A study on usability of mill scale in pellet production

Osman Işıkgül

Bar and wire rod rolling mill engineer,
Kardemir Iron and Steel Works Co.,
Karabük 78170 Turkey

Fikri Erdem Şeşen*

Postgraduate student,
Metallurgical and Materials Engineering Department,
Istanbul Technical University,
Maslak Istanbul 34469 Turkey
E-mail: sesen@itu.edu.tr

Cevat Fahir Arısoy

Assistant Professor,
Metallurgical and Materials Engineering Department,
Istanbul Technical University,
Maslak Istanbul 34469 Turkey

Mustafa Kelami Şeşen

Professor,
Metallurgical and Materials Engineering Department,
Istanbul Technical University,
Maslak Istanbul 34469 Turkey

Abstract
Mill scale is an iron oxide layer that is formed as a result of the oxidation that occurs during continuous casting, annealing and rolling of slabs and ingots in steel making. This material, which is composed of oxides of the elements in steel, is made mainly of iron oxide. Mill scale, which has been considered a waste in mini steel making plants with EAF (Electric Arc Furnace), must be recycled in every case. In this study, it was aimed to determine whether mill scale is able to be used in pellet production by mixing it with magnetite ore concentrate, without grinding it in very fine dimensions. The pellet production experiments were carried out in a laboratory-scale pelletizing disc. Effect of mill scale content in pellet production was investigated in means of mechanical properties. The mill scale was used after grinding it under 1 mm dimension while the magnetite ore concentrate was used in the pelletizing size. Optimum mill scale/magnetite ore concentrate ratio was determined as a result of the study. Pellets that were produced with the addition of mill scale which had a size of up to 1 mm possessed sufficient mechanical properties for charging into the blast furnace unless mill scale content in pelletizing blend exceeded 50% in weight.
Keywords: PELLETIZING, MILL SCALE, CAPILLARITY, BALL FORMATION, MAGNETITE ORE CONCENTRATE

Introduction

Steel is produced by two main methods in current iron-steel industry. The first one is carried out in blast furnace integrated iron-steel plants by using iron ore, pellets, sinter and coke, the second one is done in EAF by using steel scrap and directly reduced iron (DRI and HBI).

Steel industry has begun to search for alternative production methods due to high set up and management costs, energy requirements and environmental effects which are caused by the integrated steel making plants. In this manner, plants with EAF gain priority since they require less set up and management costs and they are able to run in a small scale. However, scrap usage in the EAF causes several difficulties; these can be classified as decrease in the availability of the scrap, rapid changes in the scrap price and chemical composition that may not be assured because of trace elements.

The individual units in an integrated steel making plant are connected both in terms of product flows and internal flows of residues (mill scale, fly dusts and sludges, furnace gas, etc.). These interdependencies have been installed in order to both minimise emissions and to optimise productivity and reduce costs[1].

Inevitable output of the iron-steel industry is the waste. Mill scale, which is an oxide layer that is formed as a result of oxidation on the surface of slabs and ingots during continuous casting, annealing and rolling mill stages, is one of the most important solid wastes in iron-steel industry.

Mill scale, basically, is the oxides of the elements that make up the chemical composition of the produced steel. Mill scale is an important iron source. Recycling of mill scale causes the production of a ferrous raw material while an output that has been considered a waste can be recovered into the plant in this way.

It is important to obtain the raw material on low cost basis in steel making. Therefore, transformation of mill scale, which has been considered a waste, into a ferrous raw material in low cost is meaningful. Mill scale that is formed in rolling mill facilities is in a greasy state. This greasy mill scale can be used after cleaning it by pyrolysis or convenient chemical treatments. In this circumference, mill scale can be added to the sintering blend prior to the sintering operation. Unfortunately, mill scale usage in sintering facilities within integrated steel making plants in high ratios is not convenient since mill scale causes reduction in permeability of the sintering blend[2]. Furthermore, mill scale that is produced in steel making plants with EAF cannot be used within the same plants since this kind of plants do not possess a sintering facility. More than 50% of the steel production is carried out in plants with EAF in countries like Iran, Turkey, Italy, Spain, Mexico, India and United States[3]. Therefore, using all of the mill scale that is produced in steel making plants with EAF in these countries as ferrous raw material for integrated steel making plants in the same countries is impossible. Recycling/using the mill scale out of these plants is possible with the application of some special treatments. One of these treatments is recycling it by special processes such as DK and Primus together with other ferrous residues that come out in steel making plants[1]. Another treatment is grinding it to the pelletizing size (~40 μm) followed by pelletizing[4,5]. However, this operation is not practically acceptable because of the low grinding efficiency resulting in a high cost since mill scale, which is in magnetite phase, has a hard structure[6-8].

