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Sintering of Iron Ores in a Millipot in Comparison with Tablet Testing and Industrial Process

Abstract

To explore the feasibility of small-scale sintering pot testing, a 'millipot' facility (diameter of 53 mm and height of 400 mm) was established and used to examine the sintering performance of iron ores and other non-traditional ferrous materials. The sintering performance of a millipot was examined across a range of different operational conditions (coke rate and suction pressure) and compared with an industrial sinter strand operation. Tablet tests were also performed to assist in the design of the millipot experiments and identify conditions for achieving mineral composition similar to the industrial sinter. For the millipot experiments, the materials used need to be compacted to increase the bulk density, and a higher coke rate is required to compensate the high heat loss caused by wall effects. A higher suction pressure is also necessary to maintain an oxidizing atmosphere in the sinter bed. As expected, it was not possible to eliminate the wall effect, which resulted in more primary hematite at edges of the sintered column. However, the sintered material from the center of column simulates industrial sinter reasonably well. As such, millipot provides a practical way to evaluate the sintering process and material performance at laboratory scale, helping to bridge the gap between tablet sintering and large scale pot sintering, or full scale plant trial. The results of millipot testing can be used for designing larger scale experiments or commercial sintering trials.

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1 Sintering of Iron Ores in a Millipot in Comparison with Tablet Testing 2 and Industrial Process

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Abstract

To explore the feasibility of small-scale sintering pot testing, a ‘millipot’ facility (diameter of 53 mm and height of 400 mm) was established and used to examine the sintering performance of iron ores and other non-traditional ferrous materials. The sintering performance of a millipot was examined across a range of different operational conditions (coke rate and suction pressure) and compared with an industrial sinter strand operation. Tablet tests were also performed to assist in the design of the millipot experiments and identify conditions for achieving mineral composition similar to the industrial sinter. For the millipot experiments, the materials used need to be compacted to increase the bulk density, and a higher coke rate is required to compensate the high heat loss caused by wall effects. A higher suction pressure is also necessary to maintain an oxidizing atmosphere in the sinter bed. As expected, it was not possible to eliminate the wall effect, which resulted in more primary hematite at edges of the sintered column. However, the sintered material from the centre of column simulates industrial sinter reasonably well. As such, millipot provides a practical way to evaluate the sintering process and material performance at laboratory scale, helping to bridge the gap between tablet sintering and large scale pot sintering, or full scale plant trial. The results of millipot testing can be used for designing larger scale experiments or commercial sintering trials.

KEY WORDS: sintering of iron ores, tablet testing, millipot, industrial sinter, mineral composition of sinter, microstructure of sinter

1. Introduction

At present, sinter is the major ferrous burden material used in the blast furnace (BF) for the production of hot metal, which accounts for about 70% of the world's steel production annually. [1, 2] However, with ever changing ore costs and specifications, steelmakers are increasingly motivated to use iron ore resources with a wider range of grades and mineral types previously considered unsuitable or uneconomical for sintering, as well as other iron-bearing materials such as plant by-products. This means that new issues requiring further investigation and understanding continue to arise, including the sintering of ore types with a) overall higher gangue content, b) elements that cause problems in the steel manufacturing operations, and c) distinctive sintering performance compared with traditional hematite-rich iron ores.

Laboratory-based investigation of the sintering performance and the behaviour of the gangue components during sintering is an important step towards the successful utilization of these resources in steelmaking. In terms of laboratory-based sintering investigations, there are two generally accepted experimental scales utilized prior to industrial-scale trials being undertaken, viz. bench-scale tablet (compact) testing [3-7], and pilot-scale pot testing [2, 8-12]. The former has the advantages of flexibility and more precise control of sintering conditions, but the effects of particle size and heterogeneity of the blend are neglected. The latter, which is carried out in pots with diameters between 150~500 mm, simulates the industrial sintering process and conditions, producing product sinter suitable for standard testing regimes, but is time consuming and labor-intensive. It is therefore desirable to develop a smaller scale pot testing facility, a "millipot", which avoids the above disadvantages of a large sinter pot but still provides industrially relevant information.

Neither bench- nor pilot-scale can fully simulate the industrial sintering process. In order to obtain better simulation performance, especially in the formation of mineral phases during

high temperature sintering, the selection of the operating parameters in bench- and pilot-scale testing is crucial. In previous tablet testing investigations, an oxygen partial pressure of 0.5 kPa and 4 minutes sintering at target temperatures were used to simulate the local atmosphere in the sintering hot zone. [6, 7] In sinter pot testing, parameters, such as bulk density of sinter bed, suction pressures during ignition and sintering, and ignition time were considered. [2, 12, 13] In this work, the parameters of millipot runs were adjusted on the basis of the previous investigations to get better sintering performance. The mineral composition of the sinter samples from the millipot was investigated at different coke rates and compared with an industrial sinter obtained from the same green feed. Corresponding sintering conditions to generate similar mineral phases in tablet testing were also explored. The objectives were to develop a fundamental understanding of the microtextural characteristics at three scales (tablet, millipot and industrial) and to demonstrate the suitability and application of the millipot set-up to simulation of the industrial sintering process.

