THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 3 - 2017, ISSN 1453-083X

RECYCLING OF HEMATITE FINE WASTE BY PELLETISATION

Anișoara CIOCAN, Beatrice TUDOR
"Dunarea de Jos" University of Galati
e-mail: aciocan@ugal.ro

ABSTRACT

A large volume of by-products and residues is generated during iron and steel production. Much of these represents valuable materials and can be recovered and recycled inside the flow of integrated steel plants. The fine-grained residues, which are rich in iron, are usually recycled through sinter plants. This study aims at investigating the potential of palletization of two types of hematite fine waste resulted from process of chemical pickling of steel strip. The pelletizing tests were performed in an experimental disc pelletizer. The hematite was mixed with different fluxing and binding agents. The green pellets were then dried, sintered and cooled. The effect of materials mixtures on the physical and chemical characteristics of pellets was determined and analyzed in relation with nature of pelletized components.

KEYWORDS: hematite, recycling, pelletizing

1. Introduction

The rolling is an essential industrial process for steel sheet production. During the deformations of steel, oxygen from the air reacts with the iron and forms iron oxides or scale as a fine layer on the surface of the steel strip. The constituents of mill scale are wustite (FeO), magnetite (Fe_3O_4) and hematite (Fe_2O_3) phases. FeO is usually closest to the metal surface while Fe_2O_3 forms the outer layer (Figure 1).

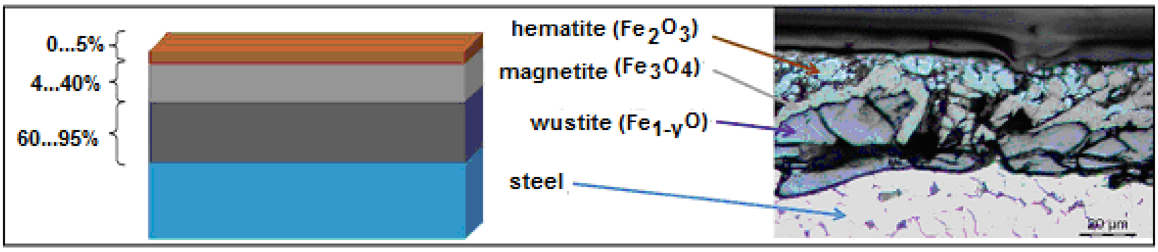

Fig. 1. *Cross section of the three-layers steel oxide scale formed during the hot rolling stage on surface of the steel strip* [1]

The oxides layer must be removed before as other processing to be applied to steel band. The scale or oxide film can be removed from surface of steel strip by immersing in acid solution, usually in hydrochloric acid bath. This is named ″batch pickling process″. When steel is pickled, iron oxides and metallic iron react with the hydrochloric acid. From chemical reactions involved in this process result ferrous chloride, water and hydrogen gas [2].

$$FeO_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_2O_{(l)} \quad (1)$$

$$Fe_3O_{4(s)} + Fe_{(s)} + 8HCl_{(aq)} \rightarrow 4FeCl_{2(aq)} + 4H_2O_{(l)} \quad (2)$$

$$Fe_2O_{3(s)} + Fe_{(s)} + 6HCl_{(aq)} \rightarrow 3FeCl_{2(aq)} + 3H_2O_{(l)} \quad (3)$$

$$Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_{2(g)} \quad (4)$$

During the pickling process, a large amount of waste pickle liquor or spent acid is produced. In the exhausted pickling solutions, a metal content of up to 150-250 g/L is accumulated [3]. The recovery of the pickling acid waste from environmental and economical cleaning process is an important issue, from points of view. By treatment the acid is regenerated and can be reused. During the treatment the metallic oxide appears (Figure 2). Thus, the regeneration reduces the cost of fresh acid supply and eliminates the cost of disposal of spent acid. There are more methods that allow efficient reuse of the pickling liquor [4, 5].

