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STUDY ON THE QUALITY OF INDUSTRIAL WASTE DEPOSITED IN PONDS

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Abstract: The industrial processes, besides the main manufacturing product, results in secondary and waste products, some of which being further processed, either within the industrial unit that generated them or within another one, or are deposited in ponds or slag dumps. Also, significant quantities of ferrous waste are resulting from the mining industry, from the processing of ferrous and non-ferrous ores, from the energy industry, chemical industry, etc. This paper presents the results of a study regarding the recovery of some wastes containing iron (and other elements or compounds, i.e. Mn, C, CaO), by recycling them in the processes of making pig iron, steel and ferro-alloys. For the purpose of the above, the waste materials for recycling have been carefully chosen, in order to study their chemical composition and grain size, determining elements for selecting the recycling / recovery process and the destination of the obtained product.
Keywords: secondary and waste products, ponds / slag dumps, recycling, recovery

1. INTRODUCTION

In the economic activities, the technological processes are always resulting in one or more primary and secondary products. Worldwide, the reported by-products obtained from the steel producers' practice, i.e. small and powdery waste, are:

- ✓ carbon dust;
- ✓ dust and slurry from sintering plants;
- ✓ dust and slurry from blast furnaces;
- ✓ dust and slurry from oxygen converters;
- ✓ steel plant dust;
- ✓ scale and scale slurry;
- ✓ sludge from heat treatments, thermo-chemical treatments and anticorrosive coatings;
- ✓ the ferrous fraction from the steelworks slag.

The small and powdery ferrous wastes, which can be used in the steel industry after a prior processing, can be also obtained from the technological processes of other industries, of which we mention:

a) aluminum industry – the red sludge;
b) chemical industry the pyrite ashes;
c) energy industry – iron concentrate from fly ashes;
d) mining industry – iron concentrate from sideritic waste, iron and manganese concentrate from manganese ore preparation, etc.

The significant generated quantities, the negative impact on the environment, and the economic potential thanks to the useful component – Fe, C, Mn, etc., imposed finding solutions for recycling the by-products. The different physicochemical properties of these materials determine different processing conditions, aiming at:

- ✓ Reuse of the iron content;

- ✓ Bringing the generated waste to an environment-friendly state;
- ✓ Use of waste for the production of other materials, especially construction materials, alkaline soil amendments (in agriculture) [1, 2, 5, 7, 8].

2. STUDY OF THE SUBJECT

The siderurgical industry generates, from the technological processes of making pig-iron, ferro-alloys and steel, largest amounts of waste containing iron. Depending on the specific conditions of each siderurgical plant and the market demand (time-varying) of each usable material, any waste can become by-product and any by-product can become waste (Table 1) [1, 2, 5,]. In the mining industry, besides the metalliferous concentrate(s) are resulting waste, which can be often processed for recycling or for other purposes (other destinations).

Table 1. Waste from siderurgical industry [1, 2, 3]

Sr. no.	Waste type	Percentage relative to production
	Coke and chemical plants	
1.	Coal dust	7.19 %
2.	Tar fuses*	4.90 %
3.	Acid tar	3.70%
4.	Tar sludge	1.00%
5.	Coke Slurry	0.90%
6.	Debris	14.9%
7.	Coke dust	2.90%
	Sintering plants – Blast furnaces	
1.	Sintering dust	1-2.5% of the sinter production
2.	Blast furnace dust + sludge	1.1-3% of the pig-iron production
3.	Coke breeze	< 0.5 mm from the sintering plants
4.	Blast furnace slag	25–30% of the pig-iron production
	Steel plants – Continuous casting	
1.	Steelworks dust	1-1.8% of the steel production
2.	Steelworks slag	15-20% of the steel production
3.	Continuous casting scale	2.8% of the steel production
	Rolling-Mills	
1.	Scale and scale sludge	2-2.8% of the steel production
2.	Steel filings from rolled products polishing	1.5-2.0% of the steel production
3.	Turnings from rolled products peeling	2.2% of the steel production
	Heat treatments, thermochemical treatments and anticorrosion coatings	
1.	Sludge	1.2% of the treated steel production

* tar sands or residues from tar decantation

The study of wastes aims to know their characteristics, in particular their chemical composition and grain size, these ones being the main factors based on which we can assess the recycling possibility and choose the processing process for recovery. Therefore, the knowledge of the chemical composition helps us to assess the content of the main recoverable element(s) (Fe, Mn), the profitability of the process, and the content of harmful elements (Zn, Sn, As, Cu, etc.); if the content of the latter exceeds certain limits, the obtained product can not be recycled. Knowing the grain-size composition helps assessing the most suitable processing method, in order to use them effectively or, whether an intermediate processing, to choosing it.

