Leaching Dicalcium Silicates from Iron Ore Sinter to Remove Phosphorus and Other Contaminants

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Although dicalcium silicates can constitute up to 10 vol% of many modern hematite/goethite iron ore sinters, traditional mineralogical investigations of such sinters have largely overlooked this phase and focused on the more abundant iron oxides and ferrites. However, dicalcium silicates have a range of properties that make them unique in sinter parageneses. These properties may contribute significantly to bulk sinter properties and also make dicalcium silicates potentially exploitable in novel upgrading processes. Analyses on a pot grate test sinter have shown that phosphorous (and possibly other elements including potassium and chromium) was heavily concentrated in the dicalcium silicates. A series of etch tests have demonstrated that dicalcium silicates can be selectively removed from the surface of polished sinter samples using weak acids. In addition, bulk leaching trials showed that the phase can also be removed from powdered and coarser (−5 mm) sinter in mild acids. These leaches resulted in a >90% reduction in phosphorous with a 7% improvement in iron grade for the powdered material and a 70% reduction in phosphorous with a 5% improvement in iron grade for the coarser material. Two novel processes are proposed to exploit the leachability of contaminated dicalcium silicates from sinter: one being a potential route to a high-grade iron product, the other being a return fines washing circuit.

KEY WORDS: sinter; slag; dicalcium silicate; leaching; phosphorus; return fines.

1. Introduction

Currently, world blast furnace burden is composed of ~80% sinter (Fe ~57%) and ~20% lump ore and pellets (combined Fe ~65%) with the proportion of pre-treated agglomerates increasing as world stocks of high quality lump iron ore decrease.

The growing reliance on sinter as a feed material and the continuing need in ironmaking to maintain productivity and quality has provided impetus for researchers to understand and categorise sinters in terms of their mineralogy, microstructure and formation.1–16) Commonly, these investigations have characterised the properties of the ores, granules and other raw feed materials as well as the various mineral assemblages and microstructures of sinters. Data generated have been related to important production and quality parameters (such as strength, reduction degradation and reducibility) with the goal of understanding the complex relationships between raw materials, processing conditions, sinter mineralogy and sinter productivity and quality. Ultimately the aim of such research has been to develop new techniques—or modify existing procedures—of materials preparation and processing, in order to maximise the formation of ‘desirable’ sinters (i.e. those with mineralogy and microstructures considered to be superior in terms of productivity and quality) in plant operations.

While sinter can potentially be highly variable in its phase composition, low temperature sintering (<1300°C) of many hematite-goethite ores fluxed to a fixed basicity produces sinters that are reasonably consistent in terms of their mineralogy. Such sinters are generally composed of four groups of phases: iron oxides (~40~70 vol%), ferrites (most of which are SFCA: Silico-Ferrite of Calcium and Aluminium; ~20~50 vol%), glasses (up to ~10 vol%) and dicalcium silicates (up to ~10 vol%).1,2,4,6,9,11,13,14,17–19) Minor phases including quartz, sulphides, pyroxenes, serpentine and lime can also be present, but the total of these rarely accounts for more than a few percent of the total sinter volume.4,13,14,20)

To date, research addressing the mineral constituents of sinter has concentrated on the iron oxides1,3,12,14,21,22) and ferrite phases.1,3,6,9–12,22) The iron oxides have been considered to be important because there is evidence that the various oxidation/reduction reactions that they undergo during sintering or preheating in the blast furnace can contribute to the formation of cracks which result in sinter degradation.3,7,12,21,23–25) The different forms of ferrites have been variously attributed with high strength and reducibility by some researchers and considerable effort has gone into both characterising these phases3,6–20) and developing techniques to maximise their formation in sinters.1,4,6–9,12)

Although dicalcium silicates and glasses are present in most fluxed hematite/goethite sinters in considerable proportions, their formation in sinters and their effect on sinter properties have not yet been fully explored by researchers. This paper intends to promote the necessity of sintering re-
search that focuses on the dicalcium silicate polymorphs as this group of phases may have some significant impacts on the properties of sinter.

