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MANAGEMENT AND CHARACTERISATION OF INDUSTRIAL WASTE CONTAINING IRON

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Abstract: In the steel industry, a significant amount of waste is frequently generated, the vast majority having a high content of iron and other useful elements; for this reason, it is necessary and recommended that small and powdery industrial waste containing iron be recovered and not stored, within the same manufacturing flows where it was generated following the principles of the circular economy or, where it is not possible (due to limiting factors related to chemical composition, granulation, technological limitations, etc.), recycling is carried out in other industries (e.g. nonferrous, building materials, etc.). Their capitalization and return in the form of by–products in the steel industry or other industrial sectors produces economic and ecological effects. The work presents the possibilities of managing and characterizing some industrial waste with iron content, historically stored, and results on manufacturing flows.
Keywords: steel industry, industrial waste containing iron, management, long storage

INTRODUCTION

A significant amount of iron–containing industrial waste is generated annually in Romania, especially by the steel industry. Approximately 45–50% of the generated waste is currently reintroduced into manufacturing streams, while 55–50% of the waste is deposited, accumulating in storage ponds or other types of sites (dumps), leading to a major negative impact on the environment [1].

For these reasons, the situation of the sites where the storage of iron–containing industrial waste was carried out, on the territory of Romania, is being investigated.

Within the work, the objective is to carry out an analysis of inventory and identification of the main industrial wastes with iron content predominantly from the steel industry that are historically deposited on the territory of our country and for which it is necessary to take recovery measures (following the principles of the circular economy and introducing the waste with iron content in the processes in which they were generated, basically in the steelmaking process).

METHODOLOGY

In this paper, the authors sought to identify iron–containing waste that has historically been stored and to present a detailed description of their situation, on the territory of Romania, supported by current data.

TYPOLOGY & SOURCES OF IRON–CONTAINING WASTE HISTORICALLY STORED

Steel industry

≡ Slag

At the national level, the storage of slag in dumps has been uncontrolled, which is why there is no record of the quantity and quality of this type of waste. These sites are in fact undeveloped areas, exposed to the action of chemical and physical agents, which makes it difficult to efficiently capitalise on the heaps [2,3]. The theoretical concept of a "zero dump" is a goal that is tended towards; from a realistic point of view, the purpose of this concept is to continuously minimise the existing heaps by finding and applying modern technologies to harness the slags [2,4].

In Romania, at the moment, there are dumps where a large amount of steelworks are stored; these dumps are presented in Table 1, specifying the years related to the start of the storage activity, respectively, of the recovery activity. It should be noted that some of the sites are still in the recovery phase [2].

Table 1. Slag dumps in Romania [2–6]

Location of the dump	The beginning year of the dump	The beginning year of the capitalisation processes of the dump
Reșița	1771	2002
Oțelul Roșu	1857	1999
Hunedoara	1965	2007
Călan	1871	2000
Câmpia Turzii	1920	2002
Galați	1968	2003
Târgoviște	1971	1998

Capitalisation of the slag dumps is carried out by specialised companies. The slag dumps located in Târgoviște, Câmpia Turzii, and Reșița began to be capitalised by companies such as Alexander Mills Service and Slag Recycling Enterprise (Reșița). To capitalise on the slag dump from Galați, DSU Duisburg was contracted in the first phase. For the capitalisation of the Hunedoara dump, companies such as Slag Processing Service and S.C Grampet S.A. were contracted [2,3,7].

And in terms of the slag dump in Călan, this was also concessioned; On the ruins of the former Victoria Călan complex, greening activities were carried out that led to the opening of an industrial park.

The old slag dump of the Hunedoara plant was arranged in 1965, occupying an area of 40 hectares on which about 21 million tons of slag were stored [8]. At the beginning of 1978, the area was extended by another 40ha, due to the increase in the company's production capacity and implicitly, the increase in the amounts of slag generated in flows (furnaces, steelworks) [9].

Currently, the slag stored in the Buituri landfill is being processed. Since 2018, the company that deals with the activity of slag exploitation stored on the dump site is S.C. Grand Smithy Works International S.R.L., which has the responsibility of processing the slag (12200t/day) to obtain the ferrous fraction, sorted by three categories of dimensions, respectively, of the non–ferrous fraction [8].