In this study, research on recycling of mill scale was carried out regarding mixing it with pelletizing iron ore concentrate. Mill scale which was not ground in very fine dimensions (used as -1 mm), pelletizing magnetite ore concentrate and bentonite were used as raw materials. Green pellet production was done in a laboratory-scale pelletizing disc. The effect of mill scale content on the mechanical properties of the pellets was investigated. Samples that were taken during different stages of the experiments and final products were characterised by several analysing methods to understand whether they are industrially compatible, e.g. can be used as a charging material for the blast furnace.

Experimental Materials and Method

The mill scale was obtained from an ingot in the continuous casting facility of Kroman Steel Works Co. The used mill scale was in an ungreased state. The chemical composition of the mill scale is given in Table 1. The chemical composition of the pelletizing magnetite ore concentrate which was supplied from Ermaden Divriği plant is given in Table 2.

Table 1. The chemical composition of the mill scale in weight per cent

Component	Total iron	Elemental iron	Fe^{+2}	Fe^{+3}	Cu	Mn	Si
Content, wt%	71.06	1.15	39.06	30.85	0.35	0.67	0.22

Table 2. The chemical composition of the pelletizing magnetite ore concentrate in weight per cent

Component	Total iron	Fe^{+2}	Fe^{+3}	TiO_2	$CaCO_3$	SiO_2	$MgCO_3$	Al_2O_3
Content, wt%	68.90	22.41	46.06	0.23	0.95	1.74	1.05	0.40

The mill scale was made to pass through a 1 mm-aperture vibratory sieve; the oversize content was ground in a rod-grinder (KHD Humboldt Wedag) before it was made to pass through the 1 mm-aperture sieve again. Undersize content, to which sieve analysis was applied, was mixed with the pelletizing magnetite ore concentrate in 0, 40, 50, 60 and 70% ratios during pelletizing operation. The binder, bentonite, was added in the weight ratio of 0.8% to each of the pelletizing blend. Batches in 3 kg weight were prepared for each composition. One batch was prepared without using mill scale in order to evaluate the properties of pellets that are made of pelletizing magnetite ore concentrate only. The flow chart of the pelletizing operation related to the mill scale is given in Fig. 1. The pelletizing operation was carried out in a 40 cm-diameter Multipex pelletizing disc by adding water to the mixture. The produced green pellets were dried in a Devotrans oven at 110 °C for approximately 10 hours. After that, they were fired in a Huppert electric-resistant furnace at 1250 °C for one hour.

Properties of the green and fired (product) pellets were investigated. The green pellets were first subjected to free fall from a height of 50 cm; the number of drops to fracture was recorded. Crushing strength test was applied to the wet, dry and fired pellets. The microstructure of the product pellets obtained from the batches which contained 40% and 50% mill scale was investigated by using an Olympos GX71 light microscope.