1.1. Dicalcium Silicates

Twenty years ago both Ostwald\(^{13}\) and Matsuno\(^{15}\) identified the potential for loss of sinter strength as a result of the \(\beta\) to \(\gamma\) transition that dicalcium silicate (\(\text{Ca}_2\text{SiO}_4\), herein referred to as \(\text{C}_2\text{S}\)) undergoes during cooling. Ostwald (1981) noted the potential to stabilise \(\text{C}_2\text{S}\) with foreign atoms and the ability to etch the phase from sinter with water.\(^{13}\) Some consideration on the formation and reactivity of the phase was also given in Shigaki et al., (1985).\(^{16}\) Aside from these works, several researchers have reported the abundance of \(\text{C}_2\text{S}\) in sinter,\(^{7,8,11,13,14,17}\) but beyond this there is little discussion of the role of the phase or the potential to manipulate it to produce higher quality sinters.

Dicalcium silicates are well known from disciplines outside iron ore sintering. Cement manufacture,\(^{30–33}\) magnesia refractory related research\(^{34,35}\) and other parts of the iron and steelmaking process\(^{36–38}\) either rely on, or are affected by, the properties of \(\text{C}_2\text{S}\) and therefore an appreciable amount of research has been conducted into various aspects of these phases. A review of this literature on the \(\text{C}_2\text{S}\) polymorphs reveals that some of the properties of this group of minerals are unique amongst sinter phases and this fact may potentially make them exploitable for the upgrading or further processing of sinters. Some of the pertinent properties of \(\text{C}_2\text{S}\) are listed below.

\begin{itemize}
\item 1) They are the only essentially Fe-free phases in sinter. Small amounts of Fe can substitute into dicalcium silicates in sinters but it is usually \(<1\) mass\%.\(^{13}\)
\item 2) They are relatively unstable, suffering from five temperature/composition/microstructure dependent phase transitions between \(\alpha\), \(\alpha'\), \(\alpha''\), \(\beta\) and \(\gamma\) polymorphs,\(^{30,31,33,35}\) which can be accompanied by significant volume changes that are known to cause the phase to break down or ‘dust’ in some cases.\(^{30,39}\)
\item 3) \(\text{C}_2\text{S}\) is known to incorporate a wide variety of impurities in several different systems, including those relevant to the cement industry,\(^{39–41}\) and steelmaking slags, where they preferentially concentrate undesirable components.\(^{36–38}\)
\item 4) The incorporation of impurities in the crystal lattice can stabilise different polymorphs of \(\text{C}_2\text{S}\) and thereby inhibit phase transformations.\(^{39,41}\)
\item 5) At least one polymorph of \(\text{C}_2\text{S} \) (\(\beta\)) is known to gelatinise in dilute HCl\(^{42}\) and the hydration of \(\text{C}_2\text{S}\) is well understood in the cement industry.\(^{32,40,41}\)
\item 6) \(\text{C}_2\text{S}\) is less dense than many other phases present in iron and steelmaking processes and segregates in iron-rich melts by floating.\(^{32,41,43,44}\)
\item 7) \(\text{C}_2\text{S}\) has a basicity (\(\text{CaO}/\text{SiO}_2\)) of 1.9.
\end{itemize}

2. Experimental

Preliminary analyses and experiments were undertaken in order to confirm that \(\text{C}_2\text{S}\) in iron ore sinter had some of the properties listed above and also to assess potential options for upgrading sinter by exploitation of those properties. The present work focused on:

\begin{itemize}
\item a) chemical and mineralogical characterisations of sinter; in order determine the amount of \(\text{C}_2\text{S}\) in sinter, the amount of Fe in \(\text{C}_2\text{S}\) and whether \(\text{C}_2\text{S}\) acts as a sink for undesirable contaminants in iron ore sinters as it does in other systems and;
\item b) leaching trials; to establish whether mild acid could preferentially remove \(\text{C}_2\text{S}\) from two-dimensional polished sinter surfaces as well as from bulk powdered and coarse sinter samples. It was anticipated that the removal of this phase would result in a proportional increase in the Fe grade of the sinter as well as a decrease in contaminants that were concentrated in the phase.
\end{itemize}

