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Mill scale as a potential additive to improve the quality of hematite ore pellet

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ABSTRACT

Hematite pellet is required to be indurated at very high temperature to achieve its good strength as there is no exothermic heat of oxidation unlike magnetite. As mill scale contains mainly FeO and Fe₃O₄, any minor amount of its addition in pellet can provide *in situ* heat and enhance diffusion bonding and sintering. In this study, the mill scale generated in steel plant is added as magnetite input in hematite pellet both in acidic and in basic condition. It has been found that in fluxed pellet, mill scale can improve the properties of pellet. In acidic pellet, the induration temperature has been reduced to a great extent (1250–1275°C) and all properties have been found to be improved due to the addition of 15% mill scale. Mill scale shows enough potential to eliminate the flux addition in producing blast furnace quality pellet from hematite ore. Thus, the flux free acidic pellet has been developed even at very low temperature (1275°C) of induration.

KEYWORDS

Hematite; magnetite; mill scale; flux free pellet; acidic hematite pellet; lowering induration temperature

Introduction

The quality of fired pellets has a strong influence on the productivity of blast furnace and its product quality. Extensive research has undergone over the years in improving the properties of iron ore pellets and making them suitable in achieving lower coke rate, better blast furnace permeability, and improved softening melting characteristics as a blast furnace burden.

Magnetite and hematite concentrates are the two main raw materials for indurated pellet production. Pellet production with magnetite concentrates was given more predominance due to the heat liberation during magnetite oxidation to hematite. However, due to the absence of any exothermic reaction and diffusion bonding, hematite ore pellets require very high induration temperature (>1300°C) which makes the process highly energy intensive. Several investigators have tried to reduce its induration temperature and increasing its strength and other properties by adding several CaO and MgO bearing fluxes. (Umadevi et al. 2011; Meraj et al. 2013; Pal et al. 2014a) However, these fluxes are costly and create complexity in operation like increasing slag volume in the downstream process. Moreover, highly fluxed pellet reduces the basic sinter acceptance capacity of blast furnace. Acidic hematite pellet is advantageous because blast furnace can accept more basic sinter and replace lump ore charging (Jiang et al. 2010; Pal et al. 2014a, 2014b)

Magnetite is an inverse spinel structure with the oxygen ions forming an ABCABC layered packing. The Fe²⁺ occupies the octahedral sites in between the oxygen atoms and Fe³⁺ occupies both tetrahedral and octahedral sites. Several investigators (Gorbachev et al. 2007; Gallagher et al. 1968; Bentell and Mathisson 1978) reported that the oxidation of magnetite particles to α -hematite at intermediate temperatures starts by the formation of hematite needles (lamellae) at particle

surfaces. The hematite needles are formed due to diffusion of Fe²⁺/Fe³⁺ ions in the magnetite phase. At the particle surfaces, Fe²⁺ ions lose one electron to surface adsorbed oxygen, so that Fe³⁺ and O²⁻ ions are formed. The Fe³⁺ ions return to most favorable sites of the hematite crystal being formed, while diffusion of O²⁻ ions is only possible to a limited extent along the hematite–magnetite crystal boundaries. At higher temperatures, fast diffusion through the hematite shell becomes possible. Heat energy is released at the rate of 490 kJ/kg on converting (Ooi et al. 2014) magnetite to hematite which supplements a good amount of heat requirement during induration.

In contrary hematite pellet has no such oxidation, therefore, bonding through recrystallization happens at very high temperature (>1598 K (>1325°C)) for hardening. It may be mentioned that investigators have tried to use cold bonding agents like portland cement (Halt et al. 2015) and fly ash (Eisele et al. 2017) to avoid high temperature induration. In hematite pellet induration, as there is no exothermic heat release, heat can be supplied by adding magnetite ore, coke fines, etc. in the raw material mix to enhance recrystallization between hematite particles (Ball et al. 1973; Ammasi and Pal 2016). During the oxidation of magnetite ore, the Fe₃O₄ gets oxidized to γ -Fe₂O₃, a kind of hematite with the same cubic lattice structure as Fe₃O₄. However, γ -Fe₂O₃ being unstable, the crystal lattice gets rearranged and converts to a hexagonal lattice structure at higher temperatures. Secondly, the induration of pellets occurs by the formation of Fe₂O₃ crystallite bonds or recrystallization of Fe₂O₃ formed by the oxidization process (Li et al. 2009). On analyzing hematite (H) to magnetite (M) blends in the ratios of 70:30 and 50:50, Jiang et al. (2008) reported that the pre-heating time can be reduced with increase in the magnetite ratio in the pellets and the maximum amount of magnetite that can be put in a hematite–

magnetite pellet is 70%. Martinez et al. (2014) observed the microstructure of magnetite–hematite mixed pellets fired at a heating rate of 50°C/min. It showed compact small grains of the sintered phase of the secondary hematite (SH), partially surrounded by a slag phase. In contrast, the fired pellet processed at 5°C/min exhibited a microstructure consisting of the SH phase with a faceted morphology surrounded by a relatively large amount of the slag phase.

Mill scale is a by-product generated during casting and rolling process, chiefly composed of magnetite and it is almost free of any silica or alumina-type gangue. Therefore, use of mill scale can also reduce the proportional amount of alumina and silica in the pellet. In this connection, it is worthy to be mentioned that several investigators have used alternative binders such as corn starch, lignin, molasses, dextrin, and bitumen (Halt and Kawatra 2017), to replace bentonite for reduction of alumina and silica input in pellet. However, use of mill scale in pellet is also an important aspect. Pal et al. (2014b) used mill scale as *in situ* heat source in their Pellet-Sinter Composite Agglomerates (PSCA) and found good strength improvement. Ahmed et al. (1997) observed low drop numbers in complete mill scale pellets which was increased with the addition of lime as binder. Umadevi et al. (2009) added mill scale in iron ore pellets containing carbon and reported that with the addition of 10% mill scale addition, the properties of pellets were satisfactory. Harp et al. (2007) mentioned that increased use of mill scale is limited in sinter as it is found to raise the FeO content of sinter lowering its productivity.

In current study, mill scale is used as magnetite input to the hematite pellet aiming to reduce the induration temperature, improving pellet properties and developing lime-free hematite pellet.

Experimental

Hematite iron ore fines from Noamundi, India, have been taken as the principal raw material for pelletization. The chemical analysis of iron ore fines, fluxes, bentonite, and mill scale used in the study is shown in Table 1. The size fraction of as received iron ore fines was 24% above 6 mm and 36% below 1 mm and mill scale size was 3% above 6 mm and 60% below 1 mm.

Table 1. Chemical analysis of raw materials (wt%).

