Factors Influencing the Bonding Phase Structure of Iron Ore Sinters

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The properties of melts formed in the flame front during iron ore sintering determine the structure of the ensuing sinter bonding phases. The tumble strength of sinter particles and yield from a sinter strand are largely determined by the inherent strength and structure of the bonding phases present. In this study, bench-scale tests were carried out to study the effect of melt chemical composition and sintering conditions on bonding phase micro-structure. The study showed that phosphorus, silica, alumina and magnesia levels, sinter basicity and maximum sintering temperature influenced bonding phase structure through the reshaping and coalescing of the melt and bubbles. Information in the literature indicates that some of the observed changes in pore properties can be explained by changes in viscosity and surface tension of the melts. The inability to explain all the changes are most likely related to the differences in chemical compositions between melts considered in the literature and the sintering melts formed in this study. The study also showed that image analysis could used to provide a reliable objective description of the obtained sinter micro-structures.

KEY WORDS: iron ore sintering; melt chemical composition; machine yield; sinter micro-structure.

1. Introduction

Sintering is the most important process used to convert iron ore fines into a suitable lumpy product for blast furnace consumption. During the process, a melt is generated which solidifies to become the bonding phase in the sinter. Typically, sinter produced in the Asia Pacific region and Australia is composed of 80 vol% of bonding material—containing phases and minerals precipitated from melt—and 20 vol% unassimilated ore particles. Melt formation occurs in the flame front where temperatures are around 1300°C. Gas volumes increase significantly at the flame front because of the high temperatures, and this makes it the major resistance to airflow during sintering.1,2)

In a recent paper,3) the productivity of a sinter machine was expressed mathematically in terms of the properties of the bed (bed height and width, average particle density, voidage, moisture and volatile content), machine speed and the return fines load. The paper then considered the effect of ore blend on airflow rate during sintering—which is an important variable determining machine speed. The study showed that the resistance of flame front to airflow was not influenced by the properties and volume of the melts generated in the flame front.3) The purpose of this study is to understand the other factors that influence productivity, in particular those that determine the return fines load. The return fines load can be expected to be a function bonding phase structure, which is, in turn, determined by the properties of the melt. It is to be noted the properties of local melts formed during sintering could vary quite significantly depending on whether there are coke or limestone or magnesia-bearing minerals particles nearby.

Even a cursory examination of laboratory and plant sinters shows that they are composed of a wide range of bonding phase microstructures. Figures 1(a) and 1(b) show that sinter particles can have dense and smooth, or porous and rough outer surfaces. Some sinter particles were then broken into smaller particles to expose fractured surfaces. Fig. 1(c) shows that when fracture occurs around grain boundaries a rough surface is obtained, and internal pores are also exposed. Other fractured surfaces have abundant, larger, more rounded pores (Fig. 1(d)) suggesting that melt temperatures have been higher and the melt just prior to solidification was more fluid. The scanning electron micrographs also indicate that sintering melts can contain trapped bubbles, which have irregular or rounded shapes—possibly depending on temperatures and melt properties. The local micro-structure of sinter bonding phases, in particular its porosity, will clearly influence its strength, and it is to be expected that large areas of porous sinter structures could lead to reduced sinter plant yield.

Prior to extending earlier pilot-scale sintering programs3) to understand the factors that influence yield, a fundamental understanding of the effect of chemical composition on sinter micro-structure is essential. This paper describes a technique to study sinter micro-structure and examines its dependence on the properties of the melt just prior to solidification.
2. Experimental

To control the chemical composition of the green sinter mix accurately, an experimental program involving the production and characterisation of analogue sinters—rather than pilot or commercial plant sinters—was chosen. Analytical grade chemical powders were mixed homogeneously, compressed into a tablet and then sintered using a simulated sintering temperature profile in an Infrared Image Furnace (typical profile has a heating rate of 2°C/s to 800°C; after holding at that temperature for 60 s heated at 20°C/s to 1300°C; after 120 s at the maximum sintering temperature the sample is cooled at 2°C/s to 400°C). The analogue sinter samples produced have quite different structures compared to sinter from a laboratory pot and plant sinters, but the forces acting on the solid–melt–gas mixture—leading to the reshaping and coalescing of bubbles present and, consequently sinter micro-structure—are similar to those present in the pot/plant sinters. This aspect will be discussed in detail later.