2.1. Materials

Product sized sinter (\(~40+5\) mm) was sourced from a batch made at CSIRO Miners’ pot grate testing facilities in Sydney, Australia. The sinter was prepared from a Western Australian, hematite-goethite fine iron ore. Phosphorous was a major impurity (0.127 mass\%) and so was selected as the primary contaminant to track in the sinter assemblies. The ore was fluxed with limestone (9 mass\%) and silica (increased to 5 mass\% total) such that it was representative of common sinter plant feeds. HCl was chosen as the leach acid for these exploratory tests.

2.2. Sinter Characterisation

2.2.1. Bulk Chemistry

Sub-samples of the sinter were pulverised in a ring grinder for one minute, dried for 1 hr at 110°C and assayed to give bulk chemistry data. Standard assay procedures for the current investigations combined 0.5 g of sample with 5 g of 12:22 flux, which was fused at 1 050°C in a Pt/Au crucible and cast into a glass bead. The bead was then analysed in an X-Ray Spectrometer (Philips PW2404). Assay results are summarised in Table 1.

2.2.2. Phase Abundances

Phase abundances were inferred by point counting two representative samples (crushed and sized to \(~1+0.5\) mm) of sinter equivalent to the one used in the experiments (made in the same testwork series and from the same ore). An optical microscope was used at a magnification of 200\(\times\), with a step size of around 300 \(\mu\)m and 1 200 points were counted per sample. The data were averaged and normalised and are presented in Table 2.

\(\text{C}_2\text{S}\) has similar reflectivity, relief and colour to glass in sinters and in many cases is difficult to distinguish optically. In the present testwork, \(\text{C}_2\text{S}\) crystals were discriminated

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
\textbf{Fe} & 57.13 \\
\textbf{P} & 0.13 \\
\textbf{SiO}_2 & 4.99 \\
\textbf{CaO} & 9.166 \\
\textbf{Al}_2\text{O}_3 & 2.14 \\
\textbf{Cr}_2\text{O}_3 & 0.034 \\
\textbf{K}_2\text{O} & 0.025 \\
\hline
\textbf{Total} & 98.6 \\
\textbf{Basicity} & 1.84 \\
\hline
\end{tabular}
\caption{Bulk sinter sample chemistry (mass\%) and basicity.}
\end{table}
from glass using a combination of their textural habit (e.g. C$_2$S is more easily identifiable when associated with large amounts of ferrites), slight differences in reflectivity and the fact that some of the C$_2$S crystals were etched during sample polishing. However, it is recognised that when using optical techniques for phase abundance determinations, the amount of glass may be overestimated and the amount of C$_2$S may be underestimated. Consequently, it is possible that the proportion of C$_2$S in sinters can be higher than optical data suggest and, therefore, the value of 5.6 area% C$_2$S for the testwork sinter (Table 2) should be considered a minimum estimate only.

Phase abundance data from the literature show that C$_2$S is commonly present in industrial sinters at similar levels as it is in the present testwork sinter. In addition, a review of phase abundance data from 52 other sinters prepared from a wide range of ore types at CSIRO Minerals showed that the mean abundance of C$_2$S in sinter was 4.6 area%, although there was a range from 1.8–9.8 area%.

