INVESTIGATION OF DRI PHYSICAL PROPERTIES UNDER HYDROGEN REDUCTION CONDITIONS

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SYNOPSIS

Transitioning to using hydrogen (H_2) as the reductant gas for producing direct reduced iron (DRI) is becoming increasingly relevant in the quest to decarbonize the global steel industry. The physical properties of DRI are important measurements of its value to the steelmaker, as well as key factors in the performance of direct reduction (DR) processes. This paper will examine how two of the physical properties of DRI – strength and clustering – are affected when produced under hydrogen reduction conditions in comparison with natural gas-based DRI.

Keywords: Direct Reduction, Direct Reduced Iron (DRI), Hydrogen-Based Ironmaking

INTRODUCTION

The combination of DRI and the electric arc furnaces (EAF) has given rise to one of the biggest iron and steel industry facelifts in history – decarbonization. Steel production via the DRI-EAF route has the lowest carbon dioxide (CO_2) emissions of any iron ore-based method.

Direct reduction (DR) plants using clean-burning natural gas are seen as the most viable near-term response to the need to reduce CO_2 emissions associated with iron and steel production. As sufficient volumes of hydrogen (H_2) at competitive prices become available for use as fuel and reductant in DR plants, these natural gas-based plants can be modified to use high percentages of hydrogen and new plants will be designed to operate on 100% hydrogen.

However, the realization that DRI produced with H_2 as reductant will contain almost no carbon has prompted other questions, such as "What will be the impact on DRI strength and clustering?".

At the Midrex Research & Development Technology Center, we have taken steps to examine the impact on the quality of DRI when using H_2 gas as reductant by comparing key physical characteristics under standard natural-gas reduction conditions and H_2 reduction conditions. The scope of our test work included:

1. Strength of DRI pellets
2. Clustering behavior of iron oxide pellets and lump ores

This paper will examine the methodology we used to compare DRI produced using natural gas and hydrogen and will present our findings related to the strength of DRI using each of the reducing gases, as well as the effect on clustering behavior of various iron oxides.

Authors' Note: Direct reduced iron (DRI) produced with H_2 gas as reducing gas will be termed as H2-DRI, and those produced from carbonaceous gas will be named as NG-DRI in this paper.

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DISCUSSION

MATERIALS & METHODS

Iron Oxide Chemical Composition

Two DR-grade pellets along with four additional iron oxide feedstocks were compared. The additional oxides included two lump ores and a BF-grade pellet with total iron content varying from 54% to ~ 65% (total iron content of the iron oxide must be greater than 67% to be classified as DR-grade).

The chemical composition of these iron oxides, as measured by Midrex, are listed in Table 1.

Table 1: Chemical composition of iron oxides

Chemical composition, %	Lump A	Lump B	BF-grade	DR-grade 1	DR-grade 2
Total iron, T.Fe	54.04%	60.41%	65.40%	68.06%	68.02%
SiO_2	5.46%	5.65%	5.51%	1.40%	0.90%
Al_2O_3	1.97%	5.97%	0.35%	0.37%	0.19%
$SiO_2 + Al_2O_3$	7.42%	11.62%	5.86%	1.78%	1.09%
CaO	0.04%	0.03%	0.67%	1.06%	0.89%
MgO	0.06%	N/A	0.32%	0.51%	0.64%
CaO + MgO	0.10%	0.03%	0.99%	1.58%	1.53%
P	0.03%	0.095%	0.021%	< detect	0.037%
S	< detect	< detect	< detect	< detect	< detect
C	< detect	< detect	0.01%	0.057%	0.03%
TiO_2	0.09%	0.31%	0.03%	0.06%	0.15%
Na_2O	0.048%	< detect	< detect	< detect	< detect
K_2O	0.071%	< detect	< detect	< detect	< detect
MnO	< detect	0.077%	< detect	0.223%	0.061%
Fe^{++}	0.31%	0.41%	0.17%	0.34%	0.32%

Iron Oxide Particle Size Distribution (PSD) and Physical Properties

The PSD and physical properties of the lump ores and iron oxide pellets were evaluated. Due to the different characteristics of lump ores and iron oxide pellets, the PSD measurement and physical properties of lump ores and iron oxide pellets were measured differently and are presented in separate tables, as shown in Table 2 and Table 3.

Typically, the desired bulk density for lump ores and pellets is at least 2200 kg/m^3 and the preferred tumble indices for lump ores and pellets are 90% +6.73 mm (>85% is acceptable) and 95% +6.73 mm (>92% is acceptable), respectively. Furthermore, the preferred oxide sizes are >95% of 9 – 16 mm and <3% of 5 mm for oxide pellets, and >85% of 10 – 35 mm and <5% of -5 mm for lump ores.