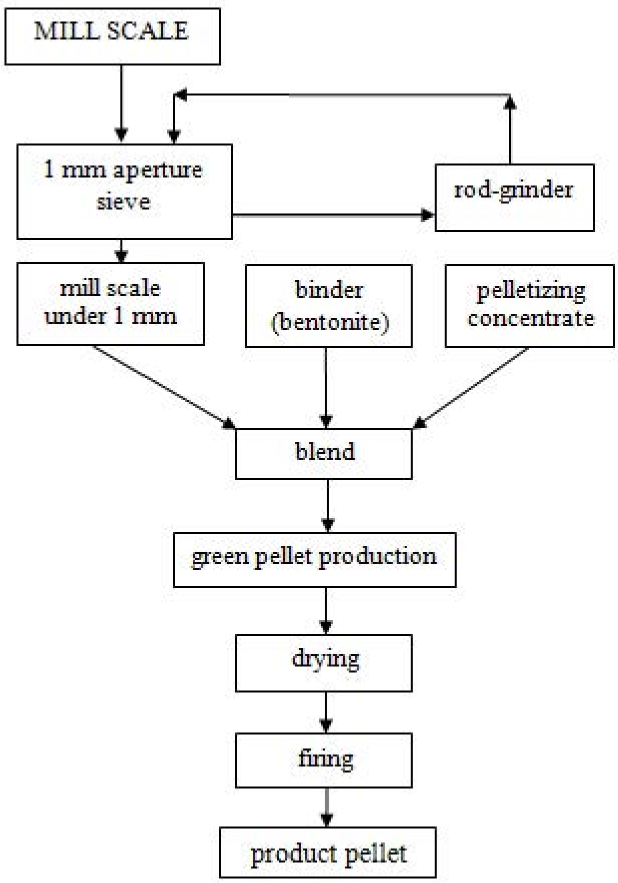


Figure 1. The flow chart of the pelletizing operation

Experimental Results

The mill scale is composed of manganese, copper and silicon, besides iron, which is the principal constituent (Table 1). X rays diffraction analysis scan of the mill scale used in the study is given in Fig. 2. Peaks that present all of the three stable iron oxide phases were detected in the scan.

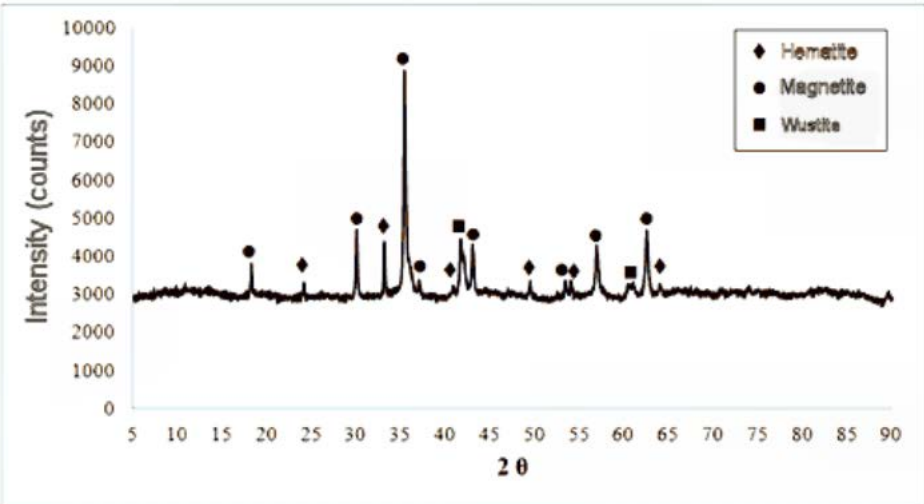


Figure 2. The x rays diffraction analysis scan of the mill scale used in the study

Sieve analysis was applied to the mill scale that was used in the study. The undersize and oversize weight results of 1 kg mill scale before grinding are given in Table 3. 42.54% of the used mill scale is under 1 mm dimension.

Table 3. The sieve analysis of 1 kg mill scale before grinding

Size range	Over 1.40 mm	1.00-1.40 mm	Under 1.00 mm
Weight	407.1 g	167.5 g	425.4 g
%	40.71	16.75	42.54

Grinding behaviour of the used mill scale was investigated by grinding it in the rod grinder. The sieve analysis of the 1 kg content after grinding in the rod grinder for 15 minutes is given in Table 4. Nearly all of the mill scale, 93.60%, was under 1 mm dimension after grinding for 15 minutes. Additionally, a great amount (81.17%) of the mill scale was between 125 μm and 1 mm dimensions.

Table 4. The sieve analysis of the 1 kg content after grinding for 15 minutes

Size range	Over 1.00 mm	500 μm-1.00 mm	125 μm-500 μm	45 μm-125 μm	Under 45 μm
Weight	64 g	397.4 g	414.3 g	79.0 g	45.3 g
%	6.40	39.74	41.43	7.90	4.53

It was understood that the wet-drop number of the green pellets decreased with increasing mill scale content in the batches. The green pellets that were obtained from the batch having a mill scale content of 50% resisted an average wet-drop number of 5 before falling into pieces. A similar correlation was observed regarding wet-crush strength. At this stage, the average wet-crush strength of the green pellets that were obtained from the batch having the same mill scale content was 9 N.

Dry-crush strength test results of the pellets obtained from each batch which was dried in the oven are given in Fig. 3. Dry-crush strength of the pellets which were made of the batch having a mill scale content of 50% was a little more than 70 N.

Cold crushing strength test results of the product pellets, which were fired in the electric-resistant furnace at 1250 °C, are given in Fig. 4. Cold crushing strength of the pellets which were made of the batch having a mill scale content of 50% was about 1850 N, which is a sufficient value for charging into the blast furnace.