A part of the processed slag in the pile in Buituri–Hunedoara (the non–ferrous fraction) was used for the construction of roads/ highways and as levelling material for parking spaces (for example, rehabilitation works of the county road section Sântuhalm–Hunedoara, parking spaces in Deva, parking spaces Kaufland Hunedoara) [3].

On the site of the slag dump initially generated by the Steel Plant in Galați, accelerated slag processing activities are currently being carried out, the activity being subcontracted by the current management of Liberty Galați S.A., to two companies, namely Phoenix Slag Services Galati and GSWI Galați [10]. To reduce the operating period of the slag dump, the amount of slag processed annually has increased according to the data presented in Table 2.

Table 2. Quantities proposed and processed at the Liberty Galati S.A. [10]

Year	Amount of slag proposed for mill.t/year processing	Amount of slag processed mil.t/year
9 months 2013	4,170	5,678
2014	5	7,638
2016	5	7,972
2017	5	8,308
2018	5	9,744
2019	5	9,446
2020	5	9,840
2021	9	–
2022	6	–
2023	Greening activities	

According to the analyses carried out in the framework of the study project "Closing the nonhazardous waste deposit Slag Dump from Liberty Galați S.A" on the stored waste, it was found that in the various areas of the dump there is steel slag, furnace slag and mixed slag.

The slag dump in Resita was organised in 1771 when the blast furnaces of the Reșița Steel Plant [5], which became TMK Reșița and now Artrom Steel Tubes, were put into operation, forming as a result of the storage of residues from the technological flows of the production of cast iron and steel.

In 2005, slag storage activities were stopped at the dump site and as a result a warehouse was designed and arranged for temporary storage of the fresh slag generated by current flows of steel elaboration [5]. Starting in 2018, the TMK Reșița plant slag was under the concession of the Swiss Swiss Trade S.R.L. company, which is the only operator responsible for the processing and maximisation of fresh slag in the warehouse and old slag in the slag dump [5]. For 7 years (the dump concession), Swiss Trade S.R.L took the risk of processing a minimum amount of old slag of about 620000 tons [5], the proposed quantities are presented in Table 3.

Table 3. Total amounts of slag expected to be processed from TMK Resita dump [5,11]

Year	Total processed slag, fresh slag + old slag, [tonnes]
2019	106 000
2020	124 000
2021	154 000
2022	154 000
2023	154 000
2024	154 000
2025	154 000

In the case of this dump, some of the processed slag amounts were used to build roads and highways.

The need for pile exploitation activities is justified by the negative impact that these sites generate on environmental factors (air, water, soil).

In these dumping's where steel slag is stored, there is a significant amount of iron, the recovery of which is carried out by magnetic separation, and this processing process can represent an important source of savings, by reducing the import of raw materials [4].

Concerns regarding the capitalisation of the slag have generated a lot of research in recent years, according to which, depending on the elaboration process within which it was generated, the ferrous fraction of the slag can be reintroduced in the steel elaboration process and the nonferrous fraction has uses in different sectors of activity (road constructions, railway constructions, hydrotechnical constructions, civil, in agriculture, cement industry, etc.) [2–4].

In conclusion, slag is waste that, if properly exploited, can be used in various fields without significantly influencing the production processes, respectively, the finished products.

≡ Dust & sludge agglomeration furnaces

In the process of drawing cast iron, through the preliminary operations that are carried out to optimise the metal load, a fine, powdery ferrous fraction is obtained, which should not be introduced into the blast furnace. In addition, a quantity of blast furnace dust is obtained from the treatment of the blast furnace gases resulting from the elaboration of the first fusion cast iron.

The amounts of blast furnace dust that results in the casting iron process are directly influenced by the quality of the load, the operating regime of the blast furnace, etc. [2,4,12,13].

In the case of the agglomeration plant, the same situation is encountered, in which the gases captured in the vacuum chambers are purified, resulting in waste such as dust and agglomeration sludge.

Within the technological process, the main areas where the largest amount of dust is generated are the area near the agglomeration belt, the agglomerate classification area, and transport areas [2,12,13].

Agglomeration dust is the result of the purification of gases collected in the agglomeration installation, and blast furnace dust and slurry are generated as a result of the blast furnace gas treatment processes that resulted in the cast iron elaboration processes.

Furnace charge preparation and agglomeration facilities are important sources of dust and sludge generation, these wastes contain around 30–40% Fe, an aspect that recommends their reintroduction into the steel circuit [2].