Table 2: PSD and physical properties of Lump Ores A and B		
Particle size distribution	Lump A	Lump B
+50 mm	0.0%	0.0%
+38.1 mm	6.1%	7.4%
+31.5mm	14.9%	19.7%
+25 mm	28.1%	35.4%
+22.1 mm	34.9%	43.5%
+19 mm	45.1%	57.3%
+12.7 mm	67.2%	80.4%
+6.73 mm	93.4%	95.7%
+3.36 mm	96.1%	97%
-3.36 mm	3.9%	3.0%
Physical Properties		
Bulk density (kg/ m^3)	1945	1983
Tumble test indices		
+6.73 mm	81.8%	83.7%
+3.36 mm	85.1%	86.3%
+0.6 mm	88.2%	89.3%

Table 3: PSD and physical properties of BF-grade and DR-grade oxide pellets			
Particle size distribution	BF-grade	DR-grade 1	DR-grade 2
+16 mm	0.1%	0.3%	0.4%
+12.7 mm	27.8%	47.3%	40.4%
+9.53 mm	89.6%	95.3%	95%
9 x 16 mm (spec > 95%)	89.5%	95.0%	94.6%
Compression strength (kg) (spec > 225)	351	225	299
Bulk density (kg/ m^3)	2116	2180	2262
Apparent density (kg/ m^3)	3844	3744	4022
True density (kg/ m^3)	4693	5140	5195
Porosity (%)	18.1%	27.2%	22.6%
Tumble test indices			
+6.73 mm	95.7%	95.2%	94.5%
+3.36 mm	96.6%	95.3%	94.7%
+0.6 mm	96.9%	95.4%	94.8%

Linder Test

The Midrex Linder Test, adapted from ISO-11257, was conducted to evaluate degradation due to abrasion under both natural gas reduction and hydrogen reduction conditions. The Linder furnace was operated for 5 hours at 760° C under reducing atmosphere to determine the metallization of iron oxides. The Linder furnace is designed so that the retort constantly rotates axially, and the material is subjected to abrasion. This is intended to simulate the frictional forces on the material as it moves through the shaft furnace. The Linder Test is run with two replicates.

Test parameters and analysis are listed below.

- 93% metallization and <2% -3.36 mm for indurated oxide pellets
- CO 36%, CO_2 5%, H_2 55%, CH_4 4% reducing gas composition for natural gas reduction, whereas the gas composition for H_2 reduction consists of 100% H_2
- Testing conducted at 760° C for 5 hours
- Test portions approximately 500 g of representative sample
- Chemical analysis performed for + 3.36 mm DRI product
- Screen size distribution to measure degradation of agglomerations

Degradation during reduction was quantified by screen analysis of the Linder product. For indurated oxide pellets, the preferred degradation is <2.0% -3.36 mm and <5% max is acceptable, whereas the preferred level for lump ore is <5% -3.36 mm and <10% max is acceptable. The results of the Linder Test using the standard Linder gas and 100% H_2 are shown in Table 4.

Table 4: Standard (NG-based) and H_2 Linder Test results of the different iron oxides

Linder Test	Lump A		Lump B		BF grade		DR grade 1		DR-grade 2	
	NG	H_2	NG	H_2	NG	H_2	NG	H_2	NG	H_2
Total Iron (T. Fe%)	83.1	82.6	89.8	94.5	87.8	89.4	91.9	95	93.2	95.5
Metallic Iron (M. Fe%)	74.1	74.6	85.1	91.1	85.2	87.7	84.8	92	86.5	94.3
Metallization (MET%)	89.2	90.3	94.7	96.4	97.1	98.1	92.2	96.8	92.8	98.7
Carbon (%)	1.5	0	1.9	0	1.6	0	1.5	0	0.5	0
Fragmentation (-3.36mm)	20.8	19.9	13.6	19.9	2.4	1.7	0.4	0.3	1.8	1.0
Comp. Strength (kg)	N/A	N/A	N/A	N/A	55	44	49	53	65	76

Cluster Test

Midrex uses the Cluster Test (ISO 11256) to evaluate the clustering behavior of iron oxide pellets and lump ores when reduced under conditions resembling those prevailing in shaft-type direct reduction processes. The test is conducted in what Midrex terms an "ISO furnace" that measures weight loss during reduction. The sample is heated to 850° C in an inert environment and then undergoes isothermal reduction under loading in a reducing gas until 95% of reduction is achieved or a set time. After reduction, the sample is cooled and removed from the retort vessel. The test sample is disaggregated in a tumble drum. The Clustering Index (CI) is calculated from the accumulated clusters after specific disaggregation operations. A clustering index of less than 20 is desirable.

Test parameters and analysis conducted are listed below. The Cluster Test is run with at least two replicates.