2. Experimental

2.1 Sintering Feed Materials

As one of the objectives of the present work was to closely simulate industrial sintering conditions, green feed from the exit of the granulation drum at BlueScope's Port Kembla Sinter Plant was used as the base feed for the millipot experiments. The components of the base green feed were (wet-wt%-green feed basis at a total free moisture content of 6%):

- Iron ores (Ores 1 to 5): 45.7, 1.82, 1.51, 1.69 and 8.31 wt%, respectively.
- Manganese ore, ferrous recycles, metallic recycles and returned fines: 0.34, 4.70, 3.23 and 15.65 wt%, respectively.
- Limestone and dolomite: 10.62 and 2.28 wt%, respectively.

- Coke: 4.17 wt%.

The mixed green feed was sampled and then stored in sealed plastic bags to prevent loss of moisture. To determine its particle size distribution, a sub-sample was dried and sieved, resulting in a distribution (wt%) of: +0-2mm 37%, +2-4mm 29%, +4-6.3mm 19%, +6.3-8mm 6%, +8-10mm 4% and +10mm 5%.

Due to the small diameter of the millipot, large particles have a disproportionate effect on the local sintering conditions. [11] To mitigate this, the feed was sieved with the +6.3 mm fraction being jaw crushed and recombined before manual regranulation in a laboratory drum to ensure the final green feed had a top size less than 6.3 mm. The indicative green feed composition was (wt% dry basis, including all components in the blend): total Fe 47.8 (1.76 FeO), SiO₂ 5.56, Al₂O₃ 1.51, CaO 8.71, MgO 1.01 and carbon 3.99 yielding a basicity (CaO/SiO₂ weight ratio) of 1.57.

The coke rate was defined as follows:

$$\text{Coke rate (CR)} = \frac{m(\text{coke})}{m(\text{green feed})} \times 100\% \quad (1)$$

where m(coke) denotes the mass of coke and m(green feed) the mass of green feed including coke, both on a dry basis.

For tablet experiments, an equivalent blend comprising the ore and flux components (coke and recycles were not included) was sourced from the plant raw material stockpiles, with each raw material component ground to < 200 µm. These materials were then mixed in the proportion corresponding to that of the industrial sinter plant and mixed thoroughly to ensure homogeneity.

2.2 Sintering Equipment

Figure 1(a) shows a schematic of the millipot: it consists of an insulated sinter tube (pot), air suction and waste gas treatment components, and a process monitoring and control system. The sintering tube is a stainless-steel column (53 mm internal diameter, 490 mm high) surrounded by 50 mm of thermal insulation material. Six ports on the side of the column allow for insertion of thermocouples to monitor the sintering temperature, or connection with a differential pressure transducer for pressure drop measurement. Two extra ports are available at the bottom extended section (T7) for the measurement of off-gas temperature and the pressure drop across the sinter bed. The sintering process is initiated using an LPG burner located at the top of the millipot. The air suction system includes a water ring vacuum pump and a buffer container or windbox to stabilize the system suction pressure. The windbox is half filled with water so that the flue gas generated during sintering can be cooled and cleaned before passing through the suction pump. The suction pressure can be controlled using a bypass valve on the windbox providing additional dilution air, *i.e.* without flowing through the sinter pot.

The process monitoring system measures the sintering temperature and pressure drop within the sinter pot. The temperatures at different locations of the sinter pot are monitored using bare Type K thermocouples connected to a Thermocouple C Series Module (Model NI 9212, National Instruments). Bare thermocouples were used to increase the sensitivity and accuracy of the measurement. The suction pressure is monitored using a differential pressure transducer (26PC series, Honeywell, supplied by RS Australia) with one side connected to port P and the other to ambient. All of the temperature and pressure data are logged using a computer with LabVIEW software (version 2013.0.1, National Instruments).

Figure 1. Schematics of laboratory sintering set-ups: (a) Millipot; (b) vertical electrical furnace.

The tablet sintering experiments were carried out using a vertical electric heating tube furnace as presented in Figure 1(b). Tablets were loaded into a steel wire basket and located in the furnace hot zone. The oxygen partial pressure was adjusted by mixing air and nitrogen, with flow rates controlled via mass flow controllers. The parameters of individual experiments are covered in the Results and Discussion section.

2.3 Sintering Procedures

For the millipot testing, the green feed was added to the stainless steel column in approximately 120g aliquots and compacted with a rod after each aliquot was added. Thermocouples were placed in the corresponding port as filling approached the level of each port. Sintering was initiated by adjusting suction pressure to 5.3 kPa and then placing the burner over the top of the bed for 90 s. The burner was then removed and the suction pressure increased to 10.6 kPa, matching the pressure gradient used by Lu. [2, 13] After the flame front had passed through the bed, suction was continued until the flue-gas temperature cooled to 80 °C, following which the pump was turned off and the sinter pot unloaded. Sintered

lump products excluding the wall area were collected for analysis. A more detailed procedure for the millipot operation is reported elsewhere. [12]

Flame front speed (FFS) is an important operational parameter for sintering. In this investigation, the FFS is defined as follows:

$$FFS = \frac{\text{Bed height}}{\text{Sintering time}} \quad (2)$$

It is calculated using the distance between ports 1 and 6 (bed height) divided by the time difference at which the peak temperatures were reached at the two ports (sintering time).