The studied waste materials can be recovered by traditional methods, i.e. pelletizing, briquetting and sintering. The very fine-grained waste (particle size up to 100 μm) is usually processed by pelletizing, the waste with the particle size up to 1.5 mm by briquetting, and the waste with the particle size up to 3 mm by sintering.

Depending on the carbon content dosed in the processing heat, we can obtain common products or reduced products, with a certain degree of metallization. The table below contains the chemical compositions and grain-sizes of some types of waste, which will be studied in the PhD thesis, in order to recycle them in siderurgy. The wastes resulted from the siderurgical processes, whether carried out in integrated plants or mini-mills, can be completely recovered (at least 98% of them are recovered in siderurgy). The table 1 shows the percentages of the types of wastes resulted from the siderurgical industry [1, 2, 5, 7, 8].

Of the total waste generated in the steel processes, presented in Fig. 1, the powdery wastes, potential by-products, raised issues in the recovery process because, on the one hand, of the unsatisfactory grain-size composition, i.e. the finely dispersed fraction, being in large amount, has a negative influence on the environment, and, on the other hand, due to the presence of heavy metals (Zn, Pb, Cu, Cd) in their composition. The heavy metals usually come from wastes containing iron, resulted from non-ferrous ore processing or, in the steelworks, the zinc comes as a result of use, in the EAF metal charge, of galvanized scrap (metal sheet and pipes). Also, from an improperly sorted metal charge, can come Sn, Pb and Cu, elements that cannot be removed from the liquid metal bath and downgrade the steel.

The Figure shows the quantities of small and powdery wastes relative to the tonne of product, the data being specific to the global siderurgy [1, 2, 3, 4, 5].

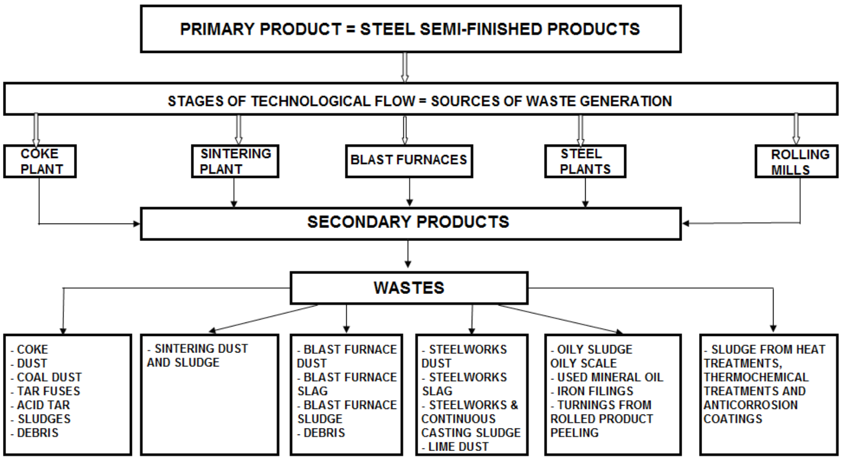

Fig.1. Types of wastes and their generation sources within an integrated iron and steel plant [1, 5]