Many studies at these Laboratories have been carried out using analogue sinters produced in Infrared Image Furnaces and the standard experimental procedure has been documented.4–7) These studies clearly show that small changes in chemical composition and furnace temperature can have a very large effect on the structural properties of the sinter. For a study involving the characterisation of bonding phase structure, it is crucial that sintering temperatures are accurately controlled. To this end, the Infrared Image Furnace was serviced prior to use, and samples for sintering were placed at the same exact location in the furnace to ensure that the thermal treatment experienced were identical for samples sintered at the same maximum sintering temperature.

Prior to commencing the experimental program, a considerable amount of time was also given to improving experimental procedures to ensure acceptable repeatability. This is particularly important since an aim of this work is also to provide quantitative description of the images using image analysis. Improvements made in experimental technique included:

a) Sinter mix preparation—The mix was accurately weighed, homogenised and pressed using the same load to ensure that all the tablets had similar green porosity.
b) Mounting sinter sample—Changes in the area involved the use of a low reflectance resin, and not subjecting the sample to vacuum to decrease resin penetration into the sample. After the resin had hardened solid block was cut to expose a consistent circular cross-section of the sample. The surface was then polished to a constant depth using standard procedures. The final polish involved using 0.5 μm alum paste.
c) Image capture—Before photographing the sample at the same magnification, calibration using a standard grey colour was carried out to ensure that the same light intensity was used.

When these changes and precautions were taken the ‘background noise’ reduced and sinters of comparable microstructure could be produced under similar test conditions. Differences between samples caused by changes in mix composition or sintering temperatures could, therefore, be identified at a high level of confidence.

2.1. Phosphorus

To test the basis of the proposed study, experiments were carried out on samples containing different levels of phosphorus. Phosphorus was added to the base mix—containing Fe₂O₃, SiO₂, Al₂O₃, MgO and CaO (in proportions shown in Table 1, for the base mix). The effect of phosphorus was examined by increasing the P₂O₅ from 0 to 0.5 to 1.0 wt%.

It is well established in the literature that phosphorus is a surface-active constituent, and that it preferentially migrates to the surface and alters the surface tension of iron containing melts.8) This should have an impact on the behaviour of the melt and properties of pores in the analogue sinters.

Figure 2(a) shows that with no P₂O₅ in the mix, the macro-pores were branch-like, irregular elongated shapes.
At 0.5 wt% P$_2$O$_5$ the macro-pores were able to reshape and transformed into more circular shapes. Further increasing the P$_2$O$_5$ content in the mix resulted in reduced pore coalescence and the formation of more circular pores. These results show that bubble properties just prior to solidification are highly dependent on melt composition. Further, they indicate that the proposed experimental technique is capable of providing information on the relationship between melt composition, melt properties and the micro-structure of the solidified phases formed—in particular the properties of the pores present. The experimental program was then extended to other mix compositions and conditions, as given in Table 1.

2.2. Basicity and Silica Level

Figure 2(b) shows that increasing basicity from 2.0 to 3.0 resulted in the formation of larger and more regular (less branch-like) macro-pores. The micrographs suggest that at increasing basicity the melts formed were more fluid. Increasing lime addition to increase basicity further to 3.0 also resulted in further reduction in total pore area, indicating increased expulsion of bubbles from the melt prior to solidification.

Figure 2(c) shows that pore area was the highest at a silica content of 5.5 wt%. When the silica level was increased or decreased from the base level of 5.5 wt%, there was greater degree of melt reshaping, resulting in more circular pores.

2.3. Alumina and Magnesia

Figure 2(d) shows that pore area increased with increasing alumina. At 1.6 wt% alumina, there was a high proportion of circular pores. The shape of the pores became very irregular (less rounded) as the alumina level increased to 2.0 wt%. It is apparent that melt fluidity had decreased, which reduced the ability of the bubbles in the melt to coalesce and reshape. Further increases in alumina content resulted in the formation of branch-like pores, caused by reduced melt fluidity and, decreased melt generation because of increased liquidus temperature (grey areas are unreacted particles). These pictures indicate that increasing the alumina content from 2.0 to 2.4 wt% should have a dramatic effect on sinter strength and yield.

Figure 2(e) shows that the sample with no MgO had comparatively rounded large discrete pores and a small amount of fine pores. At 2.0 wt% MgO, the larger pores formed were more irregular and the density of fine pores also increased. There was reduced reshaping of pores at increasing MgO levels, probably because of changes in melt liquidus temperature.

