]
Landfilled stainless steel slag from EAF	Dicalcium silicate; Magnesiochromite; Quartz; Gehlenite; Bredigite; Magnesite; Merwinite; Calcite; Cuspidine; Akermanite; Iron carbide; Magnetite; Calcium chromate; Wollastonite.	Wang et al. [64]
EAF slag	Wustite; Spinel; Chromite; Brownmillerite; Calcium chromite; Larnite; Calcite; Quartz.	Herbelin et al. [65]

Reusing the valuable components of these wastes is possible by physical or chemical processing techniques such as: crushing, grinding, classification, magnetic separation and flotation, followed by hydrometallurgical or pyrometallurgical processes [66].

The recycling processes, which can be considered for metallurgical wastes landfilled in the slag dump, can be divided into two categories:

- lower added value applications, are basically direct applications that utilize the physical aspects of the metallurgical wastes, such as construction aggregates;
- higher added value applications, utilize the chemical and mineralogical compositions of the metallurgical wastes and require further processing procedures, such as: crushing or grinding, screening and magnetic separation; higher added value recycling applications of metallurgical wastes are as a raw material for steel industry, ceramic building materials, Portland cement, etc.

Significant European examples of feasible projects that are financed by the European Commission are [67–69]:

- “Dissemination of results of the European projects dealing with reuse and recycling of by-products (REUSteel)”; focused on the reuse and recycling of by-products in the steel sector;
- “Recycling of residues from metallurgical industry with the arc furnace technology (Recarc)”; focused on the recycling of residues from the metallurgical industry;
- “Slag NO Waste: Innovative system for 100% recycling of white slag and for ZERO WASTE electric steel production (SNOW-LIFE)”; focused on demonstrating the potential of SNOW technology to act as a cost-effective waste reduction and reuse solution for white slag, from EU steel plants.

The treatment of the metallurgical wastes is possible by using the following methods [70]: pyrometallurgical; hydrometallurgical; biohydrometallurgical.

Pyrometallurgy is the oldest method for the recovery of metals and involves chemical reactions among different solids, gases or molten materials at a high temperature inside a furnace, where valuable metals present in these solids are converted into their elemental form. Pyrometallurgical processing of metallurgical wastes involves processes such as: dressing, roasting, calcination, smelting and refining. This method is not widely accepted due to high energy fuel consumption, which makes it cost ineffective and impracticable on an industrial level [71,72].

The hydrometallurgical method is favorable only for high concentrations of recoverable metals from wastes. The major advantage of this method is that it does not emit toxic gases. Hydrometallurgical methods use aqueous media to extract metals from metallurgical wastes. These methods involve the following steps: leaching, concentration and purification of the solution and recovery of metals. In the leaching step, the metallurgical waste is brought in contact with a suitable lixiviant (sulphuric acid, nitric acid, hydrochloric acid, mixtures of hydrochloric acid, nitric acid and sulphuric acid, aqua regia, hydrogen peroxide, potassium iodide, potassium iso-cyanate, ferric chloride, thiosulphate, thiourea, iodine, iodide–nitrite mixture and cyanides), which mobilize the metals present in the waste. After mobilization, the concentration and purification is performed (adsorption, distillation, precipitation, solvent extraction, ion exchange, cementation and filtration) and finally, metals are recovered [73–75].

In the case of biohydrometallurgical methods, microbes convert solid metals into their water soluble forms. These microbes undergo oxidation–reduction reactions and lead to the dissolution or mobility of metal ions by the transformation of metals to their oxides, hydroxides and sulphates. Biohydrometallurgy incorporates processes such as bioleaching, biooxidation, bio-induced surface chemical changes and bioremediation. This technology is environmentally friendly as compared to other chemical methods and is considered as a green technology since it produces a small quantity of waste and suitable substitutes for conventional recovery methods [76,77].

The control methods of the toxic metals are possible through biohydrometallurgy. This method is considered environmentally friendly and a profitable method for the extraction of toxic metals utilizing microbes. Most commonly, the microbes used in bioleaching are chemolithotrophic archaea and bacteria (*Acidithiobacillus thiooxidans*, *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Sulfolobacillus thermosulfidooxidans*, *S. thermosulfidooxidans*, *Sulfolobacillus acidocaldarius*, *Sulfolobacillus solfataricus* and *Sulfolobacillus brierleyi*) and heterogenous bacteria, fungi and yeast (*Chromobacterium violaceum*, *Acidianus ambioalens*, *Acidianus brierleyi*, *Acidianus infernus*, *Bacillus megaterium*, *Pseudomonas fluoresceni*, *Aspergillus niger*, *Penicillium notatum*, *Penicillium simplicissimum* and *Saccharomyces cerevisiae*) [70]. Using this method of controlling toxic metals eliminates the negative impact on human health and environmental factors.