2.2.3. Phase Compositions

Unground sub-samples of the testwork sinter were set in epoxy resin, polished under kerosene and examined using electron probe microanalytical (EPMA) techniques to determine the composition of the five major phases present (hematite, magnetite, ferrites, glasses, C$_2$S). The data were collected using a computer-automated electron microscope (JEOL JXA-8900R Superprobe) operating in wavelength dispersive mode. Standards were hematite (Fe$_2$O$_3$), wollastonite (CaSiO$_3$) and fluorapatite (Ca$_5$(PO$_4$)$_3$F). An accelerating voltage of 15 kV and a beam current of 30 nA were used with a beam diameter of 1–3 μm. Standard counting time was 20 s. Mean phase compositions are presented in Table 3.

Elemental data for the glass and C$_2$S phases have high standard deviations, reflecting their high compositional variability (Table 3). Some of the ‘C$_2$S’ crystals were found to contain elemental P over 8 mass% and may be more properly considered to be calcium silico-phosphates. As a result of this chemical variability, the mean data presented for these phases should be considered to be approximations of their true mean compositions. However, even after accounting for this approximation, it remains clear that P was very heavily concentrated in the C$_2$S phases of the testwork sinter (around 70% of the total P in the sample) and also somewhat enriched in the glass (remaining 30%). Ostwald did not find this preferential partitioning of P into C$_2$S; most of the P in the sinters he analysed reported to the glass.\footnote{See reference 13.}

2.3. Leaching Procedure and Results

Two methods were used to establish the leachability of C$_2$S from the iron ore sinter.

(a) Etching a polished surface of a large lump of sinter (−25 + 16 mm size fraction). This was done so that the polished surface could be observed microscopically before and after etching and C$_2$S could be confirmed as the preferentially leachable phase.

(b) Leaching of bulk sinter samples. This was done on both powdered sub-samples, in order to determine the maximum amount of C$_2$S leachable, and coarser sinter sub-samples (−5 mm), to examine the degree to which C$_2$S could be leached from sinters with size fractions more representative of those found in operational plants.

2.3.1. Sinter Surface Etching

A lump of sinter was set in epoxy resin, polished under kerosene and examined using electron probe microanalytical (EPMA) techniques to determine the composition of the five major phases present (hematite, magnetite, ferrites, glasses, C$_2$S). The data were collected using a computer-automated electron microscope (JEOL JXA-8900R Superprobe) operating in wavelength dispersive mode. Standards were hematite (Fe$_2$O$_3$), wollastonite (CaSiO$_3$) and fluorapatite (Ca$_5$(PO$_4$)$_3$F). An accelerating voltage of 15 kV and a beam current of 30 nA were used with a beam diameter of 1–3 μm. Standard counting time was 20 s. Mean phase compositions are presented in Table 3.

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Table 2. Phase abundances for equivalent product sinter (area%).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Hematite</th>
<th>Magnetite</th>
<th>Ferrites</th>
<th>Glass</th>
<th>C$_2$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>46.8</td>
<td>18.9</td>
<td>22.3</td>
<td>6.5</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 3. Mean phase compositions and standard deviations determined by EPMA (mass%).

<table>
<thead>
<tr>
<th>Phase</th>
<th>No. Analyses</th>
<th>Fe</th>
<th>P</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Total*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>11</td>
<td>68.74</td>
<td>0.45</td>
<td>0.04</td>
<td>0.271</td>
<td>98.6</td>
</tr>
<tr>
<td>Magnetcite</td>
<td>7</td>
<td>68.30</td>
<td>0.75</td>
<td>0.14</td>
<td>0.228</td>
<td>99.5</td>
</tr>
<tr>
<td>Ferrites</td>
<td>14</td>
<td>52.13</td>
<td>1.32</td>
<td>5.25</td>
<td>14.289</td>
<td>94.1</td>
</tr>
<tr>
<td>Glasses</td>
<td>4</td>
<td>8.77</td>
<td>4.71</td>
<td>1.07</td>
<td>31.50</td>
<td>47.695</td>
</tr>
<tr>
<td>C$_2$S</td>
<td>12</td>
<td>2.58</td>
<td>2.757</td>
<td>3.004</td>
<td>2.926</td>
<td>2.072</td>
</tr>
</tbody>
</table>

