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DEVELOPMENT OF HEMATITE ORE PELLET UTILIZING MILL SCALE AND IRON ORE SLIME COMBINATION AS ADDITIVE

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Abstract

Iron ore slime is generated from mines during processing and washing of iron ore, and it is not considered for pelletizing due to its excessive fineness and high gangue content, despite its good green bonding property. Mill scale is generated from steel rolling mills and reheating furnaces; it has almost nil gangue content, but is not individually considered for pelletizing due to its poor green bonding property. If both of these two wastes are blended in combined form with hematite ore, the high gangue of slime would be balanced by the gangue free mill scale. While mill scale provides exothermic heat of oxidation of FeO and Fe_3O_4 in it and enhance the diffusion bonding, slime provides good green bonding property to the pellet. Therefore, in this study a good quality pellet was developed by the combined mixing of these two wastes in hematite ore without much increase in gangue content. Up to 15% of mill scale and 15% of slime could be used successfully. The developed pellets provide improved cold compressive strength (366 kg/ pellet), reducibility index (82%), and reduction degradation index (8.5%). Induration temperature could be reduced by 75 °C, which indicates a considerable energy saving in induration furnace.

Keywords: *Mill scale; Slime; Pelletizing; Gangue content; Diffusion bonding; Induration temperature*

1. Introduction

During iron ore washing 15-20% ultra-fines are generated in a form of slurry which is contained in dams/tailing ponds for their settling. This settled material is termed slime. The slime generated from hematite ore mainly contains hematite with a small amount of goethite and the gangue minerals like gibbsite, kaolinite and quartz [1,2]. It is a very fine material, even below the grade of palletizing. With decrease in fineness, its gangue (silica and alumina) content increases [1]. The average total alumina and silica content varies to be around 8-20 wt%. Thus, due to its very fine size and high gangue content, it still remains unused and severely accumulated, occupying a huge area of land, which poses environmental threat. Its reuse is required to reduce the environmental load and to conserve mineral resources as well. Although several investigators [1,3-8] have developed flow sheets for its beneficiation, the use of the beneficiated concentrate is still under the scope of the study. Some investigators [9,10] have tried to use it directly in the form of cold bonded briquettes as coolant in the steel making converter. However, due to the lack of any suitable technology, almost 100% of slime is still unused.

If this slime is used as a mix material with iron ore fines, it will proportionally increase the silica and alumina content of the pellet, which may deteriorate the pellet property and increase the slag volume in the downstream process of iron making. Mill scale is another waste material generated in steel mills and reheating furnaces, which is nearly a pure iron oxide (mainly, FeO and Fe_3O_4) of different grade. It has very negligible gangue contents. If it is pelletized individually with bentonite binder, it shows very poor and unacceptable green pellets properties [11]. If slime and mill scale are mixed together with hematite ore for pellet preparation, the additional gangue as a result of the slime can be proportionally controlled in the mix by the absence of gangue in the mill scale. Furthermore, mill scale can provide many other advantages in hematite ore pellets, as described below.

Very high temperature is required for the induration (> 1300°C) of pure hematite ore pellet because of the absence of any exothermic oxidation of iron oxides during induration. If the mill scale is added in the pellet mix, FeO and Fe_3O_4 present in mill scale oxidize during induration and provide in-situ heat to the pellet like magnetite ore. The presence of

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magnetite may also exhibit diffusion bonding [12]. Bentell et al. [13] showed that hematite needles are formed due to diffusion of Fe^{2+}/Fe^{3+} ions in the magnetite phase. At the particle surfaces, Fe^{2+} ions lose one electron to surface adsorbed oxygen, so that Fe^{3+} and O^{2-} ions are formed. The Fe^{3+} ions return to the most favorable sites of the hematite crystal being formed. Since mill scale is a source of magnetite in a pellet, it may improve the strength of pellet. Pal et al. [14] used mill scale as in-situ heat source in their Pellet-Sinter Composite Agglomerates (P-SCA) and found a good strength improvement. Rajshekar et al. [15] found a better sintering property by using mill scale in hematite ore than by using pure hematite ore.

Thus, the combined use of mill scale and slime in hematite ore pellet can improve the pellet properties and reduce the requirement of induration temperature without considerably altering the gangue content of the pellet. Therefore, the present study focuses on the direct use of iron ore slime and mill scale as additives in hematite ore for the development of good quality acidic as well as basic pellet.

2. Experimental

Hematite ore fines of Noamundi, India, have been used as the principal raw material for palletization, and iron ore slime of Noamundi, India, and the mill scale from Tata Steel, India, have been used as additives for the pelletization. Bentonite has been used as binder for pelletization. The initial size fractions of iron ore fines, slime, and mill scale used in the study are shown in Table 1.

Raw materials were ground to around 2200 cm^2/g Blaine fineness as per the optimized value for the same ore in our previous study [16]. Their particle size distribution is given in Table 2. Fluxes including limestone, olivine, and bentonite were ground to less than BIS mesh size#200 for use in pellet making. The chemical analysis of iron ore fines, slime, mill scale, fluxes, and bentonite used in the study are shown in Table 3. X-Ray diffraction analysis of these three iron bearing materials are shown in Fig. 1. From the chemical analysis and XRD study, it is clear that iron ore fines and slime contain mainly hematite and mill scale contains mainly FeO and Fe_3O_4 with some Fe_2O_3. XRD analysis (Fig. 1) also shows the presence of FeOOH, $Al(OH)_3$ and SiO_2 phases in slime. However, LOI is slightly higher than iron ore, which indicates that quantity hydroxides phases are not very high.

