



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

by J.D. Steenkamp* and P.C. Pistorius*

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 reported¹. 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 Dyk¹. 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 consumption². TiO₂ pigments are used in surface coatings, plastics and paper³. 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

(JD Gouws and JD Steenkamp is the same person)

distillation and oxidized to titanium dioxide⁴. 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 ilmenite².

According to Hammerbeck⁵ 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 feedstock². The Cr₂O₃ levels are unacceptable for ilmenite slag production, which requires ilmenite with a Cr₂O₃ content of less than 0.1% to produce slag with Cr₂O₃ contents acceptable to the sulphate pigment production process⁶. In the sulphate process the Cr₂O₃ that reports in the slag during ilmenite smelting can degrade the optical properties of TiO₂ pigment product, or end up in the waste acid stream. Its presence in the waste acid stream makes it difficult to dispose of or recycle into a useful product². Secondary beneficiation of the ilmenite concentrate is therefore required^{6,7}.

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 separation⁷. Nell and Den Hoed⁶ found that the bulk of the chromium in the ilmenite concentrate is present in spinel of

* Department of Materials Science and Metallurgical Engineering, University of Pretoria.

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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 Prest⁸ and Nell and Den Hoed⁶ 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 Hoed⁶.

and

'...At the same time the chromite phase, the major Cr₂O₃ contaminant in the ore, remains relatively unchanged...' - Bergeron and Prest⁸

Nell and Den Hoed⁶ stated that the difference in magnetic susceptibility properties could be used to decrease the Cr₂O₃ levels of the ilmenite concentrate during secondary beneficiation. Figure 1 and Figure 2 are redrawn from the separability curves reported by Nell and Den Hoed⁶.

Beukes and Van Niekerk⁷ compared three secondary beneficiation processes, which produce ilmenite with low

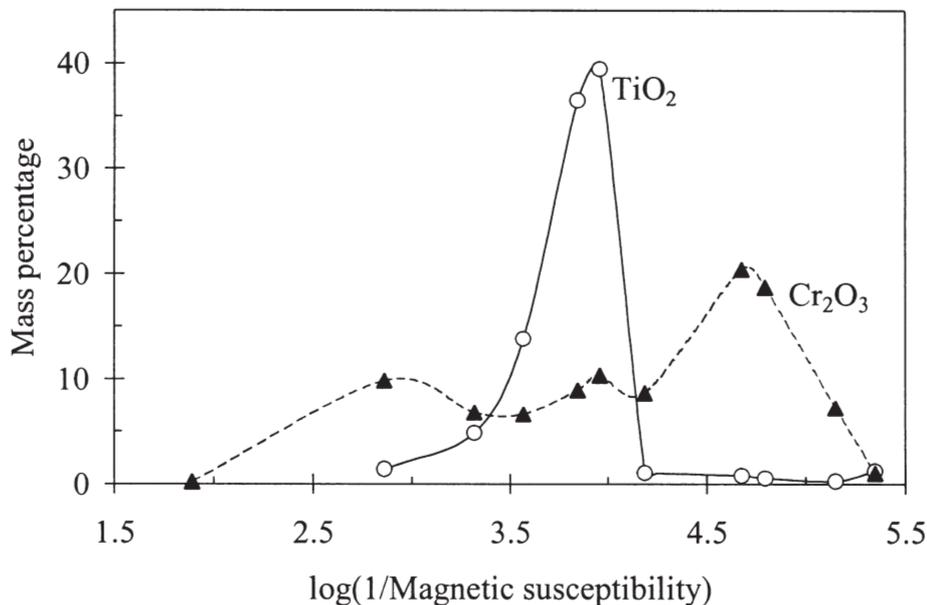


Figure 1—TiO₂ and Cr₂O₃ distribution of unroasted ilmenite concentrate. Redrawn from the results of Nell and Den Hoed⁶

