Review

A Perspective of Goethitic Ore Sintering Fundamentals

C. E. LOO

Newcastle Technology Centre, BHP Billiton Technology, PO Box 188, Wallsend, NSW 2287 Australia.

The main purpose of iron ore sintering is to produce a strong agglomerate for the blast furnace. This is achieved by partially melting a sinter mix at high temperature and then allowing the melt to solidify into a bonding phase for the unreacted material. The melt formation and subsequent solidification processes are highly dependent on the composition of the blended mix. This paper summarises the differences in sintering behaviour between hematite ores and goethitic ores based on past research programs carried out at BHP Billiton. From a fundamental evaluation of the sintering process, it is clear that productivity can be an issue with goethitic ores because of their low bulk density and high porosity. This paper recommends steps towards overcoming losses in productivity. The effect of goethitic ores on coke rates is also a matter of general concern and this study shows that the addition energy required to dehydrate goethites and remove the additional water introduced into the system is comparatively small. The properties of melts have been shown to be particularly important in determining yield from a sinter machine and it is evident that the easy-melting properties of goethitic ores will also have an impact on this area. This paper also reviews our current understanding of how goethitic ores can influence sinter quality. The implication of fundamental knowledge on practical sinter plant operation is discussed throughout and collated at the end of the paper.

KEY WORDS: iron ore sintering; goethitic ores; productivity; coke rate; yield; sinter quality.

1. Introduction

The Pilbara region of Western Australia was developed to produce iron ore in the 1960s. In recent years, increases in iron ore production rates from this region necessary to meet strong market demands, particularly from Asia, have been spectacular. Over much of the first three decade of operation, mining has centred predominantly on low-phosphorus Brockman hematite ores. For over a decade now, several good chemical grade goethitic ore deposits—those containing significant goethites, *viz.*, pisolite ore and Marra Mamba ores—have been developed in the region. Pisolitic ore is now firmly established in the marketplace and forms a significant component of most Asian sintering blends. Marra Mamba ores have only been offered to the marketplace as a separate product recently although they are have been added as minor components in commercially traded Brockman ore for a long time.

BHP Billiton and its partners have a number of projects in the Pilbara and currently export three products of quite different properties: blends of predominantly hematite ores, a pisolite ore and a Marra Mamba ore. **Figure 1** shows that these ores have quite different microstructures and, therefore, will possess different chemical and physical properties. A fundamental research program was initiated at the BHP Billiton's Newcastle Technology Centre (NTC) in Newcastle, Australia, in the late 1980s to understand the sintering properties of goethitic ores. The program commenced with pisolite ore and is still continuing at a significant pace on Marra Mamba ore.

It is clear from the literature that since the early 1980s, Japanese Steel Mills (JSM) have given considerable attention to the development of appropriate sintering technology for high goethitic ore blends. The perspective of goethitic ores sintering behaviour, as expressed in this paper, are based mainly on the author's work. From around 1990, there have been many noteworthy ISIJ International publications in the areas covered by this review—for example, melt properties,[1,2] behaviour of ore blends containing significant goethitic ores,[3–5] bed structure,[6,7] green and sintering bed permeability[8]—but these are not included (to limit the length of this review). The development of ideas given in this paper will follow a historical timeline to enable the reader to understand the author's thinking behind past experimental work and how current views have been reached.

Discussions will be classified under the four commonly accepted sinter plant performance indicators: productivity, coke rate, yield and sinter properties. Early sinter pot test-work were generally based on ore blends containing no more than 30 mass% pisolite ore to reflect practices at that time. In more recent years, ore blends containing up to 61 mass% goethitic ores have been considered to reflect current interests in Marra Mamba ores.

2. Productivity

At the time when NTC commenced research in the area, the main issue confronting users of pisolitic ore was productivity. It was widely observed that introducing pisolite ore into blends composed predominantly of Australian and
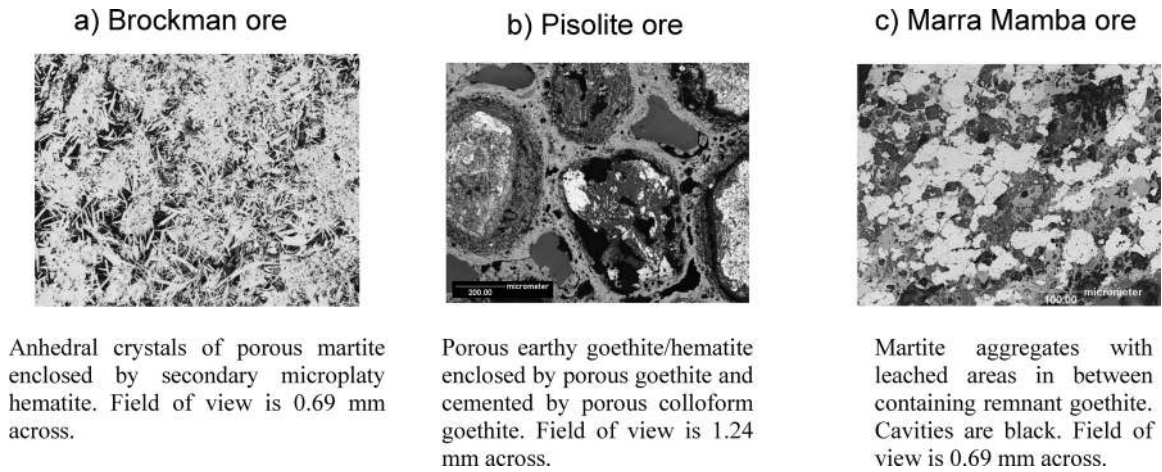
a) Brockman ore b) Pisolite ore c) Marra Mamba ore

Anhedral crystals of porous martite enclosed by secondary microplaty hematite. Field of view is 0.69 mm across.

Porous earthy goethite/hematite enclosed by porous goethite and cemented by porous colloform goethite. Field of view is 1.24 mm across.

Martite aggregates with leached areas in between containing remnant goethite. Cavities are black. Field of view is 0.69 mm across.

Fig. 1. Typical microstructure of a) Brockman, b) Pisolite and c) Marra Mamba ores.
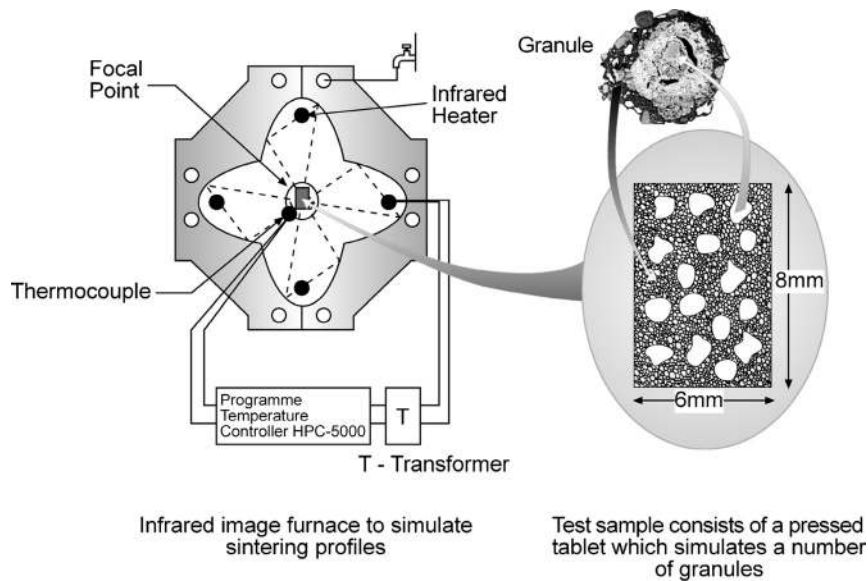

Fig. 2. Experimental technique used to quantify ore assimilation behaviour.

