Characterisation and Corrosion of Laboratory Scale Briquettes of Reduced Iron

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While considerable work has been reported in literature on the corrosion behaviour and products of direct reduced iron and sponge iron, very little work has been reported on hot briquetted iron, particularly on the effects of the conditions under which the iron ore is reduced and briquetting parameters have on subsequent corrosion behaviour of briquettes.

To investigate this, a laboratory briquetter produced briquettes from finely granulated direct reduced iron (DRI), under pressures of up to 160 MPa and at temperatures up to 700°C. Briquetting variables such as heating time, temperature at which compaction takes place, pressure applied and atmosphere under which briquetting took place were all strictly controlled.

Influences of the briquetting parameters of temperature and pressure during compaction on the density and surface area of the HBI were established. Characterised briquettes were then utilised in a study of re-oxidation behaviour of hot briquetted iron under various conditions including temperature and salt contamination to simulate storage and transportation related conditions. The studies have established that the influence of reduction and briquetting parameters and the oxidation environment variables of temperature and salt contamination are significant factors in understanding briquette corrosion.

KEY WORDS: direct reduced iron; briquetting; hot briquetted iron; re-oxidation; corrosion.

1. Introduction

Direct Reduced Iron (DRI) materials are known to be sensitive to oxidation, resulting in loss of metallisation and economic value, and posing a potential safety hazard during storage and transport. Hot briquetting, reported to be the best countermeasure to this reactivity, reduces the porosity and surface to volume ratio of DRI. Storage and handling characteristics are improved by briquetting. Bulk density is increased, bulk volume decreased and safety during handling is also improved. Porosity and density can be controlled, within limits, influencing the solubility, reactivity and heat conductivity of the final material.

Briquetting involves two main stages: compaction and sintering. Compaction is the densification of powder through the application of mechanical forces, while sintering uses a temperature approximately 2/3 of the substance’s melting temperature to encourage the building of sinter bridges in the compact, by material transport processes.

Kamiya and Tanaka produced briquettes from DRI in a briquetter under conditions of both cold and hot briquetting. Their briquettes were cylindrical having a cross sectional area of 1 cm², a height of 1.1–1.4 cm, and a density ranging between 4–5 g/cm³ depending on the briquetting parameters. Their press was an oil press of 35 tonne maximum load, allowing pressures up to 2 tonne/cm² to be applied to the DRI. An electric furnace in a nitrogen atmosphere heated the die to temperatures in the range of 400–700°C. The die was lubricated by graphite powder. They found an increase in the pressing time and pressure of compaction increased the density of the briquettes. They also found an increased density decreased the reoxidation rate in the briquettes.

Towhidi also compressed briquettes from sponge iron pellets at a temperature of 800°C and a pressure of 200 atm, reducing the specific surface area of the iron to 1/3 of its original value. His briquettes were cylindrical, having a diameter of 1 cm. A relationship between the density and subsequent reoxidation behaviour was found, indicating that the degree of oxidation increases with an increase in oxidation temperature, and decreases with increasing powder compressibility. As the apparent density increases, the rate of reoxidation decreases. Changing the structure of the briquettes also influences the reoxidation; sintering decreases the rate.

The limited work that has been done on HBI reoxidation indicated that the porosity of the briquettes has a very important influence on both the reaction rate and extent. The nature of the briquettes’ surface also affects the corrosion; briquettes passivated in air have a much slower oxidation rate at room temperatures.

As briquetting is the common technique to change DRI’s physical characteristics to make it safe to transport and store, this study was initiated to gain a fundamental understanding of briquette corrosion behaviour. Production and briquetting parameters such as the nature of the ore reduced and the briquetting pressure and temperature can affect briquette density and therefore the reoxidation behaviour. The
oxidation environment variables of temperature and salt contamination were also considered to be significant in understanding the corrosion behaviour of the briquettes, and hence significant to those involved in storage and transportation of merchant HBI.

Briquette properties of density and surface area were investigated as a function of the briquetting parameters of pressure and temperature, and carbon content of the DRI. Corrosion behaviour of the characterised briquettes was then considered in terms of oxidation extent and products, for environments of varying temperatures and contamination by salt.

