Kinetics of chromite vs. ilmenite magnetization during oxidative roasting of ilmenite concentrates

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Synopsis

In a paper presented at the Heavy Minerals Conference 2001 a laboratory scale investigation on the beneficiation of an ilmenite containing waste stream by magnetizing roasting was reported. This waste stream contained a high concentration of ilmenite, which was contaminated by chromite and other gangue minerals. Interpretation of the results of the investigation was based on the assumption that during magnetizing roasting of an ilmenite concentrate, under the oxidizing conditions, the magnetic properties of the chromite would remain constant. In this article the following hypothesis was tested: The magnetic susceptibility of chromite would remain constant during magnetizing roasting of an ilmenite concentrate under the oxidizing conditions reported by Gouws and Van Dyk. The results of this study indicated that the hypothesis is not true. The increase in the magnetic susceptibility is not significant though and it is expected that it will not influence the final ilmenite quality to a large extent. Based on the assumptions that the bulk magnetic susceptibility of the waste stream samples represents that of the ilmenite in the waste stream, and the bulk magnetic susceptibility of UG1 chromite that of the chromite in the waste stream, the results also served to confirm that the waste stream with a high chromite content should be roasted under oxidizing conditions, in a reactor with a well-defined retention time distribution (i.e. a fluidized bed reactor), at a roasting temperature of 750°C (rather than the higher temperature ranges of 800°C and 850°C).

Introduction

The largest application of titanium dioxide is as white pigment, representing between 95% and 98% of the worldwide TiO₂ consumption. TiO₂ pigments are used in surface coatings, plastics and paper. There are two commercial processes for the production of TiO₂ pigment: the sulphate process and the chloride process. In the sulphate process TiO₂ feedstock is dissolved in concentrated sulphuric acid. TiO₂ pigment is recovered by selective hydrolysis of the solubilized titanium. In the chloride process feedstock is fluidized in a chlorine gas stream at elevated temperature to produce metal chloride vapour. Titanium tetrachloride is separated from the other metal chlorides by distillation and oxidized to titanium dioxide. Feedstock for the chloride process includes natural rutile, synthetic rutile, slag, leucoxene and primary ilmenite. Feedstock for the sulphate process is slag and primary and secondary ilmenite.

According to Hammerbeck ilmenite concentrates from heavy mineral sands in KwaZulu-Natal has 49.0–49.7% TiO₂ and 0.19–0.38% Cr₂O₃. This ilmenite is mostly upgraded to 85% TiO₂-slag (by smelting), but some of the ilmenite is also used as sulphate feedstock. Feedstock for the chloride process includes natural rutile, synthetic rutile, slag, leucoxene and primary ilmenite. Feedstock for the sulphate process is slag and primary and secondary ilmenite.

Background

In a typical South African East Coast heavy minerals operation the ilmenite concentrate is produced during the primary beneficiation stage, which entails mining of the beach sand deposit and production of a heavy minerals concentrate by gravity separation methods and low intensity magnetic separation. An ilmenite concentrate is produced from the heavy minerals concentrate by wet high intensity magnetic separation. Nell and Den Hoed found that the bulk of the chromium in the ilmenite concentrate is present in spinel of kinetic of chromite vs. ilmenite magnetization during oxidative roasting of ilmenite concentrates

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variable composition. They also found that the magnetic susceptibility of the chromium-rich spinel is similar to that of ilmenite. Bergeron and Prest\(^8\) and Nell and Den Hoed\(^6\) observed that roasting under mildly oxidizing conditions increased the magnetic susceptibility of ilmenite significantly but did not change that of chromium-rich spinel. The following statements are quoted from both publications:

"...roasting does not increase the magnetic susceptibility of the other minerals present in the concentrate and specifically that of chromium-bearing spinel..." - Nell and Den Hoed\(^6\).

"...At the same time the chromite phase, the major \(\text{Cr}_2\text{O}_3\) contaminant in the ore, remains relatively unchanged..." - Bergeron and Prest\(^8\)

Nell and Den Hoed\(^6\) stated that the difference in magnetic susceptibility properties could be used to decrease the \(\text{Cr}_2\text{O}_3\) levels of the ilmenite concentrate during secondary beneficiation. Figure 1 and Figure 2 are redrawn from the separability curves reported by Nell and Den Hoed\(^6\).