The steel slag from metallurgical wastes can be incorporated in cement manufacturing in two different ways. First, the steel slag is used as a raw material for cement clinker; hence, it is calcined in the kiln together with other raw materials. Then, it is ground and blended with clinker as a cement additive [78]. The electric arc furnace slag could be successfully used to replace inert material in road construction and concrete production [79].

Figure 5 shows the conceptual diagram for the treatment of metallurgical wastes in order to recover the metal of interest. According to the diagram, the treatment of the metallurgical wastes involves, in the first stage, the crushing and primary milling of the wastes. After that, they are subjected to magnetic separation, to remove the magnetic fraction. Metallurgical wastes with non-magnetic fraction are subjected to the following stages: screening, secondary milling, grinding, roasting and leaching. Depending on the type of valuable metal (vanadium, molybdenum, copper, etc.) to be recovered, the following alkaline reagents can be used: sodium hydroxide, potassium carbonate, sodium carbonate, potassium hydroxide, etc. Metallurgical wastes without metals can be valorized in the civil engineering domain.

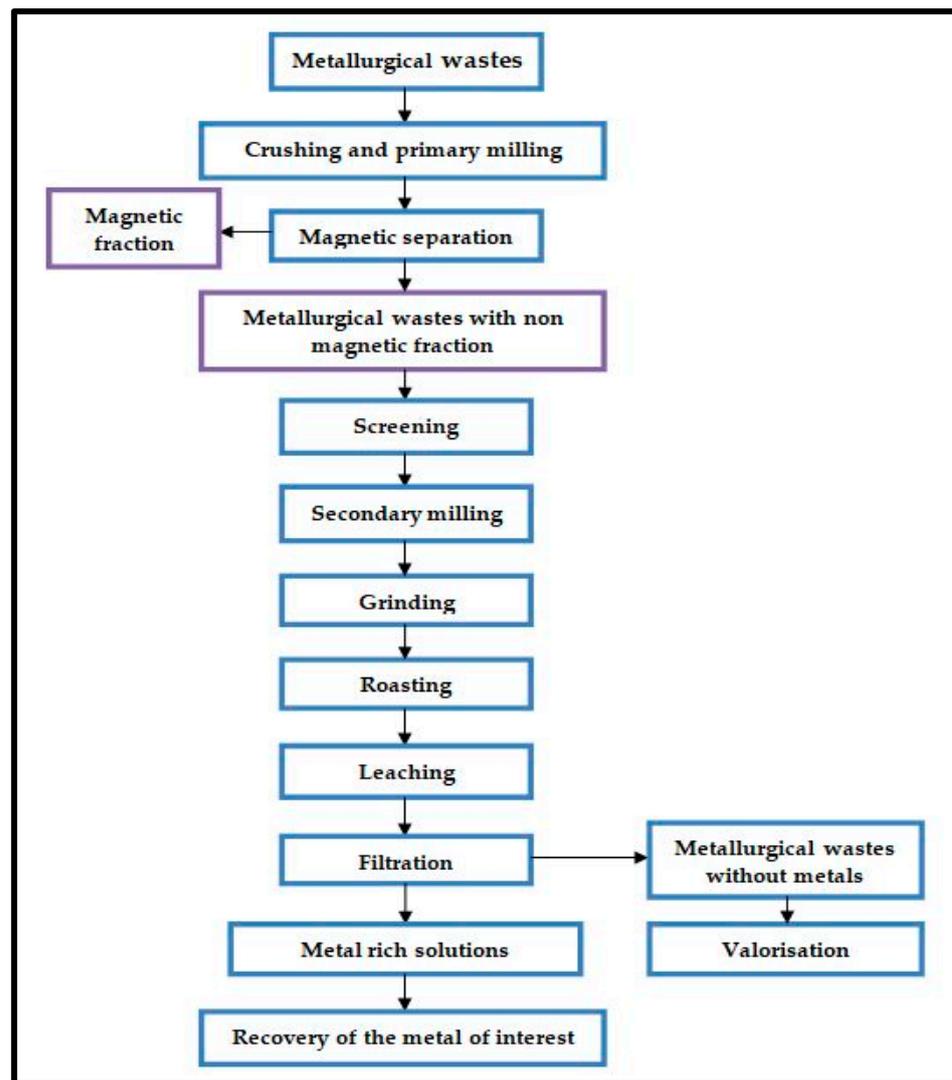


Figure 5. Conceptual diagram with stages for treatment of metallurgical wastes in order to recover the metal of interest.