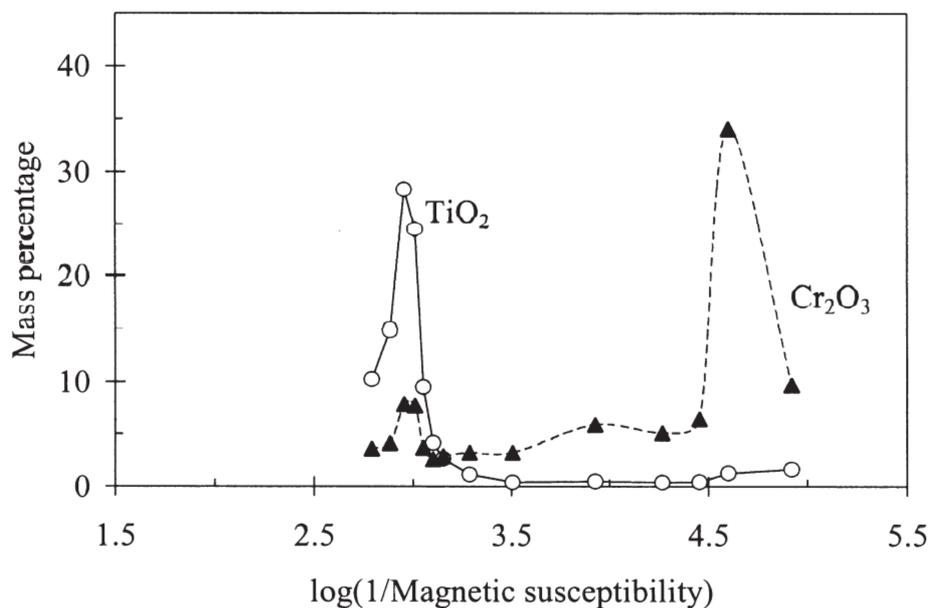


Figure 2—TiO₂ and Cr₂O₃ distribution of ilmenite concentrate roasted at 750°C in a mixture of air and CO₂ reported by Nell and Den Hoed⁶. The retention time of the sample in the roasting atmosphere was not reported

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Cr_2O_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 Dyk¹ 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 Dyk¹.

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_2O_3 content of the final product. There was therefore no reason to further investigate the bimodality of these curves. Gouws and Van Dyk¹ assumed that the bimodality in the Cr_2O_3 curve was due to analytical error

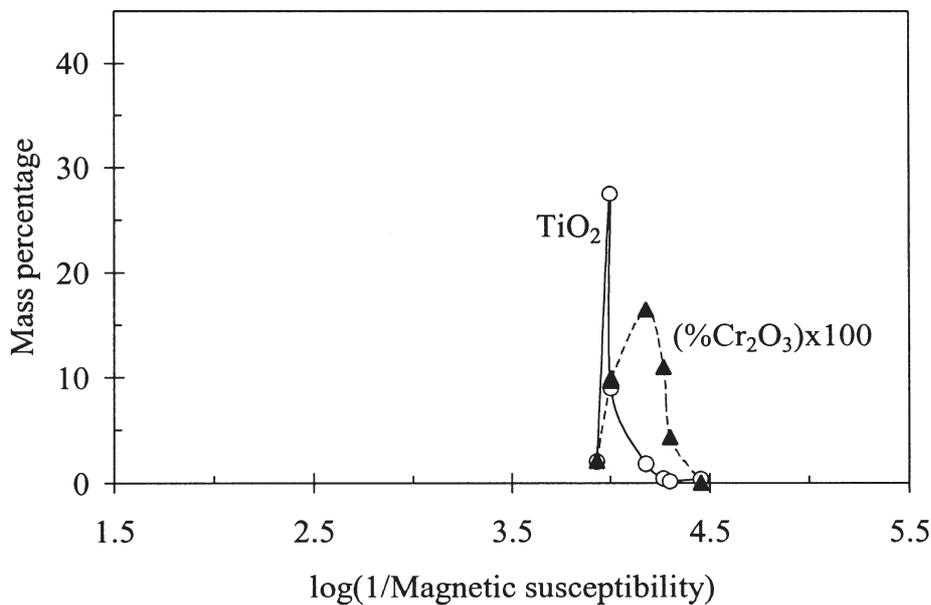


Figure 3— TiO_2 and Cr_2O_3 distribution of unroasted crude ilmenite; redrawn from the results of Gouws and Van Dyk¹