	Fe ₂ O ₃	FeO	SiO ₂	Al ₂ O ₃	MgO	P	CaO
Iron Ore Fines	91.26	0.52	2.247	2.34	0.013	0.07	0.001
Mill scale	34.32	63.21	0.49	0.28	0.06	-	0.7
Bentonite	12.58	0.1	45.62	11.43	2.79	-	1.65
Limestone	-	-	1.4	0.8	0.7	-	51.51
Olivine	-	-	40.3	0.5	48.1	-	-

Received raw materials were ground in ball mill at 6 kg/ batch for varying time of retention. Specific surface area of ground particles in terms of Blaine fineness (cm²/g) or Blaine number (B.No.) was measured by standard Blaine permeability apparatus (ASTM C-204, 2007). The fluxes, limestone, and olivine were ground to less than #200 BIS mesh.

Pellets of 9–16 mm diameter size range were prepared in a laboratory scale disk pelletizer. The raw materials for pelletization are mixed in various proportions along with various pellet codes are shown in Table 2. The blend compositions have been designed as per the desired amount of mill scale addition, MgO percentage, and basicity (CaO/SiO₂) of the pellet. The resultant chemical compositions of the pellets based upon the blending proportion are shown in Table 3.

The pellet grades A1 to A4 represent fluxed pellets with varying basicity. The pellets B1 and B2 represent complete mill scale acidic pellets with 1% and 0.5% bentonite percentage respectively without flux addition. The pellets C1 to C4 represent acidic pellets without any flux addition and varying mill scale addition. The pellets C4-a and C4-b represent acidic pellets containing 15% mill scale and varying MgO additions. The pellet codes A2-D1 to D3 represent the flux added pellets with increasing percentage of mill scale addition.

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. The average strength of 20 green pellets has been recorded as the GCS. The GDSN was measured by repeatedly dropping individual green pellets on a mild steel plate from a height of 450 mm and counting the number of drops sustained by the pellet before 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 4 hours and subsequently

Table 2. Raw material blend percentages (wt%) for various types of pellets prepared.

Type	Pellet code		Iron ore %	Mill scale %	Olivine %	Limestone %	Bentonite %	Desired MgO %	Desired Basicity (CaO/SiO ₂)
	Group	Sub Group							
Basic	A	A1	96.58	0	2	0.92	0.5	1	0.15
		A2	95.65	0	2	1.85	0.5	1	0.3
		A3	94.4	0	2	3.1	0.5	1	0.5
		A4	92.57	0	2	4.93	0.5	1	0.8
Acidic	B	B1	0	99	0	0	1	0	0
		B2	0	99.5	0	0	0.5	0	0
Acidic	C	C1	99.5	0	0	0	0.5	0	-
		C2	94.5	5	0	0	0.5	0	-
		C3	89.5	10	0	0	0.5	0	-
		C4	84.5	15	0	0	0.5	0	-
		C4-a	84.13	15	0.37	0	0.5	0.2	-
		C4-b	83.5	15	1.0	0	0.5	0.5	-
Basic	A2-D	A2-D1	90.77	5	2	1.73	0.5	1	0.3
		A2-D2	85.9	10	2	1.6	0.5	1	0.3
		A2-D3	81	15	2	1.5	0.5	1	0.3

Table 3. Chemical composition of pellet mix based upon the blend percentages and pellet codes (on dry basis before induration in wt%).

Pellet Code	Fe ₂ O ₃ %	FeO %	SiO ₂ %	Al ₂ O ₃ %	P %	CaO %	MgO %	Basicity
								(CaO/SiO ₂)
A1	88.20	0.50	3.22	2.33	0.068	0.48	1	0.15
A2	87.35	0.50	3.21	2.32	0.067	0.96	1	0.3
A3	86.21	0.49	3.20	2.30	0.066	1.61	1	0.5
A4	84.54	0.48	3.18	2.27	0.065	2.55	1	0.8
B1	34.10	62.58	0.94	0.39	0.00	0.02	0.09	0.02
B2	34.21	62.89	0.72	0.34	0.00	0.01	0.07	0.01
C1	90.87	0.52	2.46	2.39	0.070	0.01	0.027	0.004
C2	88.02	3.65	2.38	2.28	0.066	0.044	0.029	0.02
C3	85.17	6.79	2.29	2.18	0.063	0.08	0.032	0.035
C4	82.33	9.92	2.20	2.08	0.059	0.114	0.034	0.052
C4-a	81.99	9.482	2.341	2.07	0.059	0.114	0.2	0.049
C4-b	81.41	9.482	2.581	2.058	0.058	0.114	0.5	0.044
A2-D1	84.61	3.161	3.122	2.22	0.064	0.94	1.0	0.30
A2-D2	81.89	6.322	3.04	2.12	0.06	0.9	1.0	0.30
A2-D3	79.13	9.482	2.95	2.017	0.057	0.89	1.0	0.30

measuring the weight loss in the sample in wt%. The DCS of the oven-dried pellets was tested in a Hounsfield Material testing Machine (Model: H10K-S). The machine is connected with a PC having data capturing system. The properties of the green pellets are reproducible with an error band of $\pm 5\%$.

The green pellets in various batch sizes ranging between 0.1 kg and 1.5 kg were indurated in an electrically heated chamber furnace (Heating element: Mo-Si₂) at various temperatures for 15 minutes at the set temperature. 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 is 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 indicates the degradation of pellets in the upper part of blast furnace. Swelling index (SI) was measured after reduction as per JIS: M 8713–2000 at a temperature of 900°C by measuring its volume change percentage between before and after reduction by mercury displacement method. The reducibility index (RI) measured as per the standard JIS: M 8713–2000 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 was done using Siemens D500 X-ray diffractometer using Cu-K α radiation. The scanning speed has been maintained at 2 θ , 1°/min. The existence of phases has been identified by XRD analysis software Highscore Plus based on Inorganic Crystal Structure Database (ICSD) from PANalytical. The scanning electron microscope imaging was done to study the morphology of iron ore fines and mill scale. Selected pellet samples were observed under the optical microscope (LEICA, DM 2500 M) to study the distribution of phases and pores.

Table 4. Particle size distribution of ground materials.

Ground materials	Blaine fineness cm ² /g	Size range (μ m)				
		–1000 + 200	–200 + 100	–100 + 75	–75 + 45	–45
Iron ore fines, (wt%)	2200	17.84	13.58	4.65	7.5	56.43
Mill Scale (wt%)	2190	10.28	11.67	5.37	9.83	62.85

Results and discussion

Properties of Noamundi iron ore pellets

Iron ore fines were ground to about 2200 cm²/g Blaine fineness whose size fractions are shown in Table 4. Earlier investigators also used this fineness level (Pal et al. 2015) 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 and basic pellets are shown in Table 5. All properties appear very good and acceptable. In indurated condition the properties of acidic pellets and basic pellets are different as shown in Table 6. CCS is much lower in acidic pellets; i.e., acidic pellets require much higher induration temperature. Though acidic pellet is highly reducible, RDI is very high. This is because of absence of slag bond formation. Figure 1 shows minimum RDI at 0.3 basicity and beyond that both RDI and CCS increases with increase in basicity. However, a good CCS is observed at 0.3 basicity too. Thus, 0.3 basicity was considered as optimum.

