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RECOVERING TECHNOLOGY OF Fe AND Zn FROM EAF ELECTROFILTER DUST

TECNOLOGIA ODZYSKU Fe I Zn Z PYŁÓW Z ELEKTROFILTRÓW EAF

The steel production in Romania generates every year about 230,000 tons of wastes as powders and sludge containing 25-60% Fe but also important quantities of other metals like Zn (<15%) and Pb (<2%). They are also produced approximately 32% dusts (BF + EAF) and 68% sludge (BF and BOF). From this whole quantity, about 90,000 t/year is recovered and recycled inside the integrated flow, the balance being stored.

As dusty wastes unrecycled in romanian steel industry until now we can note: BOF fine sludge, blast furnace sludge and EAF dust.

The present work is developed in the framework of a research program financed by the Romanian Government, regarding „The ecology of metal cycle”, focussed especially on the EAF dust.

The paper presents the results of pilot experiments performed at the Metallurgical Research Institute in Bucharest aiming at the:

- recovery of Fe from EAF dust under the form of metallized self reducing pellets (min. 40% Fe), complying with their application in EAF;
- separation and recovery of Zn in the form of ZnO of high purity (> 99%), as required by its application in the nonferrous/chemical industry.

Keywords: EAF, dust, micropellets, selfreduction, recovery, Fe, Zn

Przemysł stalowniczy w Rumuni wytwarza corocznie około 230 000 ton odpadów w postaci pyłów i szlamów zawierających około 25-60% Fe oraz równie duże ilości innych metali, takich jak Zn (<15%) i Pb (<2%). W tym produkowane jest około 32% pyłów (wielki piec + piec łukowy) oraz 68% szlamów (wielki piec + konwertor tlenowy). Z całej ilości odpadów około 90 000 ton rocznie poddaje się utylizacji w zamkniętym obiegu wewnętrznym, reszta jest składowana. Nie są poddawane recyklingowi w rumuńskim przemyśle stalowym do dzisiaj szlamy z konwertora tlenowego i wielkiego pieca oraz pyły z pieca łukowego.

Obecnie trwają prace finansowane przez rumuński rząd, mające na celu wprowadzenie w życie programu „The ecology of metal cycle”, którego głównym aspektem jest utylizacja pyłów powstających podczas procesu EAF.

W artykule przedstawiono wyniki pilotowych eksperymentów przeprowadzonych w Metallurgical Research Institute w Bukareszcie mających na celu:

- odzysk Fe z pyłów z EAF w postaci samo redukujących się brykietów (min. 40% Fe), wykorzystywanych później jako wsad do pieców w procesie EAF,
- separacja i odzysk Zn w postaci ZnO o wysokiej czystości (> 99%), jaka jest wymagana przy zastosowaniu w przemyśle materiałów nieżelaznych lub chemicznym.

1. Introduction

The dust entrapped in the electrofilters of electric furnaces represents an excellent potential raw material for steel-making due to its physico-chemical characteristics, substituting partially the iron scrap and/or pig iron and also, after enriching with Zn, provides the raw ma-

terial required by the Zn-extraction. The double technological solution of the EAF dust valorization and the influence on the economics and environmental protection has been the main desideratum of our experimental research paper.

In resume, the experimental technology consisted in the application of a metallurgical high temperature

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process in reducing atmosphere by using a two-chamber reactor of own conception, aiming at:

- the quality control of reduced and dezincated pellets, able to be applied as raw material (especially in EAF),
- the control of specific reactor productivity,
- the thermal efficiency maximization of the reducing and dezincating equipment.

2. Characterization of the electro-filter dust used in experiments

The main physico-chemical and mineralogical characteristics of electro-filter dust were determined as follows: *mean diameter*= 0.583 μm , *specific surface*:14.62 m^2/cm^3 , *uniformity coefficient* = 0.53, *real density*=3.562 g/cm^3 , *bulk mass*=1.114 g/cm^3 , *layer porosity* =84-85%, *mean chemical composition*: Fe= 36.85%; Zn=10.8%; Pb=1.27%; PC=4.7%, etc., *the main mineralogical component*: $\text{ZnO}\cdot\text{Fe}_2\text{O}_3$ (franklinite).

