



Quantitative Determination of Phases Using Mössbauer Spectroscopy and X-ray Diffraction: A Case Study of the Fe-Ti-O System

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The relative advantages and disadvantages of x-ray powder diffraction and Mössbauer spectroscopy are considered for the investigation of mineral refinement processes involving the Fe-Ti-O system and the production of synthetic rutile. Particular emphasis is directed at issues related to the identification and eventual quantification of Ti-rich, Magnéli phases.

1. Introduction

Mineral beneficiation relies on quantitative knowledge of phases present in the process streams. This information is necessary for effective optimisation of the unit operations that constitute the flow-sheet to upgrade the mined ore. Often x-ray fluorescence is used to obtain elemental information which, by proxy and known associations, assists the metallurgists to estimate the mineral processing performance. When more accurate mineral phase information is sought, x-ray powder diffraction (XRD) is the technique that is traditionally used. However, where some or all of the phases contain iron, ⁵⁷Fe-Mössbauer spectroscopy is a particularly useful mineral phase analysis technique [1] that complements XRD. This paper will consider the relative advantages and disadvantages of XRD and Mössbauer spectroscopy for the quantitative investigation of processes involving the Fe-Ti-O system.

2. Background

A simplified representation of the sequence of processes employed for the extraction of rutile (TiO₂) from mineral sands is shown schematically in Fig. 1.

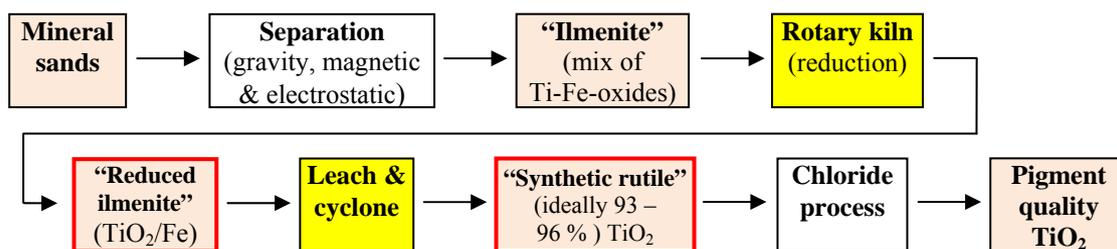
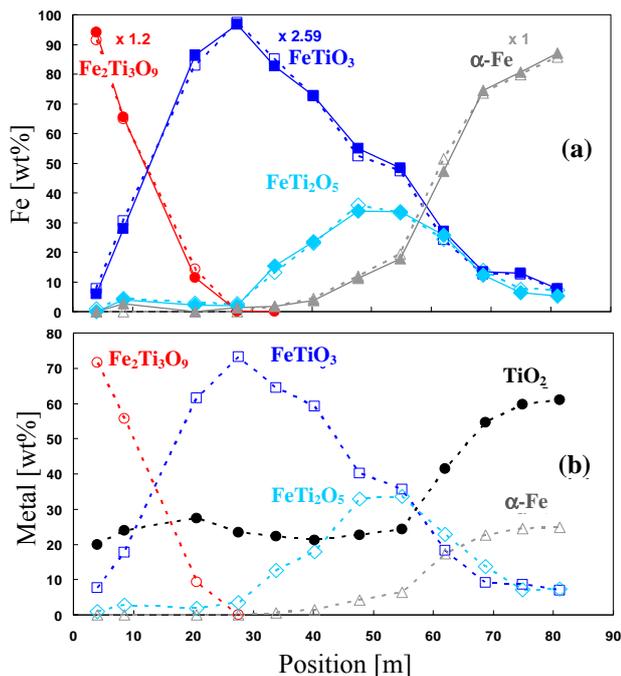


Fig. 1. Simplified representation of a typical process for production of TiO₂ from West Australian mineral sands.