Figure 6 shows the conceptual diagram for the treatment of metallurgical wastes in order to recover the heavy metals (Pb, Cd, Sb, As, etc.) by biohydrometallurgical methods and to recover of the metal of interest (the valuable metal) by hydrometallurgical methods.

According to the conceptual diagram from Figure 6, metallurgical wastes are subjected, in the first stage, to biohydrometallurgical methods, in order to recover the heavy metals (such as Pb, Cd, Sb, As, etc.), with the help of microorganisms. The recovery of heavy metals by these methods prevents the generation and elimination of toxic compounds in the environmental factors. In the second stage, the metallurgical wastes are subjected to hydrometallurgical methods in order to recover the valuable metals.

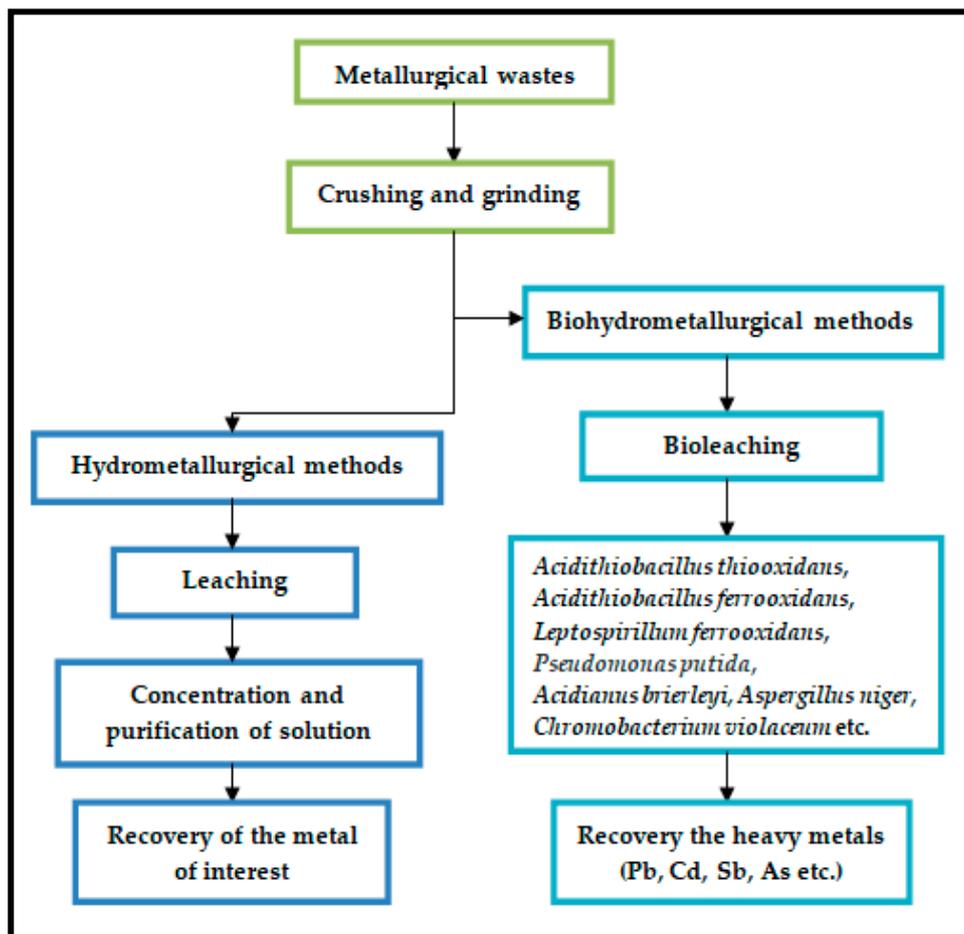


Figure 6. Conceptual diagram with stages for treatment of metallurgical wastes in order to recover the heavy metals and to recover the metal of interest (the valuable metal).

