“Research on the use of powdery and fine ferrous waste from mettalurgy industry”

PhD thesis - Abstract

for obtaining the doctor's degree at Politehnica University of Timisoara
in the doctoral field “Materials Engineering”
Author: Eng. **POPESCU Darius-Alexandru**
Scientific coordinator: Prof. Dr. Eng. **HEPUŢ Teodor**
10th October 2018

Introduction

The study of the possibilities to use the powdery and small-sized ferrous waste containing iron, zinc, carbon, etc., as well as powdery and small-sized basic waste in the metallurgical industry, involves the use of the powdery ferrous waste resulting from the various phases of the steel-making process (mostly in the steel-making industry), whose intrinsic value is determined by the ferrous content (chemically bonded iron, sometimes metallic), which can adequately replace the raw material, i.e. the iron ore or cast iron, in the steel-making processes. These powdery ferrous wastes come mostly from the iron and steel industry and generally result from the various operations of waste gas cleaning and wastewater treatment, either in dry form (coming from dry treatment plants), or as wet dust or sludge coming from wet scrubbers. The small-sized ferrous wastes come from the metallurgical processes (scale and steelworks slag - the ferrous fraction) and the mining industry – preparation of siderite ores (ferrous concentrate made from siderite waste).

In the research carried out in the laboratories of the Faculty of Engineering Hunedoara, it was experimented the use of powdery and small-sized waste by pelletizing, briquetting and sintering, taking into account the deposited wastes and those frequently produced over the technological flows.

The research was conducted in two directions, aiming to determine the possibilities of:

- recycling the zinc and iron in the non-ferrous metallurgy and steel-making industry;
- recycling the dust come from EAFs in the steel-making industry.

CHAPTER 1
EXPERIMENTS AND RESEARCH PLAN

The powdery ferrous wastes are mostly coming from the steel-making activity and, in general, they result from the various operations of waste gas cleaning and wastewater treatment, either in dry form (coming from dry treatment plants), or as wet dust or sludge coming from wet scrubbers. The small-sized ferrous wastes are coming from the steel-making processes (scale and steelworks slag - the ferrous fraction) and the mining industry – preparation of siderite ores (ferrous concentrate made from siderite waste) [1/1, 16/42]:

- the wastes resulting from the various industrial processes, especially those resulting from metallurgical processes, can be processed by sintering, pelletizing and briquetting, meaning that they can be used for iron and steel-making;
- by processing these wastes and transforming them into pieces, qualitatively appropriate for use as raw or auxiliary materials in the steel-making industry, the areas currently occupied by them can be returned to the natural environment, thus contributing to the greening of environment;
- in the industrial and metallurgical processes and in particular in steel-making, besides the main product we obtain one or more by-products, i.e. waste, which from a qualitative point of view can be recycled in the steel industry [2/2, 5/5, 16/42];
- worldwide, there are several processes / technologies for waste recovery, some of which are analysed in this doctoral thesis;

- the small-sized and powdery ferrous waste found in Hunedoara, Călan, Reşiţa and Oţelul Roşu, those with basic character, as well as those with carbon content, can be reintroduced into the economic circuit in the steel industry;

- the analysed types of waste can be processes by briquetting, sintering and pelletizing;

- the composition of recipes will be determined according to the availability of the small-sized and powdery waste and the destination of the processed material (steel plants or blast furnaces);

- under the existing conditions caused by the various industrial processes, I believe the intensification of the waste recovery process is absolutely necessary, either because it is a source of iron, which is a critical raw material, or for technological considerations and, last but not least, for ecological considerations.

The powdery ferrous wastes, in terms of granulation, are very well suited to processing by pelletization, and the small-sized ones to processing by pelletizing and briquetting [1/1, 6/6, 13/16].

CHAPTER 2

GENERAL CONSIDERATIONS ON SMALL-SIZED AND POWDERY WASTE

The waste materials are not only a potential source of pollution but, at the same time, they can be an important source of secondary raw materials and a source of energy.

The recycling operations aim at two fundamental objectives:

a) The total or partial recovery of the waste by making products or materials able to re-enter the economic circuit, as well as by obtaining secondary energy or fuels;
b) The neutralization of waste or parts thereof which can not be usually used, in order to minimize the possibility to pollute the environment in which they are disposed of.

The two components of recycling – recovery and neutralization – are closely linked; actually, the majority of recycling operations need to be dealt with together, from any such process resulting residues that must be disposed of. [11/11].

Under the current conditions of economic development (industry, transport, construction, agriculture), population explosion and large urban agglomerations, the correct management of waste becomes a priority due to the impressive increase in their volume and the impossibility of destruction at the place of production [1/1, 3/3, 16/42].

The recycling of waste in the modern era can not be realised without the existence of a powerful activity of designing, researching and production of efficient and performant facilities capable to process larger volumes of waste at a lower cost.

In the wastewater discharged from gas cleaning plants and rolling mills, there are also important amounts of powdery waste containing 60-70% Fe. This means that, for an annual production of 1.1 million tonnes of steel, it represents a total amount that exceeds 20,000 tonnes/year (currently, it represents about 7,000 tonnes/year at ArcelorMittal Hunedoara, which corresponds to a production of about 350,000 tonnes/year) [3/3].

In average, in the composition of the gases exhausted in atmosphere by the steel plant departments, about 25% is represented by particles more or less fine, of which the ferrous powders have a significant share. Thus, every million tonnes of steel produced annually result in 25,000 - 35,000 tonnes of ferrous powdery materials (2.5%), whose iron content is 40-60% and must be captured from the gases exhausted into the atmosphere [11/11].