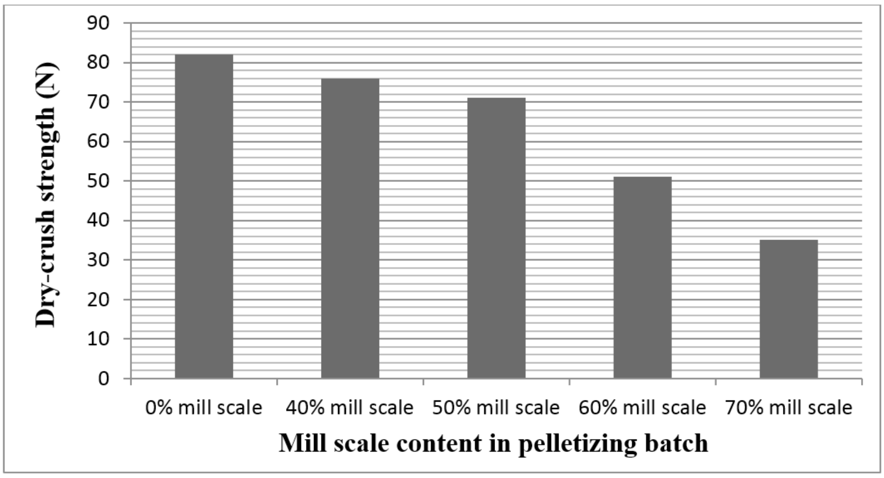


Figure 3. Dry-crush strength of the pellets obtained from each batch which was dried in the oven

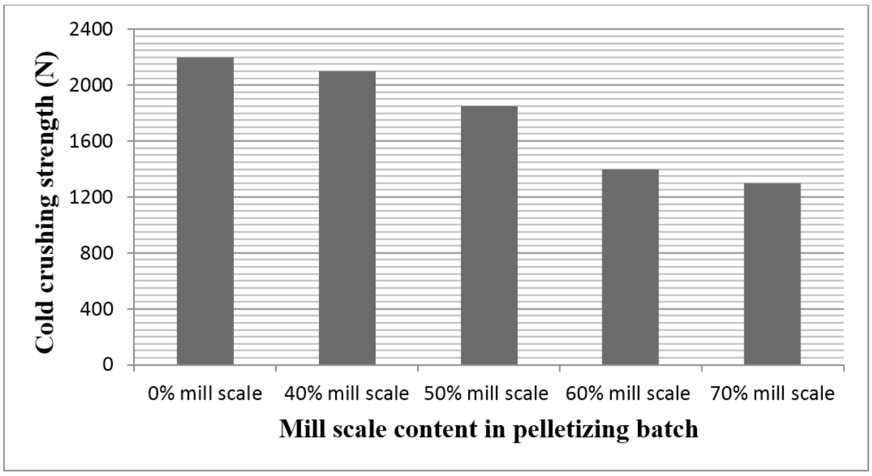
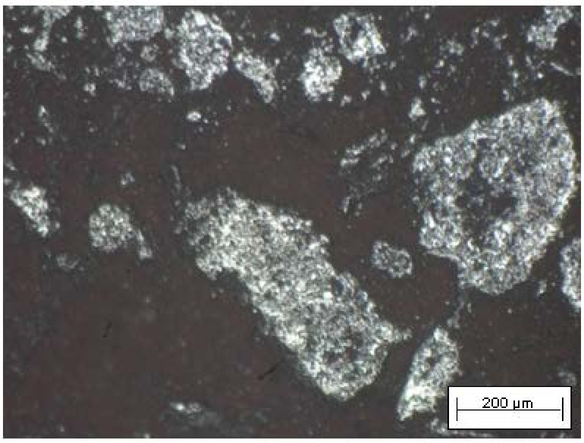


Figure 4. Cold crushing strength of the product pellets obtained from each batch which was fired at 1250 °C

Microstructure photographs of product pellets obtained from the batches which contained 40% and 50% mill scale are given in Fig. 5(a) and 5(b), respectively.