Table 1. Composition of mixes (wt%) and temperatures used in the study.

| Component       | Base mix | Other levels studied |
|-----------------|----------|----------------------|
| Fe (total)      | 52.85    | Varies depending on level of other oxides in the mix. |
| SiO$_2$         | 5.5      | 4.5, 4.5          |
| Al$_2$O$_3$     | 2.0      | 1.6, 2.0           |
| MgO             | 0.5      | 0.1, 1, 2.0        |
| Non-iron oxide content (SiO$_2$ = Al$_2$O$_3$ + MgO + CaO) | 24.5 | 19.6, 20.4 |
| Basicity (°C)   | 3.0      | 2.0, 2.5, 3.5      |
| Maximum sintering temperature (°C) | 1300 | 1275, 1310 |

* Ratio of CaO/SiO$_2$ value is larger than most commercial sizers because these sizers have silica associated with unreacted ore particles, which do not participate in the melt formation process.
2.4. Maximum Sintering Temperature and Gangue Level

Figure 2(f) shows that increasing temperature has a very large influence on sinter micro-structure. Pore area decreased and the branch-like pores also transformed into discrete elongated and more circular pores. Clearly, a temperature of 1 275°C is too close to the liquidus temperature and the sinter formed contained significant unreacted particles.

The gangue level of a sinter mix also had a very large influence on micro-structure, as indicated by Fig. 2(g). When the non-iron oxide level was low, more smaller pores were formed indicating a less fluid melt. Increasing gangue level resulted in more bubble coalescence, resulting in the formation of larger pores and greater reshaping. At 29.4 wt% non-iron oxide, a significant reduction in pore area was obtained. These pictures would confirm the general experience that a major problem with low-gangue sinters is strength.

3. Discussion

The results indicate that sinter bonding phase micro-structure is highly dependent on melt chemical composition and temperature, but the relationship is very complex. In discussions so far concepts such as melt and bubble coalescence/reshaping have been used and there is a need to further clarify these terms. Assumptions have also been made about why these micro-structures form and their dependence on the state of the melt just prior to solidification. The validity of these and other inherent assumptions are discussed and summarised in this section.

3.1. Assumptions

Inferring melt properties prior to solidification from the structure of the ensuing sinter product can be made if:

a) the pictures, which are two-dimensional measure of pore structure, provide a realistic description of three-dimensional pores in sinter bonding phase;

b) sinter microstructures (as illustrated in Fig. 2) reflect the transient properties of the melts prior to solidification, e.g. fluid melts containing no entrained bubbles will solidify to a non-porous structure, but a viscous melt containing bubbles will solidify into a porous structure;

c) bubbles freeze to become pores of similar shapes and sizes, and bubble properties can be obtained by studying pore properties;

d) the melt-gas system will naturally move towards energy minimisation; as a result there will be a tendency for bubbles to reshape and coalesce—to minimise melt surface area;

e) the degree of bubble reshaping and coalescence in a melt is determined by the relative magnitude of surface to viscous forces and melt density;

f) melt reshaping and coalescence is similarly driven by energy minimisation and is controlled primarily by the relative magnitude of surface to viscous forces;

g) parameters which define pore properties can be used to elucidate the properties of the melt, since the pore and melt reshaping/coalescence processes are dependent on the opposing effects of surface to viscous forces;

h) the influence of gravitational force on the laboratory samples is comparatively small (on a sinter machine gravitational force is also small but the flowing gases will create a drag/inertia force pulling material downwards—somewhat comparable to increased gravitational acceleration); and

i) all the oxides present react to form melt at the temperatures used (and subsequently, precipitate to form the secondary minerals and phases), even though MgO, for example, is known to diffuse in the solid state and convert hematite to magnetite—which may result in increased liquidus temperature and, possibly, reduced iron oxide assimilation into melt.

Strictly, pores in sinter could also be influenced by the texture of the precipitating minerals/phases. A good example is fine fibrous silico ferrite of calcium and aluminium (SFCA), which has significant fine inter-granular voids. In this study, no attempts were made to correct for these voids.

