



# Selective sulfidising roasting for the removal of chrome spinel impurities from weathered ilmenite ore



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## ABSTRACT

With high-grade ilmenite ( $\text{FeTiO}_3$ ) ores becoming scarce, there is a need to process lower-grade and more weathered ilmenite ores. These alternative sources provide complexities in terms of physical characteristics, mineral compositions, and impurity levels, all of which can significantly affect the subsequent processing route. In the production of high purity white pigment from ilmenite, chromia ( $\text{Cr}_2\text{O}_3$ )-containing impurities such as chrome-rich spinels need to be removed from the ilmenite concentrates down to commercially accepted levels. Existing magnetising roast processes currently used in the industry do not allow a clean separation of the chrome-rich spinels from the ilmenite due to overlapping physical properties. It has been suggested that selective sulfidation of chrome-rich spinels could be a potential route for chromia separation from ilmenite. However, the detailed conditions under which the selective sulfidation can occur are not well known. This work focuses on a systematic study of selective sulfidation of chromite  $\text{FeCr}_2\text{O}_4$  (one end member of the spinel series) for the purpose of chromia impurity removal from a weathered ilmenite concentrate. Detailed thermodynamic assessment and experimental studies have been carried out to determine the conditions at which selective chrome spinel sulfidation occurs. The results suggest that there are two regimes (Area-1 and Area-2) where selective chrome spinel sulfidation is possible. Area-1 is in the range of  $p\text{O}_2 \approx 2.37 \times 10^{-09}$  atm to  $5.01 \times 10^{-15}$  atm, while Area-2 is at lower  $p\text{O}_2$  ( $\leq 6.92 \times 10^{-19}$  atm) and  $p\text{S}_2$  ( $\leq 1 \times 10^{-06}$  atm) region relative to Area-1. Targeted experimental analyses of the two regimes revealed that selective sulfidation of chrome spinel occur only under the reaction conditions at Area-2. It is suggested that the lack of selective chrome spinel sulfidation under Area-1 conditions is the change in activity of iron ( $a_{\text{Fe}}$ ) due to weathering action on chrome spinel grain.

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## 1. Introduction

Ilmenite is used for titania ( $\text{TiO}_2$ ) pigment production through either the sulphate or chloride route processes (Ranganathan et al., 2012). The chromium (Cr) level in the ilmenite concentrates used for the pigment feedstock must be low (i.e. less than 0.1% Cr) since even a minor amount of Cr impurities can impart colour to the white titania pigment and result in a downgrade of its market value (Harben, 2002; Fisher-White et al., 2007). The main forms of chromium impurities in ilmenite concentrates are  $\text{Cr}_2\text{O}_3$ - (chromia) bearing spinel minerals namely chrome-rich spinels, such as chromite ( $\text{FeCr}_2\text{O}_4$ ) and magnesiochromite ( $\text{MgCr}_2\text{O}_4$ ). In existing industrial practises, chrome spinel impurities are separated from ilmenite concentrates through a magnetising roasting process. In this process, the magnetic susceptibility of ilmenite increased typically from  $4.36 \times 10^{-4}$  to  $1 \times 10^{-2} \text{ cm}^3 \cdot \text{g}^{-1}$  while chrome spinel remain essentially unaffected with susceptibility around  $\approx 5 \times 10^{-5} \text{ cm}^3 \cdot \text{g}^{-1}$  (Nell and Hoed, 1997). This makes an easy subsequent separation by magnetic separation. However, in the case of weathered ilmenite concentrates, the chemical composition of the ilmenite and chrome spinel varies significantly due to prolonged weathering, which is caused by leaching, oxidation and hydration processes. This results in the magnetic susceptibilities of both the ilmenites and chrome spinels being very broad and therefore more difficult to separate via a magnetising roast treatment. In such instances, the chrome-contaminated ilmenite is either unmined, stockpiled as an unsaleable by-product or sold for low value applications such as abrasive materials, welding flux, and sand blasting medium (Grey et al., 1990).

There has been ongoing research to develop efficient and economic techniques for the removal of chromium from contaminated ilmenite feedstock without significant loss of associated  $\text{TiO}_2$  values. There are a number of studies in the literature on the processing of weathered ilmenite concentrates in order to affect a clean chrome spinel impurity separation (Grey et al., 1990; Fisher-White et al., 2007; Pownceby et al., 2011; Ahmad et al., 2014). Grey et al. (1990) patented a separation technique for chrome spinel removal from metalliferous ores (e.g. ilmenite) through a reduction process. They carried out the reduction reaction at 1000–1300 °C using char as a reducing agent. After reaction, they observed metallised-iron bearing minerals and non-metallised or partially metallised chromite grains, which needed to be separated through successive aeration-leaching and magnetic separation steps.