Brazilian hematite ores caused sinter plant productivity to drop. Many considered that the fundamental cause of this was the decline in flame front permeability caused by excessive melt formation. Bench-scale tests involving reactions between ore and limestone showed that pisolite ore reacted much more readily to form a melt compared to Brockman ores. In addition, the melt formed was more fluid in that it flowed more in the tests. The decline in productivity caused by the introduction of pisolite ore was also observed in our laboratory pot tests and plant trials in Australia.[9]

2.1. Melt Generation

The importance of flame front permeability and its ability to influence sintering airflow rates is clearly a credible concept since temperatures there are very high, resulting in very high gas velocities. In 1992, a novel NTC bench-scale technique to quantify the assimilation of iron ores by melt under simulated sintering thermal profiles was presented.[10] The use of simulated profiles to measure assimilation was considered vital since sintering reactions do not reach steady-state or equilibrium conditions.[10] Tablets used for sintering contained a blend of very fine laboratory grade reagents—hematite, kaolinite (for silica and alumina), silica, limestone and magnesia—to simulate the adhering fines layer of granules, and iron ore particles (0.71 to 1.0 mm) to simulate nuclear particles (**Fig. 2**).[10,11] When the tablets were heated in an infrared image furnace under a simulated sintering thermal profile, the fines reacted to form a primary melt encapsulating the nuclear particles. This initiated the assimilation of the nuclear particles, a process that continued until tablet temperature dropped below 1 100°C (illustrated in **Fig. 3**). The volume percent remnant ore in the sintered tablet—*i.e.*, volume of nuclear particle that have not reacted over the sintering period—was a measure of the 'assimilability' of the ore nuclear particles. Results clearly showed that pisolite ore particles assimilated at a much faster rate compared to porous or dense hematite particles.[10] From these tests it was inferred that, for a fixed sintering reaction time and temperature, more melt will be formed if pisolite ore is included in a hematite ore blend.

As excessive melt generation was believed to be detrimental to productivity, it is not surprising that considerable research effort have been directed towards 'protecting' pisolite ore particles to hinder their assimilation into melt (a more detailed discussion has been given in an earlier
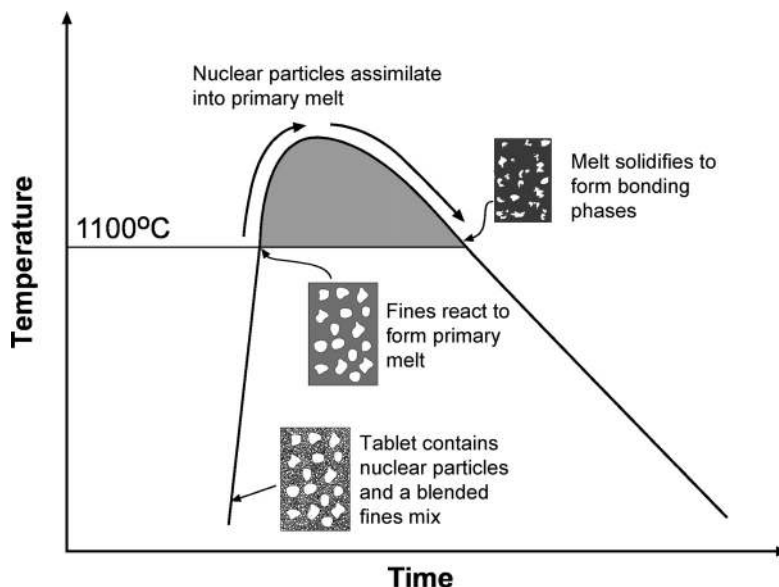
Fig. 3. Sintering temperature profile and reactions occurring within a tablet.

paper[12]). Further NTC studies showed that pisolite ore is much more porous compared to hematite ores, and between 400 and 700°C (before melt formation) it dehydrates, shrinking to form a dense structure containing significant cracks.[13] The described bench-scale tests involving a mix of nuclear particles and adhering fines also showed two other important phenomena. Firstly, SEM-EDS scans—on tablets containing nuclear particles and adhering fines, heated to 1 200°C in the infrared image furnace and then quickly withdrawn from the furnace—showed that lime from the adhering fines diffused into the pisolite ore particles very quickly and transformed the dense goethite into highly porous fine crystallites or protohematite.[13] This means that it is impossible to form a sinter containing dense dehydrated pisolite in the presence of lime. The effect of dehydration and the diffusion of lime into the goethite structure is shown in **Fig. 4**. Secondly, the shrinking of the pisolite ore particles causes a gap to develop between them and the adhering fines mix.[14] It appears that such gaps can reduce the time available for the assimilation of the formed protohematite—particularly true when a viscous primary melt forms and contact with the nuclear particle is delayed.[14] Coating pisolite ore particles with certain materials to reduce their assimilation 'works' if the coating assists in the formation of such a viscous primary melt.

All laboratory experiments using melt compositions comparable to those found in industrial sintering indicate that primary melts are highly mobile—although they have high surface tension, they are highly wetting fluids.[14] Almost as soon as the adhering fines layer transforms into a primary melt, it penetrates or is sucked into the pores of the nuclear particles by capillary forces. For this reason the reaction area available for the assimilation of porous nuclear particles is very large, and explains why the assimilation process has been shown to be so highly dependent on ore porosity.[9,14] High levels of iron oxide and alumina, and low levels of lime in the adhering fines mix have also been shown to reduce nuclear particle assimilation because of the formation of viscous melts which cannot: effectively penetrate into the pores of nuclear particles, and/or accom-
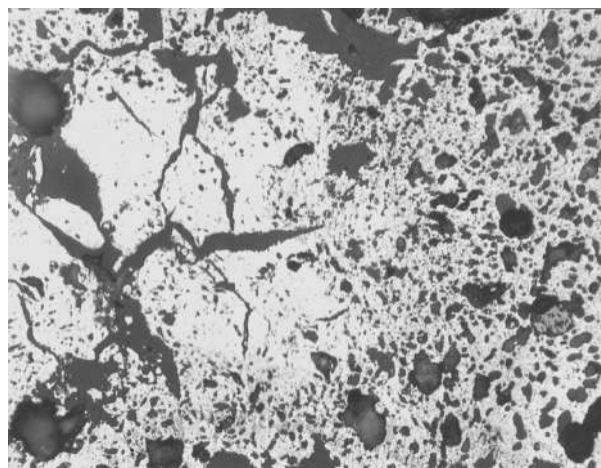

Fig. 4. Structure of pisolite ore during sintering (from Ref. 13)). Left hand side shows cracks formed as a result of goethite dehydration. Right hand side shows the effect of diffused calcium ions on dehydrated gooethite.

modate significant levels of the nuclear particle before liquidus temperature is reached.[14] A simple conceptual model was proposed to understand the factors controlling the assimilation process.[14] Studies have also confirmed that the level of protohematite in the sinter could be increased through the formation of a more viscous primary melt that cannot easily bridge across the gap to assimilate the nuclear particles.