3.2. Bubble Reshaping and Coalescence

A bed of granulated iron ore typically has a voidage of around 30% and during melt formation a proportion of void space would be transferred into the melt as bubbles. It is to be expected that porous ores, goethitic ores (which converted to a very porous hematite) and carbonaceous fluxes (which transform into very porous structures) would further increase the volume of bubbles trapped in sintering melts. The high assimilation rate of porous ores would increase melt viscosity (because of increased iron oxide to lime ratio), and this could reduce the expulsion of trapped bubbles from the melt. Therefore, goethites would be expected to have a significant influence on the micro-structure of sinter bonding phases. At this point it is appropriate to define in greater detail the three terminologies used to describe bubble behaviour in melt:

i) Reshaping

This term denotes the transformation of irregular (usually branch-like) shaped pores into more rounded shaped pores. The stresses associated with the reshaping of a bubble of radius, \( r \), as a result of surface tension is of the order of \( 2\gamma/\pi r \), where \( \gamma \) is the surface tension of the melt. For this reason, it is to be expected that small bubbles in melt will reshape much easier than the larger bubbles present. For large bubbles, minimising surface area will particularly difficult when melt viscosity is high, since the degree of reshaping is determined by the ratio of surface to viscous forces.

ii) Coalescence

When small pores combine to form a reduced number of larger pores, the total free energy in the system decreases. The coalescence process can be expected to be highly dependent on melt viscosity since melt between two approaching bubbles has to drain before coalescence can take place. Likewise, bubble expansion caused by increasing gas temperatures will push adjacent bubbles towards each other, enhancing the coalescence process.

iii) Expulsion

The ability to form denser sinter structures, for example at high sintering temperatures, indicate that bubbles can leave a melt because of buoyancy forces. As buoyancy forces acting on larger bubbles are higher, it is to be expect-
ed that they leave a liquid more easily. In addition to bubble size, melt viscosity will also influence the bubble population of a melt.

3.3. Melt Reshaping and Coalescence

Figure 3 shows a large block of sinter produced from a laboratory pot test. On stabilisation this block will break down into identifiable sinter particles (say, less than 30 mm) because of the presence of very large voids in the structure. It is clear that during sintering, major changes have taken place in the bed since voids between granules in the original green bed are comparatively small and uniformly distributed over the entire bed. The formation of melts has resulted in significant reshaping and movement of the material—which caused melts in localised regions to coalesce—giving rise to these large voids and the creation of identifiable sinter particles in the structure shown in Fig. 3. On crushing the sintered block, the sinter particles obtained are themselves also extremely porous, as shown in Fig. 1. However, intra-particle pores are much smaller in size compared to those interspersed between sinter particles (see Fig. 3). The intra-particle pores determine the strength of the sinter particles and sinter reducibility. On the other hand, the property of the large voids in a sintered bed can be expected to influence the size of sinter particles and yield, since small fractured inter-particle bridges do not report as sinter product but as return fines.

Early during sintering, large volumes of low-temperature, lime rich, iron-bearing melts are formed only where limestone particles are in close proximity to ore particles. In a sintered bed, bonding phases containing lime are quite well distributed, which suggests that local melts flow and coalesce with other surrounding melts. Only the movement, coalescence and reshaping of melts can cause the major structural transformation shown in Fig. 3. It is also clear that melt coalescence occurs during sintering for another reason. As temperatures increase, melts surrounding an iron ore particle will very quickly become saturated with iron oxide, as would melt around limestone particles be saturated with lime. In both cases, assimilation would cease quite rapidly unless the iron oxide and lime were able to diffuse away from the reaction interface to the bulk of the melt, or if the two melts of quite different chemical compositions flowed towards each other and coalesced early during the assimilation process. Coalescence triggers mixing and melt-melt reactions, and ensures that assimilation of both fluxes and ores continue until sintering temperatures fall below the liquidus temperature.

3.4. Factors Controlling Reshaping and Coalescence

It is evident that bubble and melt reshaping and coalescence are important phenomena in sintering. The forces driving these two processes are summarised in Table 2. Capillary or surface forces will oppose the reshaping and coalescing processes. Buoyancy forces exist because the melt is not uniform and the magnitude of these forces will depend on differences in density, temperature or concentration. Inertial forces are only significant if flow velocity is large. Table 2 shows that the forces causing bubbles and melts to reshape and coalesce, are very similar. These melt physical properties—surface tension, viscosity and density being the more important—are functions of melt chemical composition and temperature.