For the tablet experiments, cylindrical tablets of 6 mm diameter and ~5 mm height were prepared. An equivalent tablet blend was prepared from individual ores and fluxes (without coke and recycles) in the normalised proportions present in the plant green feed. The tablet blend was ground in a ring mill to less than 200 µm and pressed at 48.8 MPa to form each tablet. The tablets were loaded into the reaction basket and placed at the top (cold) end of the furnace tube. The furnace was preheated to the desired temperature and flushed with the gas mixture ($P_{O_2} = 0.5$ kPa) for at least 15 minutes; the basket was lowered to the hot zone and the tablet sintered for 4 minutes with gas flow of 1 NL/min (linear speed: 0.45 m/min). [6]

Adopting the methodology of Wang et al. [7], two cooling procedures were employed: a) directly lifting the basket to the cold end of the furnace tube and simultaneously switching the sintering gas atmosphere to ambient air; b) soaking at the sintering temperature or 1250 °C, whichever was lower, in air of 6 NL/min for 3 minutes, then lifting the basket to the top end of the furnace tube. All the temperatures were pre-calibrated by lowering a type R thermocouple into the empty hot zone of the furnace with the same gas flow.

The overall oxygen partial pressure in the exhaust gas of a sinter strand is high. However, due to the non-uniform gas flow, , and the progression of the flame front, the oxygen partial pressure in a sinter bed is dynamic and non-uniform over a large range (0-21%). In a local

area where the gas flow is weak and oxygen is consumed by the combustion of coke, the oxygen partial pressure can be very low. In previous investigations it was shown that 0.5% O₂ partial pressure was a representative value for the formation of mineral phases during high temperature sintering, and was determined for tablet sintering conditions to produce similar overall microstructures. [6, 7] This O₂ partial pressure value was therefore used in this investigation in assessing mineral composition effect in tablet sintering.

2.4 Characterization Methods

The sintered tablets and lump sinter samples were mounted in epoxy resin in preparation for optical and SEM-EDS analysis. After curing, the surface was ground and polished to a 1 µm finish for optical microscopic observation (Leica DM6000 Optical Microscope). The polished sample was then platinum coated and analyzed by scanning electron microscopy (JEOL JSM – 6490LV) operated at 15 kV.

The mineral phase compositions of the industrial sinter samples were determined by point counting (Olympus Vannox optical microscope) and the millipot samples by image analysis. In both cases, the samples were crushed to less than 1.7 mm, and then 32 g of representative samples were mounted in epoxy resin. After curing, the cylindrical samples were cut along the axial direction and polished to a 1 µm finish. Optical images for image analysis were taken by Leica DM6000 Optical Microscope and analyzed by Leica application Suite V4.0.

3. Results and Discussion

3.1 Industrial Sintering Conditions and Sinter Properties

Sinter quality metrics such as reducibility and mechanical strength affect BF productivity – in turn, sinter quality is governed by its microstructure. Sinter microstructure requires characterization in terms of chemical composition, mineralogy, and morphology of the presenting phases.

Figure 2 shows optical images of an industrial sinter sample of the same blend. During production of that sinter, the bulk density of green feed was 1770 kg/m³ and FFS was 13.6 mm/minute. Silico-ferrites of calcium and aluminum, SFCA and SFCA-I, are typically the major and most desirable bonding phases because of their high reducibility and good mechanical strength. [14-19] Moreover, the SFCA phases are considered the most important phases for producing high quality sinter at low temperatures and high productivity. [20-23] Secondary hematite and magnetite are the second group of major constituents in the bonding phases which are formed in more oxidizing or reducing atmospheres, respectively, and crystallized from the melt. Additionally, some relict regions (quartz and primary hematite derived from goethite ore) retain their original contours and show a reaction halo with the surrounding melt, Figure 2e.

Figure 2. Optical images of industrial sinter. Q: quartz; PH: primary hematite; SH: secondary hematite; M: magnetite; S: silicate; SFCA: platy shape of silico-ferrite of calcium and aluminum; SFCA-I: acicular shape of silico-ferrite of calcium and aluminum.

Figure 2 shows that individual particles of the industrial sinter sample, and also different regions within those particles have distinctive morphologies and mineral compositions. It is understood that the differences were caused by the changes of the sintering conditions at different locations of the sintering bed due to local non-uniformity of the blend composition, loading density, gas flow, etc., which caused differences in the maximum temperatures reached and oxygen partial pressure at different locations. However, it was the general morphology and, specifically, the overall mineral phase composition of the industrial sinter that was targeted for the millipot sinter product.

3.2 Sintering Performance of Millipot

In this millipot study, the material being sintered was derived directly from sinter plant green feed, with adjustment of coke rate being made to achieve reasonably close correspondence of sintering conditions to those in the full-scale plant. The feed preparation and experimental procedures for the millipot were adjusted by comparison to the sintering performance of the industrial process, as summarized below.

An initial set of experiments were carried out to investigate the effect of coke rate and determine an appropriate level for the millipot runs with no initial compaction of the green bed. [12] However, without compaction, the FFS was significantly higher than in the industrial sinter strand, 18~24 cf. ~14 mm/min, and approximately half of the sintered material was in the form of fines (<3.35mm), *i.e.* insufficient melting phase was formed to bond materials together. Furthermore, the bulk density of green feed without compaction was

~1650 kg/m³, which was lower than an optimum level of ~1800 kg/m³ [2] - this resulted in a high sinter bed permeability and ultimately high FFS, high heat loss and low melt formation. To increase the density, uniformity and controllability of pot filling, and to decrease the FFS during sintering, a compaction rod with a 50 mm diameter disk (weight = 1327 g) at the base was used. The green feed was loaded into the column in 120 g increments (out of a total charge of 1750 g). After each 120 g increment, the compaction rod was gently placed on the surface, lifted 100 mm and then released. This process was repeated until the column was filled to the top giving an initial bed height of 400 mm. Figure 3 presents the relationship between the loaded weight and the bed height, and corresponding average bulk density at different loading heights. Using the compaction rod, the bulk density of the sinter bed attained ~1880 kg/m³. There was a slight difference between the bottom and top of the bed and the trend was repeatable.