2.2. Recovering Productivity

While it was clear that more melt was generated with the inclusion of pisolite ore in a blend, laboratory pot tests consistently showed that it was possible to recover productivity if green bed permeability was improved. This could, very simply, be achieved by increasing water addition during granulation to increase granulation effectiveness. Clearly porous pisolite ore particles absorbed a significant amount of the added granulation water and this reduced the amount of free water available on their surfaces for inter-particle adhesion, leading to a deterioration in granulation efficien-

cy.[15,16] Studies also showed that the level of additional water could be reduced if coarser limestone was used.[15] The creation of more low-lime regions in the bed caused by such a change in limestone size did not affect the process and sinter properties probably because the presence of pisolite ore increased the reactivity (melt forming ability) of the sinter mix.[15]

A major recommendation from the pot testwork[15,16] was that when pisolite ore is introduced into blends to replace a dense ore, green bed permeability must be maintained if losses in productivity are to be avoided. Increasing granulation water addition to compensate for the water absorbed by intra-particle pores is obviously the easiest technique. However, this could incur costs as energy will be required to remove the additional water. A better way would be to alter the properties of the water to prevent or reduce its imbibition into the intra-particles pores, while not affecting its role as an inter-particle binder. The inclusion of 10 mass% sugar into the granulation water fulfilled both these requirements and sinter mixes containing 30% pisolite ore could be sintered at very high productivities even at low mix moistures (e.g., 51 t/m²·d at 5.5 mass% mix moisture).[11,17] Other additives tested gave improvements but sugar was clearly the most effective compound.[17]

2.3. Flame Front Speed

Pot test results also confirmed that the losses in productivity at the same mix moisture for blends containing pisolite ore were a direct result of increased sintering time caused by a reduction in flame front speed.[15] Increasing granulation water addition led to the formation of a more permeable bed, which increased flame front speed. Essentially blends containing high levels of pisolite ore behaved just like hematite ore blends in that green bed permeability has a large influence on flame front speed. On this basis, how then does flame front properties e.g., its voidage, temperature etc. influence the sintering process?…if it does, indeed, have an influence. A subsequent literature survey showed that there was very little understanding of flame front properties and the factors influencing the speed at which it descends down a sintering bed.

The study[18] of flame front commenced with the central assumption that flame front speed is basically determined by the time required to heat the horizontal layer of material just ahead of the flame front to around 1 000°C, the spontaneous coke combustion temperature. The conceptual model based on heat flow to and from this layer has been presented.[18] It showed that the time taken for the layer to reach 1 000°C depended on: the flow rate of gases to this layer, the thermal capacities of this layer and the flowing gases. Increasing the thermal capacity of the gases—for example, through the recycling of waste gases which have a higher carbon dioxide content—will also increase flame front speed. The flow of heat from the flame front to this layer is clearly strongly dependent on convective heat transfer and, therefore, the flow rate of gases through the bed during sintering. The thermal capacity of the layer would essentially depend on the mass of solids in the layer i.e., its bulk density. Blends containing pisolite ore would have a lower thermal capacity per unit volume compared to a hematite ore blend because[19]: pisolite ore has higher porosity and lower

bulk density, goethite has a lower inherent density compared to hematite, and goethite dehydrates prior to the arrival of the flame front, further decreasing its density.

A sinter strand operates on a fixed volume basis and the mass of ore per unit area of strand (i.e., bed bulk density) is lower with goethitic ores in the blend.[19] A drop in productivity is inevitable if strand speed is not increased.[19] If green bed permeability is maintained—and, therefore, airflow rate and convective heat transfer down a bed—the flame front would descend faster for blends containing pisolite ore simply because the thermal capacity of the thin layer ahead of the flame front is lower.[18] This increase in flame front speed should result in faster flame front speed and compensate the decrease in bed bulk density.

2.4. Flame Front Permeability

While there is no doubt that goethitic ores form more melt during sintering compared to hematite ores, the ability to recover productivity by maintaining granulation effectiveness (for blends of up to 30 mass% pisolite ore) indicates that melt volume generated during sintering does not control sintering bed permeability. The next phase of the study was aimed at identifying the controlling factors through determining in situ sintering bed permeability.

An analysis of laboratory pot test results showed that airflow rate during sintering was lower than the pre-ignition airflow rate and that it remained reasonable constant over most of the sintering period, only rising sharply when the flame front had reached the bottom of the bed.[20,21] This consistency in airflow was achieved in spite of the one-to-one replacement of the green granulated bed with the much more permeable sintered bed. Two inferences could be drawn: firstly, that the flame front controlled sintering bed permeability; and, secondly, that a meaningful averaged sintering bed permeability value could be defined.[20,21] Other studies involving a number probes located down a sintering bed to simultaneously determine pressure and temperature at various positions, showed that the pressure drop across a thermocouple and the one located below did not change until the flame front—indicated by the upward sloping section of the temperature profile (see Fig. 3)—reached the top thermocouple.[22] Only when this happened did the pressure drop between the two thermocouples increase. This was further confirmation that pressure drop across the flame front was much larger than that across the green bed.

For a large number of blends, plots of green bed airflow rate (V_i) against sintering bed airflow rate (V_s) gave an asymptotic curve (**Fig. 5**), indicating that flame front resistance R_f ($=V_i-V_s$) cannot be quantified by a single number. It was a complex function of green bed airflow rate[21,23] and confirmed that sintering bed permeability depended on green bed permeability. From theoretical considerations, the relationship was expressed by:

$$(V_i - V_s) = k_s V_s^3 \quad \text{or} \quad V_s = V_i - k_s V_s^3$$

where k_s can be considered to be a flame front structural property or flame front permeability, and the resistance of the flame front to flow is a product of k_s and flow velocity to the power of three.[21,23] Studies on a number of ore blends showed that the equation fitted experimental results well and k_s values could be determined for every blend.[21]
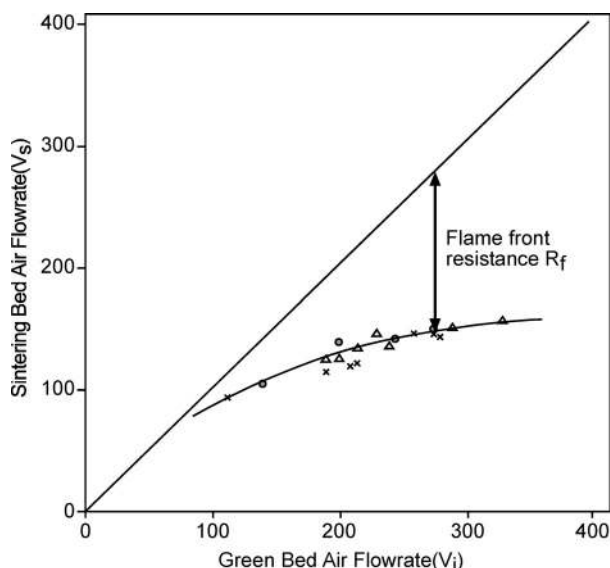
Fig. 5. Relationship between green bed permeability and sinter-ing bed permeability for three ore blends: HAEM, PISO and PIMM (from Ref. 21)).

The permeability of a green bed is commonly quantified by JPU (Japanese Permeability Units) or BPU (British Permeability Units). It defines bed structure in relation to flow resistance using a single number. Once the JPU of a bed is determined, the relationship between the pressure drop across the bed and airflow rate through the bed is fixed. For this reason JPU is a useful green bed parameter. A similar analogy can be used to understand the concept of k_s for a sintering bed. At constant sintering conditions *e.g.*, fixed coke rate, bed height and suction, it is an ore blend property, quantifying the resistance of the flame front to air-flow. It is a measure of the 'sinterability' of an ore blend,[21,24] just as JPU provides information on its 'granula-bility'. The value of k_s can only be determined experimen-tally. Once the value of k_s is defined the relationship be-tween V_i and V_s is established: for a given green bed perme-ability there is a unique sintering airflow rate, which is de-termined by the resistance of the flame front.

