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QUALITATIVE CHARACTERISATION OF SMALL AND POWDERY WASTE WITH IRON CONTENT

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Abstract: The steel industry is a sector where the concept of sustainable development is operationalized, and the circular economy must be implemented by recycling secondary products and transforming them into by–products used as components of natural capital. Small and powdery waste containing iron from the steel industry has a high content of useful elements that can be recovered by using them in the processing of aggregates as raw materials or auxiliary materials. To choose the optimal waste recovery technology, it is necessary to characterise it qualitatively. The purpose of the work is to present the provenance and qualitative characteristics of small and powdery industrial waste with iron content, highlighting the importance of the recovery process and the introduction of waste into the national economic circuit according to the principles of circular and green economy.
Keywords: small waste with iron content, qualitative characterization of waste, recovery

1. INTRODUCTION

Waste from the steel industry containing chemically bound iron may be classified according to several criteria.

According to the literature [1,2], the most comprehensive classification criterion considers the particle size (particle size structure) of the waste, according to which the waste is divided into the following two categories: powdered ferrous waste (dusty) and ferrous waste in the form of pieces.

Figure 1 shows the types of waste generated according to their place of production (blast furnace, steelworks, rolling mills, etc.).

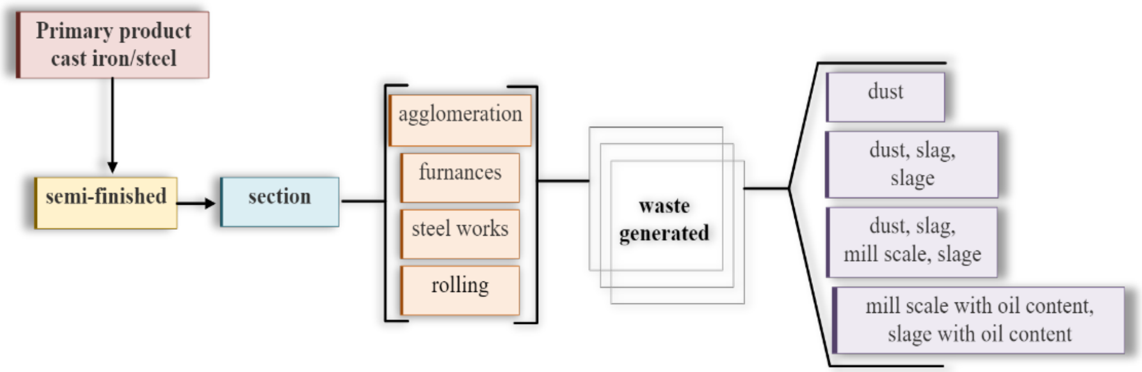

Figure 1. Types of waste in a steel plant [3,4]

Powdered ferrous waste comes primarily from steel activity being the result of various cleaning operations for exhaust gases and wastewater [1,4–6].

Small ferrous waste comes from steel processes (mill scale and steel slag in the ferrous fraction), and from the mining industry – preparation of sideritic ores (ferrous concentrate from sideritic waste) [1,4–6].

In the present work, the authors aim to identify the main types of small and powdery waste with iron content generated within the current steel elaboration flows in the electric arc furnace, presenting a brief characterisation of the identified waste as well as of the sources of origin.

2. METHODOLOGY

Within the present work, there is an extensive study of the specialised literature and reference to a set of reality research on these types of waste, the authors want to emphasise the importance of valuing and introducing waste in the economic circuit according to the principles of the circular and green economy.

Slag

The residue resulting from the metal/alloy manufacturing processes during the melting stage is known as slag.

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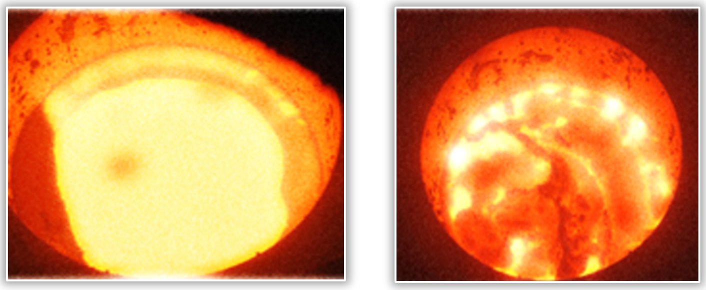
In general, steel slags are represented by residues resulting from the process of obtaining metals and represent approximately 70% of total waste generated within the steel sector, being the most common type of waste [2–4].

Currently, the main method of obtaining slag in metallurgy remains the melting process in the elaboration aggregate, where the slag decants above the surface of the melt and is removed by a special hole [7].



(a) (b)

Figure 2. The formation of the slag layer above the molten steel inside a crucible, a – the slag has not yet formed, b – the slag was formed [8]

In Figure 2 represents the process of slag formation on the surface of the metal melt.