* Fe recalculated to Fe$_2$O$_3$, P to P$_2$O$_5$. Not all elements reported; e.g. Al$_2$O$_3$, MgO, MnO, YO$_2$, ZrO$_2$, K$_2$O.
their similar optical properties. However, the distribution of these two phases is clearly identifiable in the element maps. In the Ca element map, the darkest areas have the lowest Ca and correspond to iron oxide, the grey areas have intermediate levels of Ca and are glass and ferrites, the white areas have the highest Ca levels in the map and are C2S. In the P map, P levels increase from zero in the dark areas, which correspond to the iron oxides and ferrites, through intermediate in the grey areas which are glass to a maximum in the white areas. By comparison with the Ca map, these white areas can be seen to be the C2S crystals. Thus the element maps confirm the EPMA spot analyses (Table 3) and show that the highest concentration of P was located within the C2S phases with lower levels present in the glass.

Table 4. Pre and post-leach sinter assays (mass%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pre-leach</th>
<th>Powdered</th>
<th>-5mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>57.13</td>
<td>64.49</td>
<td>62.25</td>
</tr>
<tr>
<td>P</td>
<td>0.130</td>
<td>0.011</td>
<td>0.042</td>
</tr>
<tr>
<td>SiO2</td>
<td>4.99</td>
<td>2.01</td>
<td>3.10</td>
</tr>
<tr>
<td>CaO</td>
<td>9.166</td>
<td>3.737</td>
<td>4.551</td>
</tr>
<tr>
<td>Cr2O3</td>
<td>0.034</td>
<td>0.019</td>
<td>0.021</td>
</tr>
<tr>
<td>K2O</td>
<td>0.025</td>
<td>&lt;0.005</td>
<td>0.006</td>
</tr>
<tr>
<td>Total*</td>
<td>98.6</td>
<td>100.3</td>
<td>99.2</td>
</tr>
<tr>
<td>Basicity</td>
<td>1.84</td>
<td>1.86</td>
<td>1.47</td>
</tr>
<tr>
<td>Liquor pH (after leach)</td>
<td>-</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

* Fe recalculated to Fe2O3, P to P2O5. Includes data for other elements/oxides not shown, eg. Al2O3, MgO, MnO, TiO2.

The post-etching photomicrograph differs from the pre-etch images in that the C2S that was exposed on the polished surface is absent, due to the fact that it has been successfully leached out by the weak acid, leaving only black pits (examples marked with arrows). The glass and other phases remain unaffected.

2.3.2. Bulk Sinter Leaching

A sub-sample of the testwork sinter was pulverised for one minute to be −63 μm and this powder was then leached in 1 M HCl for 18 hr. A second sub-sample of the sinter was crushed to −5 mm (a common size fraction for return fine sinter) and also leached in 1 M HCl for 18 hr. A 10 mass% pulp density was used for both of these tests. Following leaching, the liquor was separated from the solid by vacuum filtration and litmus tested for acidity. The −5 mm sample was dried and then pulverised for 1 min. Both samples were assayed and the data are presented in Table 4.