Figure 3. The changes of the bed height and average bulk density with the loaded weight. The bed height lines overlap.

The effect of coke rate on the sintering performance is presented in Table 1. With compaction, the average bulk density ranged between 1870-1880 kg/m³. The FFS at different coke rates was reasonably consistent, i.e. ~16 mm/minute. Except for the test with a low coke

rate of 5.0%, all of the tests were well sintered, with less than 15% of fines smaller than 3.35 mm in the whole sinter product.

Table 1. Effects of coke rate and suction pressure gradient on the sintering performance of iron ores

Test No.	Coke rate, %	Suction pressure				Bulk density, kg/m ³	FFS, mm/min	Fraction of fines <3.35 mm, %	Temperature profile
		Ignition		Sintering					
		kPa	kPa/m	kPa	kPa/m				
1	5.0	5.3	13.3	10.6	26.5	1876	16.6	20.9	Fig. 4(a)
2	6.0	5.3	13.3	10.6	26.5	1880	15.4	11.6	Fig. 4(b)
3	7.4	5.3	13.3	10.6	26.5	1877	15.3	12.8	Fig. 4(c)
4	8.0	5.3	13.3	10.6	26.5	1872	15.1	10.8	Fig. 4(d)
5	6.0	5.6	14.0	11.5	28.8	1874	16.5	14.3	Fig. 4(e)

Figure 4 presents the temperature profiles and the change of suction pressure during various sintering tests with different coke rates. It should be noted that these temperature profiles likely better reflect gas, rather than solid, temperatures. Furthermore, the measured peak temperature was affected by different factors such as local solid composition and local porosity surrounding the thermocouple tip. These composition/porosity effects are likely to vary between thermocouple to thermocouple and test to test. As such values are qualitative and should be considered with respect to temperature trends than absolute values. The peak temperature at the column centre was always high, increasing down the pot as sintering progressed, which is consistent with the industrial process and traditional sinter pot. The temperature measurement at the wall shows that thermal conditions were not sufficient to effectively sinter the ores. To achieve a uniform coke particle distribution radially and axially, Coke was mixed with ore and fluxing components in the form of particles to simulate the state in the industrial sinter strand, and fully granulated prior to adding to the millipot.

The temperature difference between the centre and the wall is principally a result of heat loss at the wall and not from the non-uniform coke distribution.

Figure 4 – Temperature and suction pressure profiles during millipot sintering under different coke rates. (a) Coke rate = 5.0%; T2: wall temperature, and T3, T4, T6: centre temperatures; (b) Coke rate = 6.0%; T2: wall temperature, and T3, T5, T6: centre temperatures; (c) Coke rate = 7.4%; T1 - T6: centre temperatures; (d) Coke rate = 8.0%; T2: wall temperature, and T1, T3, T4, T6: centre temperatures; (e) Coke rate = 6.0%; T2, T3: wall temperatures, and T4, T6: centre temperatures; increased suction pressure. T7: flue gas temperature in all plots.

Figure 4 also shows that the suction pressure reduced with the progress of sintering, with a sharp transition after the flame front had passed through the bottom of the sinter bed. The gas

flow after the ignition stage was measured to be 64 NL/min, corresponding to a superficial velocity of 2.9 m/s (empty column, at 0 °C and 1 atm). The gradual reduction in the suction pressure before the flame front passed through the whole bed reflects a reduction in flow resistance of the product sinter relative to the feed because of the removal of coke and moisture from the bed, and the coalescence and rearrangement of pores during sintering. Notably, the suction pressure at the end of sintering decreased from 7.2 kPa to 5 kPa (from 18.0 kPa/m to 12.5 kPa/m) when the coke rate was increased from 5.0% to 8.0%, which indicates the final permeability was higher as coke rate increased due to enhanced coalescence and higher resultant porosity.

Table 1 also includes the result of a sintering test in which the suction pressures at the ignition and sintering stages were both increased in comparison with the reference conditions with coke rate at 6% (test 5). The suction pressure was increased to 5.6 and 11.5 kPa (14.0 and 28.8 kPa/m) during ignition and sintering, respectively, in order to increase the oxygen potential. With similar starting bulk density, the increase in suction pressure caused an increase in FFS, with increased fines generation being observed compared to test 2. Despite the negative effect on the extent of sintering, increased suction pressure increased the air flow in the sintering bed, which is beneficial to maintaining a high oxygen partial pressure and the formation of SFCA and hematite.

Figure 5 shows the coherent core of the sinter product from testing with 6% coke rate with increased suction pressure (test 5). In general, the core was well sintered except at the edge where some embedded, weakly sintered ore and flux particles can be observed.

Figure 5. Photographs of the sinter core from testing with 6% coke rate at increased suction pressures. (a) Side view; (b) cross-section view.