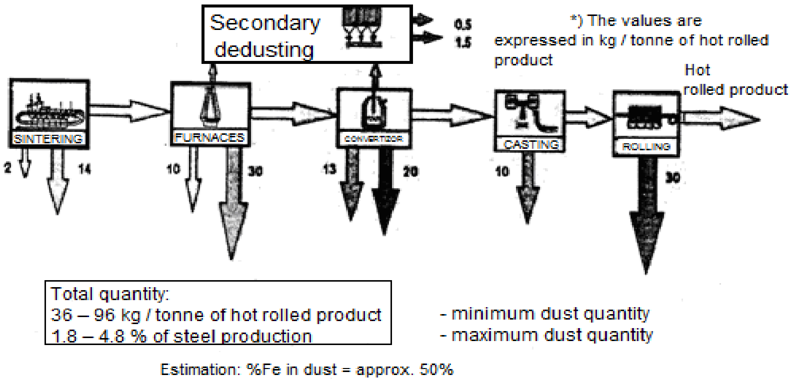

Fig.2. Specific quantities of powdery wastes generated withîn an integrated iron and steel plant [1, 5, 6, 7, 8]

The table 2 shows the grain-size distribution of these types of wastes, and the table 3 shows the chemical compositions of some of them [1, 7, 8]. Under these conditions, various pyrometallurgical, hydrometallurgical and other types of processes have been developed worldwide for removing the non-ferrous metals existent in this waste category, adjusting the grain-size and recovery of its iron content [1].

Table 2. The grain-size distribution of the powdery wastes [1, 7, 8]

Size	Sintering plant	Blast furnace		Oxygen converter		EAF	Rolling mill	
μm	dust	dust	sludge	dust	sludge	dust	scale	sludge
1.000	-	-	-	-	-	-	9	-
500	-	2	-	8	-	-	17	-
250	3	19	1	26	-	-	28	-
150	-	-	-	-	-	-	-	5
125	25	41	27	41	1	-	26	-
105	-	-	-	-	-	-	-	-
74	35	24	14	20	2	-	13	7
44	21	10	6	4	5	-	6	5
<44	16	3	52	1	92	100	1	83

Table 3. The chemical composition of the sludge from the sintering plant, blast furnaces and steel plant, for some steel plant units in Romania [1, 2, 3, 7, 8]

Component, %	Coarse slurry from L.D. - Arcelor Mittal Galați	Thin sludge from L.D. - Arcelor Mittal Galați	Sludge from blast furnaces L.D. - Arcelor Mittal Galați	Sludge from Mălina Galați	Sludge from Bataga Hunedoara	Blast furnace dust from Arcelor Mittal Galați	Blast furnace sludge from Călan
SiO_2	2.57	1.11	8.0	9.10	14.06	6.06	13.93
CaO	23.89	2.31	3.86	21.4	10.01	5.81	13.35
MgO	2.16	0.34	0.97	0.2	2.57	1.59	2.19
Al_2O_3	0.19	0.11	0.93	0.0	6.44	2.04	4.5
MnO	1.21	4.32	0.55	0.6	0.96	0.29	0.48
Cr	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Fe	41.91	57.31	29.24	52.6	30.35	31.19	23.91
Cu	0.0076	0.0227	0.0077	0.0	0.0	0.0	0.017
Zn	0.447	1.464	2.343	0.0	4.79	0.1	0.47
Ni	0.0012	0.0032	0.0	0.0	0.0	0.0	0.0
Pb	0.0078	0.2144	0.5812	0.0	0.0	0.0	0.07
Cd	0.0085	0.0041	0.0085	0.0	0.0	0.0	0.0
C	0.95	0.26	8.45	0.0	10.9	36.82	15.55
S	0.05	0.06	0.73	0.0	1.11	0.0	0.056
P	0.13	0.06	0.07	0.0	0.0	0.046	0.47
PC	0.0	0.0	28.74	3.4	0.0	0.0	0.0

Currently, arises worldwide the problem of recovery through recycling of the small and powdery waste generated in siderurgy, being proposed the concept of integrated recycling. This concept is exemplified in Figure 3, in which we can see that the entire quantity of powders, sludge, scale, steelworks slag – the ferrous fraction, generated within an iron and steel integrated plant, are recycled in the technological flow stages [1, 4, 6, 7, 8].

Compared with the worldwide practices and trends, the Romanian siderurgy is lagged behind either regarding the collection, transportation and disposal of the powdery waste, or regarding the technologies of recovery through recycling or reuse. In these circumstances, I considered necessary and appropriate to approach the problem of higher recovery of the powdery wastes generated within an iron and steel integrated plant, recovery achievable with minimal costs [1, 4, 5].