In a previous study [2], samples were taken at positions along a rotary kiln and we employed XRD and Mössbauer spectroscopy to monitor the evolution of the mineral phases during the reduction stage. In that investigation, the "ilmenite" feed material was predominantly pseudorutile (Fe³⁺₂Ti₃O₉) and the "reduced ilmenite" product was predominantly rutile (TiO₂) with metallic iron. As shown in Fig. 2, the rutile production was found to proceed via the reduction of the Fe³⁺ to metallic Fe through the intermediate production of ilmenite (Fe²⁺TiO₃) and ferrous pseudobrookite (Fe²⁺Ti₂O₅). Mössbauer spectroscopy is particularly well suited for the determination of the Fe valence state via the fitted isomer shift. It



Fig. 2. Previous Mössbauer spectroscopy (broken lines) and XRD (solid lines) results from ref [2] for a reduction kiln producing predominantly pure rutile:
(a) Comparison of techniques for the iron-based phases
(b) XRD analysis of all phases, highlighting the evolution of rutile (solid circles) in the last stages of the kiln.



also provides a “clean” spectrum for pseudorutile, a phase whose XRD pattern is notoriously broadened and difficult to analyse [3]. The advantage of XRD is that it yields component patterns for all phases (including the rutile phase), regardless of whether they contain Fe. Very good quantitative agreement was achieved between the Mössbauer and the XRD-derived data, allowing for constant multipliers of the Mössbauer data for each Fe-bearing mineral phase (Fig. 2(a)). The lower graph (Fig. 2(b)) shows the full XRD data analysis, which reveals the evolution of the rutile (TiO₂) in the final stages of the kiln.

We recently revisited the ilmenite reduction process with the same rotating kiln operated under much different conditions, aimed at producing “reduced ilmenite” with an increased overall Ti content and greater throughput. These new results are considered below.

3. Results and discussion

Samples were supplied with sieved particle size $\leq 250 \mu\text{m}$ and further ground for both the ⁵⁷Fe Mössbauer and XRD (Cu K_α) measurements which were all conducted at room temperature. All Mössbauer spectra were recorded with the same absorber thickness of 31-33 mg/cm² of specimen material. In this new work, the phase analyses were confined to “reduced ilmenite” (RI) and “synthetic rutile” (SR) samples (framed in red on the simplified representation in Fig. 1).

Representative Mössbauer spectra are shown in Fig. 3(a) with their corresponding XRD patterns immediately to their right in Fig. 3(b). As expected, the dominant component of the RI Mössbauer spectra is the six-line sub-spectrum of metallic Fe. For the SR spectra the Fe is still dominant but its signal has now dropped from approximately 12% to 1.2%, indicating that the leaching process (Fig. 1) has removed about 90% of the metallic Fe. This reduction in metallic Fe content reveals a number of additional less prevalent sub-spectra associated with a range of iron-containing phases. The advantage of Mössbauer spectroscopy is that complex superpositions of sub-spectra can be analysed into a self-consistent suite of singlets, quadrupole-split doublets and magnetic-split sextets, which can then be identified from the literature. The parameters for these sub-spectra are constrained to physically realisable values. Using this approach, small quantities of magnetite, cementite, ferrous pseudobrookite and ilmenite have so far been identified and their relative quantities determined.

