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REINTRODUCTION OF IRON–CONTAINING WASTE AND STEEL ALLOYING ELEMENTS INTO THE ECONOMIC CIRCUIT

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Abstract: As a result of the activity in the metallurgical and anti–corrosion industries, there is an important mass of waste, for which there are still no efficient recovery solutions. Besides environmental issues, this waste is enormous and consumes significant amounts of money, as it could be valuable sources of recyclable material in the steel industry and beyond. The main object of the researched theme was the identification of the technological systems / processes approached both at the theoretical and practical / experimental level, regarding the utilization of the waste resulting from the corrosion coatings and those resulted from the steel fluxes. The proposed recovery procedure is a complex one and covers the following aspects: quantitative and qualitative determinations of waste used for experiments performed; their physico–chemical characterization; performing laboratory experiments on pelleting and briquetting processes; establishing their own recipes for these experiments; mathematical correlation to optimize the best results (using Excel, Matlab, DataFit); establishing optimal areas of variation of different technological parameters of waste processing; the interpretation and scientific substantiation of the results obtained; developing strategies for the implementation of the results obtained in industrial practice. The relevance of the paper is the contribution made to the solution of some pressing environmental problems regarding environmental pollution, as well as the concern for the production of new materials with an economic and technological role.

Keywords: waste treatment & recovery, ferrous concentrates, galvanic waste recovery, waste management and treatment.

GENERAL CONSIDERATIONS

The development of technologies and methods of waste treatment and recovery and their implementation is an important environmental and applicative issue. The studies carried out have shown that using the proposed recovery technologies there are obtained ferrous concentrates containing at least 85% metallic iron, the recovery of these concentrates in the furnace and steelmaking sectors and the improvement of the environmental conditions in the areas where they are currently stored waste. From an ecological point of view, the implementation of the galvanic waste recovery process allows to reduce the environmental pollution hazard with the listed metal compounds.

Studies on waste management and treatment in Romania are carried out under the European Union Framework Directive 2008/98/EC on waste. The aim of this directive is to protect the environment and human health by emphasizing the importance of proper waste management and the use of recovery and recycling techniques to reduce resource pressures and improve them. The legislative act establishes the waste hierarchy: prevention, reuse, recycling, recovery for other purposes – such as energy and disposal.

The environmental aspects of waste management, in accord with the waste hierarchy concept, are:

- reduction of waste volume and their environmental impact through rational use and minimization of their quantity;
- reducing the consumption of natural resources and its impact on the balance and status of ecosystems by making full use of waste as a secondary raw material (energy source, fertilizers, building materials, etc.);
- recovery, use, neutralization and disposal of waste, through environmentally friendly and human health procedures.

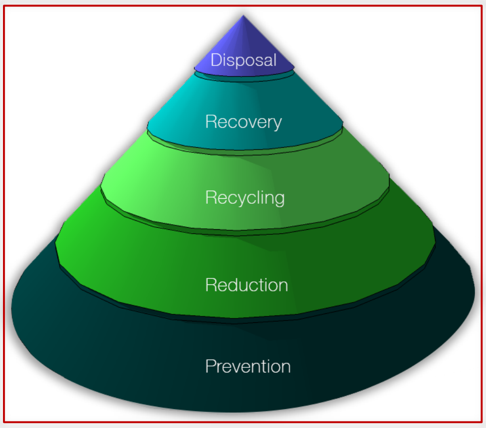


Figure 1. The waste hierarchy concept

Galvanic enterprises are the most uneconomic by their harmful working conditions and large amounts of waste generated. It is considered that in enterprises where galvanic sections operate, the waste water produced by these sections accounts for 30–50 % of their total volume. The average waste water of an enterprise with a galvanic section is 600–800 m^3/24 hours. Galvanic waste is formed in the galvanic sections of machine building machinery, machinery and apparatus in the metal pickling process. Galvanic waste is high in metals, such as Cu, Ni, Mn, Pb, Sn and W. Moreover, about 1 km^3 of toxic waste water, containing heavy metals, acids and bases, is discharged annually, and 25–30 % of these waters are deposited in aquatic basins.