2. Experimental Details

2.1. The Briquetter

The briquetter, standing 2.3 m high over an area of 1 m by 1.5 m, utilises a 30 tonne hydraulic press and a furnace, which can reach temperatures of 1200°C. The supporting structure is mild steel and most of the areas subject to high temperatures are a heat resistant grade of stainless steel (MA 253). The valve between the sample loading chamber and the heated zone of the briquetter is a 20 mm ball valve. An option of cooling water before the valve is available. Insulating material used in the rig is Kaowool. The die is made of stainless steel having an inner diameter of 40 mm. This material maintains its properties to temperatures in excess of 750°C. The upper and lower punches are made of the hot die steel H113, having a hardness of HRC 40–50. K-type thermocouples both monitor and maintain temperature control of the system. One is placed in the die, the other in the furnace. Generally there is a 50°C temperature difference between the two. A schematic of the briquetter is found in Fig. 1, where (1) is the hydraulic press, (2) is the DRI sample hopper, (3) is the upper punch, (4) is the furnace, (5) is the cooling zone and (6) is the lower punch.

The hydraulic press (1) forces a top punch (3) of heat-treated metal onto a similar, but stationary lower punch (6). The die, located in the hot zone of a furnace (4), creates a briquette 4 cm in diameter. Furnace temperature is set, and the system allowed to equilibrate. Due to limitation of the material of die and punch, temperatures have not exceeded 700°C in the die.

2.2. Briquetting Procedure

DRI is placed in a sealed sample feeder (2), and, under an inert atmosphere, allowed to fall into the position between die and lower punch. Pressure up to 160 MPa is applied by the hydraulic press. After pressing is completed, pressure can be released, and the briquette lowered into a cold zone (5), still within an inert atmosphere. The sample is removed from the top surface of the lower punch, which can then be raised into position, in readiness for the next briquette. Once a number of briquettes are made, and cooled in the inert atmosphere, the access plate to the cooling zone can be removed, and samples retrieved.

2.3. Oxidation Procedure

After characterisation, briquettes were placed in a series of vessels, each containing a solution. Most trials were done in distilled water, but the influence of salt was investigated using a variety of salt concentrations; seawater (26.7 g/l NaCl) and ±10% (29.4 g/l and 24.0 g/l NaCl respectively). This simulated the concentration of salt in seawater, and seawater subject to environmental evaporation or dilution. All solutions were stirred and aerated with 200 ml/min air bubbling through them. Briquettes were submerged in the solutions, and elevated from the bottom of the vessel. Reoxidation extent was measured as a mass change over an eight weeks time period, and corrosion products were identified using XRD and Raman Spectroscopy.

2.4. Characterisation of Briquettes

DRI was sized before compaction to <1 mm. This was to reduce sticking problems in the briquetter due to the larger fractions. The chemical composition of the DRI was analysed chemically by the BHP Hunter Laboratory, and size fractions of the DRI determined (see Table 1). DRI was then compressed under a variety of pressures in the range 63.7–159.2 MPa, and at temperatures ranging from 25 to 700°C.

The resulting briquettes had a density 3.5–6.0 g/cm³, determined by measurement of the briquette mass and physical dimensions of height and radius. Surface area was determined by using a Micromeritics (ASAP 2400) surface area analyser to be between 1.3 and 2.0 m²/g. Surface area decreased as density increased. Structure of the briquettes was investigated and illustrated using scanning electron microscopy (SEM).

3. Results and Discussion

3.1. Influence of Pressure

The influence of pressure on the physical characteristics of the briquettes was examined by maintaining the temperature at 500°C and altering the pressure in the range of 0.64–
1.43 MPa. Influence of pressure on density and surface area is shown in Fig. 2. Figure 2 shows that an increase in pressure increases the apparent density of the briquette at a decreasing rate, approaching a maximum of about 4 g/cm³, at this temperature. Surface area, determined by BET analysis, showed no conclusive dependence of surface area on pressure under which the briquettes were made. From these results, the application of pressure at a given temperature is responsible for a rearranging of particles allowing the increase in briquette density, however, increasing pressure does not appear to change the surface area available for reaction within the briquette at this temperature.