Beukes and Van Niekerk\(^7\) compared three secondary beneficiation processes, which produce ilmenite with low...
Cr$_2$O$_3$ levels from an ilmenite concentrate. Their third option consisted of two magnetic separation steps at different magnetic field strengths—2 350 Gauss and 6 500 Gauss—with subsequent roasting and magnetic separation of the reject stream with the lowest magnetic susceptibility. They did not recommend any process conditions for roasting. The aim of the investigation reported by Gouws and Van Dyk$^1$ was to determine what the ideal roasting conditions for this low susceptible reject stream would be and to compare the results to ilmenite roasting conditions published in literature. Interpretation of their results was based on the assumption that during magnetizing roasting of an ilmenite concentrate, under oxidizing conditions, the magnetic properties of the chromite would remain constant. Figure 3 and Figure 4 are redrawn from the separability curves reported by Gouws and Van Dyk$^1$.

From the separability curves of the roasted ilmenite concentrate (Figure 2) and the roasted waste stream (Figure 4) the chromite distribution is bimodal with a small concentration of chromite particles to the high susceptible side of the curves. This chromite reports with the ilmenite product (upon magnetic separation) resulting in an acceptably high Cr$_2$O$_3$ content of the final product. There was therefore no reason to further investigate the bimodality of these curves. Gouws and Van Dyk$^1$ assumed that the bimodality in the Cr$_2$O$_3$ curve was due to analytical error.

Figure 3—TiO$_2$ and Cr$_2$O$_3$ distribution of unroasted crude ilmenite; redrawn from the results of Gouws and Van Dyk$^1$.

Figure 4—TiO$_2$ and Cr$_2$O$_3$ distribution of crude ilmenite roasted at 750°C for 20 minutes in air; redrawn from the results of Gouws and Van Dyk$^1$.
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because of their interpretation of the statements made by other authors that roasting under mildly oxidizing conditions does not change the magnetic susceptibility of the chromite. A comment made by another delegate at the 2001 Heavy Minerals Conference on the bimodality of the chromite separability curve led to the decision to test the hypothesis in the work presented here:

“The magnetic susceptibility of chromite would remain constant during magnetizing roasting of an ilmenite concentrate under the oxidizing conditions reported by Gouws and Van Dyk.”

Dana and Dana and Deer et al. define the naturally occurring chromite spinel series as variations on the pure spinels magnesiocrinite (MgCr₂O₄) and chromite (FeCr₂O₄). Deer et al. stated that all natural magnesiocrinites contain a considerable amount of Fe²+ (which replaces Mg²+) and Al³+ or Fe³+ (replacing Cr³+). In natural chromites a considerable amount of Mg²⁺ replaces Fe³⁺ with generally appreciable replacement of Cr³⁺ by Al³⁺, but less so by Fe³⁺. De Waal and Copelowitz quoted Rait stating that in the system MgAl₂O₄-MgCr₂O₄-MgFe₂O₄ the straight line connecting the point, 30 mole per cent MgFe₂O₄-70 mole per cent MgAl₂O₄, with the point, 10 mole per cent MgFe₂O₄-90 mole per cent MgCr₂O₄, serves as the room temperature magnetic boundary. Therefore, chrome spinels richer in MgFe₂O₄ than this boundary or rich in Fe₃O₄ are magnetic at room temperature.

Experimental procedure

To test the hypothesis that the magnetic susceptibility of chromite remains constant during magnetizing roasting of an ilmenite concentrate under the oxidizing conditions reported by Gouws and Van Dyk, the following approach was followed:

➤ The results from the study by Gouws and Van Dyk on the waste stream was considered representative of the behaviour of unroasted and roasted ilmenite in the waste stream
➤ The test programme (roasting) was repeated on a natural chromite which is similar to the chromite in the waste stream
➤ The results of the unroasted and roasted chromite and the unroasted and roasted ilmenite were then compared to test the hypothesis.

The flow of the experimental steps is indicated in Figure 5 and the details are discussed below.

To source a natural chromite that is representative of the chromite in the waste stream, the chemical composition of the chromite in the waste stream had to be characterized first. This was conducted by energy dispersive X-ray analyses (EDX) and wavelength dispersive spectrometry (WDS). For the EDX analysis a JEOL Low Vacuum 58100 Scanning Electron Microscope was utilized. For the WDS analysis a JEOL super probe 733 was utilized. A natural chromite sample was sourced in rock from the UG1 layer in the western limb of the Bushveld Igneous Complex, South Africa. The gross sample was prepared from this rock by crushing it (by, in sequence, a jaw crusher, a gyratory crusher, and a laboratory rod mill) to a top size of 850 µm, screening with a laboratory sieve at 106 µm, and finally by performing magnetic separation with a Readings magnetic separator (set to reject the non-chromite gangue). The magnetic fraction was used as the gross sample for this study.