The effects of melt composition and temperature on melt properties are summarised in Fig. 4. Melt chemical composition determines melt viscosity, surface tension, density and liquidus temperature. The physical properties will change as the surrounding temperature is raised above the liquidus temperature, but these changes will be different for melts of different chemical compositions. For a defined sintering temperature profile, the liquidus temperature of a melt will determine the degree of superheat. For melts of

| Acting forces | Bubbles | Melt |
|---------------|---------|------|
| Surface       | Causes reshaping and coalescence | Causes reshaping and coalescence |
| Viscous       | Resists reshaping and coalescence | Resists reshaping and coalescence |
| Bouyancy      | Vertical ascent of bubbles could lead to bubble coalescence and their expansion from melt i.e. if it reaches a free surface | Flow to normalise thermal and concentration gradient across melt layer, and vertically ascending bubbles could retard the flow of melts in other directions |
| Inertia       | Could enhance the expulsion of bubbles but effect likely to be small because of low bubble rising and melt flow velocity | Enhances flow and coalescence although effect likely to be small because of low flow velocity |

Table 2. Forces acting on melts containing bubbles leading to their reshaping and coalescence.

Fig. 3. Large piece of sinter showing characteristic bed structure composed of sinter particles (P) and bridges (B).

Fig. 4. Effect of melt composition and sintering temperature on melt properties.
fixed chemical compositions, the sintering temperature profile determines the degree of superheat and, through this the physical properties of the melt.

During sintering, the time at above melt liquidus temperature is relatively short and the high degree of bubble reshaping observed (Fig. 1d)) indicates that the surface forces acting on the melts are larger than the viscous forces. Melt surface tension will also influence wettability on a specific surface and the rate at which melt surface area contracts or spreads over a surface (through the contact angle) both of which influences melt reshaping and coalescence. For most fluids, density and viscosity are closely related and increasing density will usually increase viscosity. However, it is to be expected that melts are more complex, in that the introduction of a denser oxide may modify and weaken the inter-molecular bonds in the melt, giving reduced viscosity. Melt density will clearly influence the movement of bubbles in a melt and their expulsion from melt. Intuitively, it is to be expected that surface and viscous forces will be larger in magnitude compared to buoyancy or inertia forces, and are, therefore, the more important.

4. Quantitative Measures of Microstructures

Image analysis is a technique that could be used to provide an objective measure of sinter phase micro-structure. Once a sample has been mounted and polished, it is then placed under the Zeiss Axioskop microscope for examination. A black and white CCD digital camera mounted behind the lens of the microscope captures the light reflected from the sample. The digital camera used has a maximum resolution of 756×581 pixels. A 10× objective lens on the microscope has been chosen for the current study. At this level of magnification, the equivalent frame of view on the sample surface is approximately 1.239×0.952 mm.

To capture the digital image for later analysis, the signal from the camera was fed to a personal computer via a gain correction amplifier where the signal could be corrected for optimal display. The computer software used for translating the camera signal into digital image and image analysis was the Kontron Elektronik KS300 Imaging System supplied by Carl Zeiss Vision.

Basically, the digital image captured from the black and white camera is represented by pixels having 256 shades of grey values (i.e. 0 to 255). Usually the lower range of grey values represent pores, with grains of sintered particles taking on the higher range values. A digitised black and white photograph is transformed into a binary image when the operator specify the range of grey values to be demoted to zero (black) and the remainder of the grey values to be promoted to 255 (white). The segmentation process is demonstrated in Fig. 5. Once the image has been processed into a binary picture, the various image analysis tools from the KS300 software were used to measure the physical appearances of the pores.

From an image, the Kontron software allows a very large number of parameters to be determined. It is obvious that not all of these provide useful quantitative information on sinter structure. After careful consideration three parameters were selected as being relevant and they are described in Fig. 6. Other measures of pore geometry—feret ratio, concavity and solidity—were also determined but trends obtained using these measures were consistent with the trends indicated by circle factor. This is not entirely surprising as they are influenced by the same melt properties.

The micrographs in Fig. 2 show typical areas. For image analysis studies, three sintered samples were used and 20 images were processed for each test condition. The values obtained for the three pore parameters are consistent with observations made under an optical microscope. Pore properties were found to be dependent on pore size and presented results are divided into four arbitrary categories: fine (<50 μm), small (>50 μm≤100 μm), medium (>100 μm≤200 μm), and coarse (>200 μm). All the results are

| Parameter | Schematic representation | Relevance to understanding resharding/coalescence |
|-----------|--------------------------|--------------------------------------------------|
| Area      | ![Area Schematic](image) | If melts are sufficiently fluid, bubbles can be expelled to lower the energy level in the system. Pore area or density, which is a measure of area occupied by pores, could provide information on the ability of melts to expel bubbles. |
| Size distribution | ![Size Distribution Schematic](image) | Two small spherical bubbles have a larger surface area that one spherical bubble of equivalent volume. There will, therefore, be a tendency for bubbles to coalesce, to reduce the energy level in the system. From pore size distribution, information on the melt properties that favour or allow bubble coalescence can be obtained. |
| Circle factor (C/π) | ![Circle Factor Schematic](image) | The energy level in a melt also decreases when bubbles transform from irregular to more spherical shapes because this leads to a decrease in the bubble/melt interface area. The circle factor is a measure of deviation from sphericity and could provide information on the opposing effects of two forces: surface tension ending to transform bubbles into a spherical shape and viscosity forces tending to moist such a change. |