3.2. Influence of Temperature

Briquettes were pressed at 1.43 MPa and temperatures ranging from 25 to 700°C. Influence of the temperature on the apparent density and surface area is shown in Fig. 3. These results indicate that the apparent density rapidly increased with temperature. This increase is more significant than the increase that occurred under increasing pressure. Surface area, determined by BET analysis decreased as the temperature increased. At the lower temperatures, there is no obvious particle deformation, while at the higher temperatures, sintering starts to create material bonding between particles increasing the density and lowering the surface area available for reoxidation.

Scanning Electron Microscopy (SEM) of the HBI samples was done, identifying the more open structure obtained at lower temperatures and pressures. The influence of pressure is shown in Figs. 4(a) and 4(b). The individual grains of DRI making up the HBI retained their round shape to a higher degree at the lower temperatures and pressures, when compared to the structure of those compressed at higher temperatures and pressures, whose structure appears more compressed. This deformation of particles is thought to be due to some softening of the materials at the higher temperatures and more efficient packing at the higher pressures, especially in conjunction with the increased temperature.

3.3. Influence of Carbon Content

A series of briquettes were produced from DRI varying in their carbon composition, by using different reducing techniques. Increasing the carbon content from 0.92 to 2.07 wt% corresponded to a decrease in density of the laboratory briquettes from 5.1 to 4.7 g/cm³.

This decrease in density is greater than would be predicted from the densities of the individual components of the DRI, so significant differences in porosity must exist. Carbon in DRI is predominantly present as iron carbide (Fe₃C), and a 1% carbon content is in reality around 15% Fe₃C. It is known that Fe₃C is much less malleable than iron, so it is not surprising that particles of DRI containing Fe₃C do not compact as well during briquetting as metallic iron.

Figure 5 shows micrographs of the 0.9 and 1.8% carbon briquettes, and an equivalent micrograph that has been etched in Nital to reveal the iron carbide. The high carbon
sample contains many particles of iron carbide and metallic iron particles with rims of iron carbide. This has led to a high degree of porosity, both inter-particle and intra-particle.

3.4. Reoxidation of HBI

3.4.1. Reoxidation in Salt Water

All briquettes immersed in solution were seen to corrode, but to different extents depending on the time of immersion and the salt concentration as shown in Fig. 6. Briquettes immersed for only 1–2 weeks showed little corrosion deposits. By eight weeks, the briquette surface was almost entirely covered by corrosion product that emerged at some points up to approximately 5 mm above the original briquette surface. Briquettes exhibited significant surface cracking, suggesting oxidation was not limited to the surface of the briquettes, but occurred also within the interior, as illustrated in Fig. 7.

Corrosion products were identified by Raman spectroscopy as lepidocrocite (γ-FeOOH), iron trihydroxide (Fe(OH)₃), magnetite (Fe₃O₄), goethite (γ-FeOOH) and maghemite (γ-Fe₂O₃). X-ray diffraction identified lepidocrocite (γ-FeOOH) as the primary corrosion product with magnetite (Fe₃O₄), being the next most common product. Investigation of a cross-section of a briquette immersed in saline solution for four days indicated that the centre core of the briquette had traces of iron trihydroxide (Fe(OH)₃) present, whereas the outer portions had magnetite (Fe₃O₄) and hematite (γ-Fe₂O₃). After 14 days submersion, magnetite (Fe₃O₄) was found throughout the centre.

These results can be compared to earlier reports of corrosion products found under various conditions. Music et al. said that γ-FeOOH, Fe₃O₄ and amorphous oxides were found in distilled water at 20°C, and the fraction of γ-FeOOH increased as the chloride concentration increased. In seawater, they found γ-FeOOH and β-FeOOH (aka-ganeite) and FeOCl. In an earlier study, they reported the transformation of β-FeOOH to α-FeOOH in solutions containing chloride ions at 90°C.