3. Experimental practice

The designing and realization of a reliable two-chamber reactor, which would fulfilled the above mentioned desiderata, the realization and validation of premises for technological and material solutions were the main targets of our experiments.

3.1. Description of reactor

From the point of view of construction, the two-chamber reducing reactor (DCR) consists of three parts: the upper one which contains the reducing chambers (1); the lower one constituting the crystallization chamber (2), separated one from another by a splitting plate and the gases exhaust chambers (3), positioned on both ends of the reactor. The gases leaving the dust layer during the process are collected in the gas exhaust chambers and then enter the crystallization chamber through three holes at both ends and leave definitively the reactor through two rectangular holes in the lateral walls. Two sections of the reactor are schematically presented in Fig.1

Due to the maximum work temperature previously established in the range from 1100°C up to 1200°C, the cast iron with 16% Cr was chosen as heat-resistant material for reducing chamber. The other parts, which operate at lower temperature and do not have any direct contact with the burners flame, were made of the usual cast iron. The cast iron wall thickness is 10 mm according to working and casting requirements.

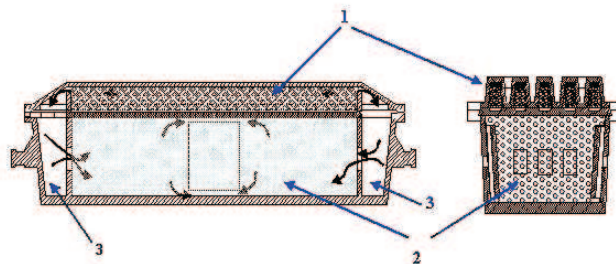


Fig. 1. The two-chambers reducing reactor (cross section): 1 – reducing chambers; 2- crystallization chamber; 3 – gas exhaust chambers

This type of pilot-reactor consisting of two chambers ensures the efficient use of the available space and corresponds to the difference of heat conditions between two chambers.

The reactor is termed a two-chambers one, because only two chambers are in operation and two completely different processes take place. In order to provide a heat source during experiments, the reactor is placed in a tunnel kiln fitted with plane-flame burners (5 Nm^3 CH_4/h). The upper chamber (the reducing one) takes over the heat from outside provided by the burners in the continuous furnace and the lower chamber (the crystallization one), where one expects a non-ferrous metals vapors condensation and their precipitation as crystals or dust, is partially heated up by exhaust gas from the dust layer and partially through the lateral walls heated up from outside by waste gas.

The total length of the reactor was restricted by the length of the tunnel kiln car (1 m). The length of the reducing chambers is 700 mm. Each chamber has a stocking volume with a capacity of approximately 1200 g pellets (having a mean bulk density of about 1.4 kg/dm^3). Taking into account 5 parallel chambers, the reactor has a capacity of approximately 6 kg crude pellets, wherefrom ca. 3.6 kg reduced pellets results. The outer dimensions of the reactor (900x300x250 mm) have been correlated with the inner dimensions of the tunnel kiln. Thus, one cannot implement more than 5 parallel chambers on a 300 mm wide front of the furnace section. For this reason the height of the crystallization chamber was restricted to 170 mm.

The pellet layer in the DCR has following sizes: thickness 12.5 mm, width 500 mm, length 700 mm, the mean volume 4.375 dm^3 and the mean capacity 6.125 kg of material with a bulk density of 1.4 kg/dm^3 . The methane gas specific consumption will be based upon the average superficial dimensions of the layer. The resulting total surface of the layer amounts to 0.35 m^2 and the capacity of charging the crude pellets for a layer is 17.5 kg/m^2 .

3.2. Organization of experiment

During the whole period of experiments, the continuous furnace is operated without interruptions. Three DCR reactors having the same dimensions and containing the same material are used in parallel. In the case of a sample, which has been programmed for a certain temperature, through the tunnel kiln will pass three DCR containing the same amounts of mini-pellets. Each charge is a parallel sample and the frequency by which cars are entering the furnace remains constant in order to maintain the charged cars in the burning zone a constant period of time.

The mixture and the self-reducing mini-pellets were prepared before starting the reducing experiments in the furnace. The required amount of mini-pellets has been estimated as 180 kg.