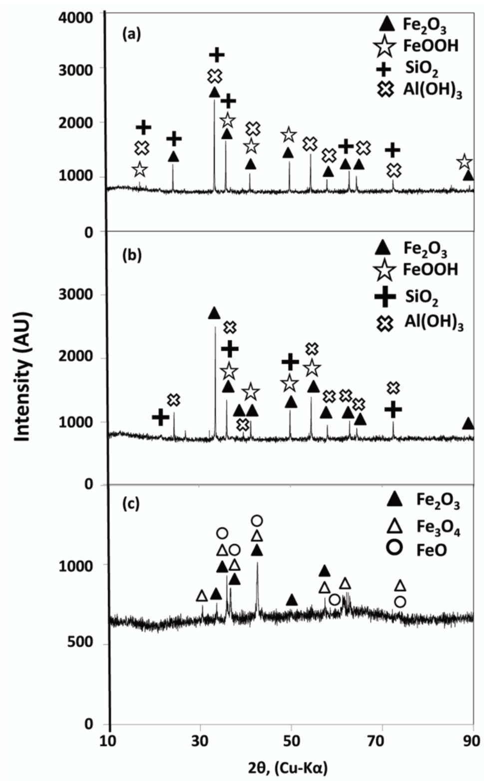


Figure 1. *XRD analysis of iron ore, slime and mill scale; (a) iron ore, (b) iron ore slime, (c) mill scale*

Table 1. *Size fraction of as received iron ore fines, slime, and mill scale, (wt% retained)*

Sieve size (mm)	Iron ore	Iron ore slime	Mill scale
-10+6	24.64	-	3.64
-6+3	10.8	-	3.19
-9+1	28.2	-	34.13
-1	36.36	100	59.04

Table 2. *Particle size distribution of raw materials after grinding*

Sieve size (µm)	Iron ore fines (wt% retained)	Iron ore slime (wt% retained)	Mill scale (wt% retained)
-1000+200	17.84	5.57	10.28
-200+100	13.58	5.38	11.67
-100+75	4.65	3.68	5.37
-75+45	7.5	10.88	9.83
-45	56.43	74.49	62.85
Blaine fineness, cm^2/g	2200	2190	2200

Table 3. *Chemical analysis of raw materials, wt%*

	Fe_2O_3	FeO	SiO_2	Al_2O_3	MgO	P	CaO	LOI
Iron Ore Fines	91.26	0.52	2.247	2.34	0.013	0.07	0.001	4.07
Iron ore slime	83.36	0	4.67	5.18	0.15	0.173	0.21	6.2
Mill scale	34.32	63.21	0.49	0.28	0.06	0	0.7	-
Bentonite	12.58	0.1	45.62	11.43	2.79	0	1.65	-
Limestone	0	0	1.4	0.8	0.7	0	51.51	-
Olivine	0	0	40.3	0.5	48.1	0	0	-

The ground raw materials mixed in various proportions, and their individual codes for pellet preparation are shown in Table 4. The blend compositions were decided as per the desired amount of mill scale and slime addition, MgO percentage, and basicity (CaO/SiO_2) of the pellet. The estimated chemical compositions of the pellets based upon the blending considerations mentioned in Table 4 are shown in Table 5, code wise. It has to be mentioned that the pellet without any flux is termed 'acidic' pellet, and the pellet with lime stone addition is termed 'basic' pellet in this study.

The pellet types A1-A3 represent acidic pellets with complete hematite ore, slime, and mill scale, respectively, without blending. B1-B4 represent acidic hematite pellets with 15% mill scale and

Table 4. *Raw material blend percentages for various types of pellets prepared*

Pellet code			Iron ore %	Iron Ore slime %	Mill scale %	Olivine %	Limestone %	Bentonite %	Desired MgO %	Desired Basicity (CaO/SiO_2)
Type	Group	Sub Group								
Acidic	A	A1	99.5	0	0	0	0	0.5	-	-
		A2	0	99.5	0	0	0	0.5	-	-
		A3	0	0	99	0	0	1	-	-
Acidic	B	B1	84.5	0	15	0	0	0.5	-	-
		B2	79.5	5	15	0	0	0.5	-	-
		B3	74.5	10	15	0	0	0.5	-	-
		B4	69.5	15	15	0	0	0.5	-	-
Basic	C	C1	95.65	0	0	2	1.85	0.5	1	0.3
		C2	80.5	15	0	2	2	0.5	1	0.3
Basic	D	D1	81	0	15	2	1.5	0.5	1	0.3
		D2	75.95	5	15	2	1.55	0.5	1	0.3
		D3	70.9	10	15	2	1.6	0.5	1	0.3
		D4	65.85	15	15	2	1.65	0.5	1	0.3

Table 5. *Estimated chemical composition of the pellet blends prepared*

Pellet Code	Fe_{total}	Fe_2O_3 %	FeO %	SiO_2 %	Al_2O_3 %	P %	CaO %	MgO %	Basicity (CaO/SiO_2)
A1	63.61	90.87	0	2.46	2.39	0.07	0.009	0.027	0.004
A2	58.1	83	0	4.88	5.21	0.172	0.217	0.163	0.045
A3	72.54	34.1	62.58	0.94	0.39	0	0.017	0.087	0.018
B1	65	82.33	9.48	2.2	2.08	0.059	0.113	0.023	0.05
B2	64.72	81.93	9.48	2.32	2.22	0.064	0.124	0.03	0.053
B3	64.45	81.54	9.48	2.44	2.36	0.069	0.134	0.038	0.055
B4	64.17	81.14	9.48	2.56	2.5	0.075	0.145	0.045	0.056
C1	61.14	87.35	0	3.21	2.32	0.067	0.961	1	0.3
C2	60.22	86.03	0	3.57	2.74	0.082	1.07	1	0.3
D1	62.76	79.13	9.48	2.95	2.02	0.057	0.887	1	0.3
D2	62.46	78.69	9.48	3.07	2.16	0.062	0.922	1	0.3
D3	62.15	78.25	9.48	3.19	2.3	0.067	0.958	1	0.3
D4	61.84	77.81	9. 48	3.31	2.44	0.072	0.995	1	0.3

varying slime. The pellets C1 and C2 represent basic hematite pellets and pellets with 15% slime, respectively. D1 to D4 represent basic pellets containing 15% mill scale and varying additions of iron ore slime. It may be mentioned here that in our earlier study on the same ore, 0.3 basicity and 1% MgO was found [17] to be optimum. Therefore, for this study also 0.3 basicity and 1% MgO were maintained.

After the preparation of green pellets, they were subjected to various tests such as Green Compressive Strength (GCS), Green Drop Strength Number (GDSN), Dry Compressive Strength (DCS) and moisture content. The GCS of pellets was measured using a Hounsfield Material testing Machine (Model: H10K-S) measuring the load on an individual green pellet to withstand, before cracking. The average strength of 20 green pellets has been recorded as the GCS. The GDSN was measured by repeatedly dropping a green pellet on a mild steel plate from a conventional height of 450 mm [12] and counting the number of drops the pellet sustains without cracking. The moisture content in green pellets was measured by heating a representative sample of 30-40 g at a temperature of 110°C for four hours and subsequently measuring the weight loss in the sample as a percentage. The DCS of the oven dried pellets was measured in a Hounsfield Material testing Machine (Model: H10K-S). The machine is interfaced with a personal computer having data capturing system. The green properties of the pellets are reproducible with an error band of ± 5%.