The purpose of this paper is to establish the reintroduction in the economic circuit of iron–containing wastes and elements for alloying steel, expressed by ecological, chemical–technological and economic aspects. Ensuring the presence of environmental and chemical–technological aspects provides for modern approaches such as minimizing the impact of waste using the pollution prevention principle, which consists in implementing technologies that generate a minimum volume of waste.

In the present paper the ecological and chemical–technological aspects foresee the use of advanced production technologies, which ensure obtaining products with a net technical characteristics superior to the previous ones. The approach, solving and implementation of the proposed technologies depend to a large extent on the nature of the materials subject to processing, namely waste as secondary materials to be recycled, as well as the shape of the finished product under which these materials are processed. The study of waste recovery experiments is essential both for the understanding of the recovery process and the reintroduction into the economic circuit of solid waste, as well as for the development of some theoretical and practical analyzes in this field.

MATERIALS AND METHODS

The waste used in the experiments came from different points: pulverulent iron powder (dust) from ponds and industrial waste dumps, agglomeration and iron fluxes, steel production in arc furnaces and oxygen converters, continuous casting, rolling mills, etc. It is necessary that in the supply of raw materials / waste they are stored in well–defined spaces so that they do not mix or impregnate them with earth, concrete, refractory materials. We considered it of interest to use in pelletizing and briquetting recipes, waste from ArcelorMittal Hunedoara, Cemtrade Oradea, Galvano Alco Oradea, IUS Braşov.

Under laboratory conditions, the waste was stored in plastic containers both before processing (grinding, volumetric classification) for pelletisation/briquetting, and after this processing, mentioning the name of the waste and its quality characteristics. Experimental determinations were carried out at Hunedoara Faculty of Engineering/Polytechnic University of Timişoara, CEMS – Politehnica University of Bucharest (Special Materials Research and Expertise Center) and at ArcelorMittal Hunedoara. These three institutions have laboratories equipped with installations and equipment that have been used to carry out the experiments.

The proposed experimental technological solutions (pelletizing and briquetting) aimed at capitalizing the secondary materials, consisting of small and powdered waste such as: blast furnace dust, red mud, corrosion protection sludge, as well as some basic additions (lime, bentonite). Experiments were carried out on the granulometric class of blast furnace dust, steel dust, gut (originated from ArcelorMittal Hunedoara), red mud (from Oradea), anticorrosive protective sludge (originating from Oradea and Brasov) , weighing 10 kg of these types of waste.

For the production of raw pellets and briquettes, the used waste (composition of recipes) and their chemical composition are presented in the Tables 1–5. The granulometric composition of the mixture obtained from all these components is influenced by the weight of each waste in the recipe, determining the quality of the recyclable product, namely a more uniform particle size distribution.

Table 1. Composition for each recipe (pellets): PO – steel dust; PAF – aglomerating–furnace dust; NR –red sludge; NG – galvanically sludge; G – graphite; B – bentonite; V – lime; T – thermal power plant ash

NUMBER RECIPE	WASTES TYPE							
	P.O.	P.A.F.	N.R.	N.G.	G	B	V	C.T
R1	37	28	14	9	4	6	2	–
R2	18	45	7	18	5	5	2	–
R3	29	29	10	20	5	4	3	–
R4	32	32	10	10	4	4	4	–
R5	21	42	11	11	–	5	4	5
R6	11	53	11	11	–	5	5	4
R7	57	11	11	11	–	3	3	2
R8	72	–	12	12	–	4	–	–
R9	–	72	12	12	–	4	–	–
R10	72	–	–	24	–	4	–	–
R11	–	72	–	24	–	4	–	–
R12	69	–	–	23	1	3	2	–
R13	69	–	23	–	2	5	2	–

Table 2. Composition for each recipe (briquettes): PAF – aglomerating–furnace dust; PO – steel dust; NR – red sludge; NGO – galvanically sludge Oradea; NGB – galvanically sludge Braşov ;G – graphite; B – bentonite; V – lime

