A Preliminary Study of Influence of Atmosphere on Reduction Behavior of Iron Ore–Coal Composite Pellets

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1. Introduction

The term 'Composite Pellet' refers to pellet containing mixture of fines of iron bearing oxide and carbonaceous material (coal, coke, char) in general. These are imparted sufficient green strength for subsequent handling by cold-bonding at or around room temperature. The pellets should also have sufficient strength to withstand high temperatures and stresses during reduction at high temperature. Use of these pellets offers advantages, such as high rate of reduction due to intimate mixing of oxide and carbon, utilization of fines, as well as non-coking coal or char. As a result they are promising feed materials for alternative ironmaking outside blast furnace. The following two joint ventures by Midrex Corporation, USA and Kobe Steel, Japan have adopted the composite pellet route for ironmaking.¹ ² The first one is FASTMET process which produces sponge iron, whereas the more recent ITmk³ process would produce liquid iron.

There have been some laboratory studies on reduction behavior of composite pellets. Dutta and Ghosh ³– ⁵ carried out reduction in non-isothermal apparatus. The pellets were slowly lowered into the hot zone of the furnace, and withdrawn thereafter. A gentle flow of argon gas was maintained in the reaction chamber all through.

However, in industrial reactors, the gaseous atmosphere in the furnace would actually be reactive, consisting of gases such as CO, CO₂, H₂, H₂O along with N₂. Therefore, laboratory studies are required about reduction behavior of composite pellets in reactive atmospheres. The investigation reported here is a short study. Its purpose was to gather some preliminary data before embarking on further investigation.

2. Experimental Apparatus and Procedure

2.1. Reduction Experiments

Gaseous atmospheres employed in this study were Ar, Ar+CO₂, Ar+CO₂+H₂. The composite pellets had been obtained from the R & D Centre, Steel Authority of India, and contained the following:

1. 86% 'Bluedust', i.e. fine iron ore (~100 mesh) from Bailadila Mines, India, containing 95.3% Fe₂O₃, 1.6% SiO₂, 1.8% Al₂O₃, 0.7%. Loss on Ignition.
2. 8.6% coal fine (~100 mesh) from Parascoal Mines, India. Proximate analysis was: volatile matter 37.5%, ash 11.4% and fixed carbon 51.1% on moisture-free basis. The ash analyzed 51% SiO₂, 23% Al₂O₃, 15.5% CaO, 7.8% Fe₂O₃, rest minor constituents.
3. rest dextrin and phenol (4:1 ratio) as binder. Density of pellets was 3.15 g cm⁻³ on average.

A dried and weighed pellet was quickly introduced into the hot zone of a vertical resistance furnace, and kept there for a predecided time. It was then withdrawn into the colder zone of the furnace. The gas flow was maintained in the furnace chamber throughout. After the pellet was cooled in the colder zone of the furnace, it was taken out and further cooled to room temperature under a cover. Then it was weighed again.

Some auxiliary experiments were carried out to measure rates of heating and cooling of pellets after introduction into and withdrawal from hot zone of the furnace. The thermocouple tip was embedded into the pellet half-way between surface and centre of pellets for this purpose. Heating and cooling rates were approximately 300°C and 250°C per minute respectively for small and large pellets.

2.2. Determination of Degree of Reduction

Let the weight loss of the pellet during its residence in furnace hot zone be ΔW₉,

\[ ΔW₉ = ΔW_O + ΔW_C + ΔW_V \]  

where, \( ΔW_O \) = weight loss of oxygen of iron oxide,

\( ΔW_C \) = weight loss of carbon of coal due to formation of CO and CO₂ and

\( ΔW_V \) = weight loss due to evolution of volatile matter of coal as well as chemically held \( H₂O \) etc.

It may be noted that carbon not only reacts with oxygen of iron oxide, but also is gasified by reaction with chemically combined or strongly adsorbed \( H₂O \), as well as with CO₂ of the gas mixture flowing through the furnace chamber.

The objective of this investigation was to ultimately find out the degree of reduction (F) as defined by

\[ F = \frac{ΔW_O}{W₂} \]  

where, \( W₂ \) = total weight of oxygen initially contained in the iron oxide of the ore.

The weight pct. Fe in pellets was 57.3%. Since the initial oxide is Fe₂O₃, \( W₂ \) could be calculated from pellet weight. Therefore, determination of \( F \) requires the value of \( ΔW_O \). Various techniques have been proposed in literature. Dutta and Ghosh ⁵ considered all these and concluded that none of them was satisfactory for composite pellets. They had developed a technique, ⁵ which was employed in the present investigation.

The technique consisted of crushing the partially reduced pellet sample, and then subjecting it to further...
reduction in flowing hydrogen at 1023 K for 1 hr. The weight loss in H₂ can be taken as due to removal of residual oxygen of iron oxide by H₂. Let us designate it as \( \Delta W_\text{O} \). Then,

\[
\Delta W_\text{O} = W_\text{O}^\text{initial} - W_\text{O}^\text{final} 
\]

### 3. Results and Discussions

All reduction experiments were carried out at furnace hot zone temperature of 1256 K. Majority of the composite pellets were approximately spheres of 8-13 mm dia. with 2-3 g weight. Total gas flow rate was 2.5 cm³ s⁻¹ (STP). The Ar + CO₂ mixture contained 30% CO₂. In Ar + CO₂ + H₂ mixtures, Ar concentration was 33.3%. Rest was CO₂ + H₂. 3 ratios of \( p_{\text{CO}} / p_{\text{H₂}} \) were employed, viz. 3/1, 2/3, 1/3. Residence time in hot zone (\( t \)) ranged from 5 min to 60 min.