The pellets have been indurated at different temperature in a chamber furnace in an inconel or mollite crucible. After the furnace cooling of the pellets, cold compression strength (CCS) of the indurated pellets was measured as per the standard ISO 4700, using Hounsfield Material testing Machine (Model: H10K-S). The Apparent porosity (AP) of indurated pellets was measured as per the standard IS: 1528 (Part VIII) – 1974 (Reaffirmed 2002).

The Reduction Degradation Index (RDI) measured as per the standard JIS: M 8720-2001, indicated the degradation of pellets in the upper part of blast furnace. Swelling Index (SI) was measured by measuring the initial volume and the final volume of the pellet by mercury displacement method after reduction at 900 °C under 30 % CO- 70 % N_2 gas flow. The Reducibility Index (RI) was measured as per the standard JIS: M 8713-2000 and it indicates the ease with which oxygen combined with iron could be removed from iron ore pellets with a reducing gas at the time of reduction.

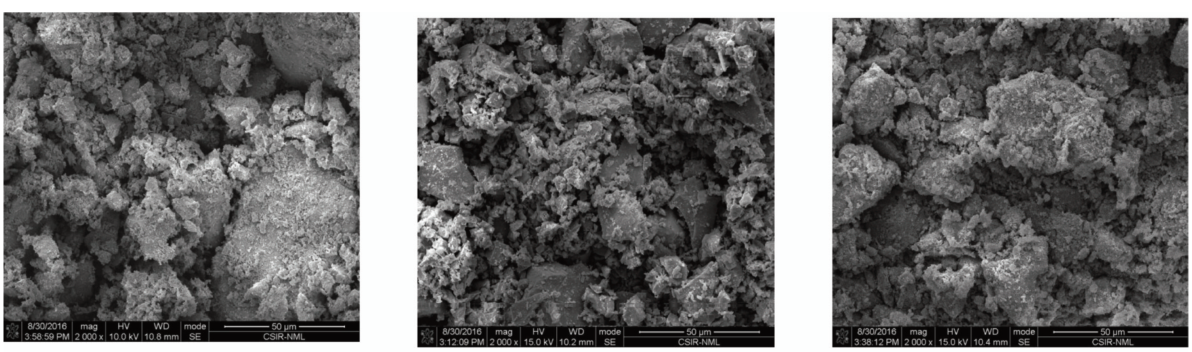
The phase analysis of raw materials and prepared pellets was done using Siemens D500 X-ray diffractometer using Cu-K∝ radiation. The scanning speed was maintained at 2θ, 1°/min. The existence of phases was identified by XRD analysis software, High score Plus from PANalytical which uses ICSD (Inorganic Crystal Structure Database). Thermo Gravimetric Analysis (TGA) of iron ore fines, slime, and mill scale was done in a TGA set-up (Model: TherMax 700) under normal air atmosphere conditions to observe the change in weight of samples with temperature. Heating rate was maintained at 10 °C/min with set temperature of 1200 °C. Selected samples were observed under the optical microscope (LEICA, DM 2500 M) to study the distribution of phases and pores.

The possibility of phase formation during induration was also estimated by the commercial thermodynamic software, FactSage 6.4 (Thermofact and GTT Technologies) through equilibrium study at their induration temperature. Though the pellet induration process is not an equilibrium reaction, it is done only to predict the thermodynamic feasibility of several phase formation at the induration temperature, which is important to understand the pellet character.

3. Results and discussion

3.1. Green properties of pellets with iron ore, mill scale and slime individually

In order to study the pelletizing properties of all the individual materials, the green properties of pellets with iron ore, mill scale, and slime are



(a) Iron ore fine (b) Mill scale fine (c) Slime fine

***Figure 2**.Surface morphology of different fines under SEM microscope*

Table 6. *Green pellet properties of complete iron ore fines, slime and mill scale pellets*

Pellet Code	GCS (kg/pellet)	GDSN (number)	DCS (kg/pellet)	Moisture (%)
A1	2.13	30.5	9.73	9.52
A2	1.77	71.2	7.86	10.33
A3	1.815	2.4	8.18	6.57

individually presented in Table 6. Mill scale has very poor green properties because of its smooth surface properties as shown in Fig. 2. Due to this smooth surface property, it has less water holding capacity, which is unfavorable for green bonding. Despite the fact that mill scale is a very pure iron oxide, it cannot be pelletized individually. On the other hand, slime shows very good green properties because of its uneven surface properties (Fig. 2) and adhesiveness. However, pellet preparation with only slime was observed to be very difficult due to its coagulation problem. Furthermore, due to high alumina and silica contents, pure slime cannot be used for pelletizing. Thus, none of the two materials can be used in pelletizing either in pure form or in high proportion. However, the effect of their varying proportion and optimization for good pellet preparation is very imperative.

The Thermo-gravimetric Analyses (TGA) % of iron ore fines, slime, and mill scale are shown in Fig. 3. The pellets A1, A2, and A3 which are respectively constituted of complete iron ore fines, iron ore slime, and mill scale are heated to a temperature of 1200°C in air atmosphere, and the percentage change in weight is recorded.

From the Fig. 3, it can be observed that with the increase in temperature, the iron ore fines and slime were found to show a continuous decrease in weight. The continuous decrease in weight may be attributed to the release of water of crystallization up to a temperature of 800°C associated with various phases such as FeOOH, $Al(OH)_3$, which could be observed in XRD (Fig. 1). The mill scale on the other hand was found to increase in weight, starting from 200 °, continuously with the increase in temperature. The increase in weight is attributed to the adsorption of oxygen from air by phases such as FeO and Fe_3O_4 present in mill scale and getting oxidized to Fe_2O_3.

The above study indicates that the green pellet characteristics of above three raw materials are different. Thermo-gravimetric analysis also shows the different behavior of pellets under high temperature induration. Since the green pelletizing with both slime and mill scale is not feasible, the possibility of blending these two materials in suitable proportion was explored.

3.2. Properties of iron ore pellets

Before mixing, we should know about the properties of pure iron ore pellets. For this purpose iron ore fines were ground to 2200 cm^2/g Blaine fineness: the size fractions are shown in Table 2. Earlier investigators also used this fineness level [16] for Noamundi ore. First, the characteristics of flux free pellets and basic pellets with varying basicity are studied in this work.