The fixed carbon concentration C_f is 15%. Metallurgical coke with $C=80\%$ was used as a carbon source. The mixture of the following ratio: coke/EAF dust=1/4.53 was prepared. On the whole, the following amounts were used: metallurgical coke dried – 32.52 kg; EAF dust dried – 147.48 kg. The mixing and homogenization of the mixture was realized only manually (taper-ring method).

The humidity of the mixture amounts to 9% and the quantity of water added to the mixture 8.64 l.

The preparing of mini-pellets was realized in a horizontal drum with sizes $\text{Ø}600 \times 200$ mm, the rotation speed being 24 turns/min. From the point of view of the reducing process three versions of technological time schedule were used:

a. intervals of push 20 minutes/ stationing time 40 minutes

The time of cars travel through the furnace amounts to 6 hours and 20 minutes, the distance between two charged cars being provided by two empty cars, the time of three parallel samples amounting to 8 hours and 20 minutes.

b. intervals of push 40 minutes/ stationing time 80 minutes.

The time of cars travel through the furnace amounts to 12 hours and 40 minutes, the distance between two charged cars being provided by two empty cars, the time of three parallel samples amounting to 16 hours and 40 minutes.

c. intervals of push 60 minutes /stationing time 120 minutes.

The time of cars travel through the furnace amounts to 19 hours, the distance between two charged cars being provided by two empty cars, the time of three parallel samples amounting to 25 hours.

4. Experimental results

Product quality. The chemical composition of reduced pellets is presented in table 1.

TABLE
Composition of reduced pellets %

Fe _{total}	Fe _{met}	FeO	CaO	SiO ₂	MgO	Al ₂ O ₃	P ₂ O ₅	O ₂
50.14	21.28	21.46	8.51	10.63	5.03	2.67	0.54	8.15

Parameters and indicators. The loss of mass in the case of experimental samples is a complex indicator which contains cumulated information of several processes: evaporation, oxygen dissipation due to the dissociation of hematite, volatilization of elements, carbon consumption during the reducing process, the release of oxygen from oxides etc. The highest losses appear in the high temperature zone.

The graph from Fig. 2 demonstrates the variation of mass losses versus temperature and stationing time in the high temperature zone. As one can observe, the co-ordinates area of maximum mass loss are: time of 80-90 minutes and a temperature of 1100°C. This area corresponds to the most economic conditions of process control. One obtains a high dezincation efficiency whilst consuming a minimal amount of energy. Based on the data concerning the chemical composition of pellets before and after processing, one can obtain a complete balance of elements, determining also the required removal parameter for each one.

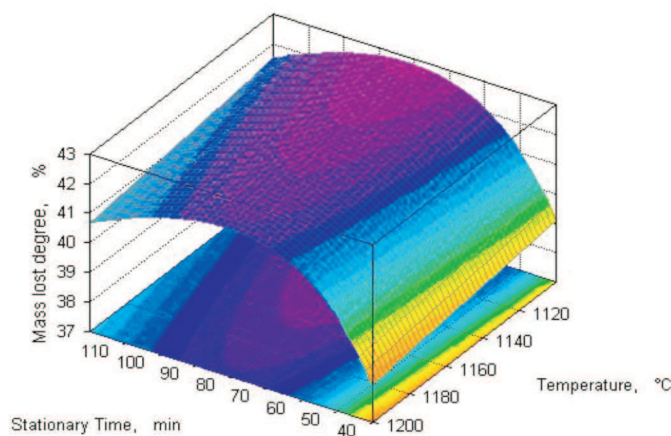


Fig. 2. The variation in mass losses

One may observe that the main removed elements are: O, C, Zn and humidity, too. At the same time one could conclude that 80% of the removed oxygen originate from iron oxides and approximately 14% from zinc compounds. As related to the share detained by various components at the process initiation (in pellets) the

efficiency of their removal resulting from the materials balance is presented in the graphic of figure 3.