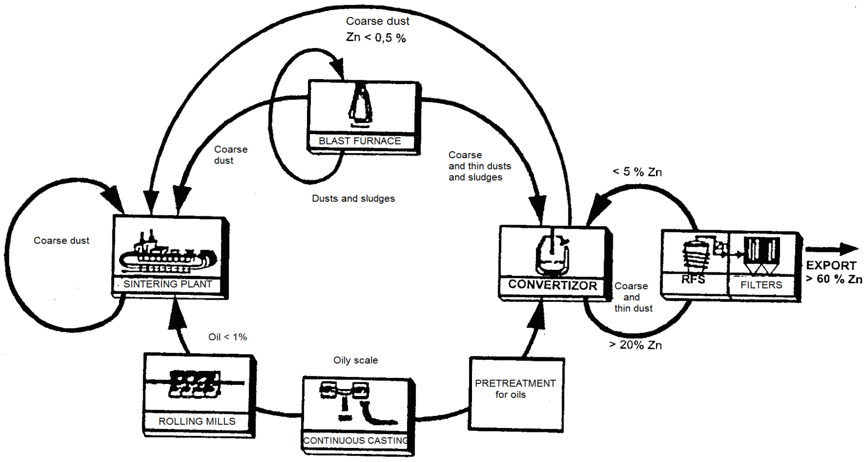

Fig. 3 The concept of integrated recycling of the powdery wastes generated within an iron and steel integrated plant [1, 2, 3, 4]

The higher recovery of the siderurgical wastes in general, and of those small and powdery in particular, represents an important issue, because their conversion into by-products, i.e. in economic assets, may lead to a rational recovery of the raw materials and energy resources, thus ensuring both the needs of the human society, and the environmental protection, major issue at the end of the second millennium and the beginning of the third millennium [1, 6, 7, 8].

In all the siderurgical plants, the slag, as waste, is resulting in the highest percentage (Table 1), the blast furnace slag being 25–30% and the steelworks slag 15–20%. In the countries with well-developed siderurgical industry (Germany, England, France, Luxembourg, Italy, U.S.A. etc.), the slag is completely recycled and not deposited on slag dumps.

In Romania, the blast furnace slag is 100% recovered, and no longer deposited on dumps. Therefore, there are no more such dumps in our country. The steelworks slag frequently resulted from the technological flows is 100% recovered, but there are still appreciable amounts of slag deposited in slag dumps (Table 4). Currently, all the siderurgical plants that have dumps made of steelworks slag are recovering the deposited slag, the slag being processed in modern mobile facilities which allow the segregation by ferrous and non-ferrous fractions, and by grain-sizes.

The properties of the types of slag deposited in Hunedoara (S.C. ArcelorMittal S.A.), and the properties of the two fractions – ferrous and non-ferrous – resulted from slag processing, are shown in Table 5. Table 6 presents the grain size class limits for the types of slag processed. Figure 4 shows the fields in which the processed steelworks slag can be used, and the share of each field. The Tables 7 and 8 present the chemical composition and grain-size of the oxygen converter slag at S.C. ArcelorMittal Galați. Besides the wastes resulted from the siderurgical industry, we studied some wastes containing iron, and wastes resulted from the mining, energy and chemical industries, whose properties are shown below. To be mentioned that we had in view the large amounts of wastes deposited in ponds. This practice, although is not very frequently used, it is contrary to the environmental regulations regarding the slag dumps. We had also in view the continuation of producing such waste and its negative effect on the environment.

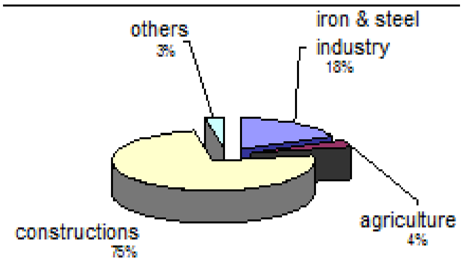

Fig.4 Application of metallurgical slag [1, 2, 3, 4]

Table 4. Evaluation of the slag dumps located in Romania [1, 5, 6 ,7, 8]