The green pellets properties of acidic pellets are already mentioned in Table 6. Basic pellets also have very good green (GCS: 1.905 kg/pellet and Drop No:22.2) and dry (DCS: 5.51 kg/pellet) properties. 1275 °C temperature was found to be optimum induration temperature for the same ore at 0.3 basicity level in our earlier study [17]. Therefore, for studying the indurated pellet properties, 1275 °C temperature is considered here. In indurated condition, the properties of acidic pellets and basic pellets are different as shown in Table 7. CCS is much lower in acidic

Table 7. *Properties of indurated pellets from Noamundi ore*

Pellet	Code	Ind Temp, °C	CCS kg/pellet	RI, %	RDI, %	SI,%	AP,%
Acidic	A1	1275	231	96.11	86.76	18.86	24.21
Basic (Basicity =0.3)	C1	1275	408	84.71	19.18	17.95	18.024

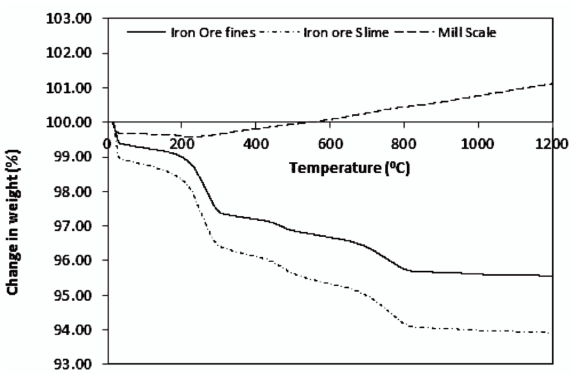


Figure 3. *Thermo-gravimetric analysis of several raw materials*

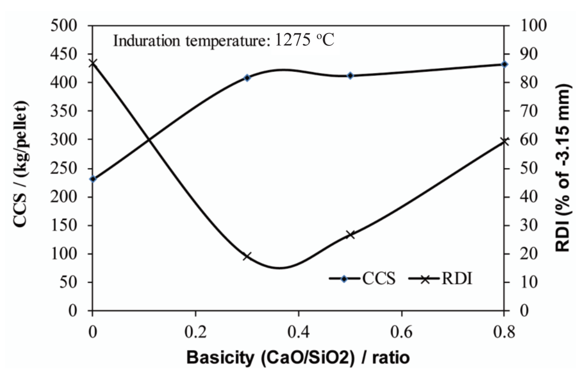


Figure 4. *Effect of Basicity on CCS and RDI of indurated fluxed pellet*

pellets; i.e. acidic pellets require much higher induration temperature. Flux free acidic hematite ore pellets have very high induration temperature because of absence of any oxidation reaction and limited amount of diffusion bonding at lower temperature [16]. Figure 4 [18] shows minimum RDI at 0.3 basicity and beyond that, both RDI and CCS increase and reducibility decreases with the increase in basicity. However, a very good CCS is observed at 0.3 basicity as well. Thus, 0.3 basicity is considered to be the optimum. The basic pellet may provide very high strength even at low temperatures. Thus, a minor increase in basicity may be one solution to increase CCS, reduce induration temperature, and decrease RDI. The addition of mill scale can reduce induration temperature and increase CCS of acidic hematite ore pellets. In a separate study [18], the effect of mill scale in hematite ore on pellet properties was studied. It was found that the use of 15 % mill scale in acidic pellet can reduce the induration temperature up to 1250 °C and improve pellet properties viz CCS, RI, RDI, and swelling index. In the present study, the possibility of slime addition in this 15 % mill scale added pellet was investigated, as explained in the proceeding sections.

3.3. Effect of iron ore slime addition in mill scale added hematite pellets

The study was carried out by making acidic and basic hematite pellets with varying additions of mill scale and iron ore slime. The green pellet properties of both types of pellets are shown in Table 8. It can be observed from the Table 8 that the green pellets properties are well above the industrially acceptable specifications (GDSN of minimum of 4 Nos, GCS of 1 kg/pellet and DCS of 2.24 kg/pellet) [12,19]. DCS and GCS are nearly within the same range (1.6-2 kg/pellet and 6.5-9 kg/pellet, respectively) for both acidic and basic pellets. However, the drop numbers for the basic pellets are smaller than for the acidic pellets. This may be due to the addition of limestone and olivine in the pellet. Since these are in carbonate form, they have inferior green bonding properties with respect to iron ore.

Table 8. *Green pellet properties of acidic and basic hematite pellets with varying additions of mill scale and iron ore slime*

Pellet Code	GCS, kg/pellet	GDSN, Nos	DCS, kg/pellet
B1	2.09	26.8	6.85
B2	1.54	16.5	6.11
B4	1.66	31.9	9.16
D1	1.74	17.5	6.44
D2	1.58	16.6	6.21
D3	1.63	20.7	7.48
D4	1.67	16.3	6.64

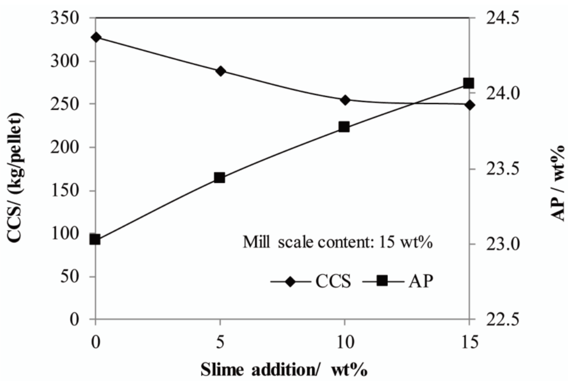
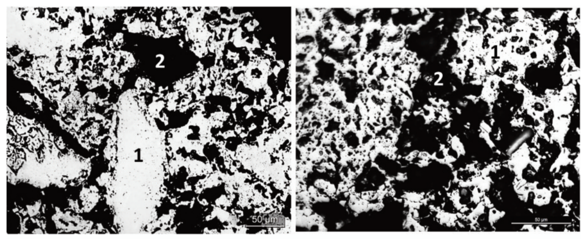


Figure 5*. Effect of increasing addition of iron ore slime on the CCS and Apparent Porosity of mill scale containing acidic hematite pellet*



15% mill scale containing pellet without slime

15% mill scale containing pellet with 15% slime

1. Hematite, 2. pore

Figure 6*. Optical microstructure of mill scale added acidic pellets with and without addition of iron ore slime*