Fig. 5. Application of binary segmentation process to produce an image for quantification.

Fig. 6. Quantifying pores in bonding phase structure and the relevance of these to understanding melt properties prior to solidification.
given in Figures 7 to 10 and a summary is given below.

Phosphorus: Pore areas were comparable and quite independent of P\textsubscript{2}O\textsubscript{5} level. Increasing P\textsubscript{2}O\textsubscript{5} level altered pore size distribution but the results did not indicate any trends. Increasing P\textsubscript{2}O\textsubscript{5} level from 0 to 1.5 wt%, resulted in increases in circle factor for all the pore sizes i.e., all the pores became more spherical and/or have smoother surfaces. At all P\textsubscript{2}O\textsubscript{5} levels, the finer pores were more circular compared to the larger pores, and this is to be expected from theory.

Basicity: Pore area decreased only when basicity increased from 3.0 to 3.5. At increasing basicity the proportion of fine and coarse pores gradually increased, while the proportion of medium and small pores decreased. When basicity is increased the medium and coarse pores became smoother and/or more spherical. All the results show that as pores became smaller they became more circular.

Silica: Pore area was highest at a silica content of 5.5 wt%. There was a trend of decreasing proportion of fine pores and increasing proportion of medium pores as silica level increased. There was a small increase in the percent of small pores with increasing silica. At 4.5 wt% silica, the differences in circle factor between the four pore size ranges were the smallest observed in this study.

Alumina: Increasing alumina increased pore area and decreased the proportion of fine and small pore, while the proportion of medium and coarse pores increased. At 1.6 wt% alumina no coarse pores were present. The differences in circle factor for the four sized pore fractions increased with increasing alumina.

Magnesia: Pore area increased with increasing magnesia content. With this increase, the proportion of fine and small pores decreased, while the proportion of coarse pores increased especially from 1.0 to 2.0 wt% MgO. For the same pore size range, the circle factor decreased as magnesia levels increased.

Maximum Sintering Temperature: At increasing temperature, pore area decreased while the proportion of fine pores increased because of decreases in the level of coarse pores. The medium and coarse pores became more circular when temperatures are increased from 1275 to 1300°C. A further temperature increase to 1310°C did not have an effect on the circle factor values.

Non-Iron Oxide Content: Pore area decreased only when the non-iron oxide content reached 29.4%. Together with this change, the circle factor values for the different sized pore fractions became more comparable. When the non-iron oxide level was increased, more fines pores were also formed.

5. Comparison of Results with Information in the Literature

The literature was surveyed to understand the possible effects of chemical composition on melt viscosity, surface tension and density to determine if there is agreement with the results obtained in the present study. The survey showed that only qualitative comparisons of results could be carried out for three important reasons. Firstly, the chemical composition of systems studied in the literature is quite different to those found in iron ore sintering—and for these reasons results obtained in this study may not follow expected trends. Secondly, trends cited are based on experimental results obtained well above liquidus temperature. In sintering, melt formation temperature is much closer to liquidus temperature. Finally, there is no certainty that the analogue sinters have not reached equilibrium conditions even though very fine powders were used. Works cited from the literature have mainly been carried out under equilibrium conditions.
The work of Nowok et al.12) showed that the physical properties of solidified slags were dependent on melt viscosity and surface tension. The porosity of the silicate and aluminosilicate deposits from pulverised coal fired utility boilers was found to strongly influence by the surface tension to viscosity ratios of the melts. The physical properties of the molten phases were measured at temperatures above the temperature of critical viscosity at which flow behaviour changes from Newtonian to non-Newtonian. It was also shown in this work that the porosity of the sintered material increased with increasing ratio of surface tension to viscosity.