After leaching, the powdered sample residue showed a reduction of around 60% in both SiO2 and CaO and around a 13% (7% absolute) increase in Fe. Assuming that area% of phase is equivalent to volume% of phase, mass balance calculations using the data in Tables 1 to 4 indicate that leaching in 1 M HCl removed all of the C2S from the powdered sinter.\(^\ast\)\(^1\) Phosphorous in the leached sample had also been reduced by more than 90%, and this is consistent with it being primarily concentrated in the C2S. In addition, assay data show that Cr and K (expressed as Cr2O3 and K2O) were substantially reduced (38% and 76% respectively), suggesting that they too may have been concentrated in the C2S phase of the testwork sinter. The −5 mm sub-sample leached in 1 M HCl had approximately 40% of the SiO2, 50% of the CaO and 70% of the P removed and a corresponding increase in Fe of 9% (5% ab-
solute). Cr and K were also reduced by around 80% and 60% respectively. From these data (and also the data in Tables 1 to 3) it was estimated that 97% of the C$_2$S had been leached. Optical examination of fresh sinters shows that C$_2$S is often located in glass-rich regions and it is hypothesised that the <5% of C$_2$S not leached from this sample was protected from acid attack by a surrounding glass barrier. The molar ratio of Ca:Si removed during the leaching of the powdered sample was very close to 2:1 (as expected for Ca$_2$SiO$_4$) and as a result, the basicity of the sinter residue was almost maintained (Table 4). On the other hand, the ratio of Ca:Si removed from the ~5 mm sample was closer to 5:2, affecting a reduction in sinter basicity (Table 4). Although it is unclear why the ~5 mm sample should have had proportionally more Ca than Si removed, it may be that the sub-sample contained a small component of unassimilated lime flux that was not present in the powdered sub-sample. Heterogeneous distributions of unassimilated lime are relatively common in iron ore sinters and it is likely that these would be removed by acid leaching. If a depletion of Ca at greater than 2 times the depletion of Si occurred consistently in a larger scale operation, lime addition may be required after leaching to restore basicity.

### 3. Discussion

#### 3.1. Chemistry and Crystal Structure of C$_2$S in Sinter

EPMA data from the current investigation found that P levels in the C$_2$S phase of the testwork sinter were around 2.5 times higher than the levels of P in the glass, with none of the other phases containing any P (Table 2). A review of EPMA data from six other iron ore sinters (including two made from blends used at Japanese steel mills and four from blends containing magnetite concentrates) confirmed that P is commonly heavily concentrated in the C$_2$S phase in iron ore sinters—up to 6.9 times greater than its concentration in the glass. In addition, leaching results indicated that the C$_2$S in the testwork sinter was also enriched in Cr and K with respect to the bulk composition. Many researchers have investigated the substitutions of various components into C$_2$S and in the fields of iron and steel-making there has been a particular focus on P (because it is an undesirable contaminant). Some iron-making literature contains data for the partitioning of foreign components into C$_2$S at low temperatures (down to ~1300°C) but the great majority of research to date has focused on P ($\geq$36-38) because it is an undesirable contaminant. Some iron-making literature contains data for the partitioning of foreign components into C$_2$S at low temperatures (down to ~1300°C) but the great majority of research to date has focused on P ($\geq$36-38) because it is an undesirable contaminant.

The crystallographic form of C$_2$S in the testwork sinter was not directly determined and it is difficult to postulate which polymorph was present due to the complexity of C$_2$S stability, the sinter chemistry and the sintering process. Figure 2, from Chan et al. (1992) shows the phase stability for the various C$_2$S polymorphs. At sintering temperatures the $\alpha'_0$ (orthorhombic) polymorph should be stable (1177–1425°C) although it is also possible that thermal heterogeneities could result in local zones of stability for either the $\alpha$ (hexagonal; 1425–2150°C) or $\alpha'_0$ (orthorhombic; 850–1177°C) polymorphs. As noted above, the incorporation of contaminants into the C$_2$S lattice also needs to be considered as this can have the effect of stabilising the various polymorphs at temperatures different to those determined for pure C$_2$S compositions. Another complication is that the sintering process (including air cooling) is relatively fast, and so kinetic effects may also play an important role in determining which phase will crystallise.

The ‘dusting’ phenomenon may be highly significant for sinter quality parameters such as strength and reduction degradation. For example if an industrial sinter contained a considerable proportion of C$_2$S that suffered the $\beta$–$\gamma$ transition while cooling (and the associated 12% volume increase), the detrimental effect on the bulk strength and yield of the product may be significant. Conversely, a sinter with proportionally little C$_2$S may not degrade to the same extent during cooling.