The gross sample was characterized by determining its chemical composition, magnetic susceptibility and size distribution. The chemical composition was determined with WDS analysis utilizing an ARL SEMQ microprobe. The magnetic susceptibility was determined with a Barrington MS2 magnetic susceptibility meter. The size distribution was determined with a Malvern size analyzer. Secondary samples of the chromite were prepared by milling with a Bond ball mill, determining the size distribution with a Malvern size analyzer, and splitting with a rotary splitter. The secondary chromite samples had a d₅₀ of 90 µm. The individual secondary samples were roasted in batches at the different roasting conditions, stated in Table I, utilizing a custom-made fluidized bed roaster. The roasted samples were characterized by determining their magnetic susceptibility with a Barrington MS2 magnetic susceptibility meter.

Results and discussion

Characterization of the chromite before roasting

Both the EDX results in Table II and the WDS results in
Table III confirmed that the chromite in the waste stream was of the magnesiochromite spinel series. The results of the two analysis methods can be seen to be similar. In both cases, the distribution of iron between the divalent and trivalent states was estimated, based on the assumption that all the chromium is trivalent, and that the spinel is stoichiometric.

The results in Table IV indicate that the chromite in the UG1 sample was not only of the magnesiochromite spinel series, but also very close in composition to that of the chromite in the waste stream (this was indeed the reason for selecting a sample from the UG1 layer of the Bushveld Igneous Complex). The mole percentages Fe in the chromite in the waste stream and the chromite in the UG1 sample were 11.0 and 11.8% respectively. However, the match was not perfect, since the FeO: Fe₂O₃ mass ratio of the chromite in the waste stream was 2.9, whereas that of the chromite in the UG1 sample was 1.5. It was therefore expected that even though the total Fe contents in both types of chromites were similar, oxidizing roasting would have a greater effect on the magnetic susceptibility of the chromite in the waste stream than on the chromite in the UG1 sample (since trivalent iron enhances the magnetic susceptibility of chromite). Despite this limitation, this natural chromite was considered to be sufficiently close in composition to that in the waste stream to provide a test of the hypothesis that oxidizing roasting leaves the magnetic susceptibility of the chromite unchanged.

Characterization of the chromite after roasting

The effect of oxidizing roasting at different temperatures and for different time intervals on the magnetic susceptibility of the UG1 chromite samples is summarized in Table V. The results in Table V are plotted in Figure 6. The results in Figure 6 clearly illustrate that oxidizing roasting did indeed affect the (average) magnetic susceptibility of the UG1 chromite. At all the roasting conditions evaluated, the magnetic susceptibility of the roasted samples increased, by factors ranging from 1.4 to 2.6.

The effect of variation in temperature on magnetic susceptibility was not as severe for the chromite as for the ilmenite—represented in Table VI and Figure 7 by the results for the waste stream as discussed elsewhere. The different effects are shown in greater detail in Figures 8 a) to d).

As shown by Figure 8 a) and b), the ilmenite increased significantly in magnetic susceptibility after roasting at 700°C and 750°C, and significantly more so than the chromite. This is, of course, favourable for magnetic separation, where the difference in magnetic susceptibility between the ilmenite and the chromite is used to separate the two minerals. Roasting at 750°C was more favourable for magnetic separation than at 700°C, yielding differences in magnetic susceptibility (between ilmenite and chromite) of factors of three and two respectively. For these two temperatures, no significant decrease in magnetic susceptibility of the ilmenite below that of the chromite was observed for the roasting times used in this study.

As illustrated by Figures 8 c) and d), the magnetic susceptibility of the ilmenite increased strongly at first (for 5 minutes' roasting) and then decreased below that of the chromite upon further roasting. The decrease in the magnetic susceptibility of the ilmenite was due to over-roasting. Over-roasting of chromite was only observed in one case, and then it was a weak effect, namely, after 40 minutes' roasting at 850°C (see Figure 7). The large change in the magnetic susceptibility of the chromite after roasting at different temperatures and for different time intervals in air is shown in Table V.