2.5. 'Sinterability' of Sinter Mixes

This section summarises factors that influence k_s. The ex-perimental program[21] involved a base hematite ore blend (HAEM), a blend containing 35% pisolite ore (PISO), and a blend containing 61% of both pisolite ore and Marra Mamba ore (PIMM). The base blend was sintered first; coke and return fines levels, and mix moisture were adjust-ed to obtain a 'balanced' operation and produce sinter of defined tumble strength. For the other two blends these variables were altered, where necessary, so that obtained productivity and sinter strength matched those of the base case. It is obvious from the equation relating V_i to V_s that accurate measures of both are essential to obtain meaning-ful k_s values. To achieve this the three blends were studied using the modified pot test procedure, which involved the use of an annular layer of fine sand at the pot wall to reduce the ingress of air at the walls. With goethitic ores in the blend bed shrinkage was significant and the ingress of air around the wall was very high, which suggested that there would be a large error associated with the determination of

V_s. With the annular layer of sand, the value of k_s obtained for the three blends were identical, indicating that the per-meability of the flame front did not alter with increased melt generation during sintering.[21] Studies also showed that the fines content (minus 0.15 mm) of Marra Mamba ore—which would have a large impact on its reactivity—did not alter the value of k_s.[25]

Another important finding of the work[21] was that the re-lationship between sintering airflow rate and green bed air-flow rate was not linear for a sinter mix, (Fig. 5). Flame front resistance ($V_i - V_s$) increased significantly with in-creasing airflow rate (V_s), and after a point there is little value in further increasing green bed permeability. This phenomenon was also observed in earlier pot test programs involving coarse limestone.[15] An explanation given for the strong dependence between green and sintering bed perme-abilities was that gas channels in the flame front was depen-dent on the properties of gas channels in the green bed *e.g.*, in size and tortuosity.[21] It was further suggested that the momentum of the flowing gases was capable of keeping the gas channels in the flame front open regardless of the amount of melt generated. The study[21] also found that in-creasing coke rates increased the resistance of the flame front; although this was not unexpected as it greatly in-creased V_s. Reducing bed suction caused a significant re-duction in sintering airflow rates, which increases sintering time. Increasing basicity (lime to silica ratio) also produced a more permeable sintering bed—probably because in-creased calcination requirement reduced flame front tem-perature.[21] When burnt lime was used to replace limestone, the value of k_s decreased but no firm conclusions could be drawn because burnt lime has a positive influence on bed structure.

A narrower, coarser coke size distribution also reduced flame front permeability.[21] Earlier programs to study the effect of coke size on sintering showed that during granula-tion, fine (minus 0.25 mm) coke particles were incorporated in the adhering fines layer.[26] Once the primary melt formed oxygen access to these particles would decrease, causing them to burn at a very slow rate. This would broaden the flame front and increase its resistance to airflow.[27] Late coke addition increased flame front speed very significantly because of high oxygen availability to all the coke particles. The resulting high combustion rate narrowed the flame front.[26]

Before terminating discussions in this area it is worth-while noting that flame front width and temperature in-crease down a sintering bed. If the flame front is, indeed, the controlling resistance to airflow, then this should reduce sintering airflow rates. On the other hand, the one-to-one re-placement of the highly permeable sintered bed with green bed should increase airflow rate. In practice, pot test results show that the value of V_s is reasonably constant. It is possi-ble that these two opposing factors on bed permeability play an important role in helping to keep V_s constant. The other factor that could also regulate airflow rate during the course of sintering is the dilatability of gas channels in the flame front: there is greater deformation of melt as flame front temperature and thickness increase down a sintering bed, resulting in the formation of larger gas channels and, consequently, no change in flame front flow resistance.[20]

2.6. Granulation

From these studies it is very clear that with the introduction of porous ores, maintaining granulation efficiency is extremely important if productivity losses are to be avoided. It is the author's view that the factors governing granulation efficiency are quite well known. Other than ore porosity, particle size distribution is important. Fine particles in the sinter mix (<0.25 mm) adhere onto the surfaces of nuclear particles (>2.0 mm) while the intermediate sized particles (greater than 0.25 mm and less than 2.0 mm) tend to remain unattached.[28] As intermediate particles will only be captured through embedment in the formed adhering fines layer they have a detrimental influence on bed permeability, particularly at low mix moisture.

For blends containing particles of a wide range of size distribution and porosity, it is clear that particles will compete for the added water. A study,[29] carried out on a number of blends composed of different ores, showed that the granulation responses of blends were quite different and difficult to predict. There is also evidence to suggest that the intra-particle pores of porous ore particles need not be filled completely before surface water becomes available for inter-particle adhesion. **Figure 6** shows that for both pisolite ore and Brockman ore, the same bed permeability can be achieved at lower granulated mix moisture if the initial moistures of these ores are lower. Granulation is conceptually a simple process; but mechanistically it is very complex. The results in Fig. 6 also indicate that even under identical granulation conditions, mix moisture is not a reliable measure of granulation effectiveness.
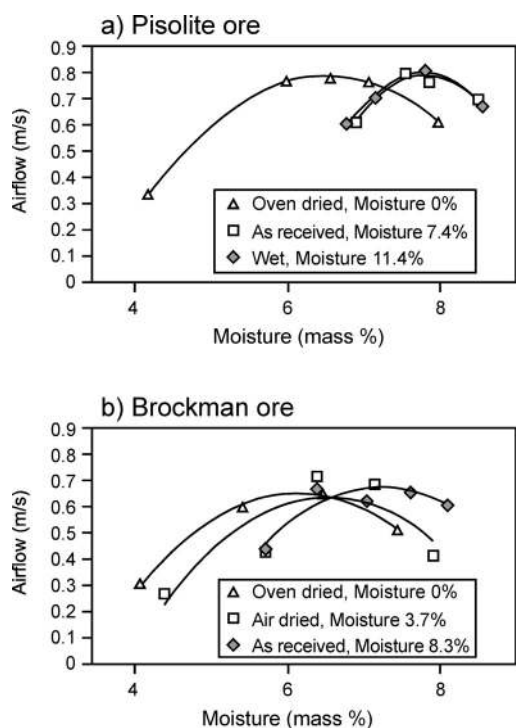
2.7. Bed Permeability

Effective granulation is a pre-requisite to obtaining a high flame front speed since granule mean size and bed

Fig. 6. Relationship between granulated mix moisture and bed permeability for ores containing different starting moistures.

voidage have a large impact on the permeability of the formed green bed. However, it is well established that plots of bed permeability *versus* mix moisture are not straight lines but inverted V-shapes. (Figure 6 shows several examples). As water addition increases, granulation effectiveness improves resulting in the formation of larger granules, with a narrower spread in size distribution—therefore, improved bed permeability. But when water addition is increased beyond the optimum value bed permeability deteriorates. Larger granules have thicker adhering fines layer containing significant intermediate sized particles and these layers deform more easily under stress *e.g.*, encountered during charging onto a sinter strand or into a permeability pot. The permeability of a granulated bed is, therefore, not solely a function of granulation efficiency but is also influenced by the strength of the granules.

Two areas were considered in an attempt to understand granule strength. The first involved the determination of ore-water contact angles[30,31] since they determine the shape and length of the water lens meniscus holding particles together and, consequently, the inter-particle adhesion strength. The contact angles of ten Brockman, pisolite and Marra Mamba iron ores from different regions of the Pilbara were determined—using a technique which measured capillary rise of water up a packed bed of ore.[31] Values varied from 0° to 48° indicating that, during granulation, water could spread more readily and preferentially over certain ore surfaces. Parallel granulation studies carried out on these 10 ores showed that ore size distribution and porosity had a greater influence on bed permeability than contact angle, but more work is required to confirm if this is true in every situation.