Specific X-ray investigations are required in order to discover which polymorphs of C$_2$S are commonly present in sinter and whether these change with bulk chemistry or crystal composition.

#### 3.2. Solubility of C$_2$S in Sinter

The quick and complete success of the direct surface etch tests at 0.001 M HCl clearly demonstrated the high susceptibility of C$_2$S in sinters to acid attack with respect to the other phases present. When the powdered and ~5 mm sinter samples were treated with 1 M HCl, C$_2$S was again easily removed. For the ~5 mm material, calculations indicated that <5% of the C$_2$S remained after leaching and this may be because this small proportion of the mineral was inaccessible to the leachant. The result of leaching out C$_2$S on the sinter’s chemical composition was very positive. Not only were contaminants such as P, Cr and K greatly reduced, the absolute improvement in Fe grade was more than 7% for the powdered sinter and 5% for the ~5 mm material (Table 4). The rapid removal of all C$_2$S in the direct surface etch tests indicates that the kinetics of C$_2$S leaching are very quick. Therefore, it is anticipated that large reductions in CaO, SiO$_2$, P, and other contaminants such as Cr and K

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**Fig. 2.** The polymorphic transformations of C$_2$S. From Chan et al. (1992)
could be achieved at leaching times significantly less than the 18 hr used in the bulk leaching experiments.

The surface etchings were also successfully conducted in a very weak acid (0.001 M HCl) and this suggests that there is potential to optimise acid concentration below the 1 M used in the bulk leaching tests. Some preliminary bulk leaching tests were carried out at lower acid concentrations (0.001, 0.01 and 0.1 M), but these were ineffective in removing C$_2$S from the sinter. The reason for this is believed to be that the weaker acids were quickly neutralised by the initial liberation of basic compounds from the sinter. pH testing of the leach liquors after the bulk leaching tests in 1 M HCl showed that the solutions remained highly acidic and neutralisation was not an issue at this acid concentration (Table 4). Other inorganic acids such as nitric or sulfuric*2 are anticipated to be suitable leachants as are organic acids. (Successful surface etching tests were carried out in H$_2$SO$_4$, lactic acid and even warm water.) Use of the latter acids in practice would be preferential to HCl for environmental reasons.

Some of the benefits of leaching iron ore agglomerates have been recognised in the past. International Patent Application WO 93/10271 published from Minas Gerais, Brazil in 1993*3 covers cool acid leaching of iron ore sinter (and other agglomerates) to achieve reductions in P and other contaminants and improvements in Fe grade. However, the explanation of the fundamental processes is inadequate in this document and there is no mention of C$_2$S. The patent application claims that contaminants migrate to the surface of ore particles (hematite and goethite) during high temperature processing such that they became more accessible to acid attack.*5 The recognition of C$_2$S as an Fe-free contaminant sink in sinters which can be easily leached is most likely the explanation of the results presented in the patent application. Having a fundamental understanding of this mechanism, we have been able to demonstrate both Fe grade improvements and contaminant reductions well in excess of those reported in the patent application.

3.3. C$_2$S and Sinter Properties

If phase transitions in C$_2$S are found to be detrimental to sinters during cooling or preheating in the blast furnace, C$_2$S stabilisation (by the incorporation of minor components) or removal (by etching) may prove to be important techniques for improving strength and decreasing reduction degradation. It therefore may not be ideal to aim for maximum dephosphorisation of iron ores prior to sintering, as the presence of minor P may actually improve the strength of cooling sinter and dephosphorisation may be more simply achieved post-sintering.

It is interesting to note that the 'skeletal rhombohedral' form of hematite has been ascribed as the phase in which much cracking in sinter is initiated*6 and our petrographic examination of sinters has revealed that C$_2$S is often closely associated with this phase and tends to crystallise along its boundaries. Therefore, there is a possibility that C$_2$S inversion may play some contributory role in the development of defects in skeletal rhombohedral hematite.