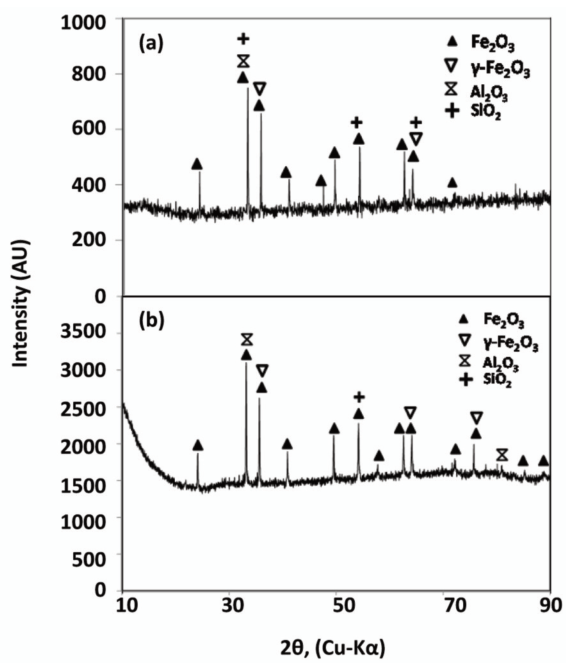


Figure 7*. XRD pattern of mill scale added acidic pellet and with and without the addition of iron ore slime (a) Mill scale (15%) added pellet without slime (b) Mill scale (15%) added pellet with 15% slime*

Table 9. *Phase analysis through XRD and FactSage equilibrium study for acidic pellets*

Pellets	Phases from XRD of cold sample (indurated at 1275 °C)	Phases from Factsage equilibrium at 1275 °C	Factsage analysis		
			Amount of molten phase, wt%	Composition of molten phase, wt%	Viscosity of molten phase, poise
Iron ore pellets	Fe_2O_3, Al_2O_3, SiO_2	Fe_2O_3, Al_2O_3, SiO_2	nil		
15% mill scale added pellet	Fe_2O_3, Y-Fe_2O_3, Al_2O_3, SiO_2	Fe_2O_3, Al_2O_3, Liquid phase	3.2	FeO: 29.5, SiO_2: 21.6, Fe_2O_3: 46.2, Al_2O_3: 2.7	0.7
15% mill scale + 15% slime added pellet	Fe_2O_3, Y-Fe_2O_3, Al_2O_3, SiO_2	Fe_2O_3, Al_2O_3, Liquid phase	3.2	FeO: 29.4, SiO_2: 22.3, Fe_2O_3:44.9, Al_2O_3: 3.4	0.8

3.3.1. Properties of indurated acidic pellets

The effect on increasing iron ore slime addition on the CCS and apparent porosity (AP) of pellets is shown in the Fig. 5. It is obvious from the Fig. 5 that the CCS decreases with the increase in slime content of iron ore. The increase in apparent porosity as shown in the Fig. 5. may be the prime reason for this strength deterioration. Moreover, the microstructure of 15% mill scale added acidic pellets with 15% iron ore slime and without the addition of slime is shown in Fig. 6. It can be observed from the microstructures in Fig. 6, that the pellets containing iron ore slime have higher pore area than the pellets without slime. It may be noted from the Fig. 4 that the acidic pellet with only iron ore shows CCS of only 230 kg/pellet. However, the minimum industrial requirement is 250 kg/pellet [19]. Due to the addition of 15 % mill scale, the strength was increased to 325 kg/pellet (Fig. 5). This may be attributed to the good diffusion bonding, bridging between two adjacent hematite grains, and recrystallization in the presence of mill scale (Fig. 6). Though the CCS decreases gradually with increasing slime content, the combined addition of 15% mill scale and 15 % slime in iron ore pellet shows much higher strength than the acidic pellet with only iron ore. Fig. 7 shows the XRD peaks with slime and without slime addition in 15% mill scale added pellet. Only iron oxides and alumina and silica peaks are visible. Rietveld analysis of the peaks shows 7.7% and 8.4% γ-Fe_2O_3 with 15% slime and without slime, respectively. However, there may exist other phases such as, fayalite in a very low quantity, which was seen in the FactSage equilibrium study at 1275°C. Since the pellets are mill scale added, FeO in mill scale is oxidized during the preheating stage: however, some residual FeO should be there, which was found to be ~2% from experimental investigation. The residual FeO can react with silica in the pellet, which yields a low melting fayalite phase in a very minor quantity (Table 9). When there is FeO in mill scale and silica is present in ore itself, the fayalite formation may happen. Although diffusion bonding plays a major role in acidic pellet, this silicate phase is molten at the induration temperature, and it may contribute in increasing the bond strength and CCS of pellet. If slime is added, the silica content further increases, which exhibits fayalite formation. Since there is high alumina in slime, the alumina can combine with silicate phase which may increase the melting point of silicate slag [20]. Table 9 shows higher viscosity of the melt phase in the slime added pellet because of its higher alumina content. The viscous slag is less prone to distribute surroundings of the grains and hence the pores remain unfilled. This may be one more reason of getting higher porosity and lower CCS in slime added pellets.

The effect of increasing addition of iron ore slime on the RDI of 15% mill scale added acidic pellets is shown in the Fig. 8. The RDI increases with the increase in slime. This is because of the proportional increase in the alumina content. As explained above, this alumina increases the melting point and the viscosity of slag phase and hence increases the pore area [17,21]. Pimenta and Seshadri [22] also reported that Al_2O_3 diffuses in hematite crystal during induration at high temperature to form solid solution. During the reduction of hematite to magnetite at low temperature, the diffused Al_2O_3 generates magnetite phase with distorted structure, which promotes crack initiation and propagation, leading to disintegrating

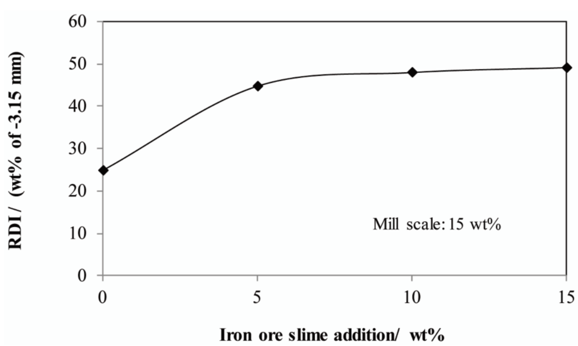


Figure 8*. Effect of iron ore slime addition on RDI of mill scale added hematite pellet*

the pellet. Though the RDI in 15% mill scale added acidic pellets came down to 25%, it significantly increases to very high level (~45%) for the addition of 15 % slime, which is much higher than industrially acceptable limit of < 20% [23].