The sample presented in Figure 5 was mounted in epoxy resin and polished to observe its microstructure and mineral phases. Figure 6(a) presents a photomicrograph of the sinter cross-section of the core in Figure 5(a) after grinding and polishing which gives an overview of sintering performance across the millipot and the influence of wall effects. The most notable feature is that primary hematite is preferentially distributed near the edge of the cross-section due to low sintering temperatures near the wall. Figure 6 (d) shows a typical photomicrograph of the sinter cross-section taken from the centre of the core in Figure 5(a), and Figures 6 (e) and (f) are the magnified images of the areas marked on Figure 6(d). Overall, the area in Figure 6(d) was well sintered; the structure contains many round pores, indicating that the solid was partially melted during sintering. A large amount of magnetite was observed which was bonded by SFCA, as shown in Figures 6(e) and (f), due to the high temperature and low oxygen partial pressure atmosphere during the peak temperature period in the sintering process. In the sinter adjacent to large pores, secondary hematite and SFCA were observed. After the passage of the flame front, colder air passed through the already sintered bed on its way to the reaction zone, providing an oxidizing atmosphere during

cooling. Needle-like larnite in glass was also observed in the lower part of Figure 6(e), reflecting the high peak temperature reached similar to that in the industrial sintering process. Based on the sintering extent as characterized by the morphology and mineral composition, it may be inferred that the temperature distribution was relatively uniform except in the thin layer close to the wall of the sinter column. This phenomenon is likely a result of the relatively fast heat transfer within the metallic millipot wall and the slow heat transfer in the sinter bed.

Figure 6 – Photomicrographs of the sinter core in Figure 5: (a) cross-section of the sinter core; (b), (c) the edge of the core at different section; (d) the centre section of the core; (e), (f) the rectangular areas as marked in (d). GO: goethite ore; HO: hematite ore; L: larnite.

Figures 6 (b) and (c) present the microphotographs of typical structures of particles around the edge of the sinter column. Remnant iron ore particles dominate which correspond to those observed macroscopically in Figure 5 (a). Limited assimilation of ore and flux particles occurred at the pot wall where heat losses are high. In Figure 6, some unreacted flux and iron ore particles are present near the edge of the sinter column. Incomplete sintering also took place in some particles: their shapes were retained but pores and secondary hematite were formed during sintering. Classification of the semi-reacted particles in Figures 6 (b) and (c) was inferred based on morphological comparison to unsintered ore samples. Partially melted areas were observed on the edge of the particles, as characterized by porous structure and rounded pores. Due to the significantly lower temperature in the edge zone caused by wall effects, some hematite ore retained its original morphology (Figure 6(b)). The goethite particles mostly kept the original morphology, but many cracks appeared in the matrix due to the dehydration reaction at relatively low temperatures (Figure 6(c)).

3.3 Sintering Conditions by Tablet Testing

To better understand the sintering process, tablet experiments were conducted under various temperatures with different quench methods. To determine the temperatures achieved, a tablet was prepared with a type R thermocouple placed at its centre. The tablet was then inserted into a furnace at 1300 °C and allowed to reach a constant temperature before it was moved to the top end of furnace tube and cooled to room temperature (Figure 7). The tablet temperature increased sharply when it was heated in the furnace, approaching the furnace temperature within a minute. The peak heating rate was 88.5 °C/s which compares to

33.6 °C/s (average of the temperature rising rates from thermocouples T1 to T4 (except located at the wall) for millipot experiments 1-4). The temperature of the tablet reached 1280 °C and 1288 °C after 1 and 1.4 minutes and plateaued at 1291 °C after 2.1 minutes. The temperature change during quenching was also very fast, decreasing to below 1000 °C in seconds. The peak cooling rate was 63.2 °C/s which compares to 20.9 °C/s (average of T1 to T6 thermocouple rates for millipot test No. 3 in Table 1).

Figure 7. The temperature profile of a tablet of 6 mm in diameter heated in a furnace at 1300 °C and then quenched in air at room temperature.

Sintering at 1250 °C for 4 minutes and then quenching formed a large amount of SFCA and SFCA-I (Figure 8). However, significant melting was not observed and a significant fraction of primary hematite was retained. With increasing sintering temperature, pore coalescence was more apparent due to increased melting as indicated by the formation of large round pores. In the tablet sintering tests, the sinter blend was crushed into fine powder and then pressed into tablets. Many small pores were present among the fine particles of sinter blend. Along with the increase in the extent of sintering with increasing temperature, the amount of sinter melt increased with improved fluidity, which helps coalesce the small pores into larger

357 pores. Especially, when a liquid phase was formed, the liquid penetrated into small pores,
358 forming denser solid/liquid phases and larger pores. The amounts of hematite, SFCA and
359 SFCA-I also decreased with increasing sintering temperature. As in Figure 8, at 1325 and
360 1350 °C, the amounts of hematite and SFCAs were minimal as hematite was not stable
361 throughout the temperature range of the tests in the atmosphere with 0.5% O₂.

Figure 8. Photomicrographs of the tablets sintered at different temperatures in the 0.5% O₂ atmosphere for 4 minutes and then directly quenched in air to room temperature.

The decomposition of hematite to magnetite as well as oxidation of magnetite would occur at different temperatures and atmospheres:

Thermodynamic calculation using FactSage shows that, in the atmosphere with 0.5% O₂, the decomposition happens above 1235 °C, which implies the decomposition of hematite could occur in all tablet tests of Figure 8. Under these conditions, oxygen released during hematite decomposition diffused through the tablet, forming an oxygen partial pressure gradient. As a result, the hematite close to the edge of the tablet decomposed faster than that at the centre. This is consistent with the observation that the remaining hematite was present internally within the tablets sintered at temperatures up to 1300 °C. Above this temperature, no residual hematite was observed; only a very small amount of secondary hematite was observable at the very surface, formed by oxidation of the magnetite during fast cooling in air.

