Rapid Reduction of Carbon-Coated Iron Ore Prepared with Heavy Oil Vacuum Residue

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Processes for the direct reduction of iron ore using coal, graphite, and coal volatiles, as well as gases such as carbon monoxide and hydrogen, have been under study for over a decade (Abraham et al., 1979; Fruehan, 1997; Griscom et al., 1994; Hayashi et al., 1994; Miyagawa et al., 1998; Nagasaka and Banya, 1992; Sato et al., 1987). Recent work reported by Sugawara et al. (1996, 1999) was undertaken to determine the mechanisms and reaction rate phenomena that influence such processes. That work involved study of the smelting reduction of iron-ore particles coated with carbon in a drop-tube reactor that permitted rapid heating of the ore particles. Changes in the oxidation states of the iron were determined at temperatures ranging from 1073 to 1773 K and it was shown that Fe, Fe(II), and Fe(III) coexisted during reduction. Furthermore, the reduction from wustite to metallic iron appeared to accelerate with temperatures above the melting point of wustite. The carbon coating on the iron-ore particles in that work was obtained by preliminary thermal decomposition of phenolphthalein.

The present study was undertaken to obtain additional fundamental data on the reduction of iron-ore particles under solid and melting conditions using heavy oil vacuum residue as the carbon source. This material can be easily mixed with iron-ore particles, and it also offers the opportunity for effective use of carbon resources. Because the presence of sulfur in the carbon source was previously identified as a potential problem in the iron-ore reduction process (Rao, 1971) and because vacuum residue usually has a high sulfur content, the present study was also aimed at investigating the effect of sulfur on iron-ore reduction.

Experimental Studies

As in the previous work (Sugawara et al., 1999), the iron ore used in this study was Australian Hamersley containing 64.6 wt % of total iron (composed of 92.2 wt % Fe_2O_3 and 0.15 wt % FeO) crushed and sieved to $-200 + 250$ mesh. The vacuum residue selected as the carbonaceous material to cover the surface of the ore particles had a density of 1.02 g/cm^3 and contained 84.4 wt. % carbon, 10.3 wt. % hydrogen, and 4.1 wt. % sulfur. The content of metals such as iron, nickel, and vanadium was less than 1 ppm.

Figure 1 shows the results of a thermogravimetric study of the vacuum residue heated at a rate of 20 K/min in a nitrogen stream. The residue begins to melt around 573 K and decomposes rapidly from 673 to 773 K. Creation of a carbon coating on the ore particles, therefore, required a treatment temperature somewhat greater than 773 K. In this study, the process used to create the coating involved mixing a sample of vacuum residue and iron ore in a 1 to 1 weight ratio followed by heating at 20 K/min up to 873 K and then holding the sample at 873 K for 10 min. The sample was contained in an alumina crucible and heated under nitrogen in an infrared gold image furnace (Ulvac-Sinku Riko, Yokohama, Japan). The carbon-coated iron ore prepared in this manner contained 30 wt. % carbon, 0.8 wt. % hydrogen, and 2.2 wt. % sulfur. The combined water contained in the iron ore was probably removed from the solid phase during this preparation.

Some other carbon-coated samples were also prepared in the same manner but using phenolphthalein and a mixture of phenolphthalein and elemental sulfur in place of the vacuum residue to study the effect of the nature of the carbon source and its sulfur content on the subsequent ore reduction. These samples were prepared with a 1 to 1 weight ratio of phenolphthalein to iron ore and varying amounts of elemental sulfur.

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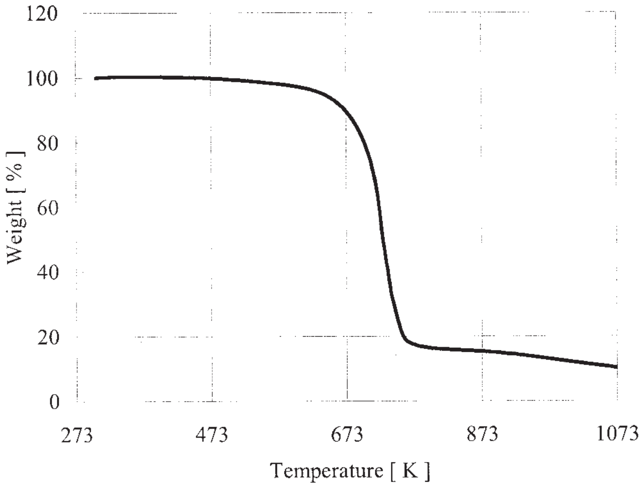


Figure 1. Thermogravimetric change of vacuum residue.