4. Recovery Potential of Metals from Slag Dump

Both the determination of average metal concentrations from slag dumps and the calculation of their recovery potential make up the basis for designing recycling processes. Therefore, the characterization of the metallurgical wastes step was completed followed by the assessment of the recovery potential of the metals from the Păgida slag dump. Table 8 summarizes the average metal concentrations and recovery potential of metals from the Păgida slag dump. Recovery potential was estimated by using the average metal concentration. The price of metals was taken from references [31–35].

According to the values presented in Table 8, iron (Fe) has the highest recovery potential from slag dumps with 183,960 metal tons and its economic value is USD 77.9990 million. Copper (Cu), vanadium (V), molybdenum (Mo) and nickel (Ni) have high recovery potential and they are also valuable metals. Economic values of their recovery are USD 25.5759 million, USD 1002.0549 million, USD 46.2840 million and USD 13.9901 million. Vanadium has the greatest economic value. The total economic value of the recovery potential of metals from the slag dump in Păgida was assessed to be USD 1175.7440 million. The recovery of valuable metals from the slag dump may be the main goal of the recycling process. The metals from metallurgical wastes can be reused as raw and additional materials in the process from which they originate or in other technological processes.

Table 8. Average metal concentrations and recovery potential of metals from slag dump.

Elements	Average Concentrations	Average Concentrations	Recovery Potential	Price of Metals	Economic Value
	(mg/kg)	(Metal Ton/Waste Ton)	(Metals Tons from Slag Dump)	(USD/ton) [29–33]	(USD Millions)
V	3098.5	0.0030985	2602.74	385,000.00	1002.0549
Cr	120.5	0.0001205	101.22	9400.00	0.9514
Ni	846.5	0.0008465	711.06	19,675.00	13.9901
Cu	3204	0.003204	2691.36	9503.00	25.5759
Zn	98.5	0.0000985	82.74	3006.00	0.24871
As	88.5	0.0000885	74.34	1310.00	0.0973
Mo	1298	0.001298	1090.32	42,450.00	46.2840
Sn	184	0.000184	154.56	36,475.00	5.6375
Sb	131	0.000131	110.04	8132.00	0.8948
Pb	42	0.000042	35.28	2469.00	0.0871
Cd	838.5	0.0008385	704.34	2730.00	1.9228
Fe	219,000	0.219	183,960	424.00	77.9990
		Total			1175.7440

Economic issues regarding the variability in metal markets include: upward trend in demand on the metals market, generated by their criticality; variability and volatility of spot price for metals on the market; variability and volatility of future price for metals on the market; the global industrial production fluctuations; variability in demand and supply on the metals market, which are factors of direct influence on the price; exchange rate; pandemic with COVID 19; disruptive factors (such as war), etc.

5. Critical Metals Connected with Market Demand

Total vanadium demand is dominated by the steel industry, which accounted for 91% of total demand in 2021 and will remain the largest source of vanadium demand in the future [80]. According to Roskill [81], vanadium demand in the steel market will grow at a CAGR of about 2.7% through to 2030, with global vanadium demand from steel reaching approximately 136,000 tones by 2030. Vanadium is rated low for green technologies, while for other applications it is rated very high. Developed economies, such as Europe, Japan and North America, have higher vanadium intensity than developing countries. China surpasses the world average in its intensity of use. The demand for vanadium in the EU is projected to increase in all applications (steel, titanium, chemicals and energy storage) [82].

Titanium demand is tied to macroeconomic factors and, accordingly, tracks global gross domestic product, avoiding the deep cyclical price volatility of many industrial commodities. Consumption is concentrated in North America and Europe, with major growth in China. In the last 25 years, overall demand has grown by about 3% CAGR per year. Global demand has proven very resilient during 2020, while post-COVID growth is forecast by industry experts of up to 1.7% CAGR by 2021/2022 [83].

The market demand for critical metals, recovered through 2000 and 2050, covering eight metals: chromium, cadmium, molybdenum, lead, zinc, tin, copper and nickel, shows an upward trend until 2050. These trends of the metals emphasize the need for a long-term, global projection of demand for critical metals, since such a global outlook will provide the underlying information needed to construct an international framework for sustainable use and technological development. [84].

From analysis of the market demand for the critical metals, it results that they show an upward trend. The analyzed metallurgical waste presents an important source of critical metals, whose demand is expected to increase until 2050. The recovery of critical metals from metallurgical wastes leads to the conservation of natural resources and to sustainable development in the steel industry.