From Figure 9, the addition of a 3-minute soaking stage after sintering for 4 minutes mostly affected the amount of hematite in the tablets. The overall appearance of the tablets was not obviously changed, although an increase of the proportion of large pores cannot be excluded. At 1250 °C, three minute holding in air increased the amount of hematite throughout the tablets. The increased amount of hematite was attributed to the re-oxidation of magnetite during soaking in air, which was predicted by FactSage to take place below 1383 °C in air. At 1300 °C, additional hematite was only present at the edge of the tablet. It is also noted that the small fraction of hematite present at the centre of the tablet in Figure 8 at 1300 °C practically disappeared during the cooling in air (Figure 9). No obvious formation of hematite was detectable in the tablets sintered at higher temperatures 1325 and 1350°C. It is speculated that the lack of formation of secondary hematite was due to multiple factors, including formation of molten phase and gradual replacement of the relatively reducing gas by air in

the furnace tube. Furthermore, the magnetite in the molten solution had a lower activity and hence was more stable, while in the early stage of cooling the atmosphere was less oxidizing compared with air.

During the soaking stage in air, oxygen diffused towards the interior of the tablets. It seems that only the external layer was affected by the oxidation of magnetite at 1300 °C. The lack of oxidation in the tablets sintered at temperatures above 1300 °C and then cooled in air is attributed to the melting of the fine particles constituting the tablets which enclosed the internal pores and suppressed the diffusion of O₂ into the tablets. The magnified image of the tablet edge (Figure 9) shows that the matrix of the tablets sintered at high temperatures was dense and impermeable, and hematite existed as a very thin layer at the periphery. The tablet sintered at 1275°C in 0.5% O₂ atmosphere for 4 minutes followed by holding in air for 3 additional minutes has the most similar microstructure to the sinter products from the millipot and industrial sinter plant when comparing the morphology and mineral phase composition.

Figure 9. Photomicrographs of the tablets sintered at different temperatures in the atmosphere with 0.5% O₂ for 4 minutes followed by holding in air at the lower of the sintering temperature or 1250 °C for 3 minutes.

3.4 Comparison of the Mineral Compositions of Tablet, Millipot and Industrial Sinters

The mineral phase compositions of the sintered tablets, millipot and industrial sinter products obtained by image analysis are summarized in Figure 10. The figure also includes the results for industrial sinter via the point counting method. In reflectance based image analysis, glass cannot be distinguished from pores, so the glass content was not quantified, and the total fractions of hematite, magnetite and SFCA were normalized to 100%. Further, only the combined amount of SFCA and SFCA-I was obtained, as the reflectance of these two phases is essentially the same, preventing separate determination via image analysis.

Figure 10. Comparison of sinter mineral phase compositions under different sintering conditions (tablets, millipot and industrial). T indicates Tablet experiment at temperature and

419 + indicates three minutes holding in air at 1250 °C during the cooling stage; M indicates
420 Millipot run at CR (coke rate) and # indicates pressure gradient increased to 14.0 kPa/m in
421 ignition and 28.8 kPa/m in sintering process; Ind indicates Industrial sample, with IA (image
422 analysis) and PC (point counting).

423 For the industrial sinter, 37% hematite, 39% magnetite, and 23% SFCA was determined by
424 image analysis, which is the closest to the millipot sinter produced with 6% coke rate and
425 increased suction pressure (viz. 35% hematite, 40% magnetite and 25% SFCA). For the
426 millipot sinter with 6% coke rate but without the increase in suction pressure, both hematite
427 and SFCA were lower. An increase in the pressure gradient in the millipot operation caused
428 an increase in the oxygen partial pressure in the sinter bed, which made the mineral
429 composition of the sinter closer to that of industrial sinter. Increasing the coke rate above 6%
430 generated sinter products with more magnetite.

431 The sinter samples from the tablet experiments changed in mineral composition with the
432 change in sintering temperature and cooling procedure, as demonstrated by the optical
433 images. The tablets consisted of finely ground and uniformly mixed blends of iron ores and
434 fluxes, so the conditions for assimilation reactions between different constituents were more
435 favourable than in the millipot or industrial sintering process. This helps explain the
436 occurrence of sintering reactions at 1250°C or even lower temperatures when the particles
437 remained in the solid state.[1, 24] With increasing temperature, the amount of magnetite
438 increased steadily, while that of hematite and SFCA decreased. Especially at temperatures
439 above 1300°C, magnetite accounted for most of the tablets.

440 Notably, a soaking stage in air at elevated temperatures prior to final cooling improved the
441 comparability of the tablet to the mineral content in the industrial and pot sintering processes.
442 Addition of the intermediate cooling stage increased the amounts of hematite and SFCA,

especially at lower temperatures. Both SFCA and hematite contents reached the maxima (~40%) under the “T-1250°C+” condition; at this temperature conversion of hematite to magnetite is low and the high hematite content favoured the formation of SFCA, because of low reduction driving force. [2, 16, 25] In the tablet sintered at 1275°C, the increased temperature caused more reduction and formation of melting phase. Reoxidation and recrystallisation during the intermediate soaking stage generated a similar mineral composition and structure to that of industrial sinter (Figure 11).

Figure 11. Comparison of three sintering scales: (a) industrial; (b) millipot under M-CR6%#; (c) tablet under T-1275 °C+.