NUMBER RECIPE	WASTES TYPE						
	P.O.	P.A.F.	N.R.	N.G.	G	B	V
R1	32	38	5	11	8	–	5
R2	27	43	3	14	8	–	5
R3	52	16	5	11	11	–	5
R4	40	20	15	10	10	–	5
R5	55	–	15	15	10	–	10
R6	–	–	–	84	10	10	–
R7	–	42	–	43	9	10	–
R8	–	84	–	–	9	10	–
R9	–	–	–	84	10	6	–
R10	–	–	–	81	9	9	–

Table 3. Chemical composition for red sludge

Fe_2O_3	Al_2O_3	CaO	SiO_2	TiO_2	Na_2O	Cr_2O_3	ZnO	Altele
36.63	27.22	16.35	8.31	5.12	3.77	0.250	0.112	1.10

Table 4. Chemical composition for the galvanically sludge from Brasov

CaO	Al_2O_3	Fe_2O_3	SiO_2	S	Na_2O	Ni	Cr2O3	MgO
63.25	7.72	6.75	5.07	3.86	3.05	2.75	1.77	1.58

Table 5. Chemical composition for the galvanically sludge from Oradea

ZnO	Fe2O3	Na2O	NiO	P2O5	SiO2	Al2O3	CaO	Altele
24.43	21.59	12.33	7.73	5.56	5.44	3.52	1.72	8.02

THE EXPERIMENTAL DATA PROCESSING

— Mathematical correlations

The character of the optimization of the metallurgical processes is largely influenced by their complex particuliarities, which take place within a large number of variables (parameters) that act independently or intercondition over time. For this reason, for the analysis of metallurgical processes and for the establishment of double correlation equations between the technological factors and the compressive strength of the raw pellets and the briquettes, the data were processed in the Matlab computing program and the results are presented both graphically and analytically.

The experimental data were modeled in the form of the equation (1).

$$z(x,y) = ax^2 + b\cdot y^2 + c\cdot x\cdot y + d\cdot x + e\cdot y + f \qquad (1)$$

where the a, b, c, d, e and f are regression coefficients

The equations of the regression hyper–surface are in the form of the above equation, for which there is a correlation coefficient R^2 and a deviation from the regression surface.

In the experimental data processing it was envisaged to obtain some correlations expressed by polynomial functions and the selection of those having representative values for the regression coefficient on the one hand, and on the other hand it was considered that the analytical expression had a shape as much as possible simple. For each correlation, we determined the expression of the functions that limit the upper and lower domains respectively.

It was intended to determine the form of mathematical functions linking dependent variables of the technological process to independent variables, based on experimental determinations, after a correlation analysis of these data was performed.

The resulted regression equations, with the multiply determination coefficients (R^2), are presented in eq. (2)–(10).

$$z = -0.0050\,x^2 - 0.0430\,y^2 + 0.0037\,x\cdot y - 0.2944\,x - 1.6302\,y + 232.8057 \qquad (2)$$
$$R^2 = 0.8742$$

$$z = 0.0173\,x^2 - 0.4860\,y^2 - 0.0193\,x\cdot y + -1.9154\,x + 12.2658\,y + 165.8485 \qquad (3)$$
$$R^2 = 0.8652$$

$$z = -0.0124\,x^2 + -0.0420\,y^2 + 0.0007\,x\cdot y + 1.3304\,x - 1.5737\,y + 194.9876 \qquad (4)$$
$$R^2 = 0.8967$$

$$z = -0.0109\,x^2 - 0.1750\,y^2 - 0.0055\,x\cdot y + 1.2592\,x + 5.8883\,y + 128.1288 \qquad (5)$$
$$R^2 = 0.9389$$

$$z = -0.0002\,x^2 + 0.0075\,y^2 - 0.0014\,x\cdot y + 0.0399\,x - 0.0270\,y - 0.2477 \qquad (6)$$
$$R^2 = 0.9858$$

$$z = -0.0002\,x^2 + 0.0061\,y^2 - 0.0003\,x\cdot y + 0.0309\,x - 0.0573\,y - 0.1376 \qquad (7)$$
$$R^2 = 0.9990$$

$$z = -0.0003\,x^2 - 0.0001\,y^2 - 0.0001\,x\cdot y + 0.0373\,x + 0.0190\,y - 0.3511 \qquad (8)$$
$$R^2 = 0.9852$$

$$z = -0.0001\,x^2 + 0.0009\,y^2 + 0.0003\,x\cdot y - 0.0080\,x - 0.0159\,y + 0.9344 \qquad (9)$$
$$R^2 = 0.9973$$

$$z = -0.0003\,x^2 + 0.0011\,y^2 + 0.0003\,x\cdot y - 0.0060\,x - 0.0137\,y + 0.7364 \qquad (10)$$
$$R^2 = 0.9854$$