As mentioned above, in case of waste briquetting process, a number of researches have been conducted, aiming the clarification of the following technological issues:

- the quality of the raw briquettes, depending on the processed materials, chemical composition and granulation, water and binder addition;

- the quality of the hardened briquettes, depending on the processed materials, chemical composition and granulation, water and binder addition, and the hardening technology;

- the reduction capacity of the briquettes, depending on the processed materials, chemical composition and granulation, water and binder addition, and the hardening technology;

- the cracking resistance of the briquettes, depending on the processed materials, chemical composition and granulation, water and binder addition, and the hardening technology;

- the crushing resistance of the briquettes, depending on the processed materials, chemical composition and granulation, water and binder addition, and the hardening technology.

CHAPTER 3

SMALL-SIZED AND POWDERY WASTE CONTAINING IRON, ZINC AND CARBON. ORIGIN AND QUALITATIVE CHARACTERISTICS

In the steelmakers practice worldwide, the well-known small-sized and powdery wastes containing carbon, iron, or iron & carbon, are [1/1, 11/11, 17/63]:

- carbon dust;
- dust and slurry from sintering plants;
- dust and slurry from blast furnaces;
- dust and slurry from oxygen convertors;
- steelworks dust from open hearth furnaces (where it is still deposited);
- dust from electrostatic precipitators (at electric steel plants);
- scale and scale slurry;
- the ferrous fraction of steelworks slag.

From the small-sized and powdery ferrous waste, which can be used in the steel-making industry after a prior processing, obtained from the technological processes carried out in other industrial branches, can be mentioned:

a) red sludge, with precautions regarding Zn, Pb, Cu, and As (in the aluminium industry);

b) pyrite ashes (in the chemical industry);

c) iron concentrate from the ashes coming from the thermal power stations (in the energy industry);

d) iron concentrate from siderite waste (in the mining industry) [1/1];

The significant quantities generated, the negative impact on the environment and the economic potential thanks to the useful component - Fe (but sometimes also other elements), required finding solutions for their recycling. Their different physicochemical properties determine different processing conditions, which are intended to:

- reuse the iron content;
- neutralise the generated waste and bring it to an environmentally-friendly status;
- using the waste for the manufacture or replacement of other materials, in particular building materials [1/1, 15/30].

Of the total waste generated in steelworks, presented in Fig.1/3.1, the powdery waste, potential by-products, have raised problems when trying to use them, due to the unsatisfactory particle size, on the one hand (i.e. the finely dispersed fraction, being in large quantity, has a negative influence on the quality of environment), and, on the other hand, due to the presence of heavy metals (Zn, Pb, Cu, and Cd) in their composition.

Methods used for finding the properties of these waste materials:

- chemical analyses carried out using various methods, such as wet chemistry, X-ray or atomic absorption spectrophotometry [2/2];
- the granulometry of materials was determined using Retsch sieve shakers with grain size of 90% over 20-30μm; the DSL method was used for finer materials (diffraction of light at sedimentation in aqueous medium), and the particle sizer "FRITSCH ANALYSETTE 22" has been used for the remaining share;
- the determination of the natural slope angle of the ferrous waste was made using the measurement in rotating drum;
- the bulk density of materials was measured according to the current standards;
- the kinetics of material wetting was determined using our own laboratory devices which enable the measurement of the total quantity of adsorbed water and the kinetics of this process (in cm^3 or grams of water/sec.);
- the mineralogical and morphological analysis was carried out using the HITACHI

scanning electron microscope (model S-2600N), equipped with an energy-dispersive X-ray spectrometer (EDX).

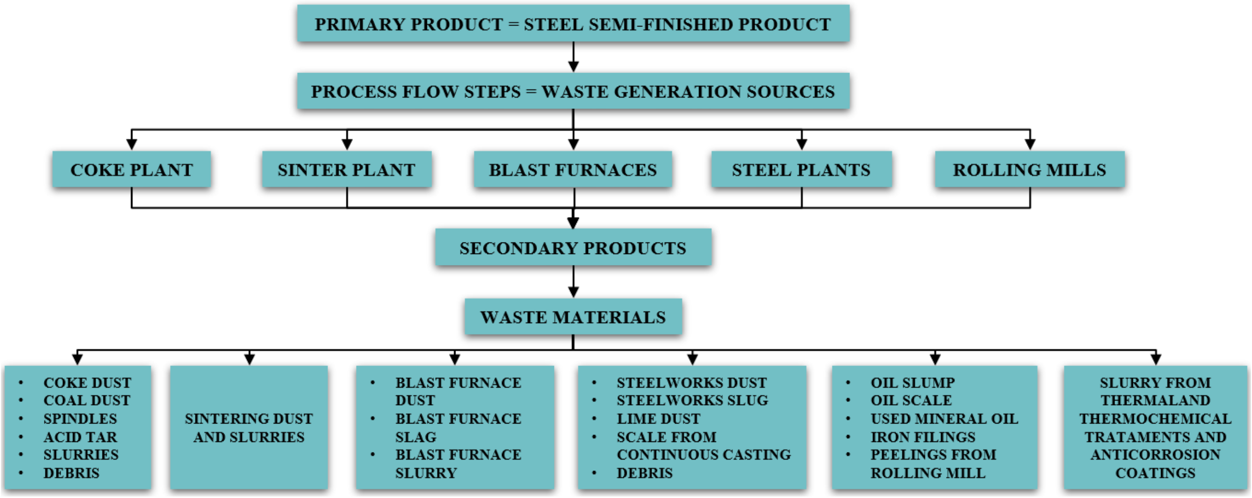

Fig. 1 Types of waste and their generation sources within an integrated iron and steel plant [1/1, 12/14]

Knowing the properties of the iron-containing wastes, in particular the chemical composition (highlighting the harmful elements) and the particle sizes, enables the selection of the technological recycling method.