The similarity between the data generated in the different salt solutions indicates that the corrosion rate was not significantly affected by salt concentration in the limited range studied. Ganguly et al. reported the same lack of influence on the rate of corrosion in their study of DRI in various salt concentrations. However, in the same paper, they reported more rapid corrosion of DRI contaminated by a saline solution than in uncontaminated DRI. This trend is also borne out in the present results. There is a significant difference in both the rate and extent of reaction between briquettes corroded in salt solution and those in distilled water.
The salt in solution increases the corrosion rate of the briquettes by improving the conductivity of the electrolyte and promoting pitting corrosion. During the early part of the trial, when oxidation was predominantly reaction rate controlled, the corrosion rate in salt was seen to be higher than in distilled water. The effect of salt decreased as the reaction became more controlled by diffusion in the latter stages, when the surface was extensively covered by reaction product.

After a period of about four weeks of dry storage in air, HBI that had been in distilled water showed little change in amount of corrosion product from when it had been removed from the solution. However HBI that had been immersed for four weeks or longer in a salt solution of any concentration showed significant degradation after four weeks storage in air. The briquettes had an internal extensive red-brown corrosion product that appeared to have caused de-lamination of the briquettes, as shown in Fig. 8. Degradation behaviour indicates that once HBI has been contaminated by a saline solution, salt precipitates are sufficiently hygroscopic to render it more susceptible to atmospheric oxidation than briquettes exposed to moisture alone.

Fig. 5. Micrographs of briquettes containing different carbon contents. The right hand micrograph in each case has been etched with 3% Nital to highlight the Fe₃C (white). (a) 0.9% C briquette showing good compaction (5.1 g/cm³ density). (b) 1.8% C briquette showing poor compaction (4.7 g/cm³ density).

Fig. 6. Corrosion of briquettes from DRI 1 in salt water of varying concentrations. 

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3.4.2. Reoxidation at Different Temperatures

The influence of temperature of the environment in the range of 25–60°C, on the corrosion behaviour is shown in Fig. 9. There is a distinct correlation between temperature and both the slope of the plots (reoxidation rate) and final mass gained (reoxidation extent). At the higher temperatures, the rate is faster and the corrosion extent is greater. At the lower temperatures, the primary reaction product is lepidocrocite (\(\gamma\)-FeOOH).

The increase in corrosion rate due to temperature is not surprising, as corrosion is a chemical reaction, and the higher temperature aids in overcoming the activation energy. However in an open system, the rate of corrosion increases with temperature up to about 80°C then falls to a very low value at 100°C, the boiling point. This falling off of the rate above 80°C is related to a marked decrease in the oxygen solubility in water as the temperature is raised, that eventually is a more prominent effect than the temperature.

3.4.3. Reoxidation of Briquettes from Different DRI Sources

Briquettes were produced from DRI reduced using a different composition of reducing gas passed through the ore under high temperatures. The different reduction conditions and the chemical and size fraction characteristics are reported in Table 1. The rates of oxidation of the briquettes of DRI 1 and DRI 2 are initially very similar (see Fig. 10), but at a later stage the DRI 2 briquettes showed a faster rate of reoxidation and to a larger extent. This may be due to a number of factors; ore source and reducing conditions contribute to the different particle size fractions and the different chemistry, which in turn effect the final density of the briquette.

Towhidî and Pietsch found that the parent ore influenced the reoxidation behaviour of DRI. The DRI 1 was produced from Mt Newman iron ore in Western Australia while the DRI 2 was produced from a Venezuelan ore. The technology used to reduce the ore can also influence the DRI in terms of carbon content and particle size. DRI 2, having been reduced predominantly by hydrogen gas, had...
the lower carbon content shown in Table 1, in comparison with DRI 1 that was reduced using a mixture of hydrogen and carbon monoxide.