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. Since, CCS increases with increase in basicity, the basic pellet provides very high strength even at the low temperature. Increasing basicity may be one option of decreasing the induration temperature of hematite ore. Though, at 0.3 basicity, RDI is very good, at higher basicity it again starts to increase and reducibility starts to decrease. Thus, a minor increase in basicity may be one solution to increase CCS, reduce induration temperature, and decrease RDI. Fan et al. (2010) also reported that 0.4 is the suitable basicity for good pellet preparation and at high basicity, excessive liquid phase formation destroys the structure of pellet. Possibility of reducing induration temperature, increasing CCS, and decreasing RDI of acidic hematite ore pellets has been explored by addition of mill scale, which will be discussed in proceeding sections.

Use of mill scale as additive

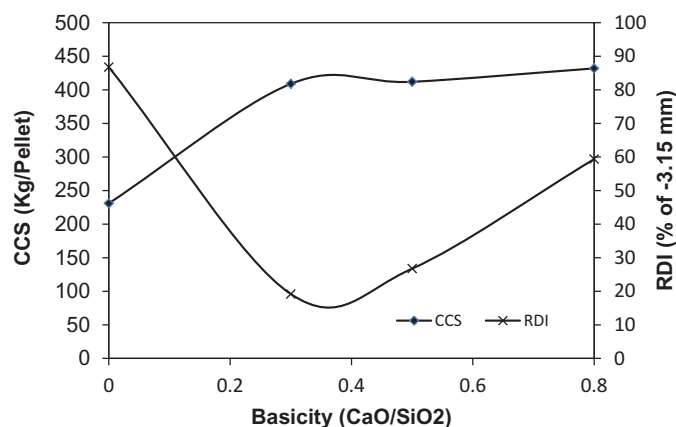
Pellets have been made in varying percentage of mill scale, using same Blaine fineness (~ 2200 cm²/g) of iron ore and mill scale. The green properties, viz. GCS, GDSN, and DCS of 0–15 wt % mill scale added pellets were found to be in the range of 1.8–2 kg/pellet, 25–30 nos., and 7–9 kg/pellet, respectively. These are found to be acceptable. However, pure mill scale pellets show very poor drop numbers (2–3 nos.) which is unsuitable for use. This is because the moisture content of mill scale green pellet is very low. Surface morphology of mill scale and iron ore particles are shown in Figure 2. It is evident that mill scale particles have smooth surfaces with sharp edges which is not favorable for green bonding. Due to this reason, any high amount of mill scale addition may affect the green pellet properties. However, up to 15% addition did not affect.

Table 5. Green and dry properties of Noamundi ore pellets.

Pellet	Code	GCS, kg/ pellet	Drop Nos	DCS, kg/ pellet	Moisture content of green pellet, wt%
Acidic	C1	2.02	30.5	9.73	9.55
Basic (Basicity = 0.3)	A2	1.905	22.2	5.51	9.62

Table 6. Properties of indurated pellets from Noamundi ore.

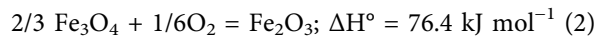
Pellet	Code	Ind Temp, °C	CCS kg/ pellet	RI, %	RDI, %	SI, %	AP, %
Acidic	C1	1275	231	96.11	86.76	18.86	24.21
Basic (Basicity = 0.3)	A2	1275	408	84.71	19.18	17.95	18.024

**Figure 1.** Effect of basicity on CCS and RDI of indurated fluxed pellet.

Physical properties of mill scale added pellets

Effect of CCS on induration temperature is shown in Figure 3 (only MS, varying MS, only iron ore). Strength properties increase with increasing addition of mill scale in pellet. Complete mill scale pellets show a CCS of >250 kg/pellet at a temperature of 1000°C. Only at 1200°C, 15% mill scale added pellet shows around 225 kg/pellet CCS, which appear to be quite attractive. For further increasing temperature up to 1275°C, CCS increases to a great extent (>300 kg/pellet) while acidic iron ore pellet without mill scale shows very low strength (210 kg/pellet). Thus, further increase in temperature is required for acidic pellets without mill scale to get good strength. Many researchers have found it to be as high as 1325°C (Pal et al. 2015). However, in 15% mill scale added acidic pellet, nearly 250 kg/pellet CCS is achieved at 1250°C induration temperature (Figure 3), which is suitable for blast furnace operation. Thus, the requirement of induration temperature in acidic pellet can be reduced by 75°C by addition of 15% mill scale. Suitability of other properties of this pellets is also discussed in proceeding sections.

Mill scale mainly contains FeO and Fe₃O₄. During induration of pellet, oxidation of Fe²⁺ to Fe³⁺ may take place with the liberation of exothermic heat of oxidation, which help in diffusion bonding and enhances recrystallization of hematite grains. The formed Fe³⁺ may return to favorable sites within the pellet forming interconnecting bridges between the individual grains and increasing bonding by diffusion even at low temperatures. The possible reactions are:



The XRD pattern of acidic iron ore pellets with and without the addition of mill scale is shown in Figure 4. Mainly, Fe₂O₃ phases have been found in both the pellets. This indicates that almost entire amount of FeO/Fe₃O₄ phase in mill scale gets converted to Fe₂O₃ as per above reaction. However, the presence of any minor amount of Fe₃O₄ is not traceable in XRD analysis.

A good quality sintering has been observed from the comparative microstructure of indurated pellets with and without addition of mill scale as shown in Figure 5. The effect of mill scale addition on apparent porosity of pellet is shown in Figure 6. Apparent porosity of acidic pellets was found to decrease with increasing mill scale addition. This may be the primary reason of strength improvement in acidic pellet with increasing amount of mill scale addition. Figure 5 shows that better bonding and bridge formation between adjacent hematite grains happens in 15% mill scale added pellet. Moreover, in mill scale added pellet the pore area is much less than the pellets without mill scale. Decreasing void space, formation of bridging and coarsening of hematite grains are also prominent in mill scale added pellets, which help increasing the CCS of pellets. However, in acidic iron ore pellets without mill scale, the sintering process occurs in a natural way as there is no such phenomena. Surface energy, grain boundaries, and lattice defects are the main driving forces and it requires very high temperature.