6. Conclusions

The mineralogical characterization of metallurgical wastes performed in this study is useful to identify their potential applications. The characterization of wastes plays a key role in their potential use and in establishing the opportunities for natural resource conservation. The results obtained from the chemical characterization of metallurgical wastes indicated the presence of the following compounds: MgO, CaO, Al₂O₃, Fe_{total}, SiO₂, MnO, P₂O₅, V₂O₅ and TiO₂. Improving the management of metallurgical waste, by reusing iron, contributes to metals' conservation. According to mineralogical characterization, in the metallurgical wastes the following compounds were identified: Magnesioferrite, Magnetite, Hedenbergite, Calcium iron oxide, Fe–Ringwoodite, Andradite, Brownmillerite, Fayalite magnesian manganoan, Fayalite manganoan and Periclase. The mineralogical compounds that present reuse potential in different domains are: Fayalite, Magnetite, Magnesioferrite and Periclase. The compounds from metallurgical wastes can be reused as: raw and additional materials in the process from which they originate; raw and additional materials in road construction and concrete production; pigments in paints; micronutrients in fertilizers; ore of iron, etc.

Metallurgical wastes from the slag dump may be treated as raw and secondary materials. The total economic value of the recovery potential of metals from the slag dump in Păgida was assessed to be USD 1175.7440 million. This research will be useful in economic activities related to metallurgical wastes, as a source of raw and auxiliary materials for various processes. The results can be extrapolated to other slag dumps if the wastes originate from steelmaking. In addition, further research activities should incorporate the development and establishment of universal analytical methods for rapid quantification of valuable metals from metallurgical wastes.

The analyzed metallurgical waste presents an important source of critical metals, whose demand is expected to increase until 2050. The recovery of critical metals from metallurgical wastes leads to the conservation of natural resources and to a sustainable development in the steel industry.

The research results of the paper can lead to an improvement in sustainability in the steel industry by: improving the metallurgical waste management from the slag dump; increasing the degree of recycling of metallurgical wastes from the slag dump; conserving the natural resources; eliminating the problems regarding the pollution of the environmental factors, due to the slag dump, by recycling the landfilled metallurgical wastes; eliminating the negative effects on human health; reusing or recycling metallurgical waste causing delays in the exploitation of natural resources.

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Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

The mineralogical compounds identified in metallurgical waste sample 1.

No.	Symbol	2 θ (Degree)	Interplanar Distance d	Interplanar Distance from the Reference Chart d _{ref}	Chart No	Mineralogical Name and Chemical Formula	Miller Indexes h k l
1	R	30.92	2.89	2.89	83–2074	Fe–Ringwoodite Fe ₂ (SiO ₄)	2 2 0
2	C	34.25	2.63	2.63	31–0274	Calcium Iron Oxide CaFe ₃ O ₅	0 0 3
3	C	35.08	2.49	2.49	31–0274	Calcium Iron Oxide CaFe ₃ O ₅	3 2 0
4	R	36.25	2.46	2.46	83–2074	Fe–Ringwoodite Fe ₂ (SiO ₄)	3 1 1
5	B	36.93	2.43	2.43	74–1346	Brownmillerite FeAlO ₃ (CaO) ₂	2 1 1
6	H	37.99	2.36	2.36	87–1705	Hedenbergite CaFe(Si ₂ O ₆)	1 3 1
7	C	42.80	2.11	2.11	31–0274	Calcium Iron Oxide CaFe ₃ O ₅	3 2 2
8	B	50.50	1.79	1.79	74–1346	Brownmillerite FeAlO ₃ (CaO) ₂	0 6 2
9	B	50.66	1.79	1.79	74–1346	Brownmillerite FeAlO ₃ (CaO) ₂	2 3 2
10	B	53.99	1.69	1.69	74–1346	Brownmillerite FeAlO ₃ (CaO) ₂	1 0 3
11	B	56.32	1.63	1.63	74–1346	Brownmillerite FeAlO ₃ (CaO) ₂	0 7 2
12	H	58.48	1.57	1.57	87–1705	Hedenbergite CaFe(Si ₂ O ₆)	5 3 0
13	A	61.68	1.50	1.50	10–0288	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	8 0 0
14	M	62.41	1.48	1.48	88–1941	Magnesioferrite MgFe ₂ O ₄	4 4 0
15	Ma	67.21	1.39	1.39	73–2273	Magnetite Mg _{0.04} Fe _{2.96} O ₄	4 4 2
16	H	67.62	1.38	1.38	87–1705	Hedenbergite CaFe(Si ₂ O ₆)	1 5 2
17	Ma	71.28	1.32	1.32	73–2273	Magnetite Mg _{0.04} Fe _{2.96} O ₄	6 2 0
18	H	72.29	1.30	1.30	87–1705	Hedenbergite CaFe(Si ₂ O ₆)	–7 1 2
19	M	73.90	1.28	1.28	88–1941	Magnesioferrite MgFe ₂ O ₄	5 3 3
20	Ma	74.46	1.27	1.27	73–2273	Magnetite Mg _{0.04} Fe _{2.96} O ₄	5 3 3