— Graphical interpretations

In graphical form is presented the regression surface, which has either a maximum/minimum point (a paraboloid shape) or a stationary point, so that it is a surface type. On the basis of the level curves, the limits of variation of the independent parameters (of the influence factors) can be determined on the dependent parameter, in this case the compressive strength of the raw pellets.

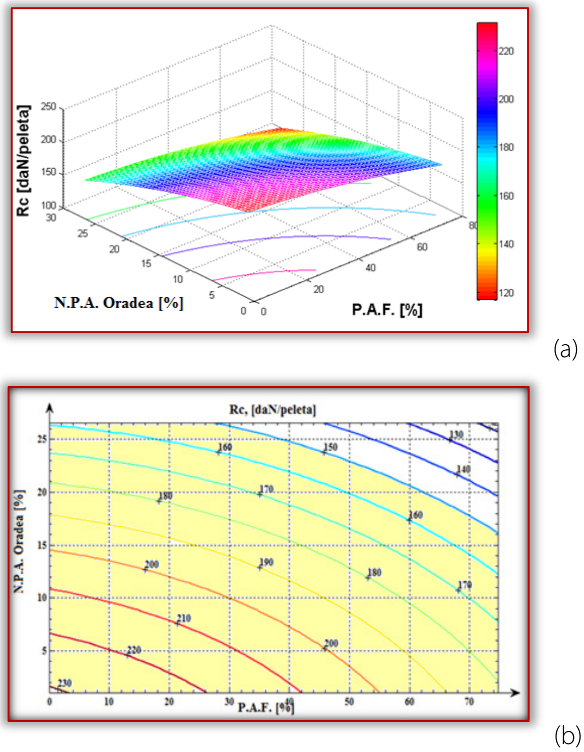


Figure 2. Compressive strength of pellets according to the percentage of agglomeration dust–furnaces (%) and the proportion of galvanically sludge Oradea (%): (a)–spatial representation; (b)–horizontal level projection curves

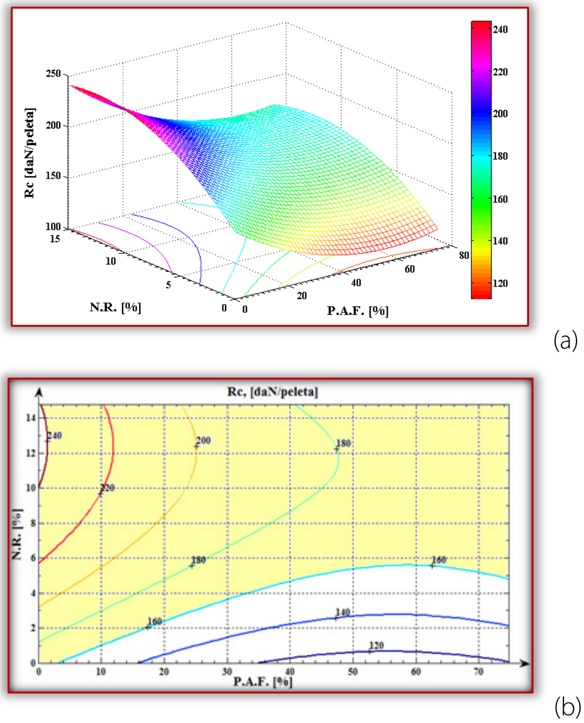


Figure 3. Compressive strength of pellets according to the proportion of agglomeration dust–furnaces (%) and the proportion of red sludge (%): (a) –spatial representation; (b)–horizontal level projection curves