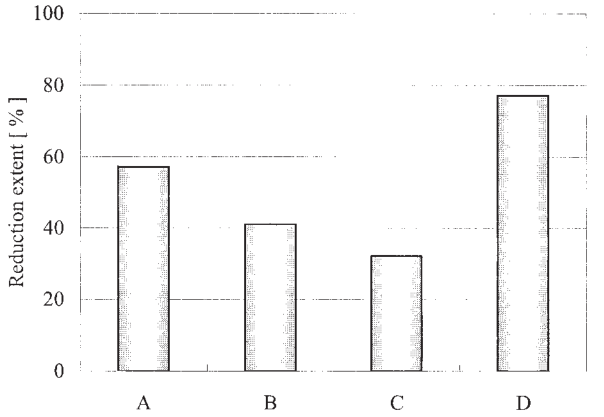


Figure 2. Effect of carbon source on extent of reduction. Samples were heated at furnace temperatures of 1273, 1773, and 1773 K.

Sample A, carbon coated by phenolphthalein; sample B, carbon coated by phenolphthalein containing 2.0% sulfur; sample C, carbon coated by phenolphthalein containing 5.4% sulfur; sample D, carbon coated by vacuum residue.

The sulfur content of the resultant carbon-coated iron ore samples was 0, 2.0, and 5.4 wt. %.

The drop-tube reactor used for the reduction experiments was the same as that reported previously (Sugawara, 1999). It consisted of an alumina tube with a 28 mm ID and an overall length of 105 cm heated by three electric furnaces in series. Iron-ore particles were supplied to the reactor from a hopper at a rate of 10 g/h along with nitrogen gas that flowed downward at 600 cm^3 NTP/min. The residence time of sample particles in the reactor was estimated to be less than 0.7 s.

Analysis of total iron, wustite, and metallic iron content of the iron-ore particles was carried out according to standard methods (JIS M8812 and M8713). FeS content was determined by application of methods for sulfur in coal (Sugawara et al., 1988). The carbon and sulfur contents of the coated ore were measured using a Horiba EMIA-1200 infrared spectrometer (Horiba Instruments, Irvine, CA) with high-frequency induction heating. Other details of the drop-tube reactor and the analytical methods used were described previously (Sugawara et al., 1999).

Results and Discussion

Figure 2 shows the change in reduction extent of the carbon-coated iron ore with four different coatings: phenolphthalein, phenolphthalein containing sulfur at two levels, and vacuum residue. In Figure 2 and subsequent figures the reduction extent of the iron ore was defined as: $\{1 - (\text{oxygen content after reduction} \div \text{oxygen content before reduction})\} \times 100\%$. Here, the oxygen content before and after reduction was determined from the amount of various iron forms (Fe_2O_3, FeO, and Fe) present. The formation of FeS was not taken into account for calculations of the reduction extent because the emphasis of the process is to obtain fully reduced metallic iron.

The data in Figure 2 were obtained with temperatures of 1273, 1773, and 1773 K in furnaces I, II, and III, respectively(furnaces numbered from the top of the reactor). Sample A (carbon coated by phenolphthalein) showed a reduction extent of 58%, whereas sample D (carbon coated by vacuum residue) exhibited a reduction extent of 77%. In samples B and C (carbon coated by a mixture of phenolphthalein and sulfur) the reduction extents decreased (compared to sample A) to 42% at a sulfur content of 2 wt. % and 32% at a sulfur content of 5.4 wt. %. It should be noted that even though sample D contains 2.2 wt. % of sulfur, the reduction achieved in that case was significantly larger than that found with sample A.

The distribution of iron states for samples A through D is shown in Figure 3, which indicates the coexistence of Fe, Fe(II) (as both FeO and FeS), and Fe(III). The amount of metallic (that is, fully reduced) iron reached 40% for sample A, 23% for sample B, and only 5% for sample C, indicating a drastic effect accompanying an increase of sulfur content in the carbon coating. At the same time, the content of unreactive Fe_2O_3 increased with increasing sulfur content. In addition, the Fe(II) content of samples A, B, and C was essentially constant, although the FeO content decreased whereas the FeS content increased in response to increased sulfur in the coating. Thus, sulfur in the carbon source caused not only the formation of