Physicochemical properties of mill scale added pellets

Effect of mill scale addition on RI of the pellets is shown in Figure 7. RI has been found to be very high (90–95%) up to 15% mill scale addition. It is similar to the acidic pellet. Since, apparent porosity decreases with increase in mill scale content (Figure 6) reducibility decreases slightly. Swelling index decreases gradually with increase in mill scale percentage and it shows below 10% for 15% mill scale addition. Better sintering and bonding between grains may be the prime reason behind this.

The effect of increasing mill scale addition (C1–C4) on the RDI is shown in Figure 8. Acidic hematite ore pellet without mill scale has exceptionally high RDI. Lu et al. (2007) reported that the presence of Al₂O₃ as solute in hematite is responsible for high RDI. Hematite containing alumina produces distorted structure during reduction at low temperature (Pimenta and Seshadri 2002). As can be observed, a significant reduction in the RDI of acidic pellets could be obtained with increasing mill scale addition. This is because with increase in mill scale percentage, bond strength not only increases but also total gangue content along with alumina content decreases. Due to the decrease in alumina content, RDI decreases. However, the RDI is found to be 25% even at 15% mill scale addition, which is apparently more than the industrially acceptable limit of RDI for BF grade pellets (<20% of –3.15 mm).

It may be recalled that we aimed to produce a lime-free acidic pellets. 15% mill scale added acidic pellet shows improved RDI and very good other properties. However,

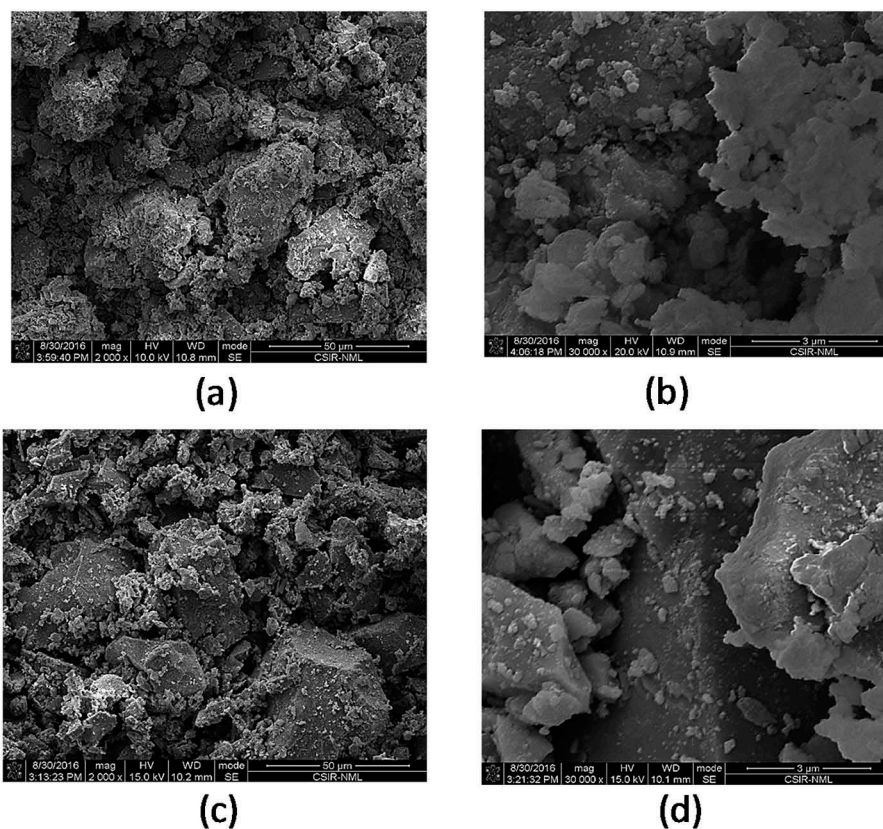


Figure 2. Surface morphologies of hematite ore fines and mill scale fines. (a) Hematite ore fines (2000x) (b) Hematite ore fines (30000x) (c) Mill scale fines (2000x) (d) Mill scale fines (30000x).

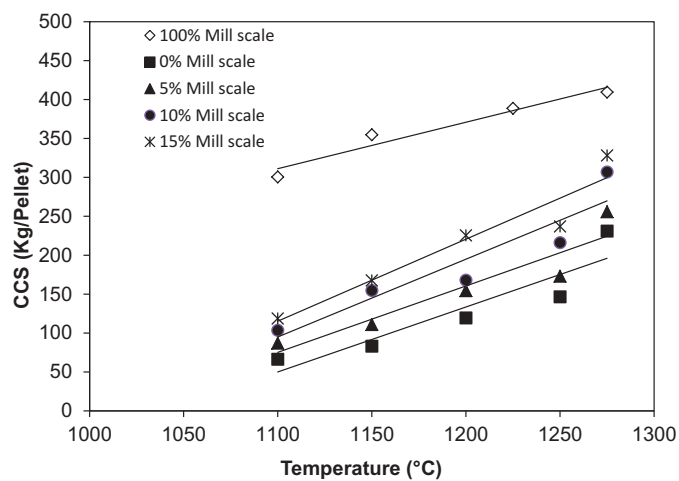


Figure 3. Effect of CCS on induration temperature of pellets with varying mill scale.

obtained RDI (25%) is not acceptable and slightly above the acceptable limit. Therefore, a minor addition of MgO is done to reduce its RDI below the acceptable limit. The beneficial effect of MgO addition has also been reported by other investigators (Thaning 1976; Pal et al. 2015). For decreasing the RDI without increasing basicity, MgO in the form of olivine was added in pellets C4-a, C4-b containing 15% mill scale.