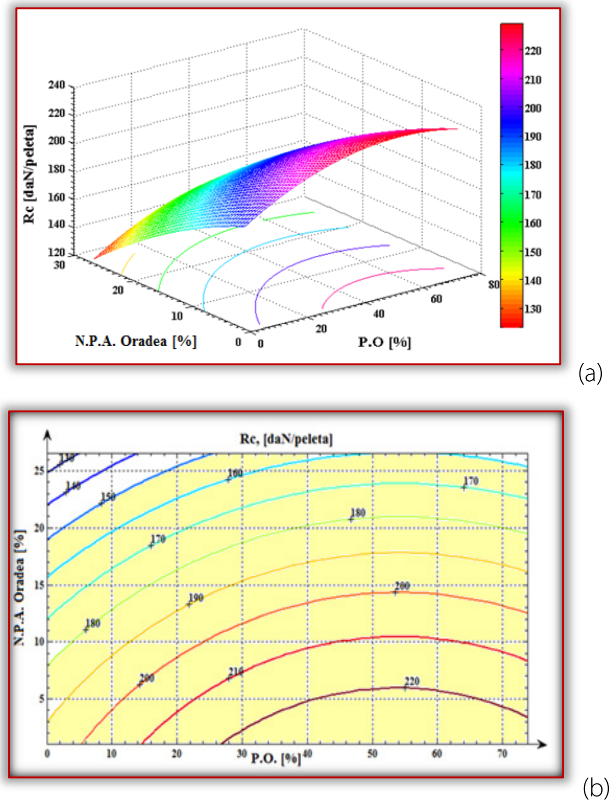


Figure 4. Compressive strength of pellets according to the percentage of steel dust (%) and the proportion of galvanically sludge Oradea (%): (a)–spatial representation; (b)–horizontal level projection curves

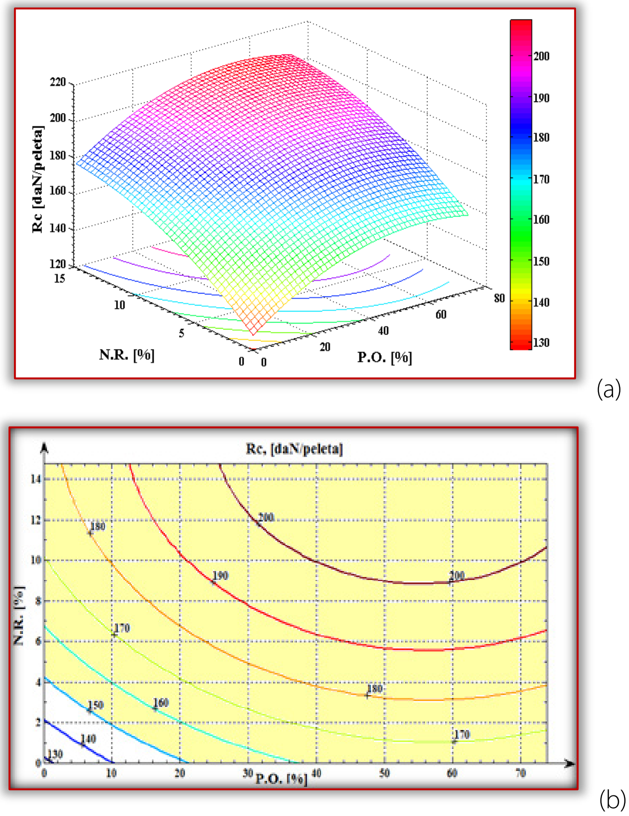


Figure 5. Compressive strength of pellets according to the proportion of steel dust (%) and the proportion of red mud (%): (a)–spatial representation; (b)–horizontal level projection curves