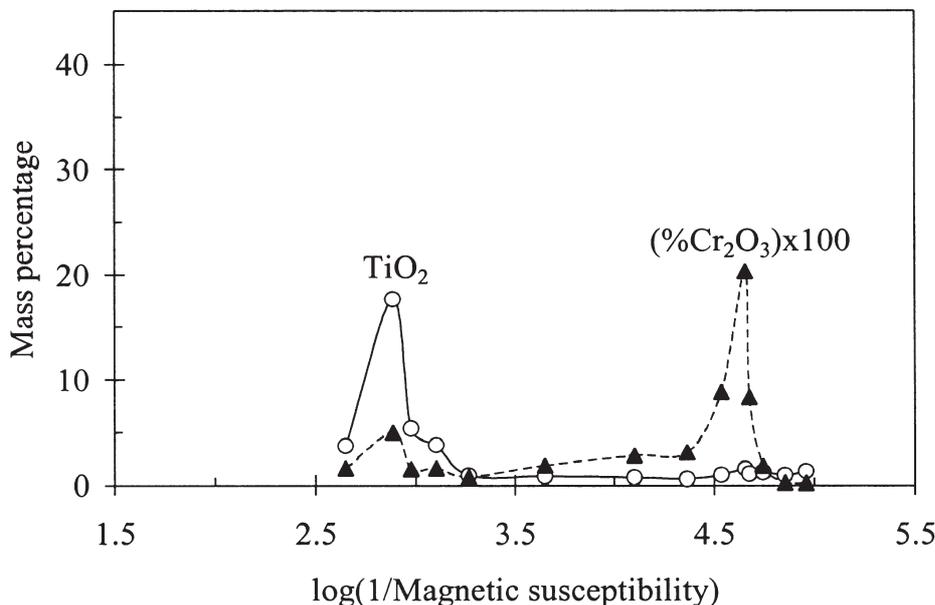


Figure 4— TiO_2 and Cr_2O_3 distribution of crude ilmenite roasted at 750°C for 20 minutes in air; redrawn from the results of Gouws and Van Dyk¹

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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^{6,8}. 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 Dyk¹.'

Dana and Dana⁹ and Deer *et al.*¹⁰ define the naturally occurring chromite spinel series as variations on the pure spinels magnesiochromite (MgCr_2O_4) and chromite (FeCr_2O_4). Deer *et al.*¹⁰ stated that all natural magnesiochromites contain a considerable amount of Fe^{2+} (which replaces Mg^{2+}) and Al^{3+} or Fe^{3+} (replacing Cr^{3+}). In natural chromites a considerable amount of Mg^{2+} replaces Fe^{2+} with generally appreciable replacement of Cr^{3+} by Al^{3+} , but less so by Fe^{3+} . De Waal and Copelowitz¹¹ quoted Rait stating that in the system MgAl_2O_4 - MgCr_2O_4 - MgFe_2O_4 the straight line connecting the point, 30 mole per cent MgFe_2O_4 -70 mole per cent MgAl_2O_4 , with the point, 10 mole per cent MgFe_2O_4 -90 mole per cent MgCr_2O_4 , serves as the room temperature magnetic boundary. Therefore, chrome spinels richer in MgFe_2O_4 than this boundary or rich in Fe_3O_4 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 Dyk¹ 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 58 100 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 d_{50} 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

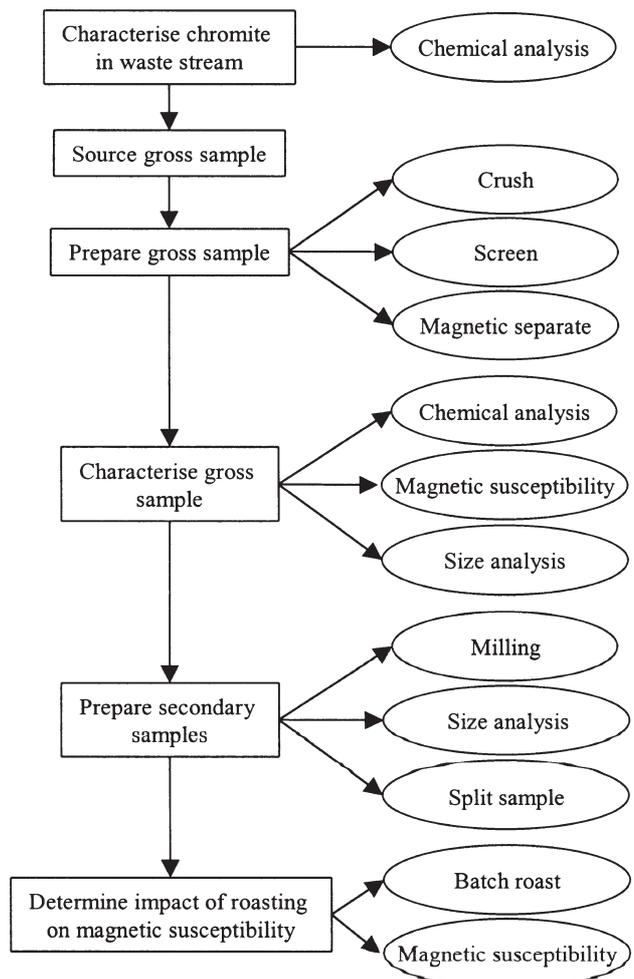


Figure 5—Flow chart of experimental plan followed in this study

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Table I

Roasting conditions applied to UG1 chromite sample

Time intervals (min)	0; 5; 10; 20; 30; 40
Temperature (°C)	700; 750; 800; 850
Atmosphere	Air