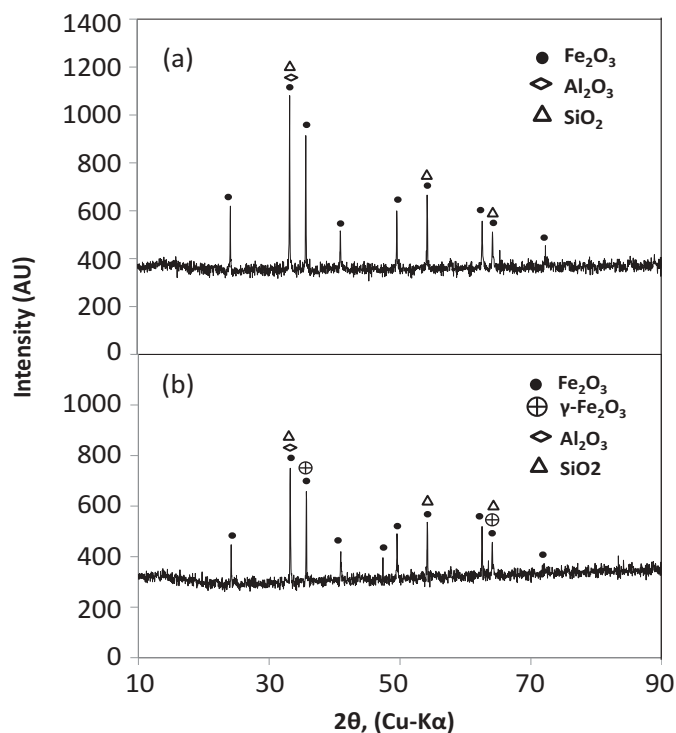
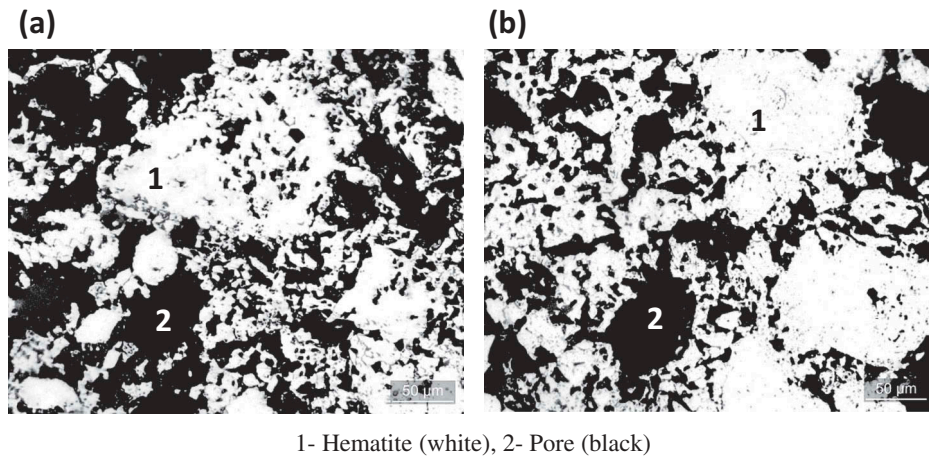
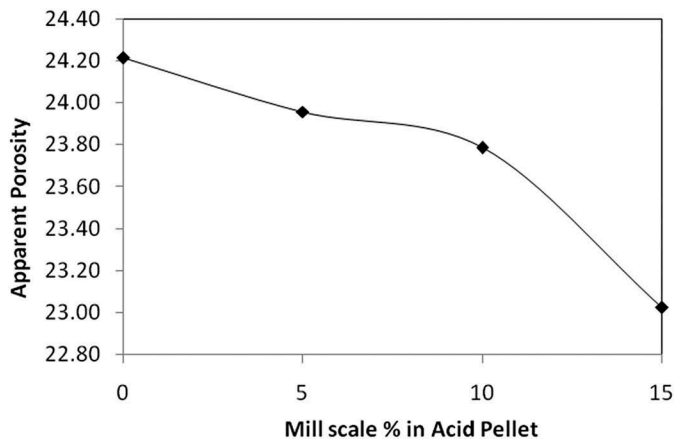
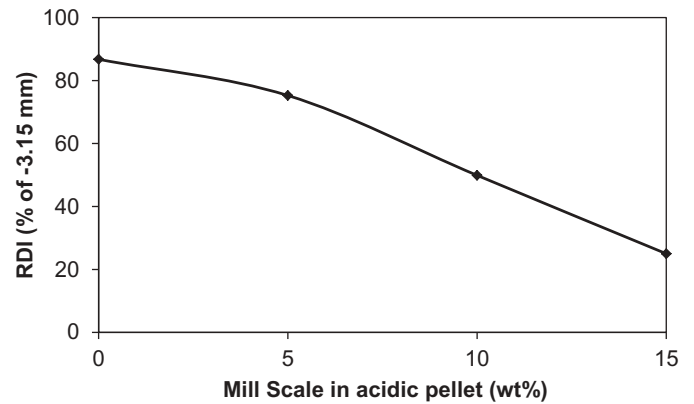
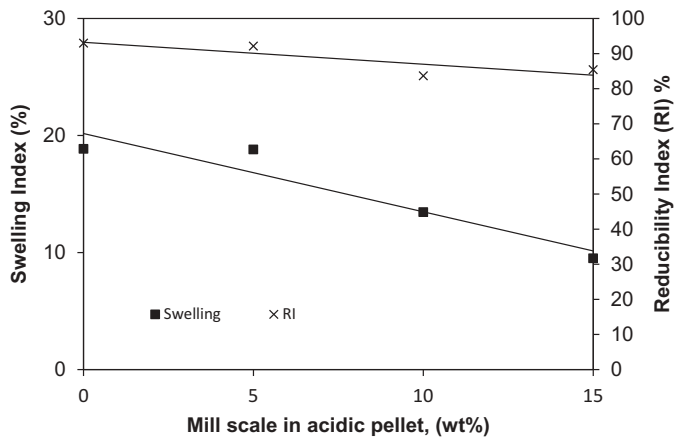
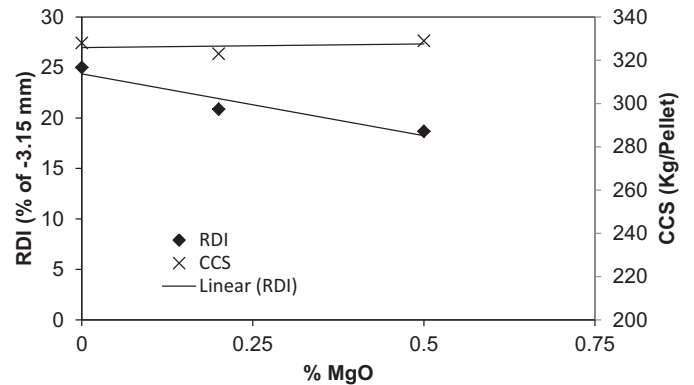


Figure 4. XRD pattern of acidic iron ore pellets with and without the addition of mill scale indurated at 1275°C. (a) Acidic iron ore pellet without mill scale (b) Acidic iron ore pellet with 15% mill scale.



1- Hematite (white), 2- Pore (black)

Figure 5. Optical microstructure of acidic pellet indurated at 1275°C. (a) Acidic iron ore pellet without mill scale (b) Acidic iron ore pellet with 15% mill scale.

Figure 6. Effect of mill scale on apparent porosity in acidic pellet.

Figure 8. Effect on RDI of acidic pellet indurated at 1275°C at varying amount of mill scale addition.

Figure 7. Effect of mill scale addition on the RI and SI of acidic pellets.

Figure 9. Effect of MgO addition on the CCS and RDI of acidic pellets containing 15% mill scale.