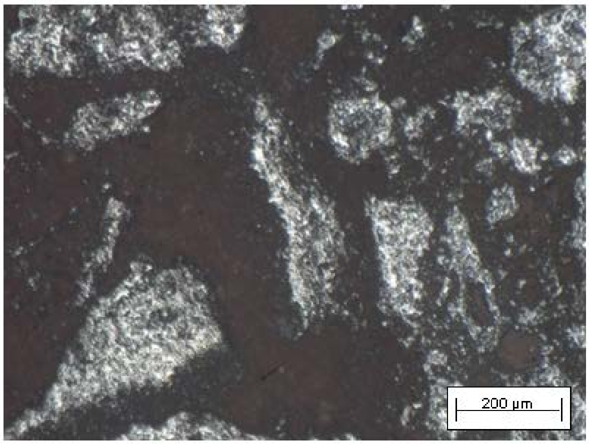


Figure 5. Optical microscope micrograph of a product pellet obtained from the batch which contained 40% mill scale-60% magnetite ore concentrate (a), optical microscope micrograph of a product pellet obtained from the batch which contained 50% mill scale-50% magnetite ore concentrate (b) (Magnification: 500 X)

Discussion

It was understood that the wet-drop number of the green pellets decreased with increasing mill scale content in the batches. Nevertheless, wet-drop number of 5, which was resisted by the green pellets that were obtained from the batch having a mill scale content of 50%, is an acceptable value for green pellets to withstand the forces they will be subjected to while they are being transported to the stages of drying and firing.

A similar correlation was observed regarding wet-crush strength. The average wet-crush strength of the green pellets that were obtained from the batch having a mill scale content of 50% was 9 N. The wet-crush strength of the green pellets must be at least 10 N. The small diameter of the pelletizing disc and failure of the charging system to run continuously and homogeneously are possible factors that affected the low wet-crush strength[9].

The wet-crush strength, dry-crush strength and cold crushing strength of the pellets that were made of batches which contained 40% and 50% mill scale were sufficient for industrial applications while the values for the pellets that were made of batches containing more than 50% mill scale were inconvenient for industrial applications, e.g. charging into the blast furnace.

The dry-crush strength and cold crushing strength of the pellets that were made of batches containing 40% mill scale and 50% mill scale were close to each other. However, the ideal values were achieved with the batch that contained 40% mill scale-60% magnetite ore concentrate.

It was understood that as the weight ratio of mill scale, which had a size of less than 1 mm, was increased beyond 50% the dry-crush strength and cold crushing strength of the product pellets were decreased. However, properties of product pellets that were produced by addition of mill scale in contents of up to 50% were considered convenient for industrial usage.

The chip-shaped structure of mill scale benefits the formation and the properties of green pellet by the way of increasing the capillarity of the wetting liquid used in pelletizing. Because of this situation, addition of coarse mill scale particles having a size of up to 1 mm did not deteriorate the properties of green pellet significantly up to the content of 50%.

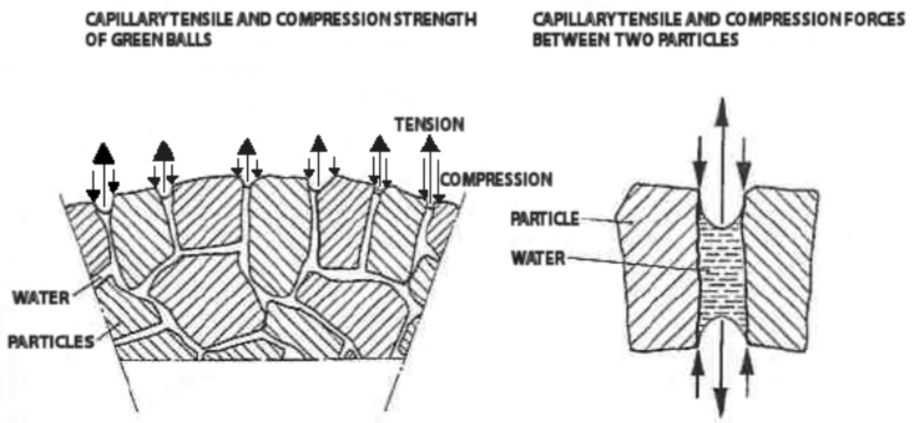


Figure 6. Influence of capillary forces on binding mechanism [9]