If recycling of the entire amount of waste cannot be achieved, it is recommended to store the waste in permanently covered ponds with water, which must be avoided because it has the potential to pollute water and soil [12].

Historical sludge deposits from agglomeration furnaces generated due to the activities of the former steel plants in Hunedoara and Călan are located on the territory of Romania. From studies carried out in the specialised literature, on the chemical composition of sludge waste stored on the territory of Hunedoara county [2–4,12], an average iron content of approximately 27% resulted, which makes it possible to recycle it in the steel industry (but in processed form, if we consider the average diameter of the blast furnace sludge particles, which is 24,721µm). If the concentration of non–ferrous elements (Cu, Pb, Cd, Zn) is above the permitted limits, the waste cannot be recovered in the steel industry, so it is recommended that it be processed in non–ferrous metallurgy [3].

At the Galați steel plant in Galați, since the first month of 2022, the project on the installation of blast furnace slurry treatment facilities was approved. The project envisages replacement of the filtration system for suspended solids in water from the treatment of blast furnace gas, to increase the capitalisation of the blast furnace slurry [14].

Currently, in Romania, slurry and blast furnace dust is still generated only in Galați, where the installations for the recovery of these types of waste are modernised to increase the speed of processing and recovery.

≡ Converter dust and sludge

The source of the generation of these types of waste is the steelmaking process in the aggregate known as the converter.

Dust from the converter is generated in the process of making steel in the converter, driven by exhaust gases. The gases discharged during the preparation process are captured and subjected to primary treatment operations which are performed predominantly wet and rarely in dry systems [3,4,15].

Wet cleaning is usually carried out in stages. In the first stage, the gas is cooled, and the coarse dust is recovered. In the second stage, fine dust fractions are captured from exhaust gases, resulting in coarse sludge with particle sizes below 90µm and fine sludge with particle sizes below 50µm [3,4,15]. After exhaust gas treatment operation, the dust content is reduced to below 15mg/Nm3, the dust obtained containing approximately 60% Fe [12].

In Romania, the converter sludge was and is generated within the Liberty Galati company, where it is stored mixed with the agglomeration furnace sludge (quantity estimated at more than 8 million tons) [2,15]. The annual quantities generated from this type of waste are approximately 50–70 thousand tons [2,4,15,16].

The high iron content of converter dust and sludge, the average values of SiO_2 and CaO compounds, and the low Zn content reflect the positive aspects according to which these wastes are suitable for recycling in the steel industry [2,3,4,12,15].

According to some studies [2,4,12,15] the recycling process of converter dust and sludge in the agglomeration process is hampered by the high degree of fineness of the waste, more than 70% of the particles having dimensions below 50 µm. Of the two types of sludge, only fine sludge presents problems for recycling.

Since 1992, the Galati steel plant has used approximately 0.4% of the sludge produced in the agglomeration process [3]. Currently, Liberty Galati has modernised its steel mill slurry processing facilities by opening a new recovery station [17].

Mining industry: Sideritic waste

This type of waste was generated as a result of the preparation activities of the siderite iron ore that was exploited intensively in the area of the Hunedoara County area. The process to which the siderite iron ore was subjected involved roasting it to remove carbon dioxide, and then it was subjected to magnetic concentration, with the aim of increasing the iron content in the roasted ore, which initially had a content between 25–40% Fe [2,4 12,15].

The magnetic concentration operation results in two components: the steel iron concentrate, which according to the research and studies carried out [2,4,12,15], has values between 49–53%Fe, and the mining tailings, which is actually the part of an ore deposit or a mining product that no longer has any utility. In the case of siderite–type iron ores, this mine waste is called siderite waste and can be stored in settling ponds.

On the territory of Hunedoara County, more precisely in the Teliuc commune, three tailings' dams are located for sideritic waste resulting from the preparation of the siderite ore used in the former Hunedoara Steel Plant — Figure 1.

Figure 1. The tailings dams where the mining tailings (sideritic waste) were stored at Teliuc [2,4,12,15]

Within a research contract carried out by a part of the team by the teaching staff of the Faculty of Engineering Hunedoara, the occupied areas and the amounts of waste deposited in the siderite sterile tailings dams from Teliuc were determined. After analysing and processing the measurements, the following were determined [12,15]:

- The area of pond no.1 is 25ha and the amount of sidereal waste stored is 7 million tons;
- The area of pond no.2 is 18ha and the amount of waste stored is 5 million tons;
- The area of pond no.3 is 32ha and the amount of waste stored is 9 million tons.