Sr. no.	Slag dump	Year of starting the slag disposal	Year of starting the slag recovery	Slag in the dump, [million tonnes]
1.	Reşiţa	1771	2006	70
2.	Hunedoara	1884	1981	100
3.	Galați	1968	2003	50
4.	Câmpia Turzii	1920	2002	1.5
5.	Târgovişte	1971	1998	5.0
6.	Oțelu Roşu	xx	xx	xx
Total				226.5

Table 5. Properties of the slag processed in Hunedoara [1, 5, 6, 7, 8]

Slag type	Chemical composition of the slag, %											B[4)]
	Fe_t	FeO	Fe_2O_3	Fe_m	SiO_2	MnO	Al_2O_3	CaO	MgO	P	S	
N[1)]	19.62	10.96	6.98	6.5	18.46	6.34	7.04	32.6	9.26	0.49	0.13	1.77
P[2)]	43.85	12.00	9.6	27.8	16.03	4.9	4.4	18.0	6.10	0.30	0.25	1.20
D[3)]	13.4	11.47	3.18	2.31	20.17	7.93	6.47	32.9	11.5	0.51	0.23	1.63

1) unprocessed slag; 2) processed slag, magnetic fraction 3) ironless slag; 4) slag basicity.

Table 6. Slag types resulted from slag processing - Hunedoara [1, 5, 6, 7, 8]

Types	Grain-size classes, [mm]			
Ironless fraction	0-10	10-60	60-250	-
Ferrous fraction	0-10	10-60	60-250	over 250

Table 7. Chemical composition of the oxygen converter slag [5, 6, 7, 8]

%Fe	%CaO	%SiO_2	%Al_2O_3	%MgO	%MnO
28.84	40.22	12.31	1.97	4.56	4.59

Table 8. Composition of the oxygen converter slag [5, 6, 7, 8]

Grain size fractions [mm]	> 14.5	10-14.5	8.0 – 10	4.2 – 8.0	3.0 – 4.2	1.6-3.0	1.0 – 1.6	0.8 -1.0	0.60-0.80	< 0.63
Weight,%	22.2	21.4	25.03	10.63	8.23	5.21	3.1	2.1	1.9	0.2

Table 9. Chemical composition of the red sludge, Alumina Tulcea [5, 6, 7, 8]

Red sludge	Chemical composition, %												
	Fe	CaO	SiO_2	Al_2O_3	MgO	MnO	TiO_2	Na_2O	K_2O	C	Cu	Zn	Pb	As
Chemistry	26.15	7.09	9.41	21.22	0.59	0.27	4.5	6.25	0.29	1.55	0.043	0.17	0.31	0.013

Table 10. Grain size analysis results, Alumina Tulcea [5, 6, 7, 8]

Grain size fractions, [µm]	>12.63	>7.29	>4.21	>3.06	>2.75	>1.48	<11.48
Weight per fraction, %	29.26	10.63	12.24	8.51	5.85	4.79	28.27

Table 11. Chemical composition of the red sludge, Cemtrade Oradea [5,6, 7, 8]

Red sludge	Chemical composition, %													
	Fe	CaO	SiO_2	Al_2O_3	MgO	MnO	TiO_2	Na_2O	K_2O	C	Cu	Zn	Pb	As
Chemistry	29.37	8.21	9.12	20.31	0.61	0.33	3.43	5.06	0.31	1.42	0.039	0.16	0.22	0.011

Table 12. Grain size analysis results, Alumina Tulcea [5, 6, 7, 8]

Grain size fractions [μm]	>12.63	>7.29	>4.21	>3.06	>2.75	>1.48	<11.48
Weight per fraction, %	31.33	11.29	11.96	8.45	5.64	4.66	29.77

Table 13. Chemical composition of the waste from sideritic ore processing [5, 6, 7, 8]

Sr. no.	Material	Chemical composition, [%]							
		SiO_2	FeO	Fe_2O_3	Fe	Al_2O_3	CaO	MgO	MnO
1.	Pond tailings waste	34.39	7.01	7.84	9.12	2.87	16.39	6.68	1.35
2.	Secondary sideritic concentrate	19.86	9.92	18.64	21.0	3.16	20.22	7.56	2.29
3.	Secondary gangue	37.60	6.30	5.58	6.45	2.87	15.16	6.58	1.41

Table 14. Composition of the fly ashes [1, 5, 6, 7, 8]

