THE PRODUCTION OF SYNTHETIC RUTILE AND BY-PRODUCT IRON OXIDE PIGMENTS FROM ILMENITE PROCESSING

A THESIS PRESENTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

by

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Abstract

A study has been carried out on the Becher and Summit Processes with the aim of understanding the mechanism and critical parameters required for the production of a range of pure iron oxide pigments, as well as high quality synthetic rutile from reduced ilmenite.

The Becher Process currently produces a large quantity of worthless mixed phase iron oxides. However, this study has shown that the range of iron oxides formed are all derived from the transformation of lepidocrocite (γ-FeOOH) through the solution phase in iron(II) solutions. The results of a kinetic study of the transformation of lepidocrocite found that the rate exhibited an induction period at low pH, was dependent on temperature and was linearly related to log $[H^{+}]$ and log $[Fe^{2+}]$. The rate determining step was found to be the formation of suitable product nuclei, following dissolution of the initial oxide at the surface of the crystal lattice.

An electrochemical study of these reactions showed that the product formed from the transformation of lepidocrocite was a function of the solution potential and an experimental Eh-pH diagram was constructed to predict the iron oxide phase produced from hydrolysis and transformation reactions. The results from this fundamental study were then applied on both a laboratory and plant scale to produce pure iron oxide phases.

A modified Summit Process, involving the removal of metallic iron from the porous reduced ilmenite matrix using $FeCl_3$, regeneration of iron(III) and the production of pure iron oxide pigments from the waste iron(II) chloride solution, was also investigated in detail.

A kinetic study of pure iron dissolution in iron(III) solutions, comparing three electrochemical techniques and a standard solution sampling method, gave consistent rate constants provided allowance was made for the reaction with the proton. The iron dissolution mechanism was found to be iron(III) diffusion controlled, while the dissolution in HCl was under mixed control. A study using both pure iron and pressed reduced ilmenite discs found that acid consumption could be minimised by the addition of citrate or by the addition of Al^{3+} or Fe^{2+}, which are believed to block the adsorption of the proton. It was found that iron(III)-citrate complexes inhibited iron(III) hydrolysis in the reduced ilmenite pores and enhanced the purity of the synthetic rutile product.

A study of the oxidation of iron(II) by atmospheric oxygen using copper(II) and activated carbon catalysts found that these catalysts were inefficient for complete iron(III) regeneration. The heating of carbon in the presence