To provide a direct measure of bulk granule strength, a uniaxial confined bed compression test was used.[32] The equipment consists of a universal testing machine, which determines the penetration/displacement of a shaft into a bed of granules as a function of applied load. From the shape of the graph an index can be derived to quantify bulk granule strength. This test is particularly useful as it can be used to determine the strength of granulated beds at the different stages during sintering: green, humidified, dried and calcined. The first study[32] in this area showed that the load bearing strength of a green bed was highly dependent on mix moisture. As water addition increased: the granules became more compressible because they had a thicker layer of adhering fines; the formed bed had more voids to accommodate the deformed adhering fines layers; and the granules became weaker because of increased lubricant (*i.e.*, water) volume. It is to be expected that the intra-particle water in porous ores would not act as a lubricant.

Results obtained to date for beds at the different stages of sintering also showed some quite unexpected trends. The dried bed was much stronger compared to the green bed. In a green bed the granules behaved as separate entities and the applied pressure was only transmitted down the bed after the granules in the upper bed had deformed into a compact bed.[32] With the dried bed, all the granules fused together into a single entity and there was no preferential compaction of upper layers at low loads. All the blends studied contained Pilbara ores and the ability of these blends to form strong dried beds could be linked to the

presence of fine clays.[32] The humidified bed strength was significantly weaker than that of the granulated bed because of the high level of inter-particle water in the bed.

3. Coke Rate

Early laboratory studies examining the introduction of pisolite ore into hematite ore blends showed very clearly that increasing mix moisture addition is essential. Blends containing up to 30 mass% pisolite ore could produce sinter of the same tumble index as the hematite blend at the same productivity without the need to increase coke addition level in the mix.[15] This finding had been confirmed at many plants. In cases where plant engineers—on the premise that these blends have higher energy requirements—increased coke rate, poorer results were obtained. The ability to maintain sinter strength whilst addition energy was expended in the sintering process to dehydrate the goethites and evaporate the additional water added during granulation required explanation.

3.1. Heat Available for the Sintering Reactions

The assimilation reaction was viewed using a simple model involving the dissolution of solid into liquid.[14] Bench-scale experiments involving the infrared furnace and pressed tablets were carried out under a fixed temperature profile. The furnace provided all the energy required for calcination (which varied depending on ore types and basicity) in addition to raising the sample to the set maximum sintering temperature. In a sinter pot test, when coke addition level is fixed, increased calcination or evaporation requirements will result in a lower maximum sintering temperature.[18] In laboratory tests and plant operation, it is clear that the substitution of a dense hematite with a porous goethite will reduce the maximum temperature achieved during sintering.[16]

In sintering, embedded thermocouples in a bed provide

information on the heat experienced by material as the flame front passes through. The information obtained from thermocouples is widely termed the sintering temperature profile and a typical profile is shown in Fig. 3 and **Fig. 7**. The heat input during the crucial melt formation period is directly proportional to the area subtended by the sintering temperature profile and the $T=1100°C$ (the start of melt formation) line. The subtended area is shaded in Fig. 7. Reducing coke rate or increasing the thermal requirements of the blend (*e.g.*, increasing limestone content) will lower the maximum sintering temperature and the shaded area. **Figure 8** also shows that the shape of the temperature profile is not an exact mirror image of the flame front profile because it also depends on flame front speed. A faster flame front speed will give a narrower temperature profile, which will also reduce the shaded area (Fig. 7). In spite of increased flame front speed for blends containing 30 mass% pisolite ore, no decreases in sinter strength were observed at many plants (an example is given in Ref. 16)), indicating
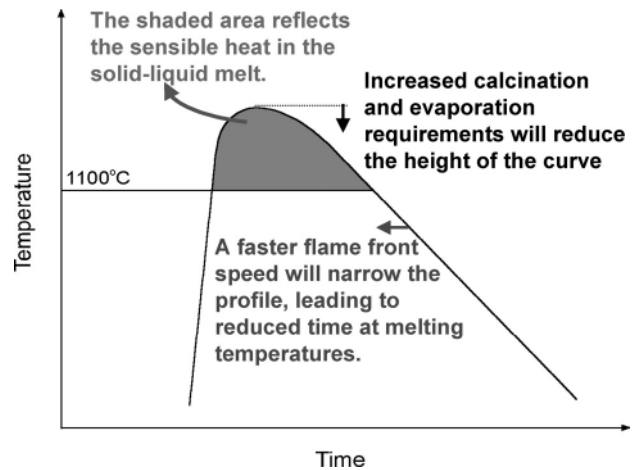

Fig. 7. Effect of changes in flame front properties on the temperature profile.
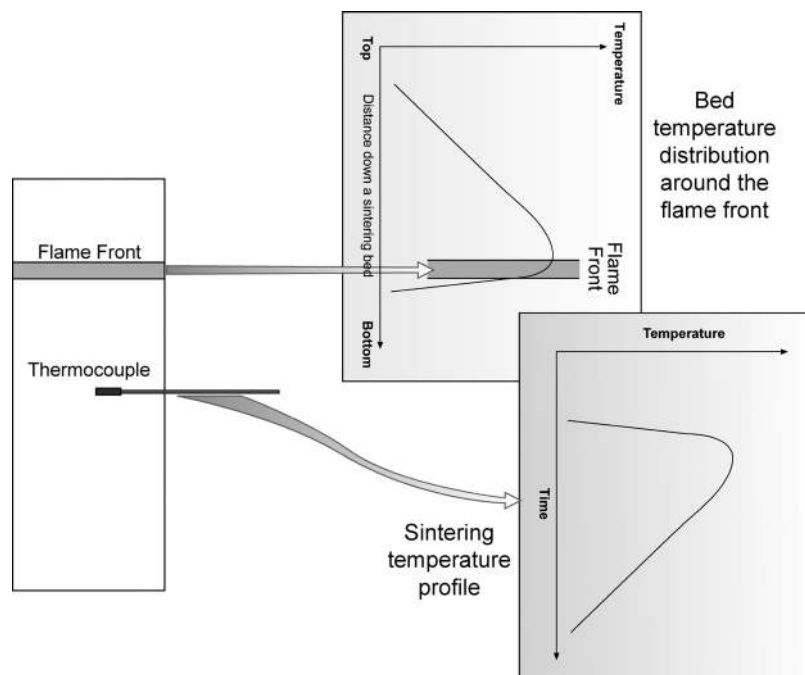

Fig. 8. Sintering temperature profile and its dependence on flame front temperature and speed.

that reducing the shaded area did not have a significant impact on melt formation and melt properties. On the other hand, improving granulation to increase flame front speed quickly results in deterioration in sinter strength for hematite ore blends. Clearly, goethitic ore blends are not as sensitive to reductions in the total heat input during the melt formation period.

There is good evidence to indicate that with lower sintering temperatures a sinter of adequate strength can still form if melt volume increases and/or melt properties improves. For example, increasing sinter basicity often does not require additional coke to produce a sinter of similar tumble strength, even though the calcination requirements of limestone is highly endothermic (see **Table 1**). From published information[33–35] the heat of reaction required to dehydrate a kg of goethite and remove the evolved water as a liquid and as a vapour (given in Table 1) is relatively small compared to the energy required to calcine a kg of limestone. Table 1 also shows that when goethite dehydrates a large part of the heat is utilised in evaporating the evolved water.