Table II

Composition of chromite in waste stream calculated from EDS analysis

	MgO	FeO	Fe ₂ O ₃	Cr ₂ O ₃	Al ₂ O ₃
Mass	9.9	35.9	6.4	60.8	31.1
Mass %	7	25	4	42	22

Table III

Composition of chromite in waste stream calculated from WDS analysis

	MgO	FeO	Fe ₂ O ₃	Cr ₂ O ₃	Al ₂ O ₃
Mass	5.3	24.5	11.6	37.1	16.1
Mass %	6	26	12	39	17

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-roasting⁶. 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

Table IV

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

	MgO	FeO	Fe ₂ O ₃	Cr ₂ O ₃	Al ₂ O ₃
Mass	10.3	18.9	12.4	43.7	15.7
Mass %	10	19	12	43	16

Table V

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

Time (Min)	700°C	750°C	800°C	850°C
	Magnetic susceptibility (x 10 ⁻⁶ cm ³ /g)			
0	149	149	149	149
5	239	231	216	205
10	322	262	262	270
20	286	321	366	315
30	308	322	387	343
40	307	326	376	296

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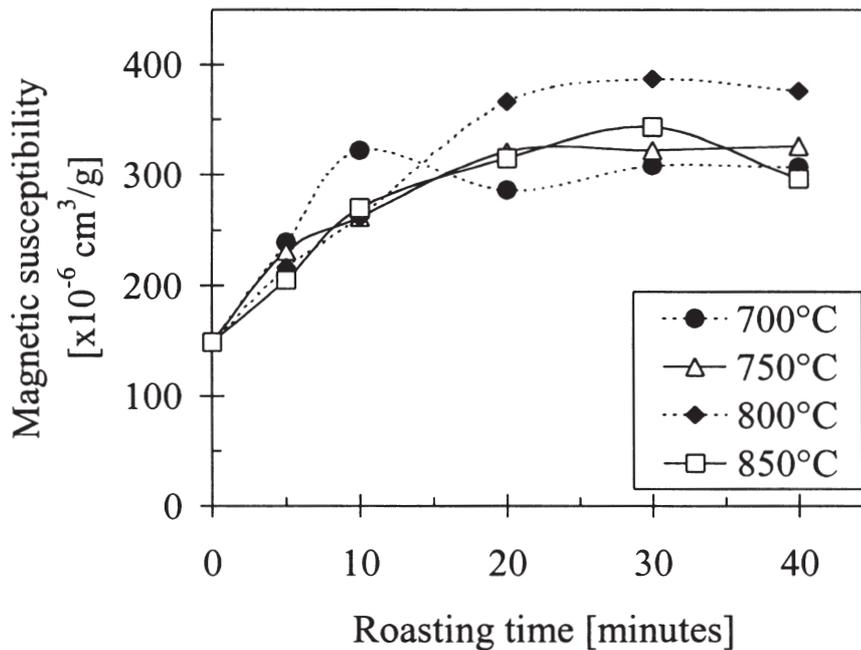


Figure 6—Magnetic susceptibility of UG1 chromite samples before roasting and after roasting at different temperatures for different time intervals in air

Table VI

Magnetic susceptibility of waste stream samples before roasting and after roasting at different temperatures for different time intervals in air, as reported by Gouws and Van Dyk¹

Time (Min)	700°C	750°C	800°C	850°C
	Magnetic susceptibility (x 10 ⁻⁶ cm ³ /g)			
0	113	113	113	113
5	310	282	1081	1110
10	394	781	1018	440
20	415	794	493	215
30	602	713	302	139
40	454	820	215	99