Experimental data had reproducibility mostly within ± 10%. **Figure 1** presents \( F \) vs. residence time data for pellets of approximately 13 mm dia. on average. It is well-established that reduction of Fe₂O₃ is stage-wise in such a mixture, *i.e.*, Fe₂O₃ would get completely converted into Fe₃O₄, which would then get completely converted into non-stoichiometric Fe₃O₄. Formation of metallic Fe starts only after that. On the basis of the above, **Figure 1** shows the stable phases of Fe–O system with increase of \( F \). Values of \( x \) for Fe₃O₄ in equilibrium with Fe₂O₃ and Fe are respectively 0.88 and 0.95 at 1256 K.³

A mixture of CO₂ and H₂ would undergo water gas shift reaction at high temperature, *i.e.*

\[
\text{CO}_2(g) + \text{H}_2(g) = \text{CO}(g) + \text{H}_2\text{O}(g) \quad \text{(4)}
\]

**Table 1** presents \( p_{\text{CO}} / p_{\text{CO}_2} \) ratio at equilibrium with various reactions at 1256 K, calculated from reaction free energy data from a standard source.⁷ Argon is neutral. It is commonly recognized that CO₂ is in thermodynamically equilibrium with Fe₂O₄. Gas mixes A, B, C are Fe₂O₃ + CO₂ + H₂ with different \( p_{\text{CO}_2} / p_{\text{H}_2} \) ratios at inlet. As Table 1 shows that gas mixes A and B are thermodynamically oxidizing to wustite, but reducing to Fe₂O₃ and Fe₃O₄, whereas mix C is reducing to all oxides.

Kinetics of water gas shift reaction has been widely studied. At lower temperatures (less than 600/700 K), solid catalyst is to be employed. But, at higher temperatures, the reaction is very fast and tends to attain equilibrium rapidly without catalyst. In one of the earlier studies, Darken and Gurry⁸ confirmed it. They also found negligible thermal diffusion error. Hence, in this preliminary study, we are assuming that Reaction (4) attained equilibrium in furnace hot zone.

The reduction kinetics is quite complex. The iron ore reacts both with coal as well as the flowing reactive gas. Several other reactions occur simultaneously. The initial period (first 10 min approximately) is most complex. It is partly non-isothermal. The coal gives off its moisture and volatile matter. Moisture chemically combined with ore and binder is also liberated during this period by and large.

Interpretation of the latter period of reduction is more clear cut. There we are basically dealing with gasification.

**Table 1.** \( p_{\text{CO}} / p_{\text{CO}_2} \) ratios at equilibrium with various reactions at 1256 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \frac{p_{\text{CO}}}{p_{\text{CO}_2}} )</th>
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<tbody>
<tr>
<td>1. ( 3\text{Fe}_2\text{O}_3(s) + \text{CO}_2(g) = 2\text{Fe}_3\text{O}_4(s) + \text{CO}_2(g) )</td>
<td>Negligible</td>
</tr>
<tr>
<td>2. ( 1.69\text{Fe}_3\text{O}_4(s) + \text{CO}_2(g) = 5.76\text{Fe}_2\text{O}_3(s) + \text{CO}_2(g) )</td>
<td>0.22</td>
</tr>
<tr>
<td>3. ( \text{Fe}_9\text{O}_4(s) + \text{CO}_2(g) = 0.95\text{Fe}(s) + \text{CO}_2(g) )</td>
<td>2.51</td>
</tr>
<tr>
<td>4. ( \text{CO}_2(g) + \frac{2}{3}\text{H}_2(g) = \text{CO}(g) + \frac{2}{3}\text{H}_2\text{O}(g) )</td>
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**Figure 1.** Fractional reduction vs. residence time for pellets in various gases at 1 256 K.

**Figure 2.** Variation of fractional reduction with pellet size for few conditions.
of char and reduction of wustite to metallic iron by CO and H₂. CO arises from the following 3 sources, viz.

1) reaction of char with CO₂, which is present in the external gas, as well as is generated as a product of iron oxide reduction
2) water gas shift reaction
3) the reaction:

\[ C(s) + H₂O(g) = CO(g) + H₂(g) \] ........................(5)

Reaction (5) is a source of H₂ also, in addition to H₂ being supplied through some gas mixtures.

In Fig. 1, for residence time of 20 to 50 min, degree of reduction was highest in pure argon. Since gas mixtures A and B as well as Ar + CO₂ are oxidizing to metallic iron, they decreased F. However that is not the case for gas mix C. Even then degree of reduction was higher in pure Ar, demonstrating that rates of reduction by coal/char fines were higher than that by externally supplied hydrogen gas. At longer residence time, there was no further reduction by char due to its depletion. Then further reduction of ore was continued by H₂ in gas mix C.

Figure 2 presents some data on variation of degree of reduction with pellet size. These pellets were obtained from Steel Authority of India, who had prepared these by laboratory pelletizer. Hence they were not very spherical. Also the reduction is primarily by internal carbon of pellet. Hence, pellet weight has been employed as measure of size in Fig. 2. However, approximate average diameters also have been indicated.

Theoretically speaking, smaller is pellet size, more significant should be the influence of external gas on reduction due to larger specific surface area. Gas mix C was reducing even to wustite. Hence F was larger for smaller pellets at the same residence time. Mix B was not reducing to wustite. Hence the effect of pellet size variation was not that much as mix C. Variation was not even monotonic for mix B at residence time of 20 min.

To sum up, this preliminary investigation has demonstrated certain behavior patterns for reduction of cold-bonded iron ore + coal pellets in reactive gas mixtures. Further studies are required for more comprehensive understanding. However, it may be stated that optimization of pellet size, its carbon content etc. would have to be done for specific applications.

REFERENCES