3.2. Water Distribution in the Lower Bed

It is well established that water vapour from the drying zone condenses in the lower bed at the early stages of sintering because the region is below dew point.[36] Water distribution in a sintering bed is an important area for study because: excessive water could make the lower bed more compressible, leading to reduced bed permeability; and how the water leaves the bed could affect energy requirements. A search of the literature indicated that there was

general adherence to one view of the condensation mechanism. Very simply it states that the condensation process moves down the bed like a wave and within a few minutes after ignition the whole bed is heated to the dew point temperature.[36] Thereafter, no further condensation occurs and the flowing gases then carry out all the water removed ahead of the moving flame front. The NTC[36] study showed that this is not possible because the flowing gases are already fully saturated and can only carry a certain amount of water out of the bed. Increasing mix moisture will certainly increase the water load beyond that capable of being carried out by the flowing gases. The dehydration of goethites will further increase the total water in the bed.

An alternative theory was put forward to explain water distribution in a sintering bed and its removal from the bed.[36,37] The basis of the theory is the heat and mass transfer—the cooling of moist air and the condensation of the water on the bed—processes ahead of the drying zone occur rapidly in a thin moisture equilibration zone (**Fig. 9**). Theoretical heat and mass considerations show that in this zone, which is just ahead of the drying zone, the hot flowing gases cool to 55°C, a value supported by sinter pot test results.[36] In their passage through the equilibration zone the gases also drag the condensed water from down the bed. Within a few minutes sufficient condensed water is present in all the lower bed gas channels to raise their temperature to 55°C. The water content of the lower bed meanwhile increases as entrained water fills dormant inter-particle voids *i.e.*, those that are not gas channels. Once these voids have been filled oncoming entrained water is directly dragged out of the bed (see Fig. 9). The ability to remove water from the bed as a liquid, rather than as a vapour, means that energy requirements are much lower. This could also help explain why the introduction of certain levels of goethitic ores does not invariably result in increased cokes rates.

In **Table 2**, water balances are carried out for the three blends HAEM, PISO and PIMM.[21] As indicated in Table 2, mix moistures are much higher with goethitic ores in the blend. The table also shows that for all three cases the flowing gases cannot carry out all the water present. For PISO and PIMM, over 2 kg of water will leave the bed as entrained liquid.

It was suggested that in an idealised sintering operation, the ignition hood provides the energy required to raise the

Table 1. Heats of reaction for coke combustion and calcination processes occurring during sintering.

Reaction	Heat of reaction at 25°C ΔH_{rxn} (kJ/mol)	Energy requirements for 1kg of reactant (kJ)
$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$*	-393.5	-32,800
$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$ *	-221.0	9,210
$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ *	183.0	1,830
$2FeOOH_{(s)} \rightarrow Fe_2O_{3(s)} + H_2O_{(l)}$ ** (evolved water leaves as a liquid at 55°C)	10.4	58
$2FeOOH_{(s)} \rightarrow Fe_2O_{3(s)} + H_2O_{(g)}$ ** (evolved water leaves as a vapour at 55°C)	53.2	300
$CaMg(CO_3)_2 \rightarrow CaO_{(s)} + MgO_{(s)} + 2CO_{2(g)}$	290.5	1,580

* Determined using information from Refs. 34 and 35
** Determined using data from Refs. 33, 34 and 35
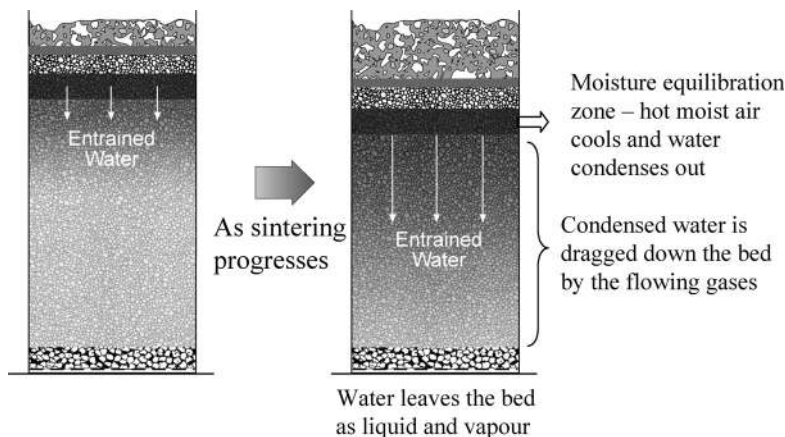
Fig. 9. Schematic representation of water transport during sintering.

Table 2. Water balance for three ore blends.

	HAEM	PISO	PIMM
Mix moisture (mass %)	5.8	6.0	6.2
Water introduced into sintering bed i.e., mix moisture, generated during ignition and humidity in the flowing air (kg)*	6.74	6.94	7.14
Water from goethite dehydration (kg)*	0	1.69	2.05
Total water in the system (kg)*	6.74	8.63	9.19
Water removed as vapour assuming a waste gas temperature of 55°C at a flow rate of 120 m³/hr and a sintering time of 23 minutes (kg)*	6.37	6.37	6.37
Water removed as a liquid from the bed (kg)*	0.37	2.26	2.82

*Basis 100 kg of sinter mix

Table 3. Energy utilised during the sintering of three ore blends.

	Energy requirement for process as a percent of total energy generated from coke combustion* (%)		
	HAEM	PISO	PIMM
Calcination of limestone	28.2	28.9	28.3
Dehydration of goethites**	0	0.91	1.10
Heat water evolved from goethite to a liquid at 55°C	0	0.25	0.30
Heat water evolved from goethite to a vapour at 55°C	0	5.0	6.0
Heat required to calcine addition limestone if sinter basicity was raised from 1.8 to 2.0	3.1	3.2	3.1
Total energy required to remove water from the bed	18.5	18.9	19.0
Energy available to break down solid lattice structure during melt formation assuming no other reactions require heat	53.3	51.0	51.3

* assuming coke combustion efficiency is defined by $CO/(CO+CO_2) = 0.2$
** assuming pisolite ore and Marra Mamba ore contain 10 and 35 mass % hematite respectively

top layer of the bed to coke ignition temperature.[18] This energy is subsequently carried down from layer to layer, to heat each to the spontaneous coke combustion temperature. Heat generated from the combustion of coke in the layers is use for calcination, evaporation and sintering reactions. If this is a first order estimate of what happens during sintering, energy consumed in the various reactions during sintering could be expressed as a percentage of the energy generated from coke combustion. Results are given in **Table 3**. The dehydration of goethite requires very little heat compared to the calcination of the limestone. Removing the evolved water as a liquid at 55°C also requires little energy (results in Table 2 show that this is how the water is removed in practice). If the water was removed as gas at 55°C, twenty times more heat is required and this could have an influence on sintering coke requirements. For comparative purposes the addition heat required for limestone calcination if sintering basicity is raised from 1.8 to 2.0 is also shown and values are about two times larger than that required to dehydrate the goethite and to remove all of the evolved water as a liquid. Table 3 shows the energy required to remove the water for the three blends are not too different, ranging from 18.5 to 19.0%.

If it is assumed that all the other heat generated by coke combustion is used for assimilation then the last row of Table 3 shows that over 50% of the energy generated is used in breaking down the solid ore lattices. This number is significant and suggest that lower coke rates will result if both the assimilation mechanism—which determines the

rate of melt formation and the total melt volume generated during sintering—and the properties of the melts were optimised.

To develop an accurate sintering coke rate model, there is a need to quantify energy required by the assimilation process. If the assimilation mechanism is similar to the dissolution of salt in water then it will involve a heat of solution, which can be viewed as occurring in two separate steps.[38] The first step involves the heat required to break down the solid crystal salt structure into gaseous ions and is termed the lattice energy. The second step involves these ions becoming hydrated, a process that is generally associated with a release of energy. This enthalpy change associated with the hydration process is termed the heat of hydration.

If these simple concepts are applicable in sintering it suggests that the energy required to break down hematite into ions (or oxides) should be the same. However, the enthalpy change caused by these ions entering into the primary melt will change depending on the properties of the primary melt.