Recently, Fisher-White et al. (2007) carried out low temperature roasting experiments for separating chrome-rich spinels from weathered ilmenite concentrates commonly found in the Murray Basin group of ilmenite deposits in southeastern Australia. They used a roasting temperature between 575 °C to 850 °C with a reducing gas atmosphere and attained 78 to 86% recovery of ilmenite. They also demonstrated that the experimental conditions employed were sensitive to crystalline  $\text{TiO}_2$  formation, which is insoluble in sulphuric acid solution during the sulphate-route process treatment. Consistent with the wide variability in ilmenite and chrome-rich spinel compositions found throughout the basin (Pownceby, 2005; Pownceby et al., 2011) the process conditions reported in the study were not generally applicable to other deposits with different compositions.

In another study, Pownceby et al. (2011) carried out high temperature sulfidising roasting experiments on weathered ilmenite concentrates from the Murray Basin, Australia. They used a mixture of char and sulphur reacted at 1075 °C (typical of the Becher reduction roast conditions used for processing highly weathered ilmenites of Western Australia) and observed the formation of a sulphide-rich rim formation around chrome spinel grains whereas the ilmenite grains remained unsulfidised. They proposed that the addition of sulphur to chrome-contaminated ilmenite concentrates under Becher-type reduction roast conditions could be a potential route for chrome spinel separation from weathered ilmenite concentrates. They proposed that the sulfidised chrome spinel grains could be separated by physical

separation techniques such as froth flotation, electrostatic separation, and magnetic separation. The detailed mechanism and conditions for the selective sulfidation reaction were not studied and reported in their work.

In follow-up thermodynamic and experimental studies by the present authors (Ahmad et al., 2014) it was demonstrated that selective sulfidation of chromite (as a representative of chrome spinel) is not a general phenomenon. Without strict control of both the effective partial pressure of oxygen ( $p\text{O}_2$ ) and sulphur ( $p\text{S}_2$ ), the selective sulfidation of chrome-bearing spinels within the ilmenite concentrates will not be possible. The aim of the current work is to present results from further studies within the Fe–Cr–Ti–S–O system to determine the specific conditions required for selective sulfidation of chrome spinel impurities in weathered ilmenite concentrates. Systematic predominance calculations of Fe–Ti–S–O and Fe–Cr–S–O systems were carried out using a thermochemical package, followed by selective experimental works to confirm the modelling results.

## 2. Thermodynamic Modelling

FactSage 6.4 thermodynamic software was used to investigate the stability of all phases in the system Fe–Cr–Ti–S–O at 1100 °C and for different  $p\text{O}_2$  and  $p\text{S}_2$  atmospheres. This temperature was chosen as it lies in the typical operating temperature range of the Becher reduction roasting process (Becher et al., 1965). For the starting point of the thermodynamic calculations, pure chromite ( $\text{FeCr}_2\text{O}_4$ ) was taken as being a representative composition for all chrome-rich spinels. Chromite is the main Cr-bearing impurity phase found in ilmenite concentrates although it also contains some minor amount of Mg, Mn and Al, present in solid solution. Ilmenite ( $\text{FeTiO}_3$ ) was also considered to be in pure form, even though it is recognised that the ilmenite may have undergone partial oxidation, alteration and/or leaching of iron. The “Predom” module of the FactSage software was used to calculate and construct the predominance diagram of the Fe–Ti–S–O and the Fe–Cr–S–O systems, which represent the ilmenite and chromite phases, respectively. Appropriate and optimised compound and solution databases were used in the study. These were sourced from NBS (National Bureau of Standards) tables of chemical thermodynamic and NIST-JANAF thermochemical tables of standard thermodynamic compilation data. The following thermodynamic assessments were carried out:

1. Analysis of phase stability of Fe–Ti–S–O and Fe–Cr–S–O systems at 1100 °C and at different  $p\text{O}_2$  and  $p\text{S}_2$  conditions to investigate the operating window for the selective sulfidation of the chrome spinel, and,
2. an examination of the effects of changing chromite activities on the selective sulfidation conditions.

## 3. Experiments

### 3.1. Materials

For the sulfidation experiments, a natural ilmenite concentrate sourced from a coarse-grained (100–250  $\mu\text{m}$  approx.) deposit in the Murray Basin, Australia was used as a representative sample of weathered ilmenite contaminated with chrome-containing spinels. The bulk composition of the ilmenite sample as determined by XRF is shown in Table 1.

**Table 1**  
XRF analysis of as received Murray Basin ilmenite concentrate (%-wt.).

$\text{TiO}_2$	$\text{Fe}_2\text{O}_3^a$	MnO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	MgO	$\text{V}_2\text{O}_5$	$\text{Cr}_2\text{O}_3$	$\text{ZrO}_2$	Others
58.8	26.3	1.29	2.53	1.61	1.08	0.19	4.44	0.43	3.33

<sup>a</sup> Total iron (Fe) calculated as  $\text{Fe}^{3+}$ .

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