Overall, the microstructure and mineral phase composition of the industrial sinter were most like the sintered tablet “T-1275°C+” and millipot sinter with industrially comparable bulk density, 6% coke rate and increased suction pressure. In millipot, compaction not only increases the overall bulk density, but also improves uniformity across the column diameter, reducing peripheral gas flow minimizing the wall affected zone. The pressure gradient and hence overall gas flowrate were increased to achieve comparable flame front speeds. With a higher coke rate offsetting heat losses to the wall and increased waste gas volume to regain target centreline temperatures. The similar microstructure and phase composition achieved indicate that the gas atmosphere in the analyzed central portion was similar to that in the industrial sinter.

Overall, based on the results in this study, the millipot sinter, except the near-wall product, can represent industrial sinter, which bridges the gap between sintered tablets and larger scale pots or full plant scale. The millipot can therefore be used as a tool for designing larger scale experiments or sintering trials.

4. Conclusions

To determine the feasibility of small-scale pot testing, a ‘millipot’ facility was established to examine the sintering performance of iron ores and other non-traditional ferrous materials.

Three sinter processing methods, viz. tablet, millipot and industrial sinter plant, were evaluated and sinter products compared using the same blend. The major findings are summarized as follows:

1) For the millipot, some experimental adjustments have to be made to achieve conditions comparable to full scale sintering, including:

- a. mechanical compaction, to increase bulk density of the sinter bed, which decreases the flame front speed (FFS) and the wall effect;
- b. coke rate increase, to offset high heat loss from the small diameter column;
- and
- c. suction pressure increase, to adjust the oxidizing atmosphere during sintering.

With these adjustments, the millipot achieved sintering conditions in a similar range to the industrial process (density of sinter bed, temperature, and FFS), and a sinter product with similar microstructure and mineral composition. It was not possible to fully eliminate the wall effect in the small diameter millipot set-up.

2) Based on a comparison of microstructure and mineral composition of the sinter products produced:

- a. a tablet sintered at 1275 °C with 0.5% O₂ for 4 minutes, followed by further sintering in air for 3 minutes; and
- b. a millipot sinter produced with coke rate 6%, suction pressure 14.0 kPa/m during ignition and 28.8 kPa/m during sintering
- were most similar to the industrial sinter investigated.

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REFERENCES

1. A.K. Biswas, *Principles of Blast Furnace Ironmaking*. Cootha Publishing House, 1981.
2. L. Lu, *Iron Ore: Mineralogy, Processing and Environmental Sustainability*. 2015: Elsevier.
3. J. Clout and J. Manuel, *Fundamental Investigations of Differences in Bonding Mechanisms in Iron Ore Sinter Formed from Magnetite Concentrates and Hematite Ores*. Powder Technology, 2003. **130**(1): p. 393-399.
4. Z. Wang, D. Pinson, S. Chew, H. Rogers, B. J. Monaghan, and G. Zhang, *Interaction of New Zealand Ironsand and Flux Materials*. ISIJ International, 2016. **56**(8): p. 1315-1324.
5. Z. Wang, D. Pinson, S. Chew, H. Rogers, B. J. Monaghan, and G. Zhang, *Mineral Phase Formation and Zinc Removal during Sintering of Filter Cake Wastes*. ISIJ International, 2016. **56**(4): p. 505-512.
6. L. Hsieh and J. A. Whiteman, *Sintering Conditions for Simulating the Formation of Mineral Phases in Industrial Iron Ore Sinter*. ISIJ International, 1989. **29**(1): p. 24-32.
7. Z. Wang, D. Pinson, S. Chew, H. Rogers, B. J. Monaghan, M. Pownceby, N. Webster, H. Rogers and G. Zhang, *Effects of Sintering Materials and Gas Conditions on Formation of Silico-ferrites of Calcium and Aluminium during Iron Ore Sintering*. ISIJ International, 2016. **56**(7): p. 1138-1147.
8. C. Loo and R. Dukino, *Laboratory Iron Ore Sintering Studies. 2. Quantifying Flame Front Properties*. Mineral Processing and Extractive Metallurgy, 2014. **123**(4): p. 197-203.