Slag, depending on its source of provenance, can be [3,4]:

- steel slag, which has a high iron content of about 20%;
- blast furnace slag where the iron content is usually 0,5 %.

Steelwork slag is the main by–product of steelmaking processes in electric arc furnaces, induction furnaces, and oxygen converters. Steelwork slags, regardless of the type of elaboration aggregate, consist of solid phases and chemical compounds, but also contain cold droplets of metal/alloy (solidified splashes) [3].

The blast furnace slag, which is not the object of this work, is formed during the cast iron manufacturing process, at elevated temperatures, and then solidifies during the cooling stage.

By directing and controlling the cooling process, since the slags in the first phase are liquid, the following three types of slags are obtained in the solid state [3,4,9]:

- slag slowly cooled in the air — found in the form of pieces (Figure 3a);
- semi–cold slag with water — it is obtained in the form of an expanded material, also called steel pumice stone;
- slag cooled rapidly with water or air — is called granulated slag (Figure 3b2).

Rapid or slow cooling affects the properties of the slag; for each tone of the slag cooled with water, about 1–1,5t of water is needed [12].

Depending on the metal elaboration phases, the slag can be primary (it is formed in the first part of the elaboration) and secondary (it is formed at the time of completion of the elaboration), respectively.

(a)

(b1) (b2)

Figure 3. Types of metallurgical slag [7,10,11]
a- raw and unprocessed slag; b- processed slag; b1- slag in pieces; b2- granulated slag

Knowledge of the chemical composition of slag is useful, but insufficient, because it does not indicate its most important characteristics. In Table 1, the chemical composition of a steelwork hole is presented for guidance purposes.

Table 1. The chemical composition of steelwork slag [2,3]

Chemical element	Fe	CaO	SiO_2	Al_2O_3	MgO	MnO
Quantity [%]	28,84	40,22	12,31	1,97	4,56	4,56

Steel slag is most often subjected to processing operations, after which the ferrous fraction (about 5–20%) [3,4], which has a high iron content, is separated from the deferrized fraction (which does not contain iron) through the magnetic separation process.

In Romania, it was found that, on average, a quantity of 250kg of slag/t of steel is obtained [4], the amount of slag resulting depending on the performance of the process, respectively 250–300kg of slag/t of cast iron [13].

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The attractiveness of reuse of this type of waste in the steel industry is due to the high Fe content, which gives it a high metallurgical value. The disadvantage encountered in the use of slag in the steel industry is caused by the variation in the Fe content (12–30%) [3].
Before actual valorisation of the slag, it is subjected to some physical–mechanical processing operations (crushing — magnetic concentration — classification), after which metallic fractions are obtained, with various granulations and content from 50–55% Fe to 80–90%Fe, which can be used in the steelmaking process as secondary raw material [14].
Figure 4 shows the diagram of the metallurgical slag processing process.

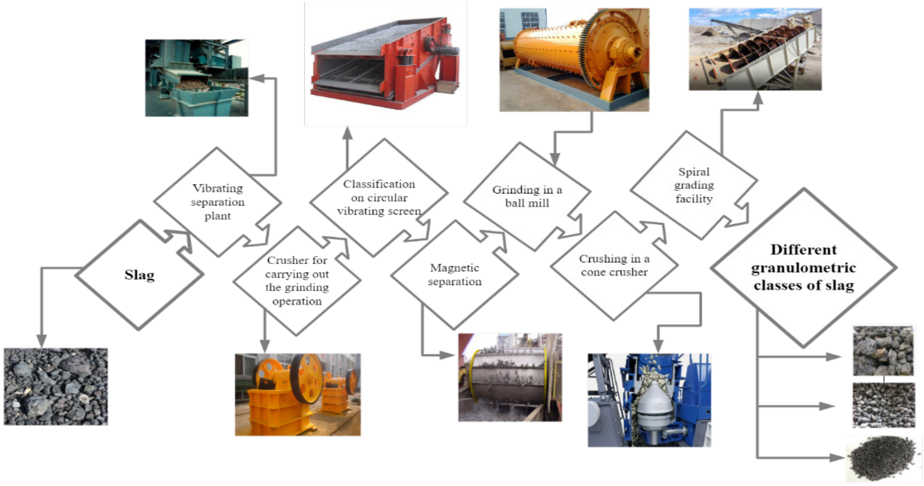

Figure 4. Exemplifying a concrete process of slag processing [10]

The capitalisation of the slags is of real interest from both an economic and ecological point of view [13].

Electric steel mill/electrofilter dust

Steel mill dust results in steelmaking flow after the dedusting of gases emitted by elaboration aggregates (electric arc furnaces) [2–5,15].
According to the specialised literature [2–5,15] steel mill dust (figure5) has a high degree of fineness, 90% of the particles having a size smaller than 60μm.
The importance of this type of waste is relevant in view of the high content of Zn, which is of interest to the nonferrous industry and the Fe content, which is why it can be exploited in steelmaking processes.