Regarding the chemical composition of the sideritic waste historically deposited in the three tailings dams, it goes without saying that it is inevitable to change it over time. Currently, tailings dams are not adequately greened and pose a substantial risk of pollution.

Due to the iron content, the steel waste deposited in Teliuc ponds has the possibility of being recovered from the steel industry only if combined with other waste rich in iron (steel mill dust, slag, mill scale) [15]. According to some studies [4,18,19], minimal amounts of precious metals (gold, silver) can be extracted from the waste deposited in the three ponds, and sideritic waste can also be used in the construction industry in addition to road construction.

At the international level, the greening of the areas occupied by the tailing's dams with mining tailings, through the full capitalisation of the stored quantities, is successfully applied in countries such as the USA, Great Britain, India, China, and Japan, etc. In this chapter, Romania is quite far behind, the research presented in the specialised literature [4,18] on these wastes aims only to recover useful minerals (in this case iron), the vast majority of the material reaching again the tailings dam.

Teliuc tailings dams are still in the conservation phase, because ecological development and rehabilitation works are very expensive. For the Teliuc ponds, the company S.C Eco Invest S.R.L Deva was contracted, with a deadline for the completion of the works set for March 2025 [20].

In Romania, at the moment, no complete method of greening the areas occupied by tailings dams has been developed and there are no known installations or projects aimed at the full recovery of the deposited waste. A method was tried to green Bălan, located in Harghita County, but the method did not involve the valorisation of the tailings, but only its introduction into the mine for final storage [18].

Energy industry: Ash from the thermal power plant ash

The processes carried out in coal power plants result in a large amount of ash that contains significant amounts of iron and carbon [2]. The amount of ash generated is represented by the amount of impurities in the coal, directly influenced by the type and method of coal exploitation [2,4].

The ashes of the thermal power plant are frequently stored in landfills, causing soil and atmosphere, due to the wind that drives the dust particles (dry ash) from the surface of the warehouse and transports them to the air [21].

On the territory of Hunedoara County as a result of the operation of the Mintia thermal power plant, one of the largest thermal power plants in the region (it was stopped at the beginning of 2022 [22]), there are deposits of slag and ash resulting from the activity of the thermal power plant — Figure 2.

Figure 2. One of the ash deposits of the Mintia thermal power plant, Source: Google maps

The amounts of slag and ash generated annually by the thermal power plant reach a value of about 1 million tons. They are stored in two warehouses, the first located near the Mureș River on the right bank, which occupies an area of approximately 70ha and the second about 4km from the thermal power plant, an area of approximately 130ha [21,23,24].

According to the literature [2,4,21], from the chemical analysis of the ash of the thermal power plant stored in Mintia it is found that it is silicoaluminal and has the highest values for SiO_2 and Al_2O_3 and an iron content that exceeds the value of 25%.

From the research present in the specialised literature, it has been found that, in terms of chemical composition, the concentrations of thermal power plant ashes resemble powdery waste (steel dust) and due to the fact that they do not contain elements harmful to the quality of cast iron or steel and can be processed together with other steel waste with a high iron content, which are subsequently used in the elaboration processes. In the processing of small and powdered waste with an iron content, the ashes from the thermal power plant are used as a binder [2,4].

The ashes of the thermal power plant can be recovered in the cement industry, representing an alternative source of raw materials that can present technical and economic advantages to producers interested in implementing new technologies to capitalise on this waste [25].

In Romania, the use of ash from power plants has been successfully demonstrated in the production of cement and concrete [26], in the manufacture of bricks [25], in road construction, in the manufacture of pavements [27], and in agriculture to correct the soil.

Chemical industry: Pyritic ash

This type of waste is the result of the sulfuric acid manufacturing process, an activity that also took place on the territory of Romania in Baia Mare (Phonix factory), the Măgurele Tower (chemical plant), Valea Călugărească (Romfosfochim plant), Năvodari (superphosphate and sulfuric acid plant), Făgăraș (Victoria chemical plant). Currently, none of these plants are functional anymore, but as a result of their activities, quantities of pyritic ash have been generated, which were deposited in landfills (Figure 3), still present today and whose quantity is estimated at almost 4.5 million tons [2,4,15].