No.	Symbol	2 θ (Degree)	Interplanar Distance d	Interplanar Distance from the Reference Chart d _{ref}	Chart No	Mineralogical Name and Chemical Formula	Miller Indexes h k l
21	R	77.59	1.23	1.23	83–2074	Fe–Ringwoodite Fe ₂ (SiO ₄)	6 2 2
22	H	80.21	1.19	1.19	87–1705	Hedenbergite CaFe(Si ₂ O ₆)	1 7 1
23	H	80.60	1.19	1.19	87–1705	Hedenbergite CaFe(Si ₂ O ₆)	5 5 1
24	Ma	83.28	1.16	1.16	73–2273	Magnetite Mg _{0.04} Fe _{2.96} O ₄	7 1 1
25	R	84.95	1.14	1.14	83–2074	Fe–Ringwoodite Fe ₂ (SiO ₄)	7 1 1
26	H	88.91	1.10	1.10	87–1705	Hedenbergite CaFe(Si ₂ O ₆)	5 1 3
27	M	89.15	1.09	1.09	88–1941	Magnesioferrite MgFe ₂ O ₄	7 3 1
28	A	99.75	1.00	1.00	10–0288	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	12 0 0
29	A	101.43	0.99	0.99	10–0288	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	12 2 0

Appendix B

The mineralogical compounds identified in metallurgical waste sample 2.

No.	Symbol	2 θ (Degree)	Interplanar Distance d	Interplanar Distance from the Reference Chart d _{ref}	Chart no	Mineralogical Name and Chemical Formula	Miller Indexes h k l
1	F	31.51	2.83	2.83	88–1998	Fayalite Magnesian manganooan Mg _{1.145} Fe _{1.742} Mn _{0.113} SiO ₄	1 3 0
2	F	31.63	2.82	2.82	88–1997	Fayalite magnesian manganooan Mg _{0.347} Fe _{1.548} Mn _{0.105} SiO ₄	1 3 0
3	Fm	33.5	2.66	2.66	12–0220	Fayalite manganooan (Fe.Mn) ₂ SiO ₄	2 4 0
4	A	33.71	2.66	2.66	03–1136	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	4 2 0
5	A	36.97	2.43	2.43	03–1136	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	4 2 2