Capillarity is an important factor in the formation of balls and agglomerates. Concave liquid surfaces and capillar voids within pores in agglomerates of ore particles keep ore particles together firmly. Tensile forces of the particles change depending on liquid-filled ratio of capillar voids of the agglomerates during ball formation. Formation of the ideal ball is achieved in case all the pores within an agglomerate are filled with the liquid but outside surface of the agglomerate is not covered by the liquid completely. If particles that make up the agglomerate are covered with liquid film completely, a rapid decrease occurs in the surface tension of the liquid causing the solid particles to fall apart and the effect of the capillary forces to cease. Binding occurs by single or combined effects of bridging, capillarity and surface tension, depending on the liquid content of capillar voids. The effect of capillarity and surface tension on binding mechanism is shown schematically in Fig. 6. It is supposed that, when the agglomeration is supplied with a liquid, optimum strength is achieved if voids between the ore particles are almost completely filled with the related liquid and the surface of the liquid-filled capillar voids within the agglomerate is concave. The capillary stress that appears in this case is the primary reason for the strength of the green agglomerate. Between 80 and 90 % of the volume of the total voids is filled with the liquid at this stage[9].

Binding force of the particles (capillary tensile stress), P_K, is dependent on the following equation:

$$P_K = \gamma s \rho_W \frac{1-\varepsilon}{\varepsilon} \qquad (1)$$

Where

γ is surface tension of the liquid (N/m)

ε is the ratio of the volume of pores

s is the specific surface area (m^2/kg)

ρ_w is the true density of the ore (kg/m^3)

Increasing the surface area of the particles that compose the green pellet, i.e. decreasing particle size, improves binding during green pellet production according to this equation.

Capillarity, on the other hand, is also important in green pellet production. Capillary tensile stress, P_K, can also be defined by the following equation:

$$P_K = h\rho g \quad (2)$$

Where

h is the column height of the liquid (m),

ρ is the density of the liquid (kg/m^3),

g is the gravitational acceleration (m/s^2).

It can be understood from these two equations that increasing the surface area of the particles and increasing the capillarity due to the chip shape of the particles improve binding.

Tensile stress, which appears between the ore particles, occurs in capillar voids compatibly with the level of liquid columns within different voids. Tensile stress is dependent on the volume ratio of the void to the entire ore particle and the surface properties of the ore particle[9].

It is already stated that capillarity strengthens bonds and increases binding during ball formation and agglomeration. Moreover, capillarity must be achieved within pelletizing materials in order to accomplish pelletizing. On the other hand, mill scale has a shape of a chip. Thus, it was understood that mill scale presented capillarity due to its chip-like shape. It was thought that the presence of chip-shaped particles, which are the characteristic structures of mill scale, in pelletizing blend, increased the tensile stress of the particles during green pellet production since this situation increases the column height (h) of the liquid. It was also understood that pelletizing properties did not deteriorate due to coarse mill scale pieces having a size of up to 1 mm even though the average size of magnetite ore concentrate particle which is ideal for pelletizing was reported to be 0.04 mm[9]. Therefore, addition of mill scale to the pelletizing mixture in contents of up to 50% is considered convenient for pellet production. Grinding mill scale to fine dimensions, which is energy-consuming, becomes unnecessary because of this opportunity.

The product pellets which were obtained from the batches containing 40% and 50% mill scale present sufficient properties of a product pellet. It can be visualised from the optical micrographs given in Fig. 5 that the mill scale has a chip-like structure.

Grinding is one of the most energy-consuming and less energy-efficient stages in industrial applications. The consumed energy is increased logarithmically as the particle size is decreased since the resistance of the particles to cracking is increased with decreasing particle size by further grinding[10]. This relation is given in Fig. 7 in which the increase in the energy consumed during size reduction with decreasing particle size is evaluated regarding different types of grinders[11]. Moreover, only a small fraction of the energy consumed by conventional grinders is used directly for grinding while the remaining is lost as heat and sound without making a useful work. Thus, the opportunity to omit grinding is economically very important.