In attempting to understand factors influencing bubble coalescence, Claderbank13) derived an equation to determine the mean size of dispersed bubbles found in metallurgical melt systems. The equation shows that the stability of bubbles in melt is very much a function of the surface tension.
sion, viscosity and the density of the melt which are governed by the temperature and melt chemical composition.

There is agreement that melt and bubble reshaping/coalescence during sintering will require knowledge of melt viscosity, surface tension and density. A survey of the literature shows that although there is information in this area on metallurgical slags, there is very little or no relevant information for iron ore sintering melts i.e. high in iron oxides and lime.

5.2. Viscosity

The Frenkel equation was developed in 1946 and it can predict the viscosity of complex silicate system reasonably well. Later work by Urbain resulted in an empirical model to better predict the viscosity of complex silicate melts based on experimental information on pure binary and ternary melts. Predictions from this model were generally accurate except for CaO–Fe₂O₃–SiO₂ systems, because of the need to know the ratio of Fe³⁺ to Fe²⁺ (Fe²⁺ has a large influence on melt viscosity). The model also could not predict the effect of increasing CaO at fixed SiO₂ well. Zhang and Jahanshahi have developed an improved viscosity model for CaO and MgO silicate systems.

Melt viscosity estimation is obviously very complex and is beyond the scope of the current study. To provide a first indication of viscosity, the degree of superheat was determined using the Multi-phase Equilibrium (MPE) model, developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO). Zhang and Jahanshahi have published a brief outline of the calculation routines for the estimation of the molten slag viscosity using this model. This model was used to estimate the liquidus temperatures of the molten slag formed during sintering of the synthetic iron ore pellets in the early 1990’s. Since then it has been upgraded several times. For a given system, the model has the capability of calculating the distribution of elements or species between phases, as well as the mass percentages of the gas, solid and liquid phases at equilibrium. It also gives a good estimate of the viscosity of the fully molten slag and slags with up to 20% solid phases.

5.3. Surface Tension

With the advent of electric arc furnaces, many studies have considered the foaming of steelmaking slags and the effect of surface tension on the process. However, these slags generally contain high FeO—greater than 30 wt%—which makes them different to high basicity melts found in the sintering of hematite ores. The Slag Atlas has information, but again these are for high Fe₂O₃ content slags. For the simple binary system of CaO–Al₂O₃, surface tension increases with increasing amount of Al₂O₃, and the addition of Al₂O₃ to SiO₂ or FeO melts also increases surface tension.

For the CaO–SiO₂ system, surface tension was found to increase with increasing CaO. This was also true for CaO–FeO–SiO₂ slags containing 30% FeO. For a simple CaO–Fe₂O₃ mixture, two references showed that increasing CaO content slightly increased surface tension, while another showed the opposite effect. In a more complex ternary system of Al₂O₃–CaO–Fe₂O₃, melt surface tension was found to increase with increasing CaO.

### Table 3. Expected changes in melt properties based on information in the literature.

| Variable                      | Literature findings and comments                                                                 |
|-------------------------------|---------------------------------------------------------------------------------------------------|
| Phosphorus                    | Nakashima and Mori[40] showed that phosphorus decreased the surface tension of FeO slags. Cluverbank[41] found that the mean size of bubbles in an agitated aqueous system was directly dependent on surface tension and inversely dependent on density and viscosity. Possibly for this same reason, the decrease in surface tension with increasing Fe₂O₃ levels could explain the transformation of more small pores in the mixer, which is a direct result of reduced bubble coalescence. |
| Basicity                      | The MPE model predicts decreasing slag equilibrium liquidus temperature with increasing lime content. Therefore, the degree of superheat increased and more fluid melt is formed. Increasing basicity to 3.0 increased bubble coalescence causing the formation of more macro-pores. At a basicity of greater than 3.0, more coalescing and reshapin occurs and the reduction in porosity indicates that some bubbles have been expelled from melt. |
| Silica                        | Over the range of silica levels considered, the MPE model predicts only a small change in the equilibrium slag liquidus temperature and melt viscosity. Silica is not a surface active constituent and should not alter melt surface tension. Experimental results show that silica is clearly having an unusual effect, which cannot be explained by current knowledge. |
| Alumina                       | Over the range of alumina levels considered, the MPE model predicts only a small change in the equilibrium slag liquidus temperature and melt viscosity. As for variations in silica, the degree of superheat and slag viscosity cannot explain the differences in sinter texture at increasing alumina levels. It is most likely that melt surface tension has also influenced the behaviour of bubbles in the melt. Nakashima and Mori[40] found that the surface tension of FeO melts were increased by the addition of alumina. A higher surface tension would encourage greater bubble coalescence. |
| Magnesia                      | The MPE model predicts that MgO raises the melting point and decreases the superheat. This explains the transformation of round pores into branch-like pores. Literature also suggests that MgO can lower melt surface tension. Changes in viscosity alone cannot fully explain the observed changes in sinter texture. It is most likely that changes in surface tension are also having an effect on bubble size, and the observed structural changes are caused by changes in both melt viscosity and surface tension. |
| Maximum sintering temp.       | The effect of superheat in reducing melt viscosity is clearly demonstrated here. While the surface forces may change slightly with temperature, the ratio of viscos to surface forces is much smaller at increasing temperatures. |
| Neo-iron oxide level          | The MPE model predicts a reduction in equilibrium liquidus temperature with increasing gangue level. The changes in sinter texture is similar to that observed at increasing basicity, and is consistent with expectations. |
sion was shown to decrease significantly with increasing Fe₂O₃ content.²⁵