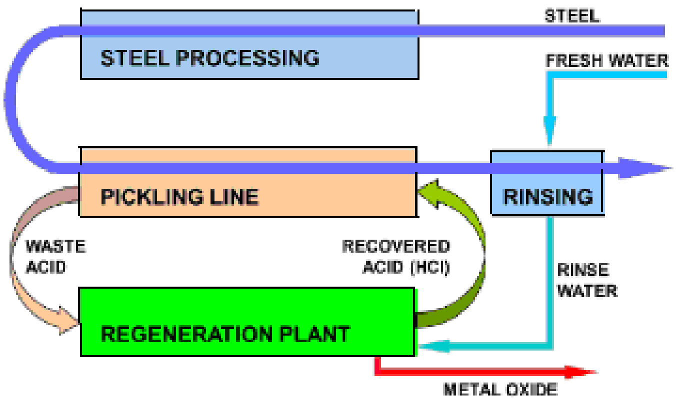

Fig. 2. *Succession of operations at ferric oxide generation* [5]

Hydrochloric acid is vaporized and heated to high temperatures without decomposing in other compounds. The technology of regeneration of pickling acid waste includes heating in two stages of the galvanic waste sludge. Firstly, to evaporate water and to recycle acid, the treatment is carried in range of 200-500 °C. A secondary treatment involves the calcination at high temperatures (850 °C). The recovery reaction, on which all HCl recovery processes depend, is the oxidation with hydrolysis of ferrous chloride. The iron chloride ($FeCl_2$) is converted into hydrochloric acid by reaction with oxygen and water vapor (hydrolytic decomposition).

$$2FeCl_2 + 2H_2O + 1/2O_2 = Fe_2O_3 + 4HCl \quad (5)$$

Thus, during regeneration of used pickling acid, additionally is obtained the ferric oxide (Fe_2O_3) as a dry powder. Very fine oxide particles are a high quality secondary material. It must be recycled due to its high iron content, low impurities and stable chemical composition. According to its properties, the iron oxide from regeneration can be used for different purposes: hard and soft ferrites production, for foundry applications, as binder for refractories, as fine aggregate in mixtures for the production of clay bricks, as coloring pigments [3, 6, 7]. A simple recycling solution is the direct using in the integrated steel production flow. Because of its physical, chemical and mineralogical properties, the iron oxide powder can be used as a raw material in metallurgical processes as feed for blast furnace, after sintering, palletization or briquetting. Thus, the recycling brings economic benefits, the iron oxide powder used as raw materials reduces the iron ore consumption. On the other hand, this solves the environmental problems of integrated steel plant, generated by own waste. In this work is studied the recovery through pelletizing. The possibility to convert the fines into valuable product, suitable for blast furnace was analyzed.

2. Experimental

The ferric oxide powder sample was supplied from a metallurgical company. The hematite used in experiments had very high content of Fe_2O_3. The fine material is composed of small particles (Figure 3).

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N°. 3 - 2017, ISSN 1453-083X

Fig. 3. *Ferric oxide powder sample*

In order to obtain pellets with suitable mechanical and chemical properties, the iron oxide micro fines must be agglomerated as larger pieces. In literature it was studied the use of various types of binders for making pellets. Some of these were applied in the industry [8]. In this work the hematite powder was mixed with solutions of sodium silicate ($Na_2OxnSiO_2$, n = 2.4-3.5) or calcium chloride (as solution 30 %) and lime. They are alternative binders to bentonite used for iron ore pelletizing. They ensure the resistance of pellets in handling operation and in metallurgical process. In addition, were used the lime for increasing of CaO content and also foundry graphite for the carbon. The coarse dust lime had the following composition: 57.50-58.74 % CaO, 1.00-3.85 % MgO, 0.74-0.88 % Fe_2O_3, 0.20-0.25 % Al_2O_3, 0.70-1.00 % SiO_2.

The pellets were prepared in laboratory using a disc pelletizer (Figure 4).

Fig. 4. *Laboratory installation for palletization*

The produced green pellets were dried in air for three days to ensure the evaporation of water used for palletization process. In accordance with mixture composition and water added were obtained pellets with different dimensions (Figure 5). The average compressive strength of oven dried pellets was controlled.