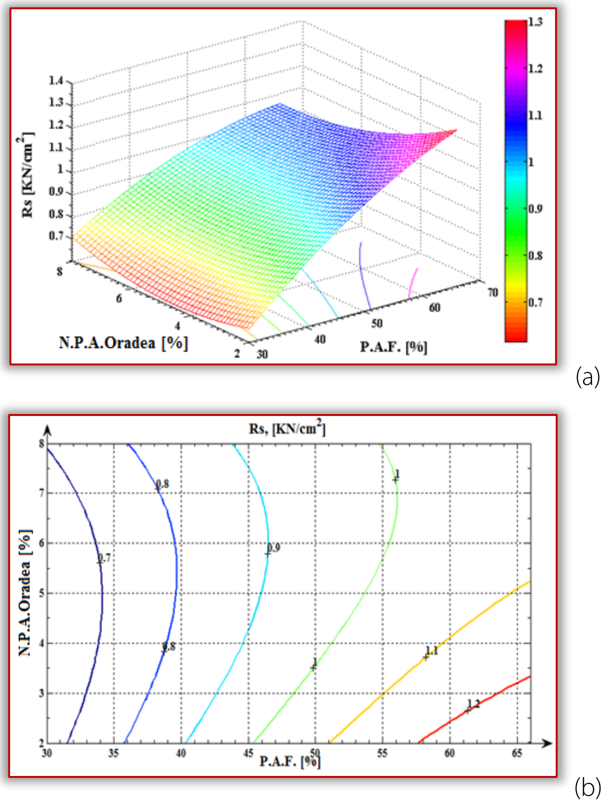


Figure 6. Crushing resistance of lighters according to the percentage of agglomeration dust (%) and the proportion of galvanically sludge Oradea (%): (a)–spatial representation; (b)–horizontal level projection curves

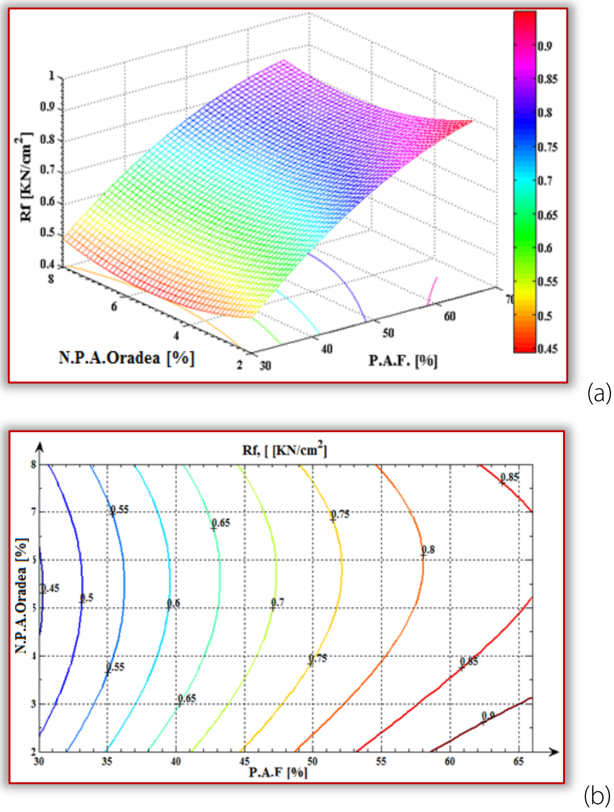
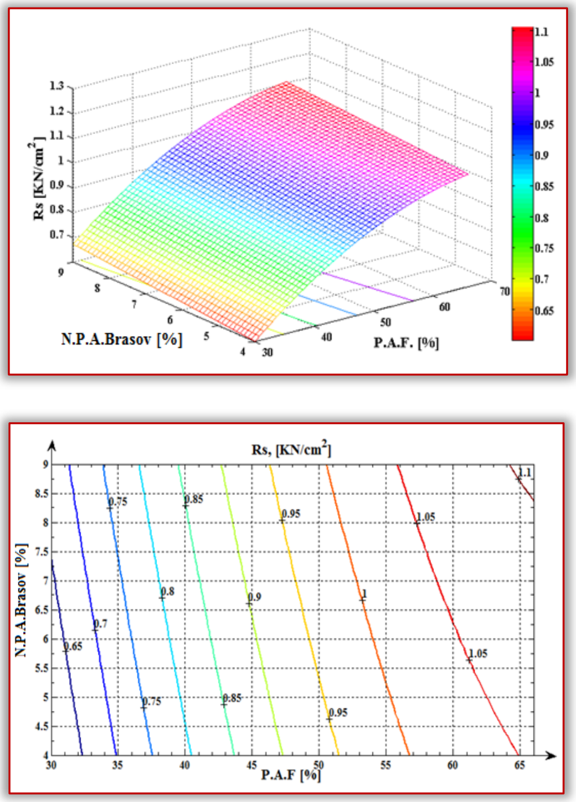