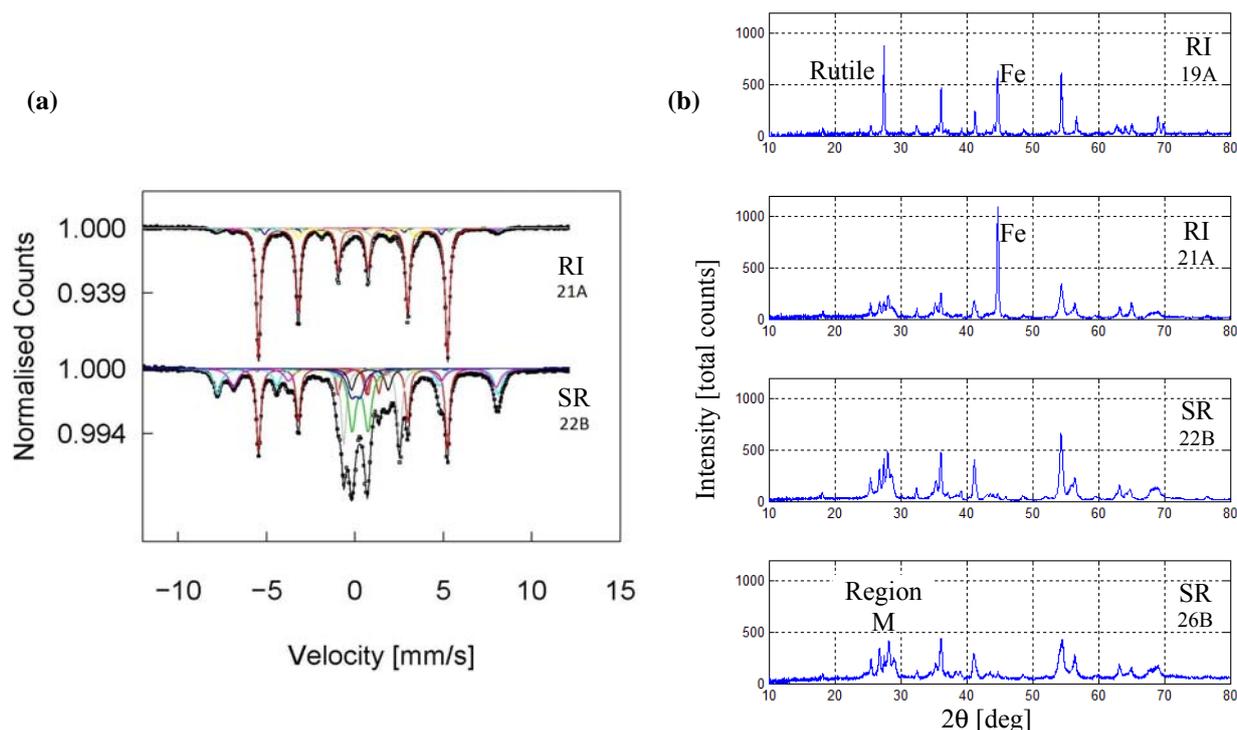


Fig. 3. Representative Mössbauer spectra (Fig. 3(a)) and x-ray diffraction patterns (Fig. 3(b)). Samples ‘B’ (synthetic rutile, SR) are derived from samples ‘A’ (reduced ilmenite, RI) after further chemical processing aimed at leaching out the metallic iron (refer to Fig. 1). The clutter that develops in “region M” is believed to be associated with Ti-rich Magnéli phases.

However, the majority phases of the RI and SR specimens are necessarily titanium based, non Fe-containing phases that are only able to be analysed using XRD. The XRD patterns shown in Fig. 3(b) are representative of the patterns recorded across all of the RI and SR samples. The removal of the Fe (in SR compared with RI) is evident as a reduction in the intensity of the Fe reflection at $2\theta \approx 45^\circ$. However, of more significance is the variation observed in the key range of $27^\circ \leq 2\theta \leq 30^\circ$ (region M) which is expanded in Fig. 4(a) on the next page and ranges from a single, well-defined rutile reflection (top pattern) through to a more complex situation in the lower three patterns where the “rutile” reflection is reduced in intensity and cluttered by additional so-called Magnéli phase reflections [4]. Because of its unexpected higher relative intensity, one of these additional reflections is almost certainly superimposed upon the ferrous pseudobrookite reflection at $2\theta \approx 25.5^\circ$.

The Magnéli phases are a suite of super-lattice derivatives of the rutile structure resulting from systematic oxygen vacancies. They have stoichiometries Ti_nO_{2n-1} where $n \geq 4$ and, in the limit of large n , the stoichiometry approaches that of rutile. The Magnéli phases form in the higher temperature reducing kiln conditions that are required to produce synthetic rutile of higher grade (i.e. higher titanium content) at commercially reasonable throughputs and were not observed for the kiln conditions prevailing in the previous study [2]. Although Magnéli diffraction lines are also present for larger 2θ , these are less intense than for the region M.