Increasing MgO content leads to more magnetite and less hematite in sinter/pellet (Lu et al. 2007), because, MgO in iron oxide crystal forms magnetite spinel during cooling and solidification. It may cause less strain in pellet during reduction.

There is not much change in green properties due to addition of up to 1 wt% olivine in the acidic mill scale pellet.

The CCS and RDI of acidic pellets containing 15% mill scale with increasing MgO are shown in Figure 9. It can be observed that the RDI is found to decrease to 18.67% at 0.5% MgO addition in acidic pellets containing 15% mill scale and CCS remains similar. RI and swelling index were 90.3 and 11.9%, respectively which looks to be very good. Hence, with 15% mill scale and 0.5% MgO addition, industrially acceptable acidic pellets with low RDI can be produced.

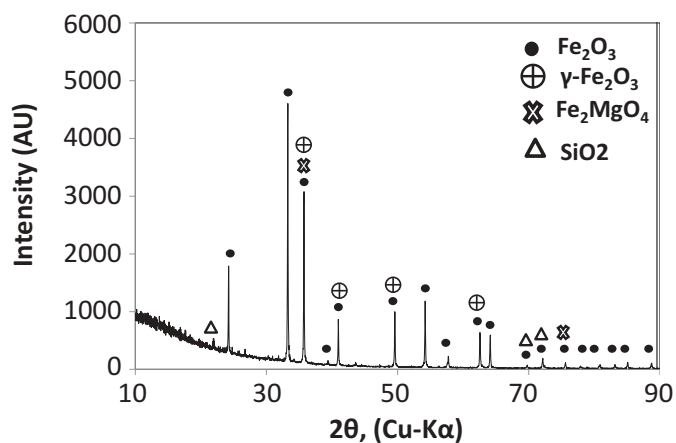


Figure 10. XRD pattern of mill scale added (15 wt%) acidic pellet containing 0.5% MgO.

Fe_2MgO_4 phase in XRD analysis has been found as shown in Figure 10, which is less reducible than hematite at low temperature. Thaning (1976) has also reported that at low temperature reduction, magnesio-ferrite does not render itself to reduction and starts reducing at later stage of reduction being converted into magnesio-wustite. Thus, the strain in pellet during low temperature reduction becomes lower and prevents breakage which improves RDI of pellet.

Thus, completely lime-free pellets (acidic) with 15% mill scale and 0.5 % MgO addition can be prepared which has acceptable RDI and other properties to be suitable for using in blast furnace.

Effect of addition of mill scale in the properties of fluxed pellets

Green and dry properties of 15% mill scale added fluxed pellet are very good which are shown in Table 7. CCS of 0.3 basicity pellet with and without addition of mill scale is shown in Figure 11. Although at lower temperature, CCS of mill scale added fluxed pellet is higher than fluxed pellet without mill scale, at high temperature above 1200°C, any significant difference has been found. This is because of high gangue content of ore and a dominant role of slag bonding. There is no significant change in apparent porosity also as shown in Figure 12. Therefore, the addition of mill scale in fluxed pellet does not influence so much on strength properties.

The XRD pattern of 0.3 basicity iron ore pellets with and without the addition of mill scale is shown in Figure 13. Basic pellets without mill scale were found to have high calcium glassy phase such as Ca_3SiO_5 when compared to the formation of CaSiO_3 in basic pellets containing mill scale. This may be attributed to the lowering of gangue content in pellets with

Table 7. Green and dry properties of mill scale added fluxed pellet.

Pellet Code	GCS	GDSN	DCS
A2-D1	1.814	14.1	6.87
A2-D2	2.36	18.6	8.97
A2-D3	1.74	17.5	6.44

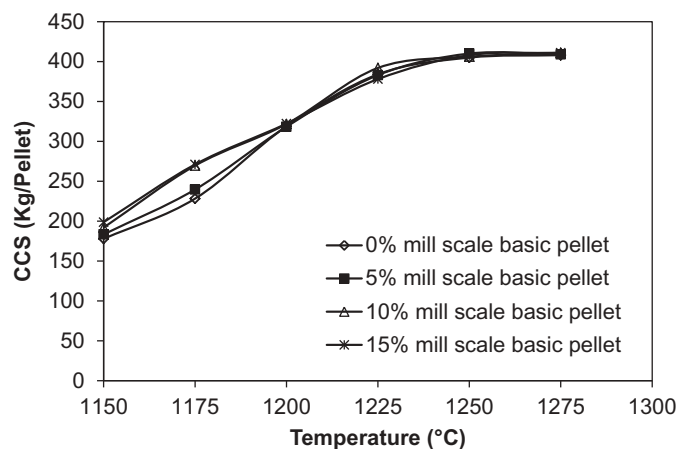


Figure 11. CCS of 0.3 basicity pellet with and without addition of mill scale.

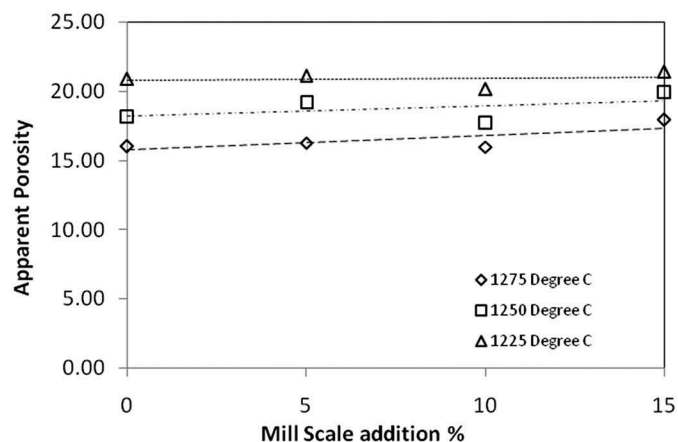


Figure 12. Effect of mill scale addition on the apparent porosity of 0.3 basicity hematite pellet at different temperature.

the addition of mill scale. CaO react more favorably with magnetite in mill scale and increases di-calcium ferrite ($\text{Ca}_2\text{Fe}_2\text{O}_5$) and the rest of CaO react with silica to form CaSiO_3 in place of Ca_3SiO_5 .

The microstructure of 0.3 basicity iron ore pellet, A2 and 15% mill scale containing basic pellet A2-D3 is shown in Figure 14. The presence of high amount of slag is observed in 0.3 basicity iron ore pellet. In the mill scale added basic pellet, the presence of magnesio-ferrite is observed in addition to slag which is filling the pores between the grains.