The similarity between the results for the DRIs up until about 2 weeks may indicate that until then, the pores and corrosion product blockage between the two are comparable. The lower rate of reoxidation in DRI 1 briquettes may be due to a greater proportion of its pores being blocked by product limiting any further reoxidation to be primarily diffusion controlled. As the DRI 2 has a lower percentage of very fine particles (−53 μm) packing order within the briquette would not be as compact as in DRI 1 briquettes. This would allow solution penetration for a longer period of time leading to a longer period of time at which the faster reoxidation rate is observed and hence a larger extent of reoxidation.

Because the ore, reduction technology, DRI chemistry, particle size distribution and density of the briquettes are all integrally linked, the following studies were conducted to investigate which of the parameters had the largest influence on the subsequent corrosion of the briquettes.

3.4.4. Reoxidation of Briquettes of the Same DRI Source but Different Density

A series of briquettes, having the same chemical content as DRI 1, but different densities were produced and corroded. The low-density briquettes were made at 500°C while the higher density briquettes were made at 600°C. This resulted in densities of an average of 4.2 g/cm³ and 5.2 g/cm³ respectively. A plot of the different corrosion behaviour can be seen in Fig. 11. This indicated that there is a difference in corrosion behaviour dependant on density, as distinct from chemistry. The higher density briquette clearly resisted corrosion better than the lower corrosion briquette did. This is due to the more open structure of the briquette of lower density as seen in the SEM pictures above.

3.4.5. Reoxidation of Briquettes of the Same Parent Ore and Similar Density, but Different Carbon Contents

A series of briquettes were corroded that were made of DRI 1 and DRI 3. These are both from the same parent ore, but due to variations in production parameters, DRI 3 has a carbon content of 1.9 wt% and DRI 1 has 1.5 wt%, as shown in Table 1. Because of the different carbon contents, different pressures and temperatures were used to make the briquettes as an increase in carbon decreases the density of the briquette, as stated previously. The resulting densities are: 4.4 g/cm³ for the DRI 1 lower carbon briquettes, and 4.6 g/cm³ for the higher carbon briquettes.

As can be seen in Fig. 12, there is negligible difference in corrosion behaviour between the HBIs containing different amounts of carbon. This could be due to the small size range studied. However, a difference of 0.5 wt% carbon corresponds to about a 20 wt% change in theoretical cementite content and a difference in corrosion behaviour was expected for two reasons. The HBI from DRI 3 is slightly denser on average than that from DRI 1 and the lower density HBI was expected to corrode faster, from the previous different density trial. In addition, Cementite (Fe₃C) is known to be more chemically stable than iron, so it was expected that HBI from DRI 1 would corrode at a faster rate than that from DRI 3. The observed lack of difference shows that carbon content doesn’t have a significant impact on the corrosion behaviour of these briquettes.

4. Summary and Conclusion

The DRI chemistry and particle size, and the temperature and pressure of briquetting all influence the briquette surface area and density. Temperature had a larger impact than pressure, producing briquettes of an increased density and decreased surface area. Briquettes formed at higher temperature and pressure had a more compact structure when observed by SEM than that of briquettes formed under less vigorous conditions. An increased carbon content decreased the density of the briquettes due to the presence of cementite (Fe₃C) which is less malleable than iron.

Ore source and reducing conditions used to produce the DRI played a significant role in determining the corrosion behaviour of briquettes exposed to oxidising conditions. HBI from DRI 1 performed better than that from DRI 2, due to the different chemical compositions derived from different reduction gas mixtures and different ore types, and different size fractions in the DRIs. Following work on briquettes with the same parent ore and similar densities and differing carbon contents showed the difference in corrosion behaviour was minimal. Corrosion behaviour of briquettes made of the same DRI, but of a different density showed that increasing the density by 1 g/cm³ (between
4.2–5.2 g/cm³) will correspond to a decreased corrosion rate.

Salt contamination of the oxidation environment increases corrosion of briquettes when compared to distilled water, as it improves the conductivity of the electrolyte. However, differences in salt concentration (3 wt%±10%) do not make a significant difference. Increasing the temperature of the environment from 25–60°C increases the rate of corrosion. The primary reaction product was lepidocrocite (γ-FeOOH).

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