The effect of increasing iron ore slime addition on the RI and swelling index of acidic pellets containing 15% mill scale and with 15% iron ore slime addition and without addition of slime is shown in the Table 10.

Table 10. *Effect on RI and SI of mill scale containing acid pellet with and without addition of iron ore slime*

% Iron Ore slime	% Mill scale	Reducibility Index, %	Swelling Index, %
0	15	85.4	9.5
15	15	90.23	12.69

It could be observed from the table that the RI increases with the addition of iron ore slime in mill scale containing acidic pellet. This may be attributed to the increase in porosity of pellets that exhibits the gas passage through the pellets for reduction. Swelling index slightly increases in 15% slime added pellets. This is because of poor bond strength as explained earlier. However, in both pellets, the swelling indices (9.5 and 12.69%) are much below the acceptable limit (20% maximum).

Form the above it is envisaged that 15% mill scale added acidic pellet has higher RDI than the industrially acceptable limit. Due to the addition of slime, alumina content of pellet proportionally increases and hence RDI increases to around 45%, which is not at all suitable for the blast furnace operation. Therefore, the flux addition is required in this pellet to minimize RDI and improving other properties, which is explained in the section below.

3.3.2. Properties of indurated basic pellets

The effect of slime addition in 15% mill scale added basic (0.3 basicity) pellet on CCS is shown in

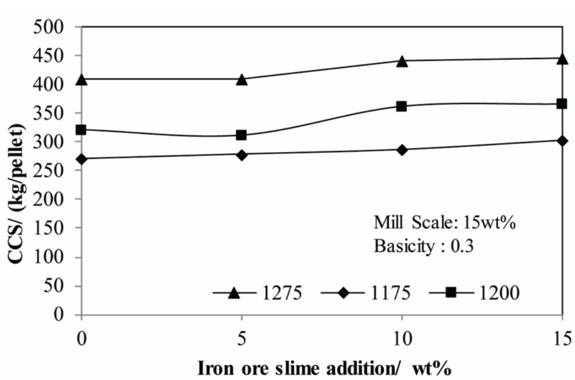


Figure 9. *Effect of iron ore slime addition on the CCS of mill scale added basic hematite pellet*

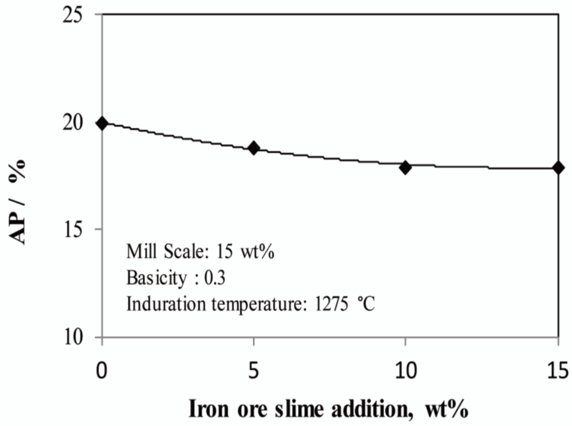


Figure 10. *Effect of iron ore slime addition on the AP of mill scale added basic hematite pellet*

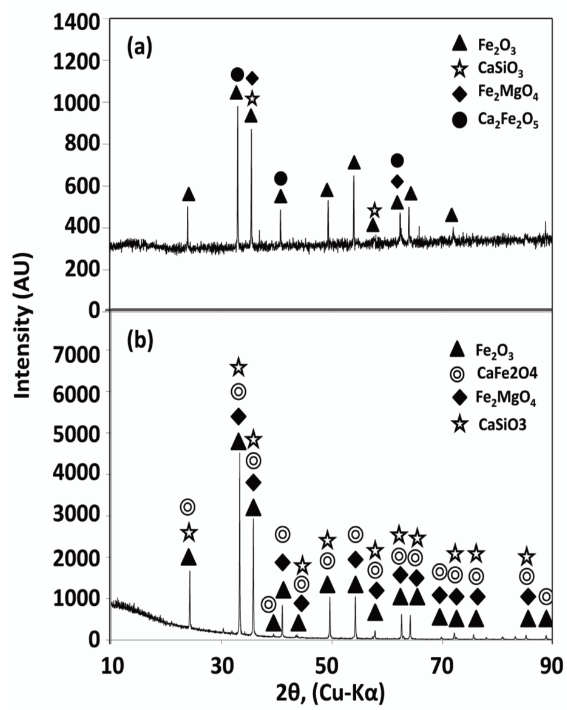


Figure 11. *XRD of mill scale added basic pellet (0.3 basicity) with and without the addition of iron ore slime (a) 15 wt% mill scale added pellet without slime (indurated at 1275°C) (b) 15 wt% mill scale added pellet with 15% slime (indurated at 1275°C)*

Table 11. *Rietveld analysis of XRD peak of mill scale added basic pellet with and without addition of iron ore slime (Indurated at 1275 °C)*

Slime	Mill Scale	Phases, wt%				
		Fe_2O_3	Fe_2MgO_4	$CaSiO_3$	$CaFe_2O_4$	$Ca_2Fe_2O_5$
-	15	80.2	4.8	4.4		10.5
15	15	93.1	1.1	3.4	2.3	

Table 12.*Phase analysis through XRD and FactSage equilibrium study for basic pellets (B=0.3)*

Pellets	Phases from XRD of cold sample (indurated at 1275 °C)	Phases from FactSage equilibrium at 1275 °C	FactSage analysis		
			Amount of molten phase, wt%	Composition of molten phase	Viscosity of molten phase, poise
Basic iron ore pellets	Fe_2O_3, Fe_2MgO_4, Ca_3SiO_5, $Ca_2Fe_2O_5$	Fe_2O_3, Fe_2MgO_4, $AlFe_2O_4$,Liquid Phase	6.6	CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO	61.97
15% mill scale added basic pellet	Fe_2O_3, Fe_2MgO_4, $CaSiO_3$, $Ca_2Fe_2O_5$	Fe_2O_3, Fe_2MgO_4, Liquid Phase	5.95	CaO, SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO	50.96
15% mill scale + 15% slime added basic pellet	Fe_2O_3, Fe_2MgO_4, $CaSiO_3$, $CaFe_2O_4$	Fe_2O_3, Fe_2MgO_4, Liquid Phase	6.68	CaO, SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO	63.96

Fig. 9. CCS has an increasing trend with the increase in slime addition at all temperatures ranging from1175-1275 °C. Further, the apparent porosity decreases with the increase in slime addition (Fig. 10), unlike acidic pellet. This characteristic may be explained from the phases present in the slag bonding, which, was analyzed by XRD study (Fig. 11) and corresponding FactSage calculation (Table 11) in equilibrium. Rietveld analysis of the XRD peaks is shown in Table 11. It is envisaged from the Tables 11 and 12 that there are good numbers of similar phases in both studies for both pellets. The apparent difference in phases between XRD study and prediction from FactSage is due to the following reasons; (i) phases in FactSage indicate the equilibrium phases at 1275 °C as explained in experimental section, and (ii) XRD study is the post induration analysis of pellets after cooling to room temperature and very minor phases may not be traceable.