Basic iron ore pellets with 0.3 basicity and varying additions of mill scale, indurated at 1275°C for 15 minutes were tested for the RDI, RI, and SI values. Figure 15 gives the effect of mill scale addition on the RDI of basic pellets. The RDI has been found to decrease with increasing addition of mill scale. This is because the possibility of formation of Ca_3SiO_5 phase becomes less with addition of mill scale. $\text{Ca}_2\text{Fe}_2\text{O}_5$ and CaSiO_3 in mill scale added pellet (Figure 13) can provide much stable bonding under reduction than Ca_3SiO_5 in pellet without mill scale. Therefore, mill scale addition in fluxed pellet reduces the degradation property of pellet. The effect of mill scale addition on the RI and SI of pellets is shown in the Table 8. It can be

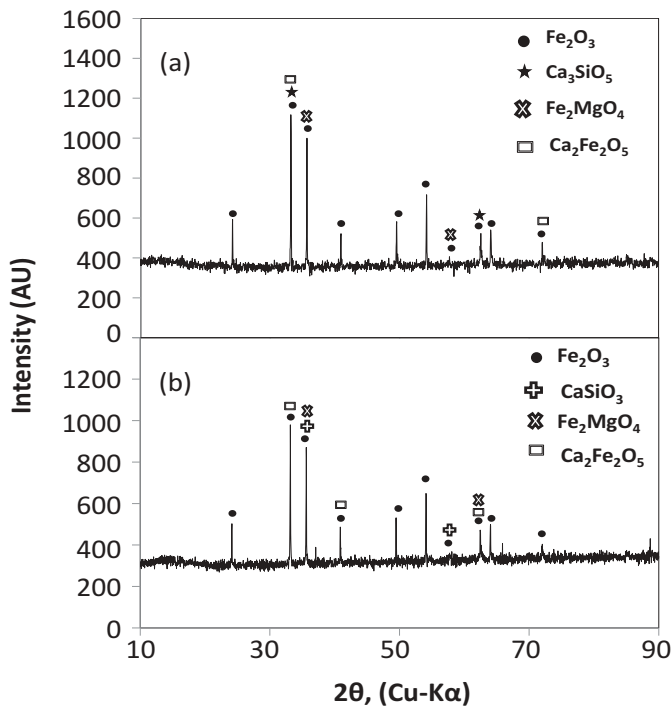


Figure 13. XRD pattern of basic iron ore pellet with and without the addition of mill scale (a) Iron ore basic pellet (0.3 basicity) indurated at 1275°C (b) mill scale added (15wt%) basic pellet (0.3 basicity) indurated at 1275°C.

observed from Table 8 that the pellets with increasing mill scale addition have almost similar RI and SI values and are found to be acceptable for blast furnace.

It may be noted from the above result that mill scale helps in improving the properties of both acidic and basic pellets made from hematite ore. The improvement has been found to be more in acidic pellet than in basic pellet. This is because, in acidic pellet, the bond formation occurs by solid state bonding mechanism through diffusion and recrystallization. The mill scale facilitates both the phenomena. In contrary, in basic pellet ($B = 0.3$), major bond formation happens through slag bonding and the slag bond formation depends upon gangue content and basicity. Since the present ore in this study has high gangue

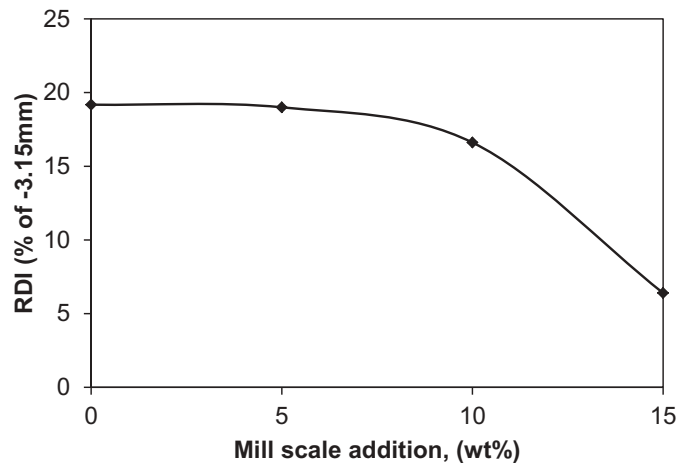


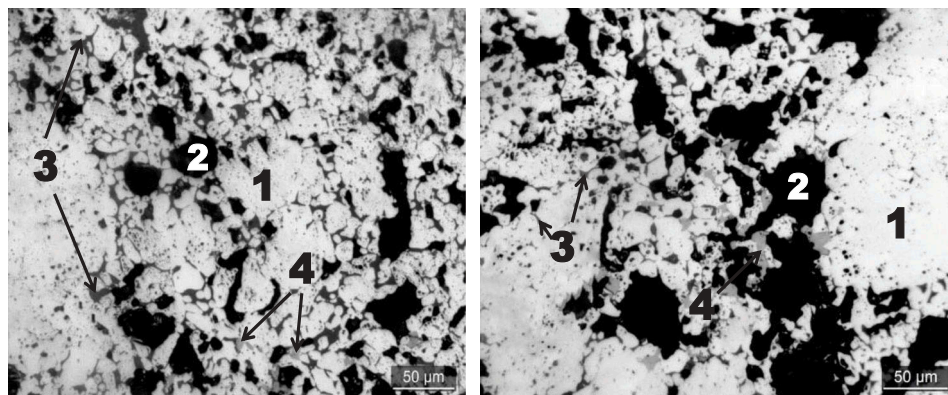
Figure 15. Effect of mill scale addition on the RDI of 0.3 basicity iron ore pellet.

Table 8. Effect of mill scale addition on the RI and SI of 0.3 basicity hematite pellets.

Pellet Code	Mill scale addition %	RI %	SI %
A2	0	84.71	17.95
A2-D1	5	92.78	18.5
A2-D3	15	87.44	17.72

content, a good amount of lime has to be added to maintain 0.3 basicity. Thus, a high amount of slag bond formation happens and takes a major role to control the pellet property. Therefore, the effect of mill scale is very minor in fluxed pellet.

It is clear from the above that mill scale has a very good role on improving properties of acidic pellet. Use of acidic pellet in blast furnace is very important for accommodating very highly basic sinter. Highly basic sinter shows better physical and metallurgical properties than low basicity sinter. On the other hand, there is a severe scarcity of good quality lump ore. In this situation acidic pellet and highly basic sinter would be a good combination in blast furnace. Thus, our developed acidic pellet can be an important charge material in blast furnace.



1- Hematite (white), 2- Pore (black), 3- Slag (dark grey), 4- Magnesioferrite (light grey)

Figure 14. Optical microstructure of iron ore basic pellet with and without the addition of mill scale, indurated at 1275°C for 15 minutes. (a) Iron ore basic pellet (0.3 basicity) (b) mill scale added (15wt%) basic pellet (0.3 basicity).