CHAPTER 4

PROCESSES AND TECHNOLOGIES FOR USING THE SMALL-SIZED AND POWDERY WASTES CONTAINING IRON, ZINC AND CARBON

The iron ore pelletization reveals several essential advantages, some of which being:

- the round shape of the pellets, as well as the particle-size distribution uniformity, which determine the increase of the charge permeability, enable boosting the operating regime through a better gas distribution in the blast furnace and intensification of the indirect reduction, with consequences on the decrease in specific coke consumption;

- the sulphur content in pellets is much lower than in sinter (0.01% vs. 0.10-0.15% S in sinter, most of it being brought by the coke);

- the specific heat consumption for making pellets is lower by approx. 50% relative to the same specific consumption required to obtain the sinter [7/7, 8/8].

- Briquetting is the process of transforming by pressing the fine and small-sized ores (concentrates, ferrous waste), whose particle size is less than 8 mm, into pieces (briquettes) with well-defined shape (oval, spherical, cylindrical, parallelepiped, cubic or hexagonal prism) using specialized machinery, followed by a drying-roasting process to increase their mechanical properties [10/10, 11/11].

The briquettes must meet the following conditions:

- resistance in variable conditions (not to deteriorate under the influence of heat changes, cold or humidity);
- high temperature resistance (900°C);
- water resistance;
- adequate gas permeability;
- mechanical resistance and shredding resistance;
- resistance to heated vapour atmosphere;
- low humidity (maximum 2%);
- high volumetric weight [9/9].

The heat sintering is the most widespread process of converting fine and small-sized concentrates and ores to be used in the ferrous and non-ferrous extractive metallurgy. The sintering process results in the concentration in useful elements by removing the volatile compounds or elements (S, CO_2, As). The obtained products are more easily reducible, due to their porosity. Sintering is a physicochemical process, depending on: [11/11, 14/25]

- the particle size of materials: small-sized ores (or small-sized ferrous waste), which are the main component of the crude sintering charge; the particle size must be less than 8 mm, even less than 6 mm (in case of magnetite ores), and less than 3 mm in case of fluxes and fuels (metallurgical coke fines);
- the humidity of material: 5-18%, depending on particle size, nature and surface properties of the material;
- the content of combustible materials (fine coke, coke dust, coal, and sulphur), which provide the heat required for the sintering process, depending on particle size, humidity and nature of the material (averaging 3-10%);

For waste recycling, it is necessary to use specific facilities/processes, of which I can mention the introduction of sinter into the liquid steel (Fig. 2 / 4.13), and the rotary hearth furnace (Waelz) (Fig. 3 / 4.14).