Figure 3. Storage of pyritc ash in landfills [2]

Pyritc ash is interesting to harness in the steel industry due to its high iron content of more than 50%. This finding was made as a result of studies in the specialised literature [2,4,15] carried out on the chemical composition of pyritic ashes stored in Valea Călugărească, Turnu Măgurele, Baia Mare, Năvodari, and Făgăraș.

In Romania, pyritc ashes have been exploited using the Kowa Swiko technology developed by the Japanese company Toyo Engineering Corporation. This technology was implemented in the pyrite ash valorisation plant established at Turnul Măgurele. Through technology, pyrite ash was converted to metallized pellets and metals such as Cu and Zn were extracted from its composition [28].

The Kowa–Seiko technology involved the separation of non–ferrous metals by roasting. Metal pellets made of pyritic ash and additions such as lime, calcium chloride, etc., were transported to Hunedoara and Galați plants to be used in the manufacture of cast iron in the blast furnace [2,28].

Currently, the pyrite ash utilisation plant in Turnul Măgurele is completely decommissioned, and the existing pyrite ash deposits cause serious environmental problems.

In conclusion, the pyrite ash obtained in the sulfuric acid manufacturing process can be processed and subsequently recovered in the steel industry due to its iron content, but there are also situations in which its use in the steel industry is practically impossible due to the heavy metal content that can affect the quality of cast iron and steel. According to studies in the literature [2,4,15], the cause that makes it difficult to use pyrite ashes in steelworks is the arsenic content, an undesirable element in ferrous metal alloys.

Aluminium industry: Sludge and red mud

The process of manufacturing alumina using the Bayer process from bauxite ore results in significant amounts of waste, such as slurry and red sludge.

The alumina factory slurry is actually a sludge with a very fine particle size fraction, which together with the red sludge (Figure 4) is usually stored in the ponds. It is recommended to always keep the surface of the ponds moist, because otherwise the air currents will scatter this dry powdery material, causing a much higher degree of pollution [2].

(a) (b)

Figure 4. Red sludge generated in the alumina manufacturing process [2]
a – red sludge; b –red sludge tailings pond

Studies in the literature [4,29,30] show that red sludge and slurry have a high content of iron oxides (35–60% Fe_2O_3).

It should be mentioned that on the territory of Romania, plants for the extraction of alumina from bauxite are in Tulcea, Oradea, and in Slatina the production and processing capacities of aluminum are located. Currently, the Oradea plant, the only one to use bauxite ore mined on the territory of our country, is no longer functional, having been completely decommissioned since 2006. However, in its wake, the landfills were used as dumping grounds for the sludge and red mud resulting from the alumina manufacturing activity.

At the ALRO–owned Tulcea plant, red sludge is stored in two waterproof warehouses with capacities of 23 and 7,5 million tons, respectively. Now, there is no integrated recovery solution for the deposited red sludge [4,15].

Because slurry and red sludge–type waste are deposited at sites that occupy large areas of land, studies and research have been carried out to find chemical composition and recovery solutions. According to studies carried out [2,4] on the chemical composition of red sludge, the predominant elements of the composition are iron and alumina.

Regarding the valorisation activity of the valorisation activity of the valorisation activity of the red mud valorisation activity, it was found that by its processing an iron alloy (pellets) can be obtained that can be used in the activity of steel mills in the charge of steelmaking furnaces [15].

CONCLUSIONS

From the data presented, it is found that most of the slag dumps on Romanian territory were and are leased to specialised companies to better capitalise the different fractions of the slag. But, nevertheless, sites still exist, the works for the greening of the occupied lands are non–existent, or, at best, they were only planned (the case of the Galați dump). The processing speed of the slag in landfills is still low and does not generate a significant reduction in the amount of waste; these types of sites continue to endure. Another factor with a negative impact on the low level of slag recovery in landfills is also the frequent change of companies specialised in the recovery of waste from the steel industry (the case of the landfill in Hunedoara, in Reșița).

It is necessary to find efficient solutions for the complete elimination, through recycling, of the blast furnace slurry and agglomeration dust historically stored in the Hunedoara and Călan areas. Finding or developing an optimal recycling solution for blast furnace sludge and dust will lead to the total elimination of this type of waste from the area, as the streams in which it was generated are completely decommissioned. For industrial waste with iron content historically deposited on the territory of Romania, it is necessary to find optimal solutions for the valorisation and greening of the land to return the environmental spaces.

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