- The natural gas reducing gas for the Cluster Test consists of CO 30%, CO_2 15%, H_2 45%, N_2 10%, whereas the gas composition for H_2 reduction consists entirely of 100% H_2
- Test portions approximately 2000 g of representative sample
- Testing conducted at 850° C until 95% reduction is achieved, or a set time has passed (Note: in our study, we waited until 95% reduction was achieved)
- Chemical analysis of the reduced product performed

The Cluster Test results of the lump ores and iron oxide pellets are shown in Table 5.

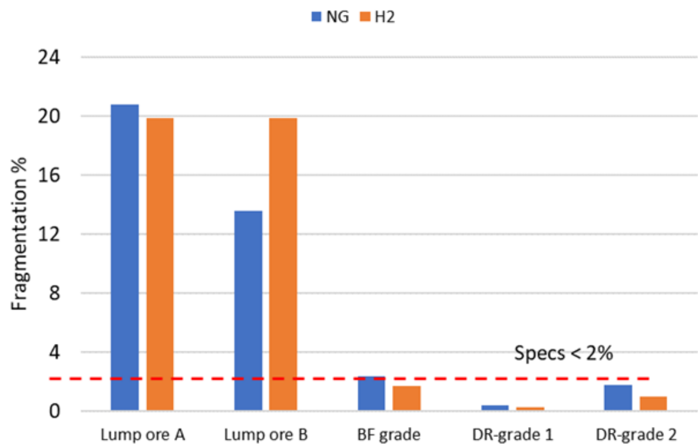
Table 5: Clustering index (CI) of iron oxide samples		
Samples	Clustering Index	
	NG	H_2
Lump ore A	0	0
Lump ore B	2	3
BF-grade	17	12
DR-grade 1	18	6
DR-grade 2	7	4

ANALYSIS

Fragmentation of Lump Ores and Iron Oxide Pellets When Using Carbonaceous Gas and H_2 as Reductants

The degradation of Lump Ores A & B was high (high fragmentation), as expected since lump ores are not indurated like oxide pellets. Figure 1 shows the percent fragmentation (-3.36 mm) of iron oxide pellets reduced by carbonaceous gas and H_2 gas. All the oxide pellets that were reduced using the H_2 Linder had lower fragmentation values than the ones reduced using the standard Linder gas. The DR-grade 2 pellets met the Midrex fragmentation criterion of <2%. Overall, using 100% H_2 as reducing gas did not have an adverse impact on the strength of DRI pellets.

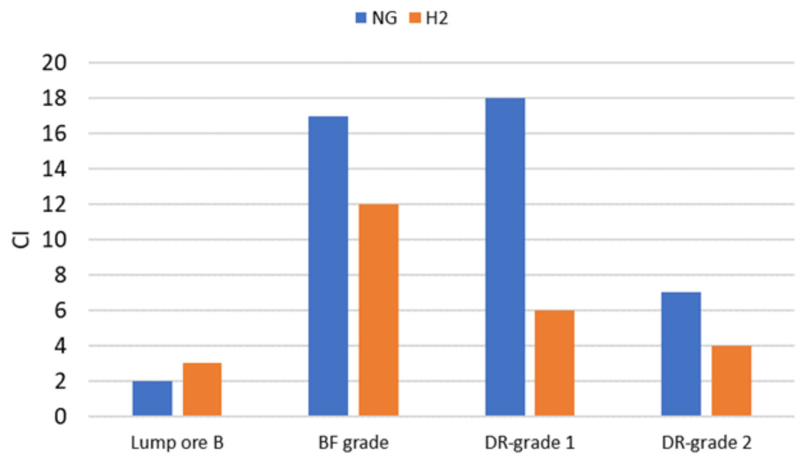
Figure 1: Fragmentation data (-3.36 mm) of DRI pellets: BF-grade, DR-grade 1, and DR-grade 2 reduced by the standard Linder gas (NG) and H_2 gas (H2). The H_2 reduced DRI pellets met the criterion of < 2% fragmentation.



Clustering Behavior of Lump Ores and Iron Oxide Pellets When Using Carbonaceous Gas and H_2 as Reductants

Figure 2 shows the clustering index (CI) of Lump Ore B and iron oxide pellets reduced using carbonaceous gas and H_2. There is significantly less clustering in lump ores than iron oxide pellets. The lack of clustering in lump ore is likely because of its low iron content [5]. As can be seen from Figure 2, the CIs of the iron oxide pellets reduced using H_2 as reductant are lower than those reduced using carbonaceous gas. The DR-grade 2 pellets satisfied the Clustering Index criterion of <20.

Figure 2: Clustering Test results of iron oxide samples. The criterion of an acceptable CI is <20.