9. H. Li, *Effect of Raw Material Composition on the Sintering Properties*. ISIJ international, 2005. **45**(4): p. 551-559.
10. R.R. Lovel, Vining K.R., *The Influence of Fuel Reactivity on Iron Ore Sintering*. ISIJ international, 2009. **49**(2): p. 195-202.
11. C. Kamijo, M. Matsumura, and T. Kawaguchi, *Sintering Behavior of Raw Material Bed Placing Large Particles*. ISIJ international, 2005. **45**(4): p. 544-550.
12. H. Li, R. Zhou, D. J. Pinson, P. Zulli, L. Lu, R. J. Longbottom, S. J. Chew, B. J. Monaghan, G. Zhang, *A Millipot Set-up for Sintering Investigation of Iron Ores*. Iron Ore 2017 Conference, 2017: p. 85-90.
13. L. Lu, M. Adam, M. Kilburn, S. Hapugoda, *Substitution of Charcoal for Coke Breeze in Iron Ore Sintering*. ISIJ international, 2013. **53**(9): p. 1607-1616.
14. K. Yajima, and S. Jung, *Data Arrangement and Consideration of Evaluation Standard for Silico-Ferrite of Calcium and Alminum (SFCA) Phase in Sintering Process*. ISIJ international, 2012. **52**(3): p. 535-537.
15. R. Chaigneau, *Complex Calcium Ferrites in the Blast Furnace Process*. Delft University of Technology, 1994.
16. J. Jeon, S. Jung, and Y. Sasaki, *Formation of Calcium Ferrites under Controlled Oxygen Potentials at 1273 K*. ISIJ international, 2010. **50**(8): p. 1064-1070.
17. N. A. Webster, M. I. Pownceby, I. C. Madsen, A. J. Studer, J. R. Manuel and J. A. Kimpton, *Fundamentals of Silico-ferrite of Calcium and Aluminum (SFCA) and SFCA-I Iron Ore Sinter Bonding Phase Formation: Effects of CaO: SiO₂ Ratio*. Metallurgical and Materials Transactions, 2014. **45**(6): p. 2097.
18. M. Pownceby and J. Clout, *Importance of Fine Ore Chemical Composition and High Temperature Phase Relations: Applications to Iron Ore Sintering and Pelletising*. Mineral Processing and Extractive Metallurgy, 2003. **112**(1): p. 44-51.
19. M.S. de Magalhães, and P.R.G. Brandao, *Microstructures of Industrial Sinters from Quadrilatero Ferriero's Iron Ores, Minas Gerais State, Brazil*. Minerals Engineering, 2003. **16**(11): p. 1251-1256.
20. N. V. Scarlett, M. I. Pownceby, I. C. Madsen and A. N. Christensen, *Reaction Sequences in the Formation of Silico-ferrites of Calcium and Aluminum in Iron Ore Sinter*. Metallurgical and Materials Transactions B, 2004. **35**(5): p. 929-936.
21. M. Sasaki and Y. Hida, *Consideration on the Properties of Sinter from the Point of Sintering Reaction*. Iron and Steel, 1982. **68**(6): p. 563-571.
22. L. Hsieh and J. A. Whiteman, *Effect of Oxygen Potential on Mineral formation in Lime-fluxed Iron Ore Sinter*. ISIJ International, 1989. **29**(8): p. 625-634.
23. Y. Hida, J. Okazaki, K. Itoh, M. Sasaki, *Formation Mechanism of Acicular Calcium Ferrite of Iron Ore Sinter*. Tetsu-to-Hagane(J. Iron Steel Inst. Jpn.), 1987. **73**(15): p. 1893-1900.
24. J.H. Strassburger, *Blast Furnace Theory and Practice*. Vol. 2. 1969: Taylor & Francis.
25. M. Gan, X. Fan, and X. Chen, *Calcium Ferrite Generation During Iron Ore Sintering—Crystallization Behavior and Influencing Factors*, in *Advanced Topics in Crystallization*. 2015, InTech.

565 Figure 1. Schematics of laboratory sintering set-ups: (a) Millipot; (b) vertical electrical
566 furnace.

567 Figure 2. Optical images of industrial sinter. Q: quartz; PH: primary hematite; SH: secondary
568 hematite; M: magnetite; S: silicate; SFCA: platy shape of silico-ferrite of calcium and
569 aluminum; SFCA-I: acicular shape of silico-ferrite of calcium and aluminum.

570 Figure 3. The changes of the bed height and average bulk density with the loaded weight. The
571 bed height lines overlap.

572 Figure 4. Temperature and suction pressure profiles during millipot sintering under different
573 coke rates. (a) Coke rate = 5.0%; T2: wall temperature, and T3, T4, T6: centre temperatures;
574 (b) Coke rate = 6.0%; T2: wall temperature, and T3, T5, T6: centre temperatures; (c) Coke
575 rate = 7.4%; T1 - T6: centre temperatures; (d) Coke rate = 8.0%; T2: wall temperature, and
576 T1, T3, T4, T6: centre temperatures; (e) Coke rate = 6.0%; T2, T3: wall temperatures, and
577 T4, T6: centre temperatures; increased suction pressure. T7: flue gas temperature in all plots.

578 Figure 5. Photographs of the sinter core from testing with 6% coke rate at increased suction
579 pressures. (a) side view; (b) cross-section view.

580 Figure 6. Photomicrographs of the sinter core in Figure 5: (a) cross-section of the sinter core;
581 (b), (c) the edge of the core at different section; (d) the centre section of the core; (e), (f) the
582 rectangular areas as marked in (d). GO: goethite ore; HO: hematite ore; L: larnite.

583 Figure 7. The temperature profile of a tablet of 6 mm in diameter heated in a furnace at
584 1300 °C and then quenched in air at room temperature.

585 Figure 8. Photomicrographs of the tablets sintered at different temperatures in the atmosphere
586 with 0.5% O₂ for 4 minutes and then directly quenched in air at room temperature.

587 Figure 9. Photomicrographs of the tablets sintered at different temperatures in the atmosphere
588 with 0.5% O₂ for 4 minutes followed by holding in air at the lower of the sintering
589 temperature or 1250 °C for 3 minutes.

590 Figure 10. Comparison of sinter mineral phase compositions under different sintering
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592 + indicates three minutes holding in air at 1250 °C during the cooling stage; M indicates
593 Millipot run at CR (coke rate) and # indicates pressure gradient increased to 14.0 kPa/m in
594 ignition and 28.8 kPa/m in sintering process; Ind indicates Industrial sample, with IA (image
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596 Figure 11. Comparison of three sintering scales: (a) industrial; (b) millipot under M-CR6%#;
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