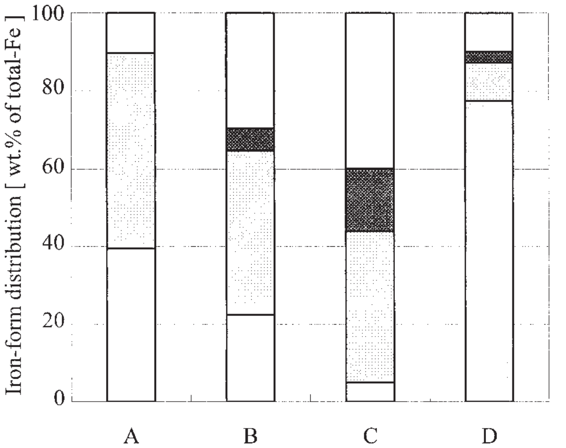
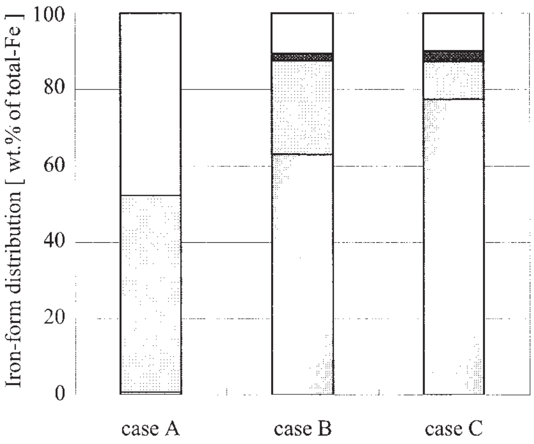


Figure 3. Effect of carbon source on iron-form distribution at 1773 K.

□, Metal–Fe; ▨, FeO; ▩, FeS; □, Fe(III). Samples A–D as in Figure 2.



Case	Furnace temp. [K]		
	I	II	III
A	973	1173	1173
B	1173	1573	1573
C	1273	1773	1773

Figure 4. Effect of temperature on iron-form distribution. □, metal–Fe; ▨, FeO; ▩, FeS; □, Fe(III).

FeS, but also a drastic lowering of reduction extent from Fe_2O_3 to FeO. Because FeS melts at 1461 K, it is possible that molten FeS, formed when the sample was heated to the terminal temperature of 1773 K, may have obstructed contact between iron oxides and the carbon-reducing agent of the coating. Note that no appreciable difference in the reduction extents was observed in either the presence or the absence of FeS at temperatures below 1461 K.

The high reduction extent (77%) for sample D resulted from the rapid reduction from FeO compared to sample A, whereas the rate of reduction from Fe_2O_3 to FeO for sample D was similar to that for sample A. This result indicates that carbon obtained from the vacuum residue is very reactive for iron reduction. Furthermore, because the FeS content of sample D was lower than that in sample B, it is apparent that the sulfur in the vacuum residue is somehow more chemically stable and has very little effect on the reduction process.

Figure 4 shows the effect of furnace temperature on the iron-form distributions obtained with coatings generated from the vacuum residue. As indicated, three different temperature distributions in the drop-tube reactor with high temperatures of 1173, 1573, and 1773 K produced reduction extents of 2.4, 66, and 77%, respectively. (The latter correspond to sample D referred to previously.) As noted earlier, the large reductions observed at the two higher temperatures resulted from smelting reduction of iron ore that occurs above the melting point of wustite. As the reduction proceeded, only a single large sphere of metallic iron in the center of the particle could be seen. In the previous study at those temperatures, using only phenolphthalein-generated coatings (Sugawara et al., 1999), the reduction extents were found to be 38 and 57%, respectively. Although those extents were larger than those obtained with reduction by graphite and close to results for the Fe—C melt system, they have been surpassed by more than 20% in the present work. Thus, it is clear that carbon-coated iron ore prepared from vacuum residue is clearly preferable for iron-ore reduction. The differences of the reduction behavior found with the different carbon sources may reflect more rapid carburization of the iron resulting from easier penetration of the iron-ore particle by carbon generated from the vacuum residue.

Conclusions

Rapid reduction of carbon-coated iron-ore particles in a high temperature drop-tube reactor was successfully demonstrated previously. The present study has shown that carbon coatings generated from vacuum residue from heavy oil produce significantly greater extents of iron reduction than those produced from phenolphthalein. It has also been found that sulfur present in the vacuum residue does not have a negative effect on reduction extent, contrary to results obtained with phenolphthalein–sulfur mixtures. Vacuum residue may thus be an effective source of reducing carbon for iron ore.

Acknowledgments

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