It can also be observed from the Table 12 that the pellets with slime and without slime show more or less similar phases in both studies. The phase quantities were also estimated from the FactSage (Table 12), and it was found that the quantity of melt phase formation in the slime added pellet is much higher than in the pellet without added slime. This is because of high percentage of silica in slime added pellet, which requires the addition of high amount of lime to maintain the basicity at 0.3 level. These combinedly increases the amount of slag phase in pellet. Due to the presence of the suitable amount of lime, the higher viscosity does not hamper the distribution of slag phase surrounding the grains and filling the cavity/ pore, in spite of high alumina in the slime. Thus, the porosity decreases in the mill scale added pellets. The microstructure, as shown in Fig. 12, also shows less pore area and good slag bonding in the slime added pellet. In addition to the diffusion bonding, slag bonding plays a major role in the mill scale added basic pellets with and without the addition of slime. Thus, higher CCS and lower porosity were found in pellet due to the better slag bonding with increasing slime addition.

The effect of increasing addition of iron ore slime on RDI is shown in Fig. 13. It is envisaged that a marginal increase in RDI has been observed with the increase in iron ore slime. This increase in RDI may

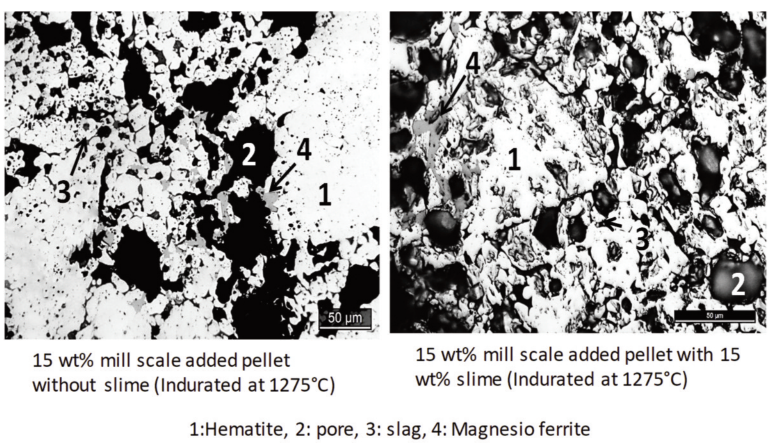


Figure 12*. Optical microstructure of mill scale added basic pellet (0.3 basicity) with and without the addition of iron ore slime*

be attributed to the increase in alumina content of pellet mix due to the addition of high alumina slime. However, even at the 15% slime addition, RDI is nearly 13%, which is not so high, and significantly better than the industrially acceptable limit of 20%. The low RDI may be attributed to good bonding in pellet, which can withstand the stresses generated due to phase transformation taking place during low temperature reduction. The effect of increasing iron ore slime on the reducibility and swelling index of pellet is shown in the Table 13. From Table 13, it can be observed that with increasing iron ore slime addition there is no significant increase in RI and SI. Thereby, it could be observed that a good quality blast furnace grade basic pellet can be prepared with the addition of 15% iron ore slime and 15% mill scale.

The properties of hematite basic pellet containing 15% mill scale and 15% iron ore slime at various

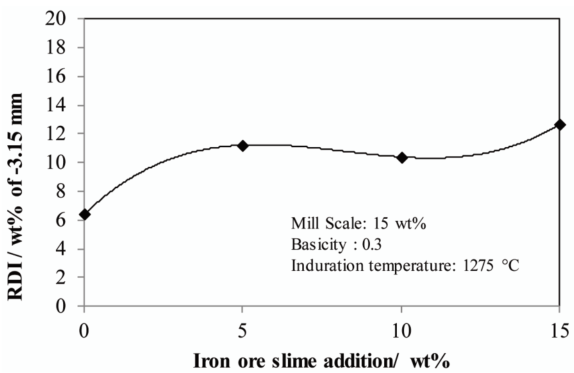


Figure 13. *Effect of iron ore slime addition on RDI of mill scale added basic hematite pellet*

Table 13. *Effect of increasing iron ore slime addition on the RI and SI of 15% mill scale containing 0.3 basicity pellet*

Slime % in 15% mill scale 0.3 Basicity Pellet	Reducibility Index, %	Swelling index, %
0	81.99	17.72
5	84.78	18.79
15	81.71	18.29

Table 14. *Physico-chemical properties of basic hematite pellet (0.3 basicity) containing 15% mill scale and 15% iron ore slime at varying temperature*

Temperature (^{0}C)	CCS (kg/Pellet)	AP, %	RI, (%)	RDI (% of -3.15 mm)	SI, (%)
1175	303	25.6	87.91	12.68	6.86
1200	366	23.6	82.44	8.5	12.81
1275	447	17.9	81.71	12.66	17.92

temperatures is shown in Table 14. It can be observed from Table 14 that the strength and physico-chemical properties are satisfactory, even at very low temperature (1175 °C). Considering unequal temperature distribution of pellet induration bed in plant practice, a little higher temperature, 1200 °C, may be considered as a required induration temperature of the developed pellet. At this temperature CCS of pellets reaches to very high level of 366 kg/ pellet, and all other properties are found to be well within the industrially acceptable limits. Microstructure of the same pellets indurated at three different temperatures are shown in Fig. 14. It is revealed from the microstructure that at 1275°C induration excessive fusion, grain coarsening thereby decreasing porosity occurred. Since the porosity is very low at 1275°C induration, this structure shows more expansion during reduction and transformation from hematite to magnetite than that at 1200°C induration. Therefore, at 1200°C both RDI and swelling index is little lower than that at 1275°C (Table 14). Hence, good blast furnace grade indurated basic pellets could be produced at much lower temperatures (1200°C) by mixing 15% mill scale and 15% iron ore slime as a blend in the pellet mix. Although, the addition of iron ore slime in acidic pellets deteriorates the physico-chemical properties, a drastic improvement in properties were found in basic pellets for the addition of iron ore slime. It was mentioned earlier that for the same iron ore, 1275°C was found to be the optimum induration temperature at 0.3 basicity level [17], when no mill scale and slime