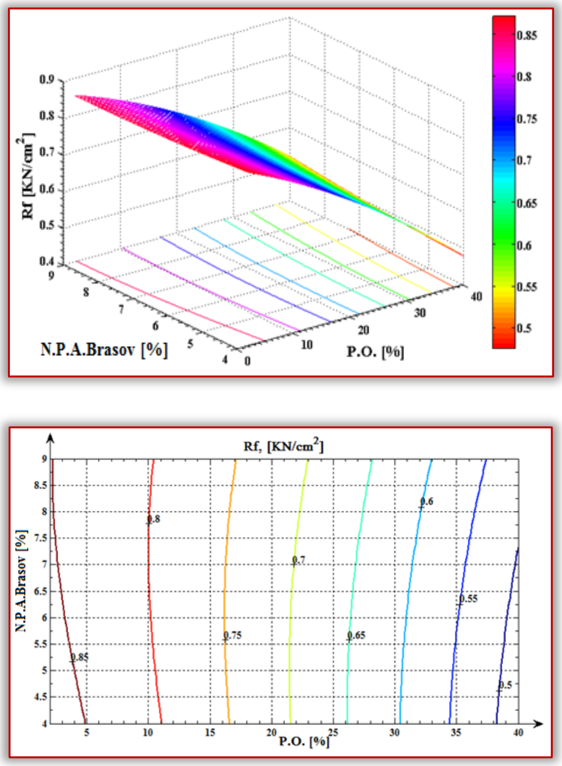
Figure 7. Crack resistance of the briquettes according to the percentage of agglomeration dust (%) and the proportion of the galvanically sludge Oradea (%): (a)–spatial representation; (b)–horizontal level projection curves



(a)

(b)

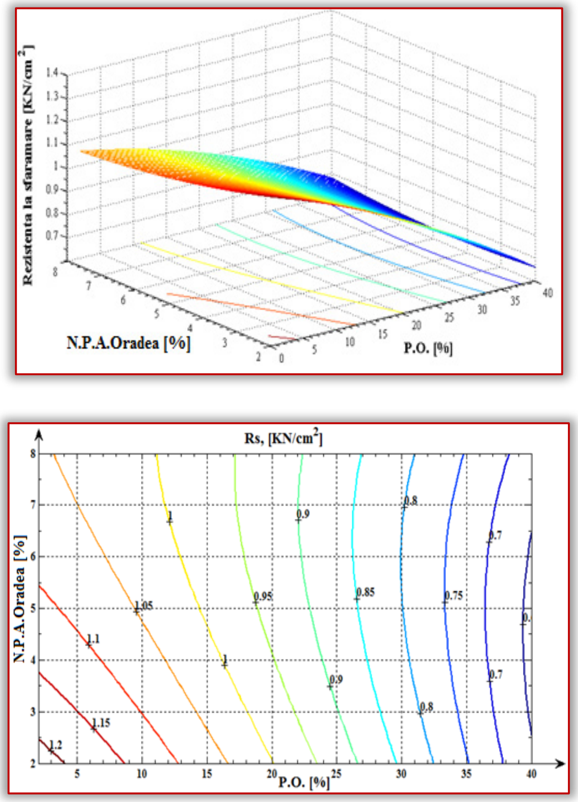
Figure 8. Briquette crushing resistance according to the percentage of agglomeration dust (%) and the proportion of galvanically sludge Braşov (%): (a)–spatial representation; (b)–horizontal level projection curves



(a)

(b)

Figure 9. Crack resistance of the briquettes according to the proportion of steel dust (%) and the proportion of galvanically sludge Braşov (%): (a)–spatial representation; (b)–horizontal level projection curves



(a)

(b)

Figure 10. Crushing resistance of briquettes according to the percentage of steel dust (%) and the proportion of galvanically sludge Oradea (%): (a)–spatial representation; (b)–horizontal level projection curves