Sticking or clustering occurs mostly during metallization of ore and depends strongly on the kind of iron ores. Clustering of iron ores can be caused by low melting eutectic mixture iron grains that soften and stick together or an interlocking of fibrous iron during reduction [1].

Three widely recognized types of sticking during reduction with CO or CO/CO_2 are [1.2]:

1. Type 1 sticking – the bonding effect of generated iron whiskers. Precipitation of iron whiskers during reduction by CO leads to the eventual interlocking of these whiskers at temperatures above 600° C. Iron whiskers form when the conditions are reaction-controlled and the generation rate of iron ions on the surface of the particles is much slower than the solid-diffusion rate. The particle acts like a reservoir for storing iron ions until the critical lowest nucleation free energy at the surface is reached and triggers the formation of iron nuclei, which eventually grow into whiskers with the continuous supplement of iron ions from the reservoir.
2. Type 2 sticking – the bonding effect of generated new metallic iron. The high surface energy and high viscosity of the highly active new metallic iron leads to increased adhesion among pellets. The solid-state diffusion of the freshly formed metallic iron eventually results in interconnected solid bridges between the pellets [2].
3. Type 3 sticking – the bonding effect due to low melting eutectics. This type of sticking occurs at temperatures above 850° C. At high temperatures, the presence of gangue generated a low melting eutectic phase between wustite and gangue components (e.g., CaO-SiO_2-FeO) that stick together in an iron ore particle. This type of sticking generally occurs after 33% reduction degree in the presence of wustite [1].

In Figure 3, we can see a drastic decrease in the CI of H2-DRI compared to NG-DRI. This phenomenon has been reported in literature. Yi et al. investigated the sticking behavior of iron ore pellets in direct reduction with varying composition of H_2 and CO in a reactor similar to Midrex cluster test reactor. The iron oxide pellets were isothermally reduced at 800 – 1000° C in synthetic gas mixtures under a load of 1 kg/cm^2. The authors reported that the sticking of pellets during reduction decreases with H_2 content in reducing gas and increases with temperature [3].

The Midrex Cluster Test isothermal reduction is run under loading in a reducing gas until 95% reduction is achieved. Since H_2 is a more effective reducing gas, the reduction time is shorter than carbonaceous gas. The reduction time when H_2 was used as reductant in the

Cluster Test was as short as 77 mins, whereas it took a minimum of 133 minutes to complete the test when carbonaceous gas was used as reductant.

There were queries that the lack of clustering among the H2-DRI could be due to the shorter reduction time. In this regard, we may refer to the study done by Guo et al. for probable explanation, where the authors demonstrated that higher H_2 concentration led to higher metallization ratio, higher speed of reduction, and shorter fluidization time in a fluidized bed iron ore reduction process [(4)]. The sticking occurred when the iron ores fines reached a constant metallization ratio and the agglomeration led to de-fluidization [(4)]. From this, we can deduce that the fundamental difference in clustering between the H2-DRI and NG-DRI observed in our study is not caused by the shorter exposure time to the H_2 reducing gas. In fact, we would expect higher CI among the H2-DRI than NG-DRI because of its higher metallization ratio. However, in our study, the CI of the H2-DRI is lower than NG-DRI, despite higher metallization ratio. Therefore, there was something else at play that caused the higher CI observed in the NG-DRI.

Yi et al. detected the presence of fibrous iron on the pellets and claimed in their study that the interlocking of these fibrous iron caused clustering; the sticking of pellets during reduction decreases with H_2 content in reducing gas [(3)]. Komatina and Gudenau reported that the growth of fibrous iron decreases with a small addition of H_2 and stops if the H_2 addition increases greatly [(1)]. Du et al. also showed that the sticking index decreases with increasing H_2 content in the reducing gas and proposed that the addition of H_2 to the reducing gas mixtures transforms the metallic iron from fibrous to a dense layer; fibrous iron is favored in pure CO and dense iron is dominant in pure H_2 [(5)]. Finally, Guo et al. did not detect the growth of iron whiskers on Fe_2O_3 surfaces under reduction with varying composition of H_2-N_2 gas mixtures; the author hypothesized that the clustering of iron ore reduced under H_2 was due to the sticking surface of the ore particles with newly generated iron [(4)]. Therefore, we hypothesized that clustering among the NG-DRI may be attributed to Type 1 and Type 2 sticking, and under pure H_2 conditions, there is little to no iron whiskers formation and the sticking among the H2-DRI may be attributed to Type 2 sticking.

CONCLUSIONS

From our test work, we were able to reach the following conclusions about the physical characteristics of DRI produced with hydrogen (H2-DRI):

1. Using 100% H_2 as reducing gas does not have an adverse impact on the strength of DRI pellets.
2. The Clustering Index of iron oxide pellets reduced with H_2 as reductant is lower than those reduced using carbonaceous gas.

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