No.	Symbol	2 θ (Degree)	Interplanar Distance d	Interplanar Distance from the Reference Chart d _{ref}	Chart no	Mineralogical Name and Chemical Formula	Miller Indexes h k l
6	B	39.88	2.2	2.2	11-0124	Brownmillerite (Calcium Aluminium Iron Oxide) $\text{Ca}_4\text{Al}_2\text{Fe}_2 + 3\text{O}_{10}$	2 3 1
7	P	42.94	2.10	2.10	43-1022	Periclase MgO	2 0 0
8	F	45.56	1.98	1.98	88-1998	Fayalite magnesian manganooan $\text{Mg}_{.145}\text{Fe}_{1.742}\text{Mn}_{.113}\text{SiO}_4$	0 4 2
9	F	45.90	1.98	1.98	88-1997	Fayalite magnesian manganooan $\text{Mg}_{.347}\text{Fe}_{1.548}\text{Mn}_{.105}\text{SiO}_4$	2 3 0
10	B	47.61	1.92	1.92	11-0124	Brownmillerite (Calcium Aluminium Iron Oxide) $\text{Ca}_4\text{Al}_2\text{Fe}_2 + 3\text{O}_{10}$	2 1 2
11	B	44.06	1.86	1.86	11-0124	Brownmillerite (Calcium Aluminium Iron Oxide) $\text{Ca}_4\text{Al}_2\text{Fe}_2 + 3\text{O}_{10}$	2 2 2
12	Fm	50.83	1.79	1.79	12-0220	Fayalite manganooan $(\text{Fe.Mn})_2\text{SiO}_4$	2 4 0
13	Fm	53.58	1.71	1.71	12-0220	Fayalite manganooan $(\text{Fe.Mn})_2\text{SiO}_4$	2 4 1
14	F	53.79	1.70	1.70	88-1997	Fayalite magnesian manganooan $\text{Mg}_{.347}\text{Fe}_{1.548}\text{Mn}_{.105}\text{SiO}_4$	2 4 1
15	F	56.50	1.62	1.62	88-1998	Fayalite magnesian manganooan $\text{Mg}_{.145}\text{Fe}_{1.742}\text{Mn}_{.113}\text{SiO}_4$	1 5 2
16	R	57.64	1.59	1.59	74-1002	Fe-Ringwoodite $\text{Fe}_2(\text{SiO}_4)$	5 1 1
17	F	60.15	1.53	1.53	88-1998	Fayalite magnesian manganooan $\text{Mg}_{.145}\text{Fe}_{1.742}\text{Mn}_{.113}\text{SiO}_4$	2 5 1
18	P	62.14	1.49	1.49	43-1022	Periclase MgO	2 2 0
19	F	66.26	1.41	1.41	88-1998	Fayalite magnesian manganooan $\text{Mg}_{.145}\text{Fe}_{1.742}\text{Mn}_{.113}\text{SiO}_4$	2 6 0
20	F	68.10	1.37	1.37	88-1998	Fayalite magnesian manganooan $\text{Mg}_{.145}\text{Fe}_{1.742}\text{Mn}_{.113}\text{SiO}_4$	2 6 1
21	F	68.46	1.37	1.37	88-1998	Fayalite magnesian manganooan $\text{Mg}_{.145}\text{Fe}_{1.742}\text{Mn}_{.113}\text{SiO}_4$	3 2 2

No.	Symbol	2 θ (Degree)	Interplanar Distance d	Interplanar Distance from the Reference Chart d _{ref}	Chart no	Mineralogical Name and Chemical Formula	Miller Indexes h k l
22	A	69.98	1.34	1.34	03–1136	Andradite(Calcium Iron Silicate)Ca ₃ Fe ₂ + 3(SiO ₄) ₃	8 4 0
23	F	70.81	1.33	1.33	88–1998	Fayalite magnesian manganooan Mg _{1.145} Fe _{1.742} Mn _{0.113} SiO ₄	3 4 1
24	R	72.03	1.31	1.31	74–1002	Fe–Ringwoodite Fe ₂ (SiO ₄)	6 2 0
25	A	73.83	1.28	1.28	03–1136	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	6 6 4
26	P	74.08	1.27	1.27	43–1022	Periclase MgO	3 1 1
27	R	75.62	1.25	1.25	74–1002	Fe–Ringwoodite Fe ₂ (SiO ₄)	6 2 2
28	F	81.44	1.18	1.18	88–1998	Fayalite magnesian manganooan Mg _{1.145} Fe _{1.742} Mn _{0.113} SiO ₄	3 3 3
29	R	83.10	1.16	1.16	74–1002	Fe–Ringwoodite Fe ₂ (SiO ₄)	7 1 1
30	F	84.44	1.14	1.14	88–1998	Fayalite magnesian manganooan Mg _{1.145} Fe _{1.742} Mn _{0.113} SiO ₄	0 6 4
31	F	83.56	1.13	1.13	88–1998	Fayalite magnesian manganooan Mg _{1.145} Fe _{1.742} Mn _{0.113} SiO ₄	1 9 0
32	R	87.02	1.11	1.11	74–1002	Fe–Ringwoodite Fe ₂ (SiO ₄)	6 4 2
33	A	87.78	1.11	1.11	03–1136	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	9 6 1
34	A	89.32	1.09	1.09	03–1136	Andradite (Calcium Iron Silicate) Ca ₃ Fe ₂ + 3(SiO ₄) ₃	8 7 3
35	P	93.90	1.05	1.05	43–1022	Periclase MgO	4 0 0
36	P	105.90	0.96	0.96	43–1022	Periclase MgO	3 3 1
37	P	108.50	0.97	0.94	43–1022	Periclase MgO	4 2 0

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