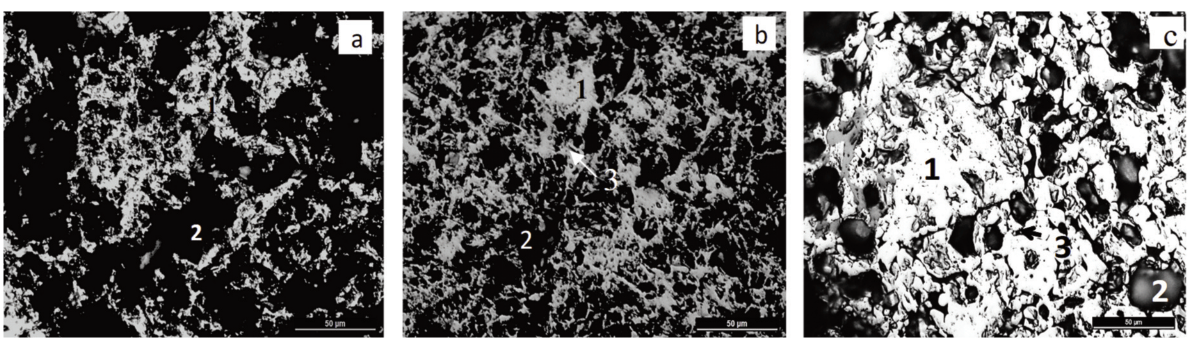


Figure 14. *Optical microstructure of mill scale added basic pellet (0.3 basicity) with addition of iron ore slime (15wt%) at different temperature; 1 - Hematite, 2- Pore, 3 - Slag; (a) 1175 °C induration, (b) 1200 °C induration, (c) 1275 °C induration*

Table 15. Chemical analysis of the indurated pellets

Pellets	Chemical analysis, wt%				
	Fe_{total}	CaO	SiO_2	Al_2O_3	MgO
Basic iron ore pellet	63.9	1.07	3.11	2.26	1.04
Basic iron ore pellet with 15% mill scale addition	64.32	1.1	2.49	2.13	1.07
Basic iron ore pellet with 15% mill scale and 15% slime addition	63.37	0.979	3.53	2.58	1.17

were added. In this respect, it can be stated that due to the addition of 15% mill scale and slime in hematite ore, a lowering in induration temperature requirement is possible by 75°C. Accordingly, it may reduce the energy requirement in induration strand.

The chemical analyses of three different pellets are shown in Table 15. From the table, it is envisaged that due to the addition of 15% mill scale there is a considerable decrease in alumina and silica content. When 15% slime is added with this pellet, the increase in silica and alumina was found. However, if these are compared with iron ore pellet, the increase is not so high. Thus, both wastes could be utilized in a suitable proportion without much increase in alumina and silica.

4. Conclusions

Hematite pellet in acidic condition shows 230 kg/pellet CCS and very high RDI (80%). However, when up to 15 wt% mill scale was used, its CCS increases to very high level of 325 kg/pellet and RDI drastically reduces to 24%.

When the slime was used in 15 % mill scale added acidic pellet, its CCS decreases with the increasing slime content. However, it shows ~270 kg/pellet CCS, which is quite acceptable for blast furnaces. Though other properties like RI and swelling indices were found to be excellent, RDI increases to around 45% for 15 wt% mill scale addition, which is not acceptable in blast furnaces.

Due to the above mentioned reason, the basicity of the pellet was improved to 0.3 by adding limestone in the presence of 15 wt% mill scale and a varying amount of slime. Here CCS and RDI had an increasing trend with the increasing slime, but not remarkable. With 15 wt% slime, RDI was found to be only up to 18%. Other properties of pellet are very suitable for the blast furnace application, and the chemical analysis does not show much increase in gangue content.

Hematite pellet with 15 wt% slime and 15 wt% mill scale shows suitable properties in 1200 °C induration and in this way the reduction in induration temperature is possible by ~75 °C.

Thus, the study provides a good quality pellet with improved properties, lowering induration temperature, without increasing gangue content.

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DOBIJANJE PELETA IZ HEMATITSKE RUDE KORIŠĆENJEM KOMBINACIJE ODGORKA I OTPADNOG MULJA NASTALOG PRERADOM GVOZDENE RUDE KAO ADITIVA

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Apstrakt

Otpadni mulj se dobija iz rudnika tokom prerade i ispiranja gvozdene rude i ne uzima se u obzir za peletiranje zbog izuzetne finoće i visokog sadržaja jalovine, uprkos dobrim ‚zelenim' vezivnim svojstvima. Odgorak se dobija u valjaonicama čelika i prilikom ponovnog zagrejavanja peći; u njemu skoro i da nema jalovine, ali se pojedinačno ne uzima u obzir za peletiranje zbog svojih slabih vezivnih sposobnosti. Ako se ova dva otpadna materijala kombinuju i pomešaju sa hematitskom rudom, visok sadržaj jalovine u mulju biće izbalansiran odgorkom u kome nema jalovine. Dok odgorak obezbeđuje egzotermičku toplotu oksidacije FeO i Fe_3O_4 koji se u njoj nalaze i povećava difuzno vezivanje, mulj omogućava dobra ‚zelena'vezivna svojstva za pelet. Stoga je u ovoj studiji dobijen pelet dobrog kvaliteta kombinovanjem mešavine ova dva otpadna materijala u hematitskoj rudi bez velikog povećanja sadržaja jalovine. Do 15% odgorka i 15% mulja može se sa uspehom koristiti. Dobijeni pelet obezbeđuje poboljšanu hladnu kompresivnu snagu (366 kg/ pelet), indeks reducibilnosti (82%), i redukciju indeksa degradacije (8.5%). Temperatura otvrdnuća se može umanjiti za 75 °C, što ukazuje na znatnu uštedu energije u peći za otvrdnjavanje.

Ključne reči: *Odgorak; Mulj; Peletiranje; Sadržaj jalovine; Difuzno vezivanje; Temperature otvrdnuća*