3.4. Potential Applications of Sinter Leaching

Removing C$_2$S from sinter is a technique for 'cold working' of the slag in the iron making process and there may be several technical (as well as economic) benefits of developing applications that rely on 'cold' removal of contaminated slag phases. Two possibilities are discussed below.

3.4.1. High Grade Fe Products from Sinter

Leaching of powdered sinter in 1 M HCl resulted in a product with an Fe grade of 64.5 mass%. It is anticipated that leaching a sinter which has been engineered such that the initial proportions of Fe oxides and C$_2$S are increased at the expense of ferrites and glass, may result in a very high-grade leach product. Recent revisions of phase diagrams in the high Fe$_2$O$_3$ portion of the Fe$_2$O$_3$–CaO–SiO$_2$ system provide good data for determining the starting compositions and temperatures required to increase the proportions of such target sinter assemblages.*27,46,47 Large reductions in ferrites and glasses may result in a loss of sinter strength. However, if a DR grade product can be achieved via this route, the required properties of the product material may not be the same as for traditional sinters.

3.4.2. Return Fines Leaching

The coarse (~5 mm) material leached in the present test-work was representative of the return fines fraction of industrial sinters. Current treatment of return fines on sinter plants involves separation from the product sinter, rewetting (during granulation) and recycling back into the sintering process. Therefore, there may be potential to incorporate a return fines leaching circuit into a sintering plant with only relatively minor alterations to standard operations (Fig. 3). The benefits of leaching C$_2$S from return fines could include:

1. Reductions in bulk Ca, Si, P, Cr, K and possibly other undesirable elements proportional to the size of the returns fraction. This would create a cleaner sinter product and reduce the amount of hot processing of molten iron required after the blast furnace. A reduction in high temperature purification should result in energy savings and therefore economic benefits. The removal of any alkali metals would also limit the chemical attack of refractories.

2. Simultaneous neutralisation of waste acid from wet scrubbers if this liquor could be successfully utilised as the leachant. Potential also exists to recycle neutralised (or Ca enriched) water to the granulator.

3. Improvements in Fe grade if the reductions in Ca and Si achieved in the leaching process can be translated to the raw blast furnace feed. This may require adjusting the bulk CaO and SiO$_2$ of sinters made with leached return fines. However, early removal of contaminants will reduce the slag volume required in the blast furnace to trap impurities and so proportionally lower slag volumes may be achievable. A more thorough understanding of the contribution of C$_2$S in the return fines fraction to bonding during resintering is required in order to pursue this further.

4. Removal of contaminants that originate from a variety of sources and are concentrated in C$_2$S in sinter. Sources of contaminants in the sinter plant may include

*2 Bulk leaching in H$_2$SO$_4$ may be complicated by the precipitation of calcium sulfates from the liquor.
4. Conclusions

Historically, iron oxides and ferrites have been the focus of mineralogical and microtextural studies of iron ore sinters. Literature from other disciplines as well as the preliminary leaching experiments reported here indicate that the C\textsubscript{2}S polymorphs may be of equal importance in determining the properties of sinter and further research into these phases may provide new avenues for development of techniques to improve current sintering practices. Analyses of a testwork sinter showed that all of the P in the sinter reported to the C\textsubscript{2}S and glass phases—C\textsubscript{2}S with a considerably heavier concentration. The leaching experiments demonstrated that C\textsubscript{2}S can be removed from polished sinter surfaces as well as bulk powdered and -5 mm sinter samples with HCl solutions. As P was concentrated in the C\textsubscript{2}S, it too was removed from the sinter. In addition, leaching reduced bulk Cr and K and it is inferred that these elements were also preferentially substituted into the C\textsubscript{2}S lattice.

Processes for producing DR grade material from iron ore sinter and leaching of return fines at sintering plants may be future practical applications of the present results.

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