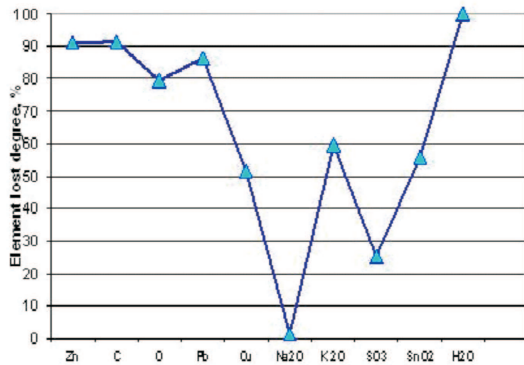


Fig. 3. Removal efficiency of various components

• Degree of metallization of Fe and removal efficiency.

Iron can be found in reduced pellets as metallic iron, wustite and residual magnetite. From figure 4 one can observe the relation between metallic iron and wustite. The curve of magnetite is not so easy to be explained, normally magnetite must disappear when the degree of metallization reaches 90%, but nevertheless remembering the reoxidation phenomenon of pellets one can appreciate that the metallization degree of iron will increase proportionally to the reoxidation degree.

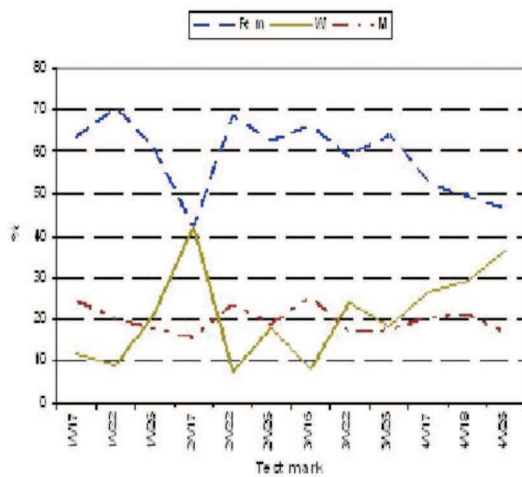


Fig. 4. Iron phases evolution

Also, one presents in figure 5 the metallization degree of iron correlated with the dezincation degree.

Both process indicators are influenced by technological parameters as maximum zone temperature and stationing time in the high temperatures zone. One observes that the dezincation degree will be higher as the temperature of the reducing zone and the stationing time in high temperatures zone increase. Where must one stop the

process? The answer to such a question will be further formulated on the basis of a techno-economical analysis.

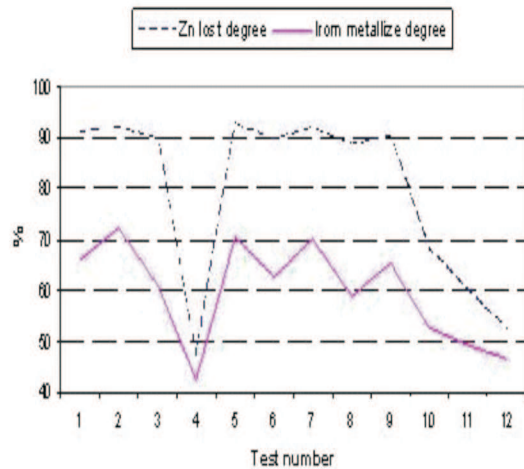


Fig. 5. Evolution curves for the degree of iron metallization and dezincation degree

5. Comments on the results

• The results of these experiments confirm the theoretical affirmation regarding the possibility of making mini-pellets by using a tubular granulator and varying the humidity content of the mixture and through the control of water atomization during the humectation process linked with granulometric parameters of the raw material. Also, the optimal humidity value of 9%, determined under lab conditions, has been confirmed by the present experiments. In the industrial scale, it is suited, nevertheless, to use a pelletizing cup, which provides better conditions to control the dimensions of pellets.

• One of our preoccupations regarding the realization of a reducing atmosphere has been solved by applying the concept of closed reducing chambers, made of cast refractory iron, which are flame-heated from the outside. The two-chamber reactor was designed for running at a positive pressure, which is generated by the reducing gases exhausted from the reactions zone and the difference between the pressure in the reactions zone and the outer atmosphere determines the velocity of gases all along the route. The experimental practice realized on the continuous furnace revealed that one has to set up special installation for gas-distillation, separately from the medium where the layer is submitted to a reducing process and these gases are produced, in order to control the gas kinetics.