Chemical composition, [%]								
SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	P_2O_5	Na_2O	K_2O	TiO_2
47.08	6.72	1.82	23.06	20.12	0.5	0.20	0.20	0.30

Table 15. Composition of the fly ash concentrate [1, 5, 6, 7, 8]

Chemical composition, [%]								
SiO_2	Fe_2O_3	Al_2O_3	FeO	CaO	MgO	Fe	Mn	P
11.89	51.96	8.85	13.39	7.31	3.85	46.71	1.15	0.028

Table 16. Grain-size analysis of the fly ash concentrate [1, 5, 6, 7, 8]

Grain-size fraction [mm]	0.315-0.20	0.20-0.10	0.10-0.071	< 0.071
Content, [%]	0.02	54	33.4	12.58

Table 17. The chemical composition of pyrite ashes [1, 5, 6, 7, 8]

Composition / source	Chemical composition, %										
	Fe	CaO	SiO_2	Al_2O_3	MgO	S	P	As	Alkalis	Cu	Pb	Zn
Valea Calugarească	52.72	2	12.2	0.5	0.6	3.8	0.2	0.6	2.5	0.5	0.5	1.2
Navodari	54	4	8	-	-	6	-	0.6	2.1	0.55	0.5	1.8
Turnu Magurele	53.8	3.03	8.3	-	-	3.28	-	0.15	1.8	0.55	0.17	0.33
Baia Mare	47.52	0.7	15.6	-	-	0.89	-	0.22	1.65	0.8	0.28	0.25
Făgăraş	21.97	3.64	13.6	-	-	5.28	-	0.28	2.31	0.14	0.41	0.46

3. DISCUSSIONS

From the study I have conducted, I found that the industrial processes and especially those taking place in the metallurgical/siderurgical, mining, energy and chemical industries are resulting in large amounts of ferrous wastes, which can be used either as such, or after a mechanical chemical or thermal processing.

Depending on the waste grain size, we can choose the appropriate process of recovery. Sometimes a certain waste, especially the powdery ones, can be recovered by applying any of the classical methods: briquetting, pelletizing and sintering.

The iron containing waste, resulted from the steel industry and deposited in ponds and slag dumps, are found in relatively high amounts in the major siderurgical plants, despite the reduction in their activity due to the economic restructuring of the industry in Romania, very sharply applied to the steel industry. Following the complete decommissioning of the integrated flow at Reşiţa şi Hunedoara, some of the wastes that used to be frequently obtained can no longer be recovered through the sintering process.

Some siderurgical facilities (for steel making and rolling) have reduced their capacity to approx. 25%, other to 5-10%, and some of them to less than 5%. In these conditions, we must find the optimal technological solutions to recover such wastes, making them suitable to be recycled in siderurgy.

The wastes from the mining, energy and chemical industries are found in large amounts, so the extension of research on their use in the non-ferrous metallurgy and the construction and building materials industry is fully justified.

4. CONCLUSION

For conducting the research on the quality of the wastes deposited in ponds, I studied the literature (referred to in the paper), on the one hand, and on the other hand I made a site documentation at the concerned ponds and slag dumps, based on which the followings can be concluded:

- The small and powdery ferrous waste are mainly resulting from the siderurgical industry, but also from other industrial branches, i.e. chemical industry (pyrite ashes), energy industry (iron concentrate from fly ashes), mining industry (secondary sideritic concentrate) and nonferrous metallurgy (red sludge from alumina making process);
- The wastes have various iron contents, from about 30% (sideritic concentrate) to over 60% (scale, steelworks dust);
- Besides the iron (the main element), some wastes have a high carbon content of 18 - 22% (blast furnace dust), and alkaline components (CaO and MgO from the secondary sideritic concentrate), or fluidifying agents (Al_2O_3 found in the red sludge), which are useful in the recycling process;
- Some wastes contain harmful elements (As – red sludge, Zn, Cu, Pb – pyrite ashes) that affect the quality of the products obtained by waste recycling and, therefore, precautionary measures must be taken to their recycling;
- From the point of view of the chemical composition and grain-size, the wastes can be recovered by recycling, and the chosen technology should consider all of their qualitative characteristics.

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