In our study, the effect of temperature on surface tension is important. Generally, over a limited temperature range, surface tension decreases linearly with increasing temperature.²⁶ There are, however, exceptions to this rule. The surface tension of some complex slag melts with high SiO₂ content can actually increase with increasing temperature because of structural dissociation—the increased number of unsatisfied molecular bonds at the surface, which increases the surface free energy. This could explain why changes in pore properties with varying silica levels could not be predicted by the MPE model²⁷ (Table 3).

5.4. Density

For most pure liquids, viscosity is a solely a function of density e.g. Arrhenius relation or Thomas’s equation (Perry.²⁸) Olives, Brungs and Liang²⁹ carried a study on slag density as a function of its composition. Their study on synthetic slags used various concentrations of CaO, SiO₂, Al₂O₃, Na₂O and CaF₂. It was found that slags containing higher concentration of SiO₂, Al₂O₃ and Na₂O had lower density, whereas higher concentration of CaO and CaF₂ resulted in higher density. Furthermore, these investigators found that the change in density per unit concentration of the varying component was linear and was independent of the initial base composition.

In the area of bubble coalescence and ejection from melt, density could be important, according to Claderbank.¹³ The size of bubbles in slags formed from small orifices at low gas flow rates were shown to depend on melts surface tension and the buoyancy forces acting on the bubbles. Higher surface tension increased bubble size but higher density resulted in smaller bubbles because of the greater buoyancy forces. It is to be expected that once bubbles formed in a melt, they can either be ejected or retained from depending on their terminal rising velocity. According to Stokes’s law, terminal rising velocity will decrease with increasing viscosity and, increases with increasing melt density. It is most likely that lower melt density would favour bubble retention and the average size of the bubbles retained would also be larger.

6. Conclusions

The structure of sinter indicates that the chipping of material from sinter particles can be expected to be a strong function of its bonding phase micro-structure i.e. pore density and size distribution. In turn this influences sinter plant productivity. Bench-scale tests were carried out to understand the influence of melt chemical composition and maximum sintering temperature on bonding phase micro-structure. Fundamental understanding in this area is required to establish relationships between yield, productivity, and ore blend composition—which is the next stage of on-going BHP Billiton Technology studies on sintering.

The following conclusions can be drawn from this work:

(1) Melt properties, which determine bonding phase structure are viscosity, surface tension and density, and they, in turn, are dependent on chemical composition and temperatures. These properties determine the degree of melt and bubble reshaping and coalescence, prior to the solidification.

(2) Assumptions were made in this study that the structure of the melt just prior to solidification were reflected by the properties of the bonding phases. Limited information available in the literature on the effect of different chemical species on the properties of the melts indicates that the assumption is valid.

(3) Bubble coalescence and the reshaping of melts/bubbles are highly dependent on the relative magnitude of ratio of the surface to viscous forces. Results indicate that the degree of superheat is a good indirect measure of melt viscosity and the magnitude of the viscous forces.

(4) Results show that pores in bonding phases vary in size distribution as chemical composition and sintering temperatures are altered to vary the degree of superheat.

(5) Lowering melt viscosity—through altering melt composition or raising the degree of superheat—encourages the expulsion of bubbles from the melt and a denser bonding phase structure is formed.

(6) On changing ore blends at a sinter plant, sinter strength and return fines load are often controlled through altering coke rates. This is not surprising as coke rate determines the degree of superheat of the melt and results in the formation of denser bonding phases.

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