4. Yield

While flame front speed has been shown to be independent of melt properties—in particular, melt volume—productivity will be influenced by melt properties through sinter yield. A mass balance equation,[21] which shows the dependence of productivity on bed properties and yield, has been derived.

As a sinter machine is operated under a balanced return fines condition—the weight of fines generated after the bed is crushed and the sinter is stabilised *en route* to the blast furnace is equal to the weight of fines returned to the sinter machine for addition into the green sinter mix—the circulating fines load is a measure of yield. It is generally observed that sinter strength and yield are often related in that improving one improves the other, but this is not always the case because they are measures of quite different things.

4.1. Source of Return Fines

A sintered bed yields a product fraction composed of sinter particles of a range of sizes, and a return fines fraction generated from the weaker parts of the bed. It is clear that because the air used to sinter the upper regions of the bed is not pre-heated, unlike in the lower regions, material from this region is comparatively weak and a larger proportion of material from here ends up in the return fines. Yield from the upper regions would be a function of the reactivity of the sinter mix, and a certain level of goethitic ore addition could increase the yield from these regions. The yield from the lower regions is likewise also dependent temperatures, which determines the structure of the bed. Based on observing the structure of a pre-shattered bed it was argued that the bed could be broadly divided into identifiable particles and narrow bridges—the latter holding the former in position.[11,14] On shattering, most of the bridges would break down into return sinter fines. Yield is predominantly a measure of the level, size and strength of the bridges while tumble index is a measure of the strength of the sinter particles.

Fig. 10. Quenched sintering bed showing major transformation in bed structure. The flame front was at the middle of the bed.

It is important to remember that before the commencement of sintering the bed is reasonably homogeneous in structure—the granules and voids are uniformly distributed in the bed. After sintering, the structure of the bed has been transformed because of material loss (*e.g.*, combustion of coke particles, calcination of limestone, dolomite and goethite) and formation of melt. To obtain the observed structural transformation of the bed during sintering (shown in **Fig. 10**), there needs to be significant movement of material—which is clearly driven by the formed melts coalescing.[39] The loss of particles uniformly distributed in the bed, such as coke and limestone, will not result in such a structure. The process is undoubtedly complex because it involves a three-phase mixture of melt, unassimilated solid nuclear particles and entrained bubbles.[39] Where there has been significant coalescing of the mix in a localised region, densification has occurred to form sinter particles. The loss of material from an adjacent region, in turn, results in the formation of voids and narrow bridges. Although it is unclear what initiates the coalescing of three-phase mixture into preferred regions to form sinter particles, there is little doubt that understanding in this area would assist in reducing return fines load and the formation of sinter of narrower size distribution.

4.2. Quantifying Melt Properties

Melt properties such as viscosity are not easy to measure and this is one reason why so little work has been carried out in the area. NTC commenced study in the area[39] by adopting indirect measures. The study focused on measuring pore properties—size distribution, mean size and pore shape—using two-dimensional image analysis. Melt properties were then inferred from these results. It was argued that melt and pore properties are related because increasing melt fluidity results in: enhanced bubble coalescence, reduced porosity because bubbles can leave the melt, and the formation of rounder bubbles.[39]

An inherent assumption of the study[39] was that the microstructure of the sinter—as measure by porosity, pore size distribution and pore shape—reflected the properties of the melt just prior to solidification. The viscosity and surface tension of the formed melts work in opposition to determine the degree of melt and bubble coalescence. It was proposed that all bubbles would naturally transform into spherical shapes to reduce the energy in the system. This transformation process is enhanced by a large acting surface force, which has to overcome the viscous forces present. The coalescence of two bubbles into a larger one would depend on the ability to drain the melt separating the bubbles, which is obviously more difficult when the melt is viscous. From these considerations, it was proposed that information on melt properties could be obtained from a study of bonding phase pore properties.

The experimental program[39] involved pressed tablets containing fine laboratory chemical grade hematite, silica, alumina, lime and magnesia. After sintering the tablets in the infrared image furnace, they were mounted in resin, polished and their structure quantified using image analysis. Results indicated that there was a clear relationship between melt chemical composition and melt properties. The level of oxides including phosphorus and alumina, and the basicity of the melt all influence melt properties through the degree of superheat—the difference between the system temperature and the liquidus temperature of the melt. For this reason, increasing the sintering temperature resulted in a more fluid melt. The program was then extended[40] to include nuclear particles in the pressed tablet. In doing this a much more complex system was obtained and knowledge obtained from the earlier program could not be applied directly to explaining all the results. In particular for porous nuclear particles, the primary melts generated did not stay on the surfaces of particles and so the influence of melt properties on sinter structure was not as significant as for the dense nuclear particles.

Melt properties are strongly dependent on temperatures and chemical composition. Consequently, these two variables will strongly influence the return fine generation. However, these two variables are not independent because raising sintering temperature will increase ore assimilation rate and, in turn melt chemical composition. For a blend composed of only porous highly reactive ores it is to be expected that increasing coke rate will only have the effect of raising melt temperatures because there are no more solids left to assimilate. On the other hand, for less reactive ores increasing temperature will increase assimilation and also raise melt temperature. The particular split in energy utilisation can be expected to be a function of the actual reactivity of the ore. In sintering a certain amount of melt will be required to produce a minimum level of bonding phases so that a strong sinter can form. Once this requirement is met,

additional heat should be used to raise melt temperatures to enhance the coalescence process rather than to generate more melt. In the former case the sensible heat is recoverable but in the latter case the energy component utilised to break down the solid ore lattice is not recoverable.

Discussions above indicate that sintering energy requirements will be a function of ore blend composition. For this reason it has been suggested[18] that blends should compose highly reactive ores to form melt quickly and efficiently, and also very dense, slow assimilating ores to ensure that energy available thereafter is not dissipated through the formation of more melt but is used to raise melt temperatures. Fundamental studies of assimilation indicate that this is achievable in sintering because primary melts—formed from the adhering fines layer[10]—are very quickly penetrated into porous ore particles, resulting in the availability of less melt for the assimilation of the dense ore particles in the blend.

4.3. Role of Fluxes

Fluxes play as important a role as ores in the melt formation process. Any discussion of melt properties and melt chemical composition must include flux reactivity and size distribution. Recently a fundamental program[41] using tablets containing flux nuclear particles and a standard adhering fines mix was also carried out with the main purpose of determining if dolomite could be used to replace serpentine to lower the silica content of blends containing high levels of pisolite (which have lower alumina and higher silica levels compared to Brockman ore). A major conclusion from this study[41] was that the lime from dolomite does not partake in the forming of melts as readily as the lime from limestone. When dolomite was used to partially replace limestone, sinter basicity had to be increased to form the same level of melt and prevent deterioration in sinter strength. Unlike dolomite, serpentine is a good sintering material. It was not as reactive and this meant that the silica it carried did not partake in the formation of melt.[41] Melt basicity was, therefore, higher resulting in the formation of a melt of lower liquidus temperature.

There is another reason why dolomite can cause deterioration in melt properties. Table 1 shows that the heat required to calcine a kg of dolomite is slightly less than that for a kg of limestone. However, during calcination, 560.4 g of CaO is formed from 1 kg of limestone, which meant that to obtain this same amount of CaO, 1.84 kg of dolomite is required. The energy required to calcine this mass of dolomite is 58.7% higher than that required to calcine 1 kg of limestone. This calculation shows that when dolomite is used as a replacement for limestone, increased coke rates could be required to form melts of equivalent properties.