Figure 5. Steel mill dust [16]

If the steel dust has a Zn content not in the range of 3–27% [4], it may not be used in the preparation of cast iron and steel, unless certain zinc abatement technologies are used.
In steelmaking practise, steel mill dust is frequently recirculated within processing flows, which is why this waste reaches a Zn content between 15–25%. When these levels are reached, the steel dust is stored or sent for processing within the non–ferrous industry [4].
This practise of storing steel dust in premises located on the site or near the steel plants is practised by S.C ArcelorMittal Hunedoara S.A, Mechel Câmpia Turzii S.A, Mechel Târgoviste S.A. [3,4], because they no longer have processing flows corresponding to this type of waste.
Steel dust generated by the current flow of steel elaboration within the ArcelorMittal Hunedoara plant is capitalised by specialised companies [17]. In the past, the quantities of steel mill dust generated within the former Simmens Martin steel mill (Simmens Martin II steelworks II) of the Hunedoara Steel Plant were recycled by agglomeration, before the decommissioning of the agglomeration furnace sector, the rest being still stored in closed spaces (disused halls from rolling mills [2]. For quantities still in the stage of permanent storage (historical storage), it is necessary to find solutions.
By processing steel mills, dust can be an important raw material for steel processes [2]. According to some research studies conducted [2–4,15], knowing the chemical composition of small and powdery waste from current streams of elaboration of Fe–C alloys (cast iron, steel) is particularly important to choose the optimal recovery technology and to determine or know the impact caused by their storage on the environment.

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In Table 2 are presented for comparison the main elements of the chemical composition of the steel dust from AcelorMittal Hunedoara and TMK Resita now owned by Artrom Steel Tubes.

Table 2. The main elements in the chemical composition of steelwork dust [3,4]

Source of provenance	Chemical element, [%]							
	Fe	C	Pb	ZnO	MnO	MgO	CaO	SiO_2
ArcelorMittal Hunedoara	43,40	3,4	1,45	13,04	3,96	2,85	5,55	2,65
TMK Resita	36,82	1,42	1,27	10,81	3,43	2,95	8,43	4,34

As seen in Table 2, the iron and zinc oxide content of the ArcelorMittal Hunedoara steel mill dust exceeds the values obtained for the steel mill dust from TMK Resita.

The chemical composition of steel dust varies depending on the type of steel manufactured and the production flow used (oxygen furnace–converter, electric arc furnace) [18]. For example, according to research in the literature, the production of one tone of stainless steel produces quantities between 18–33kg of steel dust, with particle sizes smaller than 50µm. Steel dust–type waste containing, as mentioned above, a large amount of Fe and other metals (Cr, Ni) [19].

This type of waste, due to the high degree of finesse and handling operations to which it is subjected [2], causes an elevated level of air pollution.

Mill scale and mill scale sludge

In the process of steel processing in steel plants, a burn is formed on the metal surface during the operations of continuous casting, reheating, and hot rolling; this burn is made up of iron oxides and is called scale [20,21].

This type of waste is usually removed from industrial water used to cool steel blanks. During the hot processing process and in the presence of gases containing oxygen (including air), the surface of the steel spontaneously corrodes to a layer of ferrous oxide called milling [21,22].

The mill scale comes from the hot rolling process, which is made up of iron oxides in the form of a burn that detaches and falls off the ingot during the heating, handling, and processing of the cast blanks.

In figure 6 you can see how the shredder waste appears on the continuously cast blanks.

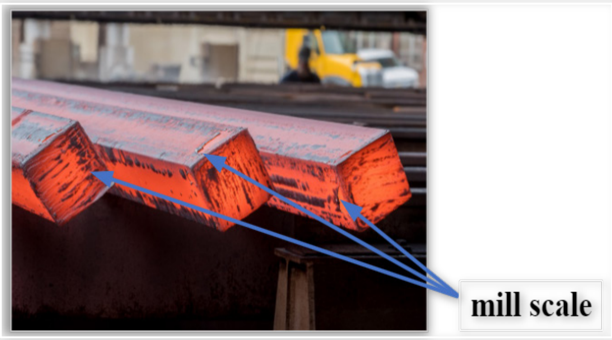

Figure 6. Formation of waste known as mill scale on the surface of continuously cast ingots [23]

According to the literature [1–4], the mill scale consists of mixtures of FeO and Fe_2O_3 (hematite) and a part of the tailings (non–useful part) between 0.5–15%. On average, the mill scale represents 3–4% of the total steel production [4].

According to the legislation, the mill scale is considered a non–hazardous waste (Figure 7). Although this is an inert waste, storing it in the soil near the waters can cause a high degree of pollution.