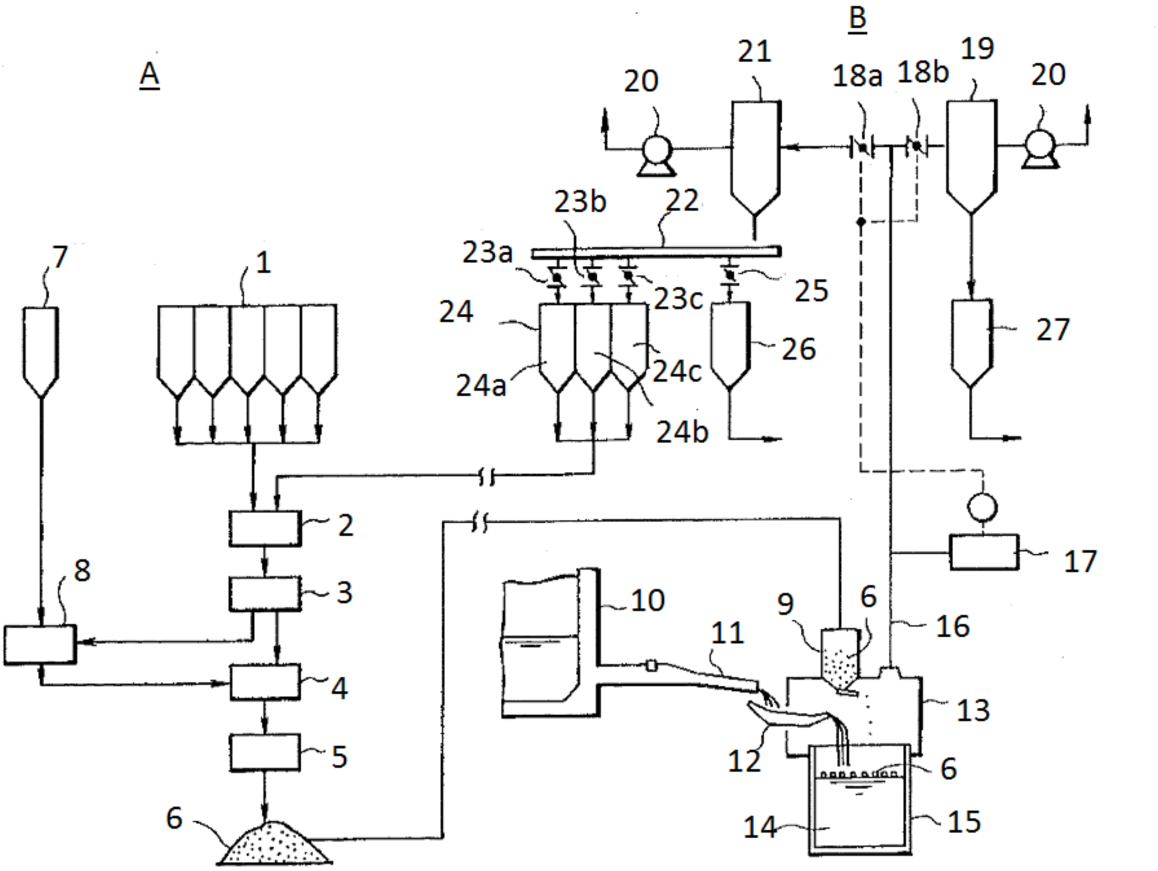

Fig. 2 Schematic diagram of a zinc reduction plant
1 - tanks containing steelworks dust and mixed material; 2 - blender; 3 - tank collecting mixed material; 4 - drier; 5 - tank collecting pellets; 6 - pellets; 7 - tank for graphite; 8 - pelletizer; 9 - pellet feeding tank; 10 - furnace; 11 - hopper; 12 - rotating retort; 13 - dust collection hood; 14 - liquid steel; 15 - liquid steel collection ladle; 16 - dust and exhaust gas transport pipe; 17 - dust analyzer; 18 - pipe closing valves; 19 - general dust collector; 20 - fan; 21 - dust collector for zinc recovery; 22 - conveyor belt; 23a, 23b, 23c - dust discharge valves; 24a, 24b, 24c - tanks for dust collection; 25 - valve for recovered recycled dust, 26 - tank for recovered recycled dust

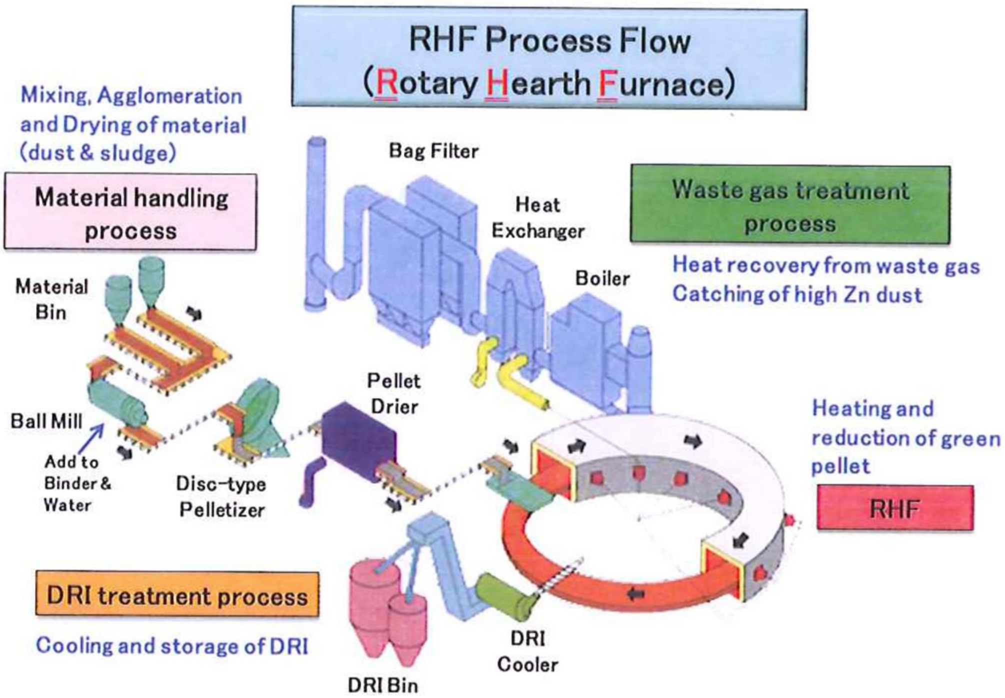

Fig. 3 Schematic diagram of a zinc reduction plant using a rotary hearth furnace

CHAPTER 5

LABORATORY EXPERIMENTS ON THE USE OF SMALL-SIZED AND POWDERY WASTES ORIGINATING FROM METALLURGICAL INDUSTRY

The experimental technological solutions, proposed within the doctoral thesis, aim at using the secondary materials consisting of powdery and small-sized wastes (from S.C. ArcelorMittal Hunedoara S.A. – steelworks dust, sinter plant dust, blast furnace dust, lime dust, scale, steelworks slag – the magnetic fraction, reducing slag from LF, graphite dust, etc., and from a company that deals with the processing of complex non-ferrous ores (PMNC), I.S.P. slag and mixed material.

The research focused mainly on the use of waste containing zinc and iron, the purpose being to determine the rate of zinc removal from the waste containing such elements, processed by pelletizing, briquetting and sintering, the first two methods being the most technically and economically convenient for the highly restructured iron and steel-making companies, as well as for other companies producing relatively small quantities of waste (up to about 6000 tonnes per year).

The types of waste used for the production of pellets, as well as the manufacturing recipes, are presented in Table 1 / 5.1. Also, the percentage of graphite used as reducing agent is shown in the same table.

Table 1 Composition of recipes used for making pellets, briquettes and sinters, [%]

Nr. Crt.	*)Used wastes	**Recipes composition,** [%]									
		R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
1.	P.O.	20	24	32	35	38	40	45	50	54	60
2.	I.S.P.	35	24	19	28	31	25	23	25	12	12
3.	M.A.	25	24	25	16	18	19	15	7	18	14
4.	G	13	16	14	13	9	11	8	10	11	10
5.	Zg LF	7	12	10	8	4	5	9	8	5	4
Total		100	100	100	100	100	100	100	100	100	100

*) P.O. – steelworks dust; I.S.P. – material from PMNC; M.A. – mixed material; G – graphite; Zg LF – slag from LF

Table 2/5.2 shows the chemical composition of the components used for making pellets, briquettes and sinters.