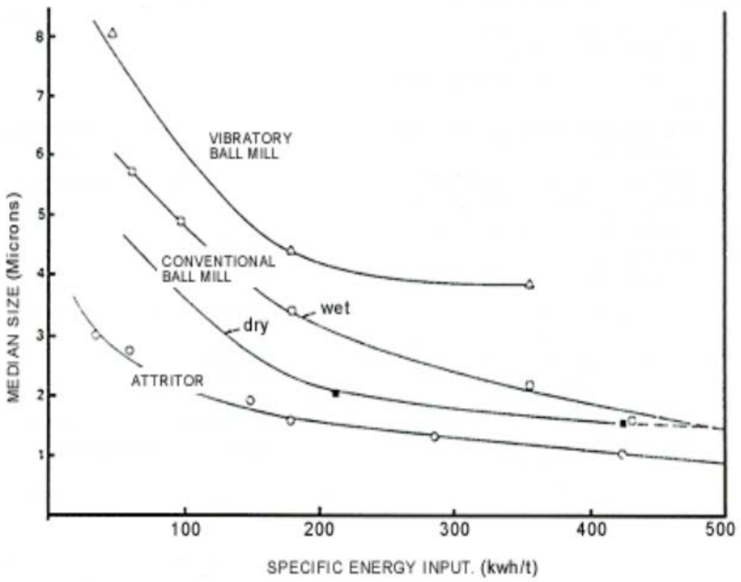


Figure 7. The variance of the energy consumed during size reduction via particle size with comparing different types of grinders[11]

Mill scale that is supplied from ingots, which are widespread production components in plants with electric arc furnace (Fig. 8 right), is smaller than that supplied from slabs, which are semi-finished products having large cross-sections in integrated steel making plants (Fig. 8 left). Because of longer heating and cooling durations of the slab due to its large cross-section, the generated oxide layer and so mill scale have coarser dimensions, according to parabolic rate law[12,13]. Therefore, under 1 mm content of mill scale produced in plants with electric arc furnace is more than that produced in integrated steel making plants. In this study, under 1 mm content of the as-received mill scale comprised about 42.5% of the total weight, which is a considerably high ratio.

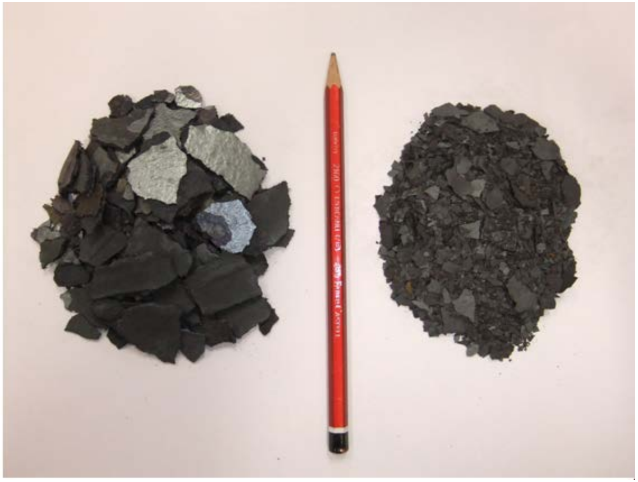


Figure 8. Mill scale that is produced during production and rolling of the ingots in plants with electric arc furnace (right) and mill scale that is produced during production and rolling of the slabs which are the components of mostly integrated steel making plants (left)

In integrated steel production plants, mill scale is used as a raw material by adding it to the sintering blend. On the other hand, getting used by mill scale that is formed in plants which produce steel in EAF can not be achieved since there is no sintering facility in this kind of plants. A great amount of steel production is carried out in plants with EAF in countries like Turkey, Italy, Spain, Mexico, India and United States (Table 5). Mill scale is generally sold for very low prices by the plants with EAF in these countries. The trade of mill scale is generally international. However, these countries require ferrous raw materials for steel production and import ferrous raw materials. While purchasing raw materials from other countries, selling mill scale, which is a kind of ferrous raw material, is a great economical contradiction. Therefore, recycling of mill scale in a useful way is essential in countries where a great amount of steel production is carried out in EAF. Amount of steel production and ratio of the applied processes are given in Table 5 related to 20 countries which are the biggest steel manufacturers. As seen in the table, which gives information according to year 2014, Iran, Turkey, Italy, Spain, Mexico, India and United States do more than 50% of their steel production in plants with EAF[3]. Among them Iran mostly uses directly reduced iron (sponge iron) as the principal raw material that is charged into the EAF. The principal raw material that is used by the other countries is the scrap.