5. Sinter Properties

There are a few internationally accepted methods of quantifying sinter quality based on the different regions in a blast furnaces. To understand the effect of goethitic ores on sinter quality it is important to understand the factors that control these standard measures.

5.1. Tumble Index

The tumble index of sinter is dependent on critical flaws in the sinter and the propagation of these flaws through a sinter particle. Flaws are unavoidable because, during the cooling cycle, the minerals and phases precipitate out of the melt at different times, and changes in volume almost always accompany the transformation of a liquid into a solid. The severity of the crack propagation process will determine the sinter tumble index which, in turn, will be determined by: the volume of bonding phases in the sinter, the toughness of the individual minerals and phases present, porosity and the shape and distribution of the pores, and the boundary adhesion strength between the minerals and phases. As discussed, increasing the heat input during the melt formation period will result in more melt, a more fluid melt, and enhanced melt and bubble coalescence. The net result is lower sinter porosity and bonding phases containing fewer larger pores rather than an abundance of very fine pores. Goethitic ores reduce the heat available during the melting period and results in the formation of a more viscous higher Fe_2O_3 melt; for this reason, at goethitic ore addition levels of greater than 30 mass% more coke is often required to maintain the level of melt superheat (which greatly influences melt properties) and prevent deterioration in sinter strength.

5.2. Reducibility

Although bed shrinkage occurs during sintering, a significant proportion of the porosity in the green bed—both inter- and intra-particle pores—is not destroyed.[9] As discussed previously, many of these voids will coalesce during melt formation to form very large voids. For the same initial inter-particle bed voidage, the sintered bed formed with goethitic ores present can be expected to be more porous because of increased small intra-particle pores—which exists in the original ore and also increases with the dehydation of the goethites.

The introduction of goethitic ores into blends improves reducibility simply because not all the intra-particle pores are transformed to become large inter-particle voids in the sintered bed (inter-particle voids are clearly evident in Fig. 10). Some have been incorporated into the sinter particles, making them more porous and less dense. It was shown that the number of particles used in a reducibility test, where the mass was fixed at 500 g, was higher for blends containing goethitic ores.[9] The presence of more pores improved the access available to reducing gases and this increased the reducibility of the sinter particles.

5.3. RDI

An extensive study has been carried to understand the process leading to fines generation during low temperature reduction.[42–44] Cracks initiate in sinter particles when hematite present reduces to magnetite. For this reason, increasing sinter porosity and the hematite content of sinter can lead to higher RDI. However, the form of the hematite and its accessibility by reducing gases is also important. Protohematite, for example, is highly porous and easily reduced but this may not form deleterious cracks because of its highly porous structure.

For most sinters, crack initiation is not the major reason why fines are generated. Of greater importance is the crack propagation process, which is controlled by the fracture toughness of the other phases in sinter. It has been shown that trace elements such as titania[43] and alkalis[45] have such a large impact on sinter RDI because they report to the glass phase. This widely distributed phase has the lowest fracture toughness value in sinter[42] and these oxides in glass cause a deterioration in its fracture toughness value.

From a discussion on how fines are generated, it is likely that sinters produced from blends containing goethitic ores would reduce more during the reduction phase of the RDI test. However, crack propagation could be curtailed by the other minerals and phases. It is difficult to predict the effect on crack propagation as it depends on the specific mineral/phase composition and their toughness values. Pores could also arrest propagating cracks and reduce fines generation.

5.4. Sinter FeO

The most popular technique used to control sinter plant coke rate is to control sinter FeO at a fixed, predetermined value. Sinter FeO is a measure of the magnetite content in sinter and, with the introduction of goethitic ores into the blend, its value can change because of a number of factors. These include:

i)   increased magnetite formed as a result of the gaseous reduction of the highly-reducible protohematite in the sinter mix by CO or hydrogen, formed as a result of the incomplete combustion of coke (increases sinter FeO),[11]

ii)   decreasing sintering temperatures which decreases the level of hematite decomposing to magnetite (decreases sinter FeO),[11]

iii)   increased level of ore assimilated leading to a decreased melt basicity, which decreases the Fe^{3+}/Fe^{2+} value of the melt (increases sinter FeO),[11] and

iv)   decreased re-oxidation of magnetite in the melt to hematite during solidification, because cooling rates are faster with increased flame front speed and lower material thermal capacity (increases sinter FeO).

For the reasons above, FeO will most likely alter when goethitic ore is introduced into a blend. It is not possible to predict which of these four factors with have the greatest influence on FeO for a particular ore blend. Hence, FeO should not be controlled during plant trials on blends containing goethitic ores. It should be allowed to float while coke rate is adjusted to maintain sinter tumble index. As indicated earlier, changes in coke rate may not be necessary when the level of goethitic ore is less than 30 wt%. Once the appropriate coke rate has been determined, a new sinter FeO value can be defined for plant control purposes.

6.   Conclusions

This paper has demonstrated the importance and applicability of fundamental research to understanding the behaviour of goethitic ores in sintering. Based mainly on the author's work, a perspective is given on the link between fundamental research results, obtained mainly from bench-scale experiments, and sinter pot test results. The following is a summary of research findings discussed in the paper

and the author is well aware that many of these are not exclusive in that they are shared by sintering researchers and practitioners elsewhere.

(1)   Goethitic ores are inherently more porous and cause deterioration in granulation efficiency, which can be recovered by the addition of more water during granulation.

(2)   Iron ores have different assimilation properties under realistic sintering heating profiles because of differences in ore porosity. Initial melts are extremely mobile and porous ores have very high reaction surface areas, resulting in the formation of increased melt volume during sintering.

(3)   Goethitic ores have lower bulk densities and will reduce sinter plant productivity if machine speed and/or yield are not increased.

(4)   For the same bed permeability, the bed containing goethitic ore should have a faster flame front speed than the bed with denser ores. For this reason it is possible that no losses in productivity results even though there is a decrease in bed bulk density.

(5)   Green bed and sintering bed permeabilities—as determined by pre- and post ignition airflow rates—are strongly dependent on each other. This explains the importance of maintaining green bed permeability in sintering operations. Appropriate attention must be given to ensuring that green bed permeability on a sinter strand is maintained when introducing goethitic ores.

(6)   The major resistance during sintering has been shown to be the flame front, and factors that cause its temperature and thickness to increase will affect its resistance to airflow.

(7)   For a sinter mix, a single number termed the 'sinterability index' can be defined to characterise the resistance of the formed flame front during sintering.

(8)   Studies to date do not suggest that increasing the level of melt generated in the flame front reduces its permeability.

(9)   A water balance carried out on sintering beds indicates that increasing the level of water during sintering—either through significantly increased mix moisture during granulation or through increased use of goethitic ores—will result in water dripping out of the bed as an entrained liquid because the waste gases, prior to burn-through, are already fully saturated.

(10)   The flowing gases cause the entrainment of this water, and for this reason condensed water does not have an adverse effect on bed permeability.

(11)   The energy requirement to dehydrate goethite is very small in comparison to that required to calcine limestone in a sinter mix. The removal of water as a liquid rather than as a vapour also means reduced energy requirements.

(12)   First order calculations indicate that the irrecoverable energy used to break down the solid lattice of particles during melt formation consumes one half of the heat generated by the burning of coke.

(13)   The heat available for the sintering reactions can be utilised in melt formation or to raise the temperature of the unreacted solids and generated melts.

(14)   A minimum level of melt is required to make a strong sinter and this is most efficiently sourced from goethitic ores. When melts form easily and early, the time

available for melt coalescence increases.

(15) Goethitic ores assist in the production of more porous sinters, which are more reducible.

(16) Goethitic ores could increase or decrease sinter FeO depending on ore blend and sintering conditions.

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