Table 2 Chemical composition of the materials to be used for making pellets, briquettes and sinters, [%]

Recipe no.	**Chemical composition**, [%]											
	Fe_2O_3	**SiO_2**	**ZnO**	**CaO**	**Al_2O_3**	**PbO**	**MgO**	**MnO**	**P_2O_5**	**Cr_2O_3**	**C**	**Other oxides**
P.O.	43,11	7,29	19,67	6,59	1,74	2,66	3,33	3,03	0,307	0,337	3,2	8,736
M.A.	33,97	24,36	11,28	8,53	6,29	5,95	1,16	0,614	0,132	0,0592	0,5	7,1548
ISP	35,62	20,82	12,99	10,87	9,11	2,33	1,53	0,527	0,191	0,0576	0,16	8,936

It has aimed at reducing the zinc content of the pellets. In this regard, Table 3/5.3 shows the chemical composition of the pellets and briquettes before reduction, Table 4/5.4 shows the chemical composition of the reduced pellets, and Table 5/5.5 shows the reduction degree of zinc.

Table 3 Chemical composition of the recipes for making pellets and briquettes from the crude charge, [%]

Recipe no.	**Recipes chemical composition**, [%]											
	Fe_2O_3	**SiO_2**	**ZnO**	**CaO**	**Al_2O_3**	**PbO**	**MgO**	**MnO**	**P_2O_5**	**Cr_2O_3**	**C**	**Other oxides**
R1	31,19	16,45	15,66	9,02	3,70	2,44	2,95	2,19	0,252	0,234	8,77	7,144
R2	28,76	11,12	11,42	14,54	6,81	1,94	3,09	1,92	0,739	0,171	13,01	6,48
R3	32,64	12,42	12,83	10,56	5,31	2,14	2,98	1,59	0,214	0,168	12,3	6,848
R4	33,60	9,39	13,19	11,48	4,79	2,08	3,15	1,67	0,193	0,21	13	7,25
R5	36,8	10,84	14,87	10,47	4,5	2,18	2,91	1,78	0,238	0,19	7,25	7,97
R6	35,91	9,08	14,47	10,48	4,02	2,13	3,05	1,88	0,202	0,227	10,6	7,95
R7	32,32	12,22	12,2	10,98	5,45	2,15	2,63	1,3	0,193	0,139	14	6,42
R8	35,49	8,64	15,15	10,11	4,25	1,98	3,08	2,03	0,229	0,221	11,1	7,74
R9	36,68	9,85	15,66	9,02	3,70	2,44	2,95	2,19	0,252	0,234	8,77	8,26
R10	35,3	6,72	17,22	6,72	2,2	2,44	3,04	4,03	0,24	0,297	12	9,79

Table 4 Chemical composition of pellets after Zn removal, [%]

Recipe no.	**Recipes chemical composition**, [%]											
	Fe_2O_3	**SiO_2**	**ZnO**	**CaO**	**Al_2O_3**	**PbO**	**MgO**	**MnO**	**P_2O_5**	**Cr_2O_3**	**C**	**Alți oxizi**
R1	38,29	23,84	2,16	15,14	8,66	0,211	3,61	1,58	0,295	0,723	0,16	5,33
R2	36,70	22,20	0,986	15,69	9,79	0,0399	3,96	1,75	0,744	1,04	0,79	6,31
R3	40,58	20,30	1,92	13,48	7,46	0,111	3,56	1,86	0,285	3,17	0,31	6,96
R4	36,15	22,15	1,68	16,02	9,64	0,174	4,24	1,91	0,332	0,247	0,01	7,45
R5	44,23	18,07	3,99	10,87	6,12	0,334	2,99	1,82	0,279	3,91	0,11	7,28
R6	36,74	21,47	2,06	14,93	8,85	0,226	4,39	2,16	0,352	0,327	0,35	8,14
R7	43,02	19,6	2,16	11,85	6,3	0,314	3,43	1,9	0,287	2,68	0,28	8,18
R8	48,95	14,81	1,12	9,57	5,58	0,0706	3,10	2,18	0,278	6,78	0,32	7,24
R9	46,94	17,17	1,02	10,45	5,79	0,092	3,71	2,61	0,319	4,67	0,17	7,06
R10	36,42	20,34	1,76	15,44	7,52	0,365	5,06	3,08	0,455	0,545	0,19	8,82

Table 5 Rate of zinc removal from pellets, [%]

Recipe no.	R1	R2	R3	R4	R5	R5	R7	R8	R9	R10
η_{eZn}, [%]	86,20	91,37	85,04	87,26	85,16	85,76	90,20	90,52	93,49	89,78

$$\eta_{eZn}=(Zn_f / Zn_{total}) * 100 \qquad (1/5.1)$$

The obtained data were processed using Matlab software, in order to obtain correlations between the main feature pursued – *zinc removal rate* – and the *percentage of recipe components*.

To establish double correlation equations between the components containing Fe and Zn (PO, ISP, MA) and the removal rate of zinc, the data were processed using Matlab software, and the results are shown graphically and analytically.

Following the processing of data using Matlab software, it was obtained a recipe which, after making pellets, the zinc removal rate reached values of 95-97%, which is the purpose of the thesis – to remove Zn from the resulted pellets, briquettes and sinters, making them suitable to be used in the electric furnace charge, and to reduce to zero the waste disposal.

Fig. 4/5.4 Pellets taken from the oven

For producing briquettes moulds were made (Fig.5/5.39). After making briquettes (Fig.6/5.40), they were subjected to reduction, and the obtained data were compared with the data obtained for pellets and sinters.