Table 5. Amount of steel production and distribution of the applied processes (basic oxygen furnace and electric arc furnace) in the 20 biggest steel manufacturers (2014)[3]

Country	Annual production (Million tonnes)	% Ratio of production processes	
		BOF	EAF
China	822.7	93.9	6.1
Japan	110.7	76.8	23.2
United States	88.2	37.4	62.6
India	86.5	42.3	57.6
South Korea	71.5	66.2	33.8

Russia	71.5	66.6	30.6
Germany	42.9	69.6	30.4
Turkey	34.0	30.2	69.8
Brazil	33.9	75.5	23.0
Ukraine	27.2	73.4	6.2
Italy	23.7	27.5	72.5
Taiwan	23.1	58.6	41.4
Mexico	19.0	29.9	70.1
Iran	16.3	16.7	83.3
France	16.1	65.9	34.1
Spain	14.2	29.5	70.5
Canada	12.7	60.7	39.3
United Kingdom	12.1	83.9	16.1
Poland	8.6	59.2	40.8
Austria	7.9	91.2	8.8

Conclusion

The results derived from the current work can be summarized as follows:

1 - Mill scale can be mixed with magnetite ore concentrate in producing pellets as a blast furnace charging material. By this way, mill scale, which had been considered a waste, can be recycled so as to obtain an economical ferrous raw material. The problem of getting rid of mill scale has also been solved.

2 - Pellets that were produced with the addition of mill scale which has a size of up to 1 mm possessed sufficient properties for charging into the blast furnace unless mill scale content in pelletizing blend exceeded 50% in weight.

3 - It was understood that mill scale presented capillarity due to its chip-like shape. It was also understood that the properties of product pellets did not deteriorate despite mill scale pieces having a size of up to 1 mm even though the average size of magnetite ore concentrate particle which is ideal for pelletizing was reported to be 0.04 mm.

4 - Mill scale that is produced during production and rolling of ingots in plants with electric arc furnace is smaller than that produced during production and rolling of slabs in integrated steel making plants. Therefore, the former one is more suitable for addition to the pelletizing blend. The usability of mill scale in pelletizing operation without grinding it to the pelletizing size results in a great economic benefit in plants with electric arc furnace which do not possess a sintering facility.

Acknowledgements

The authors would like to acknowledge KROMAN Steel Works Co. for supplying mill scale and ERMADEN Plant for supplying magnetite ore concentrate. This article was written on the basis of the Master's Thesis of the first author.

References

1. Remus R, Aguado-Monsonet M A, Roudier S, Sancho L D. (2013) Best Available Techniques (BAT) Reference Document for Iron and Steel Production. European Commission Joint Research Centre.
2. Shatokha V I, Gogenko O O, Kripak S M. (2011) Utilising of the Oiled Rolling Mills Scale in Iron Ore Sintering Process. Resour. Conserv. Recy., 55, p.p.435-440.
3. World Steel Association, World Steel in Figures 2015, p.p.9-10.
4. Pandey B K, Sharma T. (2000) Reducing Agents and Double-Layered Iron Ore Pellets. Int. J. Miner. Process., 59, p.p.295-304.
5. Sharma T. (1997) Reduction of Double-Layered Iron Ore Pellets. Int. J. Miner. Process., 49, p.p.201-206.
6. Chicot D, Mendoza J, Zaoui A, Louis G, Lepingle V, Roudet F, Lesage J. (2011) Mechanical Properties of Magnetite (Fe_3O_4), Hematite (α-Fe_2O_3) and Goethite (α-FeO.OH) by Instrumented Indentation and Molecular Dynamics Analysis. Mater. Chem. Phys., 129, p.p.862-870.
7. Magnetite, URL: http://www.mindat.org/min-2538.html, access date: 20.11.2015.
8. Magnetite, URL: http://www.handbookofmineralogy.com/pdfs/magnetite.pdf, access date: 20.11.2015.
9. Meyer K. (1980) Pelletizing of Iron Ores. Sprin-

ger-Verlag, Verlag Stahleisen m. b. H. Düsseldorf.

10. Akçiçek N. (2007) Bilyalı Değirmenlerde Bazı Öğütme Parametrelerinin Modellenmesi ve Optimizasyonu (Modelling and Optimization of Some Grinding Parameters for Ball Mill). *Master's Thesis*, Cumhuriyet University Institute of Science and Technology, Turkey (in Turkish language).
11. High Energy Ball Milling, URL: http://www.unionprocess.com/ball_mills.html,access date: 20.11.2015.
12. Olszewski T. (2012) Oxidation Mechanisms of Materials for Heat Exchanging Components in CO_2/H_2O-containing Gases Relevant to Oxy-fuel Environments. *PhD Thesis*, Rheinisch-Westfalischen Technischen Hochschule Aachen, Germany.
13. Verein Deutscher Eisenhüttenleute (VDEh). (1992) Steel: A Handbook for Materials Research and Engineering, Volume 1: Fundamentals, Springer-Verlag Berlin Heidelberg and Verlag Stahleisen m.b.H., Düsseldorf, Germany.