Figure 7. Forms under which the waste known as mill scale is found

The chemical composition of the mill scale differs depending on the steel from which it comes from, which contributes to its consideration as an important material within any steel plant, due to its high iron content.

The mill scale sludge is generated during the continuous rolling and casting process, being taken over by the cooling water and transported to the treatment plants to be separated [2–4].

The mill scale waste has thicknesses between 0.1–50mm and lengths, respectively, widths of the order of centimeters. Upon contact with water, it cracks, crumbling in small particles that resemble fine dust [2–4].

Within the iron and steel company S.C ArcelorMittal Hunedoara S.A, the mill scale produced is stored in a hall in the section of the Semi–Finished Mill 2, set up as a covered warehouse, with a platform, where the dehydrated (dry) mill scale is also stored [2–4].

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The former Hunedoara Steel Plant, currently ArcelorMittal, used the mill scale produced until 1999 within the agglomeration–furnace sector, and after the closure of the sector, it also began to dump it [2–4]. Similarly, the Galati steel plant capitalised on the mill scale in the agglomeration process and directly in the furnace load [2,4].

As a result of the expansion of the steel industry's preference for continuous casting processes, the amount of waste generated, including the mill scale sludge waste that can be successfully reintroduced into the steel circuit, has also inevitably increased.

The mill scale generated in the rolling mill sector contains significant amounts of oil, which limits the possibilities for it to be reused; however, the attributes that recommend its capitalisation are directly related to the high iron content (60–72%), the low amount of residuals contained, and the lack of elements that can harm steel quality (Pb, Cu, Sn) [1–4].

Currently, emphasis is placed on the problem of storing the mill scale generated on the current flows compared to the already stored. Currently, at the Hunedoara plant, the mill scale is not directly capitalised in the elaboration processes because the blast furnace agglomeration flow has been completely decommissioned. However, it, according to Table 3, is converted into a by–product applicable in other industries.

Table 3. Specific measures for the prevention and reduction of the resulting waste quantities, implemented in ArcelorMittal Hunedoara [17]

Waste	Provenance	Management activities			Actions taken to prevent / minimize waste generation
		Recovery	Recycling	Eliminate	
Slag	Steel elaboration	x			Transformation into a by–product
Unprocessed slag	Steel elaboration	x			Proper contracting of scrap metal sorts sorting/ compliance with technological standards
Steel mill dust	Steel elaboration	x		x	Proper contracting of scrap iron grades sorting of metal cargo / compliance with the technological norms' capitalisation with specialised companies
Mill scale	Continuous casting and hot rolling	x			Turned into a by–product
Mill scale sludge	Cooling water treatment	x			Optimisation of blum heating process and production schedule

At Liberty Galati, the mill scale is stored directly on the ground and dumped, which causes a certain degree of soil pollution. Unlike ArcelorMittal Hunedoara in Liberty Galati, mill–scale waste is capitalised and transformed into agglomerated, which is later used as a secondary raw material in the steelmaking process — Table 4.

Table 4. Management of the main waste of steel activity [25]

Name of waste	Provenance	Management methods		
		Recovery	Eliminate	Storage
mill scale sludge	rolling mill sector	–	specialised companies	temporary in the rolling mill and in temporary storage of hazardous waste
mill scale	rolling mill sector	recycled onto the production stream of the agglomerates.	–	temporarily within the section, on a concrete platform to dry
slag	steelworks/kilns sector	recovery within the temporary storage space	–	temporary at the rolling mill and in the temporary storage area for non–hazardous waste

At Liberty Galati, over the course of several years, the recovery of a fraction of the mill scale waste, of approximately 3000–7000 tons/year has been achieved [26,27].

Although this waste has a high iron content, on average 68–72% [27], it is sold very cheaply as industrial waste in the form of iron oxide, rather than being collected and valued in the steel industry.

3. CONCLUSIONS

From an environmental protection point of view, the exploitation of steel slags has the effect of freeing up the land occupied by slag dumps and restoring the landscape. If slags are used in the construction field, the raw materials that would have been used are preserved, the costs of carrying out the works being lower. The utilisation of slag has other economic advantages in addition to those presented above, such as, for example, its use as a fertiliser in agriculture.

Most of the waste resulting from current steel development streams (slag, mill scale, and mill scale sludge, steel mill dust) is processed, to some extent, after generation, but due to the fast pace of waste production, it is not possible to keep up with the processing activities that proceed more slowly, leading to the long storage of these types of waste in decommissioned halls or directly in nature.

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The small and powdery waste with iron content generated by the steel industry cause a high degree of pollution, which is why it is necessary to qualitatively characterise these types of waste, to choose the optimal recovery process that generates by–products that are subsequently used as raw materials in the cast iron and steel elaboration aggregates.

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