• The contraction of the layer's material has been performed in compliance with our prediction made during the reactor's designing, as concerns the shape of the reducing chambers section. Once the reactor has been opened one could clearly observe the five non-deformed



Foto 1



Foto 2

layers, as it is demonstrated in photo 1. The reduced pellets are intact, not melted and are lightly sintered.

But the industrial practice will require a disintegrator in order to prevent the apparition of aggregates formed from pellets stuck to each other, which hinders their manipulation (transports and the movement in the buffer bunker).

- The surface of some pellets at the periphery of layers will appear as brown, meaning that secondary hematite has been formed during the cooling process, after leaving the burning zone. This phenomenon should appear if the layer is not protected by inert gas. After the reactor left the burning zone and the reactions of direct reduction are slowed due to the decrease of temperature below the inferior limit, the reducing CO gas disappears, the pressure is becoming more and more negative because of the aspiration from the continuous furnace. The gaseous atmosphere of above the layer becomes step by step an oxidant one. Within the range of temperatures from 400 to 600°C metallic iron is oxidized and hematite is formed. This reaction is slow and cannot penetrate the inn of the reduced pellets, as confirmed by their chemical analyze.

- In the case of experimental samples, when the maximal temperature was provided a few degrees over 1180°C, but below that of the burning zone (1250°), it has been observed when opening that the reduced pellets stuck to the lateral walls of the reducing chambers (photo 2).

Also, the aggregates formed from stuck pellets were more resistant, but melted pellets could not be observed yet. Normally, after reaching 1150°C one expected to obtain a liquid phase composed of low-melting eutectics, as in the case of the agglomeration process. But, in the process of direct reduction with a big thermal energy consumption, these eutectics do not appear. The high metallization degree of iron disintegrates the compounds, which are able to form such potential eutectics under established heat conditions.

- The metallization degree of iron as well as the dezincation degree of pellets, the two targeted indicators of the process efficiency are directly influenced by the technological parameters (zone maximum temperature and stationing time in the high temperatures zone). In figures 6 and 7 this influence of technological parameters on the degree of metallization of iron and dezincation of pellets is presented.

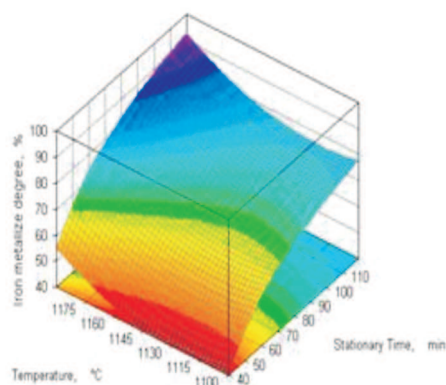


Fig. 6. Influence of temperature and stationing time on the metallization degree of iron

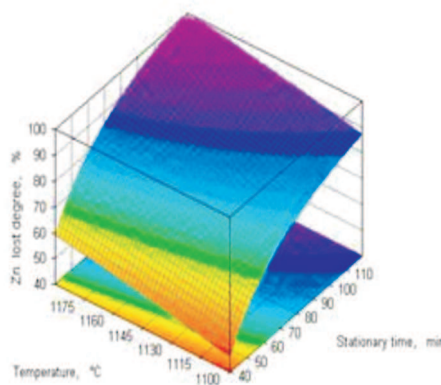


Fig. 7. Influence of temperature and stationing time on the dezincation degree of iron

The more the maximum temperature of the reduction zone and the stationing time in the zone of high temperatures increases, the higher the pellets dezincation and iron metallization degree.

6. Conclusions

1. An installation named two-chamber reactor was designed and constructed, which allows for the control of self-reduction processes of the mini-pellets obtained from EAF dust and coke and simultaneously, the control of the vaporization and crystallization processes of zinc.

2. The technological processing parameters were defined, especially the relation time-temperature. It makes easy the transfer of technology for industrial practice.

3. We estimate that the technological efficiency of the experimental method is good, the obtained degree of iron metallization amounting to minimum 70% and that of dezincation min. 90%.

4. Both products resulted from the application of our technology are qualitatively suitable to valorization as raw materials for the partial substitution of iron scrap of EAF charges and respectively, for the chemical industry on Zn extraction.