Table I
Roasting conditions applied to UG1 chromite sample

<table>
<thead>
<tr>
<th>Time intervals (min)</th>
<th>Temperature (°C)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>0; 5; 10; 20; 30; 40</td>
<td>700; 750; 800; 850</td>
<td>Air</td>
</tr>
</tbody>
</table>

Table II
Composition of chromite in waste stream calculated from EDS analysis

<table>
<thead>
<tr>
<th>MgO</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (%)</td>
<td>9.9</td>
<td>35.9</td>
<td>6.4</td>
<td>60.8</td>
</tr>
<tr>
<td>Mass %</td>
<td>7</td>
<td>25</td>
<td>4</td>
<td>42</td>
</tr>
</tbody>
</table>

Table III
Composition of chromite in waste stream calculated from WDS analysis

<table>
<thead>
<tr>
<th>MgO</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass (%)</td>
<td>5.3</td>
<td>24.5</td>
<td>11.6</td>
<td>37.1</td>
</tr>
<tr>
<td>Mass %</td>
<td>6</td>
<td>26</td>
<td>12</td>
<td>39</td>
</tr>
</tbody>
</table>

Table IV
Composition of chromite in the UG1 chromite sample calculated from WDS analysis

<table>
<thead>
<tr>
<th>MgO</th>
<th>FeO</th>
<th>Fe₂O₃</th>
<th>Cr₂O₃</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass %</td>
<td>10.3</td>
<td>18.9</td>
<td>12.4</td>
<td>43.7</td>
</tr>
<tr>
<td>Mass %</td>
<td>10</td>
<td>19</td>
<td>12</td>
<td>43</td>
</tr>
</tbody>
</table>

Table V
Magnetic susceptibility of UG1 chromite samples before roasting and after roasting at different temperatures for different time intervals in air

<table>
<thead>
<tr>
<th>Time (Min)</th>
<th>700°C</th>
<th>750°C</th>
<th>800°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic susceptibility (x 10⁻⁶ cm³/g)</td>
<td>149</td>
<td>239</td>
<td>322</td>
<td>308</td>
</tr>
</tbody>
</table>

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Figure 6—Magnetic susceptibility of UG1 chromite samples before roasting and after roasting at different temperatures for different time intervals in air, as reported by Gouws and Van Dyk.

Table VI

<table>
<thead>
<tr>
<th>Time (Min)</th>
<th>700°C</th>
<th>750°C</th>
<th>800°C</th>
<th>850°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic susceptibility ($\times 10^{-6}$ cm$^3$/g)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>113</td>
<td>113</td>
<td>113</td>
<td>113</td>
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<tr>
<td>5</td>
<td>310</td>
<td>282</td>
<td>1081</td>
<td>1110</td>
</tr>
<tr>
<td>10</td>
<td>394</td>
<td>781</td>
<td>1018</td>
<td>440</td>
</tr>
<tr>
<td>20</td>
<td>415</td>
<td>794</td>
<td>493</td>
<td>215</td>
</tr>
<tr>
<td>30</td>
<td>602</td>
<td>713</td>
<td>302</td>
<td>139</td>
</tr>
<tr>
<td>40</td>
<td>454</td>
<td>820</td>
<td>215</td>
<td>99</td>
</tr>
</tbody>
</table>

Figure 7—Magnetic susceptibility of waste stream ilmenite samples before roasting and after roasting at different temperatures for different time intervals in air, redrawn from the results of Gouws and Van Dyk.

Conclusions

The results of this study clearly indicate that the hypothesis that the magnetic susceptibility of chromite remains constant during magnetizing roasting of an ilmenite concentrate under the oxidizing conditions as used before, is not true. The increase in the magnetic susceptibility is not significant though, and it is expected that it will not influence the final ilmenite quality to a large extent.

Based on the assumptions that the bulk magnetic susceptibility of the waste stream samples represents that of the ilmenite in the waste stream, and the bulk magnetic susceptibility of UG1 chromite that of the chromite in the waste stream, the results also served to confirm that following observations regarding the conditions required for maximal separation between ilmenite and chromite:

- The waste stream with a high chromite content should be roasted under oxidizing conditions, in a reactor with a well-defined retention time distribution (i.e. a fluidized bed reactor), and applied a roasting temperature of 750°C (rather than the higher temperature ranges of 800°C and 850°C).

Acknowledgements

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References


Figure 8—Magnetic susceptibility of waste stream (predominantly ilmenite, after Gouws and Van Dyk1) and UG1 chromite samples (this work) after roasting for different time intervals in air, at different temperatures: a) 700°C, b) 750°C, c) 800°C and d) 850°C