Fig. 5. *Mixture of dried pellets obtained with different binders*

3. Results and discussion

The size analysis of the Fe_2O_3 powder sample was carried. Samples were dried previously at 105 ºC. The granulometric distribution of the hematite is given in Table 1.

Table 1. *Particle size analysis of Fe_2O_3 powder*

Sieve diameter, [mm]	Fe_2O_3 powder, [wt. %]
+0.5	0.0
-0.5, +0.1	57.20
-0.1, +0.05	39.4
-0.05, +0,04	3.40
-0.04	0.05

All particles of dry powder are below 500 microns. 96.60% of the sample had sizes between 50 and 500 microns, showing the fine nature of the studied material. Also 3.45% of the particles are less than 50 µm. This is important for transporting fine material either for reuse or disposal in landfills. The fine particles have the possibility to disperse and air pollution. The particles with sizes larger than 1 µm have different forms, from spherical to irregular.

The chemical analysis of hematite powder highlighted the high content of iron oxide (Table 2).

Table 2. *Characteristics of hematite powder*

Characteristics	Value
Fe_2O_3, [%]	99.33%
Fatty substances, [%]	2.08%
SiO_2, [%]	-
Soluble substances in water, [%]	0.23%
Soluble substances in HCl, [%]	0.24%
Moisture, [%]	-
pH (aqueous suspension)	6.0
Bulk density in compressed state, [g/dm^3]	0.704 kg/dm^3
Chemical reactivity, [%]	1.39%

The powder used in the palletization did not have a neutral nature. The value of pH when hematite particles have been suspended in water was 6. The knowledge of pH value allows to infer its possible influence on soil when this by-product is stored. The value determined exceeds the limit required for waste disposal in landfills or for temporary storage inside of metallurgical plant (Table 2). Consequently, the concrete platforms or preliminary treatments are required. For using in the metallurgical process, the literature recommends pellets with pH ranged of 5 and 8.

The hematite micro fines were bonded with sodium silicate or calcium chloride and lime. The composition of the experimented samples is presented in Table 3.

The chemical composition of pellets was determined by X-ray fluorescence analysis (Table 4).

***Table 3.** Materials participation in the mixtures for palletization*

Sample	Material, [%]				
	Hematite	Lime	Sodium silicate	Foundry graphite	Calcium chloride
R_A	80	4	8	8	-
R_B	80	4	-	-	8

***Table 4.** Chemical composition of the pellets*

Pellets	Fe_2O_3	MnO	SiO_2	CaO	MgO	Al_2O_3	PC
R_A	67.29	0.61	10.11	2.45	0.00	1.58	13.80
R_B	81.10	0.77	0.18	5.46	0.00	1.68	9.61

The pellets obtained can be considered composite materials. Their binder matrix is formed by addition of the sodium silicate or the calcium chloride and the lime. Taking this approach into account, the hematite is considered the complementary phase, homogenous dispersed in the matrix of pellets. The shape of microparticles and the binder have a positive influence on mechanical properties of pellets. Quality of the pellets is influenced by the nature of the ferrous waste, type and amount of fluxes added. These factors in turn result in the variation of physicochemical properties of the coexisting phases and their distribution during the hardening of pellets. Hence properties of the pellets are largely governed by the form and degree of bonding achieved between the particles and the stability of these bonding phases during reduction of iron oxides in the blast furnace. The formation of phases and micro-structure during heating depend on the type and amount of fluxes added. This effect of fluxing agents on quality of pellets is analyzed in terms of CaO/SiO_2 ratio and CaO content. As example, at lime addition, CaO in contact with water forms the calcium hydroxide. On palletization, this calcium hydroxide provides primary bonding amongst the particles and imparts strength to the green pellets [9].

The values of compressive strength of dried pellets confirm these appreciations (Table 5). The pellets strength was measured by a compression test. These were individually compressed to failure and the maximum load was recorded. Tests were performed on 5 uniformed sized pellets, and the average compressive strength values were calculated.