Fig. 5 Moulds used for making briquettes

Fig. 6 Obtained briquettes

For the recovery of non-ferrous metals, it was designed a hood to be placed above the furnace to capture the gases (Fig.7/5.95), as well as a gas moistening plant, so that the content of Zn, Pb, and Cd became solid (Fig.8/5.98). The gases are brought to the plant using a fan installed upstream. The operating principle of the plant involves "washing" the gases, which is possible through the upper chamber filled with water from the laboratory installation. The base plate is perforated for spraying inside the chamber in which the gases are captured (Fig.9/5.99). The obtained sludge was then chemically analysed.

Fig. 7 The new gas collection hood

Fig. 8 The gas purification installation

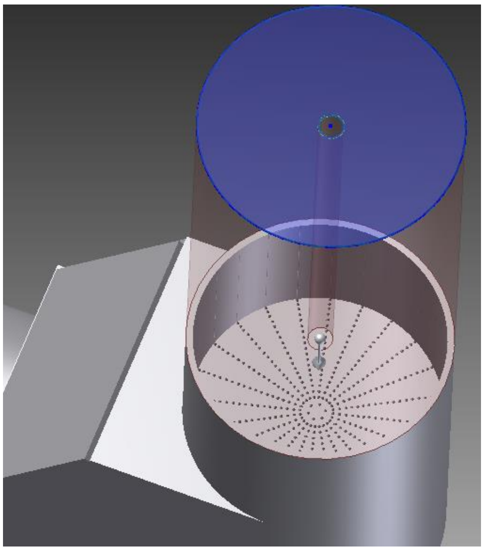

Fig. 9 The upper part of the installation

CHAPTER 6
PROCESSING OF PELLETS CONTAINING IRON AND ZINC IN ELECTRIC INDUCTION FURNACE

Experiments were carried out in the laboratory phase on the removal of zinc from the pellets made from steelworks dust containing high levels of zinc by introducing them into the liquid steel bath of an induction furnace with a capacity of 10 kg. For the formation of metal bath, samples were taken from it (steel grade S 235) to determine the chemical composition (the standard chemical composition was known).

For obtaining experimental pellets, there were used three types of pellets made from steelworks dust, following the same recipe, but with different concentrations of zinc oxide in the dust (types: C1, C2 and C3). As binder, I used bentonite and L.F. reducing slag.

The same recipe for all three types of steelworks dust, making 2 batches of pellets per recipe, 2 kg/batch (the capacity of pelletizer), which means 4 kg per type.

For the production of pellets, the materials used were dosed according to the established recipe, aiming to obtain a mixture of 4 kg for each batch. Next, the material was homogenized in the homogenization plant, after which the amount of 2.0 kg was introduced into the pelletizer to obtain the pellets. During the formation of pellets, the batch was continuously wetted to ensure the adhesion of the dust particles, binder and reducing agent. The pelletization process was appropriate, considering the addition of reducing agent. As mentioned above, when the pelletization process was completed, the pellets were dried in open air and granulometrically graded.

After the completion of the pelletization process, the crude pellets were left untouched for 24 hours, enabling the removal of moisture, and then dried in the oven at 120°C for 36-48 hours. Their chemical composition was next determined. The particle size grading was carried out after drying the pellets.

The pellets were added into the liquid steel bath, (Fig. 10 / 6.5) and the exhaust gases containing zinc were watched after the reaction with the liquid steel (Fig. 11 / 6.6).

Fig. 10 Adding pellets into the liquid steel bath

Fig. 11 Gases exhausted following the zinc reduction reaction

During the experiment, samples were taken after a chosen time and chemically analysed in order to monitor the reduction of Zn level. Upon completion of the reduction process, it was found that the reduction was realised in a percentage ranging from 98% to 99.9%.

Comparing the evolution of the zinc quantity eliminated from the pellets with the particle size of 2-5 mm and 10-15 mm, it was deduced that the zinc removal was more intense in case of large pellets. As a consequence, in case of intermediate particle size of 5-10 mm, the reduction evolution in time lies between the other two extremes. In case of stirring the liquid steel bath, the release of zinc dust lasts 14-15 minutes, i.e. 50% less compared to the case in which the pellets are added into the steel bath without stirring.

The processing of pellets using the method of addition into the steel bath in the induction furnace enables the zinc to pass through vaporization and reoxidation into the gases and to be recovered through gas purification operations, followed by further processing using technologies specific to the zinc metallurgy.

For this technological method of zinc recovery by addition of pellets into the steel bath of the induction furnace, are recommend pellets with the particle size of 2-15 mm (granulometric composition, 2-5 mm, 20%, 5-10 mm, 50% and 10-15 mm, 30%);

A very important thing in using this method is to stir the liquid steel bath (so the reduction time is 50% lower), choosing pellets with the particle size of 10-15 mm.

Also, the installation of a gas capture and purification system at the furnaces that would process such pellets ensures the capture of zinc from the dust and its further processing using technologies specific to the zinc metallurgy.

CHAPTER 7

RESEARCH ON THE USE OF DUST RESULTED FROM SIDERURGICAL PROCESSES

Given that the briquettes intended to be processed in blast furnaces undergo multiple handling operations, in many cases being transported over long distances (hundreds of kilometres), and taking into account the data from the literature [1/1, 4/4, 8/8], it is considered that, if the briquettes are to be used in a siderurgical company, they must have a certain resistance (cracking resistance, crushing interval).

For briquetting, two technological variants were applied, in both cases being used as ferrous waste the dust from sintering, dust from blast furnaces, dust from steelworks, and scale. At variant "B", was used also slag from steelworks – the ferrous (magnetic) fraction; the lime was used as binder and the graphite as reducing agent in both cases, and at the variant "A" was used also bentonite as binder, this one being substituted at the variant "B" by slag from L.F.

The qualitative features related to resistance and chemical composition of the obtained briquettes (in both cases) make them suitable to be used as feedstock for the EAF charge in percentage of 5-7% (they can be equivalent to the ferrous scale).