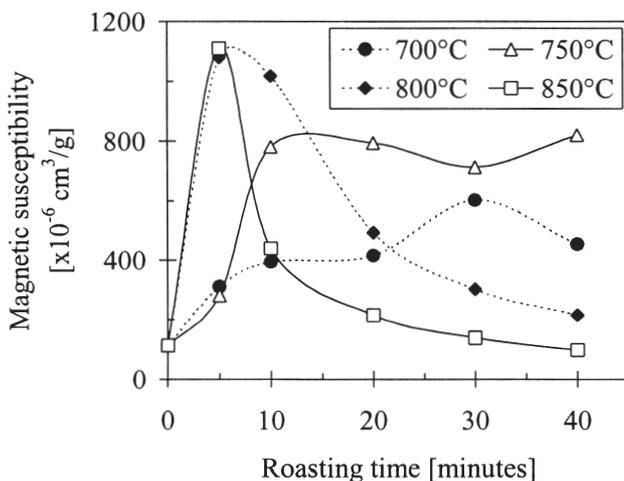


Figure 7—Magnetic susceptibility of waste stream ilmenite samples before roasting and after roasting at different temperatures for different time intervals in air, redrawn from the results of Gouws and Van Dyk¹

susceptibility of the ilmenite for roasting at one temperature for relatively small differences in retention times is an undesired effect: the control of the retention time in the roasting reactor would have to be very precise to ensure separation of ilmenite from chromite. This is unlikely to be practical in industrial-scale reactors.

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 before¹, 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 observations¹ 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).

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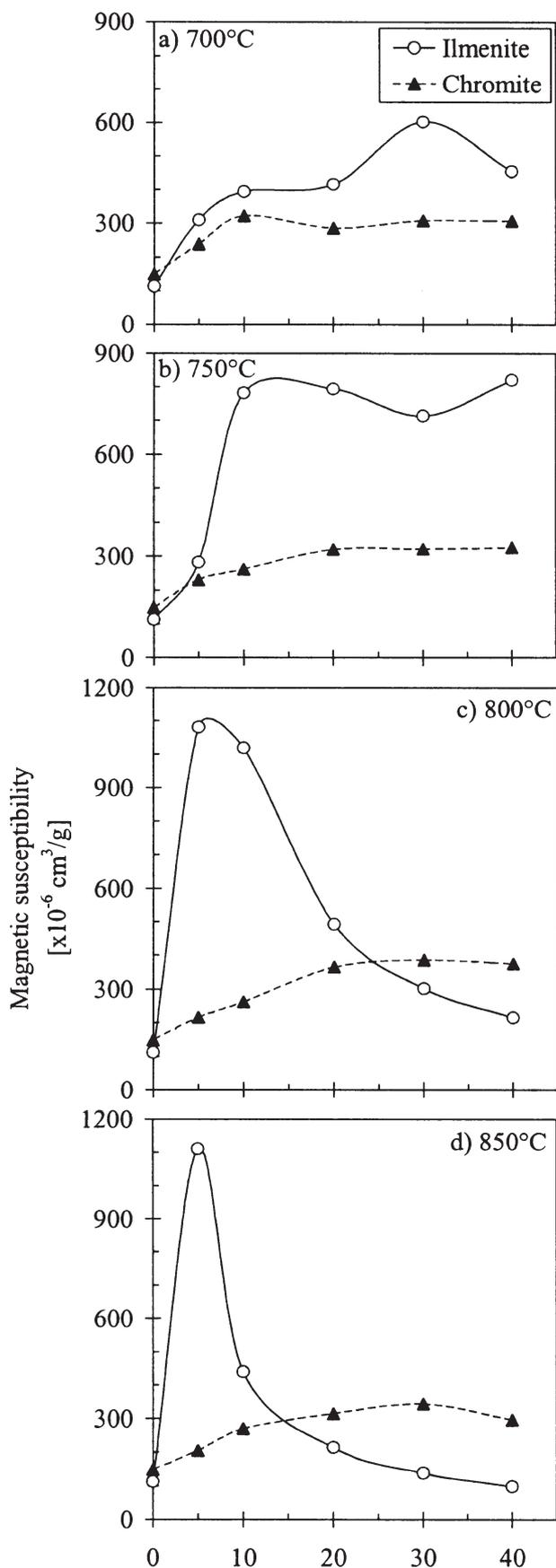


Figure 8—Magnetic susceptibility of waste stream (predominantly ilmenite, after Gouws and Van Dyk¹) and UG1 chromite samples (this work) after roasting for different time intervals in air, at different temperatures: a) 700°C, b) 750°C, c) 800°C and d) 850°C

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