***Table 5.** Compression strength of pellets*

Sample	Average pellet diameter, [cm]	Applied force*, [N]	Pressure, [bar]	Compressive strength, [daN/cm^2]
R_A	1.5	1015.594	2.3	57.5
R_B	1.2	1015.594	2.3	89.8

*piston diameter = 7.5 cm

Analyzed like composites, the aggregation of materials in pellets is the result of bonding forces. The adhesion and cohesion forces manifested at the contact surface of different components. In the experimented pellets, the additions of binders ensure the surface connection of hematite microparticles with other components, and in consequence the strength of pellets. The compressive strength obtained is within the standards required for iron ores or ores sintered introduced in the blast furnace. The values are above the acceptable limit of crushing strength: 200 kg/pellets, for conventional type, fired between 1300-1350 ^oC or 400 kg/cm^2 for lump ore-oven dried [10, 11].

4. Conclusions

The hematite pellets can be used as a substitute for ores and sinter in the blast furnace due to the properties. The hematite powder from pickling process has a high content of iron oxide and it has no other impurities. Since it results from a chemical process, it is formed of fine and uniform particles: 96.60% of samples is formed of particles sized between 50 and 500 microns.

By adding sodium silicate or calcium chloride and lime as binders were obtained pellets with suitable compression strength. Lime and calcium chloride proved to be more beneficial additives for hematite micro fines. When water glass was used, the SiO_2 content increased in the pellets. For lime and calcium chloride we obtained the so-called ″lower silica″ pellets. This is an advantage because the utilization of pellets with high values of CaO/SiO_2 ratio reduces the slag volume in the blast furnace and the pellets reducibility is higher. As a result, blast furnace productivity is increased and the coke rate requirement is decreased.

References

[1]. Graf M., Kawalla R., *Scrap development on steel hot strip rolling*, La Metallurgia Italiana, 2, p. 43-49, 2014.

[2]. Jatuphaksamphan Y., Phinichka N., Prapakorn K., Supradist M., *Pickling kinetics of tertiary oxide scale formed on hot-rolled steel strip*, Journal of Metals, Materials and Minerals, vol. 20, no. 1, p. 33-39, 2010.

[3]. Quaranta N., Caligaris M., López H., Unsen M., Pelozo G., Pasquini J., Cristóbal A., *Reuse of red powder of steel plants as fine addition in ceramic bricks manufacture*, WIT Transactions on Ecology and The Environment, vol. 155, 2012.

[4]. Regel-Rosocka M., *A review on methods of regeneration of spent pickling solutions from steel processing*, Journal of Hazardous Materials, vol. 177, p. 57-69, 2010.

[5]. Baerhold F., Mitterecke S., *Acid recovery in the steel and metallurgical industry - process characteristics and fuel saving options*, IMPC 2016: XXVIII International Mineral Processing Congress Proceedings.

[6]. Zaspalis V., Kolenbrander M., *Design principles for spray-roasted iron oxides for the manufacturing of ferrites*, Powder Technology, vol. 161, p. 169-174, 2006.

[7]. Woon H. S., Lim K.P., Puteri N., Rozaimah R., Tan C. Y., *Synthesis and characterization of hot-roll and cold-roll byproduct-derived strontium hard ferrites*, American J. of Engineering and Applied Sciences, 2 (4), p. 580-583, 2009.

[8]. Eisele T. C., Kawatra S. K., *A review of binders in iron ore pelletization*, Miner. Process. Extr. Metall. Rev, 24, p. 1-90, 2003.

[9]. Pal J., *Utilization of Microfines in Iron and Steel Making*, Steel World, p. 86-90, June 2016.

[10]. Halt J. A., Komar Kawatra S., *Review of Organic Binders for Iron Ore Agglomeration*, 2013.

[11]. Socalici A., Heput T., Ardelean E., Ardelean M., *Ferrous waste processing by pelletizing, briquetting and mechanically mixed*, International Journal of Energy and Environment, issue 4, vol. 5, p. 532-540, 2011.