DISCUSSIONS

The analysis carried out shows the following:

- as far as the influence of the red sludge is concerned, increasing its proportion leads to an increase in the compressive strength, the technological explanation being that it has a high content of Al_2O_3 and SiO_2, which also serves as a binder. In this respect, it can be used in a concentration of 10–12 %, with the mention that compared to other assortments of this material, it (deposited in the ponds in Oradea) has very low content of As on the one hand, and on the other part is currently not recycled;
- it can be seen that although the compressive strength decreases with increasing the proportion of sludge from the anticorrosive protection, it can be used without restrictions up to about 12 % in the pelleting batch. In fact, considering the quantities of about 20–25 tons/year resulting in the corrosion protection process, the waste pelletizing waste recyclers can use this waste in smaller proportions depending on the destination of the product obtained;
- in the case of the use of the corrosion protection sludge together with the agglomeration dust–furnaces it is found that higher values for the compressive strength are obtained at their lower proportions in the pelletizing batch. High quality pellets can be obtained with agglomeration–blasting dust within the maximum 50%

limit and 10–15 % anti–corrosion protection sludge, with the values for R_C in the hauling area;
- Figure 6 shows the positive influence of red sludge acting as a binder, basically a 14–16 % red slurry adds good value for pellets even if the agglomeration–baking dust content exceeds 50 %. In the assessments made it is considered that in the majority of cases the pellets are destined for recovery in the steel works;
- Figure 4 shows that an increase in the proportion of steel powder has a positive influence on the compressive strength of the pellets, and the anti–corrosion protection sludge has a negative influence (lower bonding capacity) but within the limits used to ensure the achievement of the required values for resistance (it is clearly seen in the hatched subdomains);
- Figure 5 shows that an increase in compressive strength occurs with the increase in the proportion of red mud and steel powder, the best values being obtained for the upper limits of the two components of the recipe. The technological explanation lies in the high finesse of both material assortment and the content of Al_2O_3 in the red mud. Depending on the availability of waste, it would be preferable to place their proportion to values for Rc above 140 daN / pellet, especially in the upper right corner;
- analyzing the correlations shown in Figure 7 it is deduced that the correlation surface has a point. For example, at 45% agglomeration dust and 5% corrosion protection mud from Oradea, crack resistance R_f = 0.657 KN/cm^2 (Figure 7); in order to obtain a crush resistance Rs = 1KN/cm^2, at a 50% agglomeration dust content, the anti–corrosion protection sludge must have a 3,5 % share. At 50 % agglomeration dust and 4 % corrosion protection sludge from Oradea, crack resistance Rf = 0.75 KN/cm^2 (Figure 7).
- the level curves of these dependencies can be considered as correlation–correlation diagrams of the chemical composition and can guide the conduction of a process for optimizing the chemical composition.

CONCLUSIONS

Following the analysis carried out on the processing of the secondary materials from the areas mentioned in the paper, the following conclusions can be drawn:

- analysing the pelletization process, it results that the metal coating (chrome and nickel) from GALVAN ALCO Oradea can be utilized by pelletizing;
- it was considered that for the recovery of sludge from S.C. IUS Braşov, the cold hardening variant is the most suitable, CaO having a binding character;
- the pellets obtained (metallised as a result of autoreduction) can be used in the alloyed load of the arc electric furnaces;
- it is apparent from the graphical representation that within the limits of variation of the waste used in the experiments it is ensured that the lighters with the qualitative characteristics necessary in the process of their utilization are obtained.

Experiments on the possibilities of capitalizing on small and pulverous ferrous waste have led to the obtaining of graphical and analytical correlations that allow the optimal domains of variation of the technological parameters and the qualitative characteristics of the resulting products.

The obtained products, usable as raw material or auxiliary material in the steel processes, contribute to the reduction of the costs for the ferrous raw materials and bring technological, economic and ecological benefits, namely: increasing productivity, reducing the specific energy consumption and increasing the iron recovery rate.

The reintroduction into the economic circuit of small and pulverous ferrous waste, both of those resulting from current production flows as well as those deposited on dumps or ponds, leads to the reduction of the level of water–air–soil pollution in the areas generating such of waste.

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