Conclusions

Mill scale provides *in situ* heat that facilitates diffusion bonding and recrystallization bonding to improve pellet strength. It shows much better result in acidic pellet than in basic pellet.

Mill scale addition can reduce the induration temperature of pellet and decreases the energy consumption in induration strand. Only 15% mill scale addition can reduce induration temperature by 75°C.

It is possible to produce the lime-free acidic pellet which has very good properties to be suitable for blast furnace use. Lime-free acidic pellet with highly basic sinter may be a good choice combination in blast furnace.

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Disclosure statement

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the article.

References

- Ahmed, Y. M. Z., Khedr, M. H., Mohamed, O. A., and Shalabi, M. E. H., 1997, "The role of calcium hydroxide in the production of iron oxide (Mill Scale) pellets." *Fizykochemiczne Problemy Mineralurgii*, 31. pp. 31–41.
- Ammasi, A., and Pal, J., 2016, "Replacement of bentonite in hematite ore pelletisation using a combination of sodium lignosulphonate and copper smelting slag." *Ironmaking and Steelmaking*, 43. pp. 203–213.
- Ball, D. F., Dartnell, J., Davison, J., Grieve, A., and Wild, R., 1973, *Agglomeration of Iron Ores*, 1st ed., New York: American Elsevier Publishing Company, Inc., pp. 324–327, 147.
- Bentell, L., and Mathisson, G., 1978, "Oxidation and slag-forming process in dolomite fluxed pellets based on magnetite concentrates." *Scandinavian Journal of Metallurgy*, 7. pp. 230–236.
- Eisele, T. C., Haselhuhn, H. J., and Kawatra, S. K., "Production of Inorganic Pellet Binders from Fly-Ash", Technical Report, 1995, source: <https://www.osti.gov/scitech/servlets/purl/205641>, accessed on 24th November, 2017
- Fan, X.-H., Gan, M., Jiang, T., Yuan, L.-S., and Chen, X.-L., 2010, "Influence of flux additives on iron ore oxidized pellets." *Journal of Central South University of Technology*, 17. pp. 732–737.
- Gallagher, K. J., Feitknecht, W., and Mannweiler, U., 1968, "Mechanism of oxidation of magnetite to γ -Fe₂O₃." *Nature*, 217. pp. 1118–1121.
- Gorbachev, V. A., Abzalov, V. M., and Yur'ev, B. P., 2007, "Conversion of magnetite to hematite in iron-ore pellets." *Steel in Translation*, 37. pp. 336–338.
- Halt, J. A., and Kawatra, S. K., "Review of organic binders for iron ore agglomeration", online source: http://chem.mtu.edu/chem_eng/skka/watr/2013/2013_May_OrganicBinderReview.pdf, accessed on 24th November, 2017
- Halt, J. A., Roache, S. C., and Kawatra, S. K., 2015, "Cold bonding of iron ore concentrate pellets." *Mineral Processing & Extractive Metallurgy Review*, 36. pp. 192–197.
- Harp, G., Mohring, S., Hillmann, C., and Bsirske, W., 2007, "Alternative processing of sinter plant recycling materials." *Technical Steel Research, European Commission, EUR*, 22974. pp. 1–77.
- Jiang, T., Li, G. H., Wang, H. T., Jhang, K. C., and Jhang, Y. B., 2010, "Composite agglomeration process (CAP) for preparing blast furnace burden." *Ironmaking and Steelmaking*, 37. pp. 1–7.
- Jiang, T., Zhang, Y. B., Huang, Z. C., Li, G. H., and Fan, X. H., 2008, "Preheating and roasting characteristics of hematite–magnetite (H–M) concentrate pellets." *Ironmaking and Steelmaking*, 35. pp. 21–26.
- Li, G. H., Li, X. Q., Zhang, Y. B., He, G. Q., and Jiang, T., 2009, "Induration mechanisms of oxidised pellets prepared from mixed magnetite–haematite concentrates." *Ironmaking and Steelmaking*, 36. pp. 393–396.
- Lu, L., Holms, R. J., and Manuel, J. R., 2007, "Effects of alumina on sintering performance of hematite iron ores." *ISIJ International*, 47. pp. 349–358.
- Martinez, N. P., Trejo, M. H., Estrella, R. M., Román, M. D. J. C., Esparza, R. M., and Villareal, M. C., 2014, "Induration process of pellets prepared from mixed magnetite–35% hematite concentrates." *ISIJ International*, 54. pp. 605–612.
- Meraj, M. D., Pramanik, S., and Pal, J., 2013, "Role of MgO and its different minerals on properties of iron ore pellets." *Transactions of the Indian Institute of Metals*, 69. pp. 1141–1153.
- Ooi, T. C., Hardwick, S. C., Zhu, D., and Pan, J., 2014, "Sintering performance of magnetite–hematite–goethite and hematite–goethite iron ore blends and microstructure of products of sintering." *Mineral Processing & Extractive Metallurgy Review*, 35. pp. 266–281.
- Pal, J., Arunkumar, C., Rajshekhkar, Y., Das, G., Goswami, M. C., and Venugopalan, T., 2014a, "Development on iron ore pelletization using calcined lime and MgO combined flux replacing limestone and bentonite." *ISIJ International*, 54. pp. 2169–2178.
- Pal, J., Ghorai, S., Agarwal, S., Nandi, B., Chakraborty, T., Das, G., and Prakash, S., 2015, "Effect of Blaine fineness on the quality of hematite iron ore pellets for blast furnace." *Mineral Processing & Extractive Metallurgy Review*, 36. pp. 83–91.
- Pal, J., Ghorai, S., Goswami, M. C., Prakash, S., and Venugopalan, T., 2014b, "Development of pellet-sinter composite agglomerate for blast furnace." *ISIJ International*, 54. pp. 620–627.
- Pimenta, H. P., and Seshadri, V., 2002, "Influence of Al₂O₃ and TiO₂ degradation behaviour of sinter and hematite at low temperatures on reduction." *Ironmaking and Steelmaking*, 29. pp. 175–179.
- Thaning, G., 1976, "Reduction strength on superfluxed pellets made from rich magnetite concentrate." *Ironmaking and Steelmaking*, 2. pp. 57–62.
- Umadevi, T., Kumar, M. G. S., Mahapatra, P. C., Babu, T. M., and Ranjan, M., 2009, "Recycling of steel plant mill scale via iron ore pelletisation process." *Ironmaking and Steelmaking*, 36. pp. 409–415.
- Umadevi, T., Kumar, P., Naveen, F. L., Prabhu, M., Mahapatra, P. C., and Ranjan, M., 2011, "Influence of pellet basicity (CaO/SiO₂) on iron ore pellet properties and microstructure." *ISIJ International*, 51. pp. 14.