Unlike Mössbauer spectroscopy which probes the chemical environment of the Fe atom, an XRD pattern is the product of the symmetry, atomic positions and lattice spacings of the crystalline structure. The XRD sub-patterns associated with the Magnéli phase(s) cannot be fitted unless their crystal structures are known. The region M is often interpreted as the superposition of several Magnéli phase sub-patterns. However, in this case (refer to Fig. 4(a)), the additional diffraction peaks appear to be reasonably well defined. In an effort to

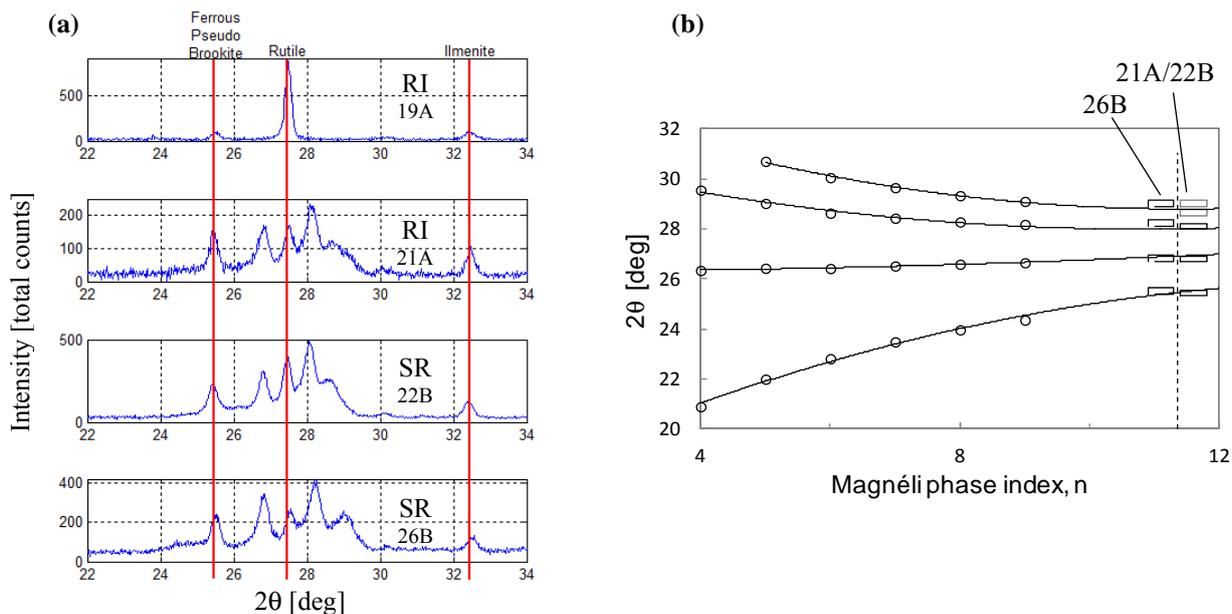


Fig. 4. (a) Expanded view of region M for the XRD patterns in Fig. 3(b), showing the ferrous pseudobrookite, rutile, and ilmenite reflections in the presence of unidentified Magnéli phase reflections. (b) Extrapolation to higher index, n, of Magnéli phase peak positions (open circles) for $n = 4 - 9$. The vertical broken line indicates that the most likely intercept with our current experimental positions (open rectangles) is for $11 \leq n \leq 12$.

identify the phase(s) present, the 2θ positions for the relevant quartet of Magnéli phase reflections with $n = 4 - 9$ were taken from the original structural refinement work of Andersson *et al.* [4] and extrapolated. As shown in Fig. 4(b), it is possible that the Magnéli reflections observed here in region M then correspond to a single Magnéli phase with $11 \leq n \leq 12$. Unfortunately, the detailed structures for the Magnéli phases with $n > 9$ appear not to have been published (at least they are not provided in the Pearson data base [5]). The next challenge is therefore to locate sources of the crystal structure for Ti_nO_{2n-1} with higher n values and conduct a quantitative phase analysis of all the XRD patterns.

4. Conclusions

The ilmenite reduction process investigated earlier [2] was found to produce a relatively simple conglomerate of rutile and metallic iron, together with lesser amounts of ilmenite and ferrous pseudobrookite. However, for the different (higher Ti grade / higher throughput) reduction conditions considered here, the rutile appears mostly to be replaced by a single titanium-based Magnéli phase, Ti_nO_{2n-1} , with $11 \leq n \leq 12$. As for the earlier investigation, ^{57}Fe -Mössbauer spectroscopy proved to be a powerful tool for the identification and determination of the relative masses of the Fe-bearing phases, leaving only the remaining titanium oxides (rutile and the Magnéli phase) to be identified using XRD.

References

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