For the waste processed by peletization, there were tested three technological variants ("A", "B" and "C", i.e. "A" and "B" with fire-hardening and "C" with cold hardening), and for each variant I tested the pellets obtained with the application of three recipes.

In all three variants, a single powdery ferrous waste was tested, i.e. the steelworks dust (very good in terms of the Fe and Zn content), in order to determine the possibilities of processing it along the gas dedusting flow.

At the variants "A" and "B", bentonite was used, lime and LF slag as binders, and at the variant "C" was used cement and LF slag; in the first case (variant "A"), were obtained self-reducing pellets and, therefore, it was necessary to introduce the reducing agent in the composition of the pellets, i.e. the graphite dust (reducing agent "C").

In case of self-reducing pellets (variant "A"), was obtained for iron a degree of metallization of 92-94% and for zinc a removal rate of 94-96%, which means that, in terms of particle size composition and resistance to compression, regardless of the processing option, the pellets are suitable to be used as feedstock for the EAF charge.

For the waste processed by sintering, three technological variants ("A", "B" and "C") were applied – 2 recipes for each variant, in all cases being added small-sized coke (a part of it as reducing agent) and LF slag (a better micro-pelletization of the dust).

In terms of ferrous waste, the variants "A" and "B" contain the same types of waste as those used for briquetting, and the variant "C" only steelworks dust and scale, in order to obtain results on two categories of waste frequently resulting along the technological flow: Electric Steelworks – Continuous Casting – Rolling Mill.

The degree of metallization for iron ranged between 68% and 74% (variant "A": 69.57-72.06%; variant "B": 68.96-73.71%, and variant "C": 71.26-73.71%), so it can be considered that the reducing sintering process underwent very well, and from this point of view the sinter is of good quality; in terms of resistance, chemical composition and harmful elements content, the sinter is of good quality, too.

CHAPTER 8
FINAL CONCLUSIONS. ORIGINAL CONTRIBUTIONS. DIRECTIONS FOR FURTHER RESEARCH

From the final conclusions highlighted in the doctoral thesis, the most significant ones are presented below:

- in the integrated iron and steel-making plants (coke plant / sinter plant / blast furnaces / steelworks / rolling mills) the following types of *powdery waste* are resulting from the technological processes: dust and slurry from the coke plant, dust and slurry from the sintering plant, blast furnaces and steelworks, scale slurry from rolling mills, iron filings from grinding the rolled products, etc.; *small-sized*: slag, scale from continuous casting and rolling mills, turnings from peeling the rolled products; *large-sized waste* (usually over 10 mm): splashes, scales, cut ends, rejected products, etc.;
- some wastes also contain harmful elements to the quality of the products obtained by recycling the wastes (As – red sludge, Zn, Cu, Pb – pyrite ashes);
- the wastes contain various levels of iron, from approx. 30% (siderite concentrate, waste containing iron and zinc) to over 60% (scale, steelworks dust);
- the variety of ferrous waste found in Hunedoara, Călan, Oţelu Roşu and Reşiţa areas, either in terms of particle size composition or chemical composition, led to the idea to subjecting them to pelletization, briquetting and sintering processes for the advanced recovery of iron and, under certain conditions, of zinc;
- the results of the experiments carried out, which are presented in Chapter 5, aimed the processing by pelletization, briquetting and sintering of some powdery and small-sized types of waste, rich in zinc (steelworks dust Zn~20%, ISP slag (Imperial Smelting Process) Zn~11% and mixed material Zn~13%), in order to recover zinc;
- the pelletization process for making self-reducing pellets (using 10 different recipes) has resulted in a zinc removal rate of 85-94%;
- determination of the correlation relationships between the zinc removal rate and the shares of components in the recipes by processing the data using the MATLAB software; the correlations presented analytically and graphically enabled us to obtain the optimal pelletization recipe for which the zinc removal rate ranged from 95% to 98%;
- the SEM and EDX analyses carried out using crude and hardened pellets (self-reducing) confirms the reduction of zinc and iron in pellets;
- by processing the waste as self-reducing briquettes and using the same types of waste as for pelletizing, were obtained close values for the zinc removal rate;
- regarding the sinters made using three different recipes, thanks to the coke addition in the sintering charge (20%), the zinc removal rate was 97-99%, the degree of metallization for iron was 59-62%, and the total iron level (Fe_{total}) was 32-34%, of which 19-21% Fe_{met};
- The experiments carried out on the processing of steelworks dust containing high levels of zinc (Chapter 6), from pelletization to addition into the liquid steel bath (induction furnace), concerned primarily the recovery of zinc and secondly the recovery of iron;
- the pellets were made in three variants (with addition of graphite as a reducing agent), varying according to the dust quality assessed through the iron and zinc levels;
- the zinc removal rate (98 - 99.99%) is influenced by the granulation of pellets and the steel bath stirring intensity;
- in the researches carried out, whose results are presented in Chapter 7, it was envisaged to establish the technologies for recycling the small-sized and powdery ferrous wastes (dust from sinter plant, blast furnaces and steelworks, scale and steelworks slag – the ferrous fraction) existing in the traditional siderurgical areas (Hunedoara, Călan, Oţelu Roşu and Reşiţa), where there are large reserves of such waste. The experiments were carried out with waste collected from Hunedoara area;

The most significant original contributions are:

1/2. Selection of waste types for experiments, determination of their chemical and particle size composition, content of harmful components, as well as of the appropriate processing technologies, and, according to them, the determination of the recipes to be used;

2/4. Determination of the recipes for waste processing by pelleting, briquetting and sintering, and determination of the qualitative features afferent to each technology and recipe;

3/5. Data processing using the Matlab software in order to determine the correlation between the zinc removal rate and the percentage of components in the pelletization charge;

4/6. Determination of the optimal pelletization recipe that provides a zinc removal rate of 95-98%;

5/7. Analysis of SEM structure, analysis of chemical composition of crude and burned pellets, analysis and comparison of results;

6/8. Designing the moulds for making cylindrical briquettes of various diameters and various shapes of the cross section (full, hollow, multi-cavity);

7/9. Making briquettes using the same recipes as for making pellets, determination of the zinc removal rate, and comparison of the results obtained at pelletization;

8/10. Waste sintering using three recipes (different shares of P.O., I.S.P. and M.A.), determination of zinc removal rate, iron reduction degree and metallization degree;

9/16. Determination of briquetting recipes, making briquettes, determination of qualitative resistance properties;

10/17. Data processing in EXCEL and MATLAB software to obtain simple and multiple correlations between the qualitative properties and the percentage of components in recipes;

11/18. Technological analysis of the obtained results and determination of the optimal recipes;

12/20. Determination of the compressive strength depending on diameter, data processing in Excel sheet, determination of the correlation between these parameters, presentation of the results in graphical and analytical form, and technological analysis of the results;

13/21. Determination of compressive strength of the cold hardened pellets depending on diameter and hardening time, data processing in EXCEL sheet, determination of the correlation between these parameters, presentation of the results in graphical and analytical form, technological analysis of the results and determination of the optimal recipes;

14/22. Determination of the sintering recipes (for the same ferrous products as in the case of briquetting), realisation of the sintering process, determination of the qualitative properties (chemical composition, resistance, metallization degree) and selection of optimal recipes.

References

[1/1] T. Heput, A. Socalici, E. Ardelean, M. Ardelean, N. Constantin, R. Buzduga – *„Valorificarea deşeurilor feroase mărunte şi pulverulente”* [Use of small-sized and powdery ferrous waste], Publisher: Editura Politehnica Timişoara, 2011;

[2/2] S. Şerban – Doctoral thesis: *„Cercetări privind valorificarea deşeurilor cu conţinut de fier şi elemente pentru alierea oţelului”* [Research on the use of iron-containing waste and steel alloying elements], Hunedoara, 2015;

[3/3] T. Heput, A. Socalici, E. Ardelean – *„Cercetări privind protecţia mediului în industria siderurgică”* [Research on environmental protection in the iron and steel-making industry], Annals of the Faculty of Engineering Hunedoara, Tome II, Fascicule 1, 2000, 84;

[4/4] V. Şerban, A. Nicolae – *„Bilanţ de materiale - instrument de analiză a eficienţei valorificării materialelor secundare”* [Material balance - tool for analysing the efficiency of using secondary materials], Metalurgia no. 1, 2004, 130;

[5/5] A. Nicolae, et al. – *„Dezvoltarea durabilă în siderurgie prin valorificarea materialelor secundare”* [Sustainable development in the iron and steel-making industry by using secondary materials], Publisher: Printech, Bucharest, 2004;

[6/6] L. Strungariu – Doctoral thesis: *„Cercetări privind valorificarea subproduselor rezultate de la epurarea apelor industriale”* [Research on the recovery of by-products from industrial water treatment], Hunedoara, 2013;

[7/7] D. Dobrovici, O. Hătărăscu, I. Şoit-Vizante, A. Alexandrescu – *„Intensificarea proceselor din furnal"* [Intensification of the processes occurred inside the blast furnace], Publisher: Editura Tehnică, Bucharest, 1983;
[8/8] O. Buzea – *„Îndrumător furnale"* [Guiding Book for Blast Furnaces], Part I, Raw materials;
[9/9] M. Guran, I. Tripşa – *„Noutăţi în pregătirea minereurilor de fier pentru furnal"* [News in the preparation of iron ores for blast furnaces], Publisher: Editura Tehnică, Bucharest, 1964;
[10/10] N. Constantin – *„Procedee neconvenţionale de obţinere a materialelor feroase"* [Unconventional processes for obtaining ferrous materials], Publisher: Printech, 2002;
[11/11] E. Popa, T. Heput, M. Ardelean – *„Procese industriale"* [Industrial processes], Publisher: Editura Politehnica Timişoara, 2012;
[12/14] Al. Rău, I. Tripşa – *„Metalurgia oţelului"* [Steel Metallurgy], Publisher: Editura Didactică şi Pedagogică, Bucharest, 1985;
[13/16] I. Dragomir – *„Teoria proceselor siderurgice"* [Theory of iron and steel-making processes], Publisher: Editura Didactică şi Pedagogică, 1985;
[14/25] N. Constantin – *„Determinarea caracteristicelor metalurgice ale materialelor din amestecul de aglomerare utilizat la U.A.F.-SIDEX Galaţi"* [Determination of metallurgical properties of the materials introduced in the sintering mixture used at U.A.F.-SIDEX Galaţi], Contract no. 9/1996, Beneficiary: I.C.E.M. - S.A. Bucharest;
[15/30] O. Buzea – *"Guide for blast furnaces",* Technical Publishing, 1994;
[16/42] E. Crişan – Doctoral thesis: *„Cercetări privind valorificarea în siderurgie a deşeurilor pulverulente şi mărunte cu conţinut de fier şi carbon"* [Research on the use in the iron and steel-making industry of the powdery and small-sized wastes containing iron and carbon], Faculty of Engineering Hunedoara, 2013;
[17/63] D.A. Popescu – *"Study on the quality of industrial waste deposited in ponds*", Annals of the Faculty of Engineering Hunedoara - International Journal of Engineering, Tome XII 2014-Fascicule 4, pp 315-321 ISSN: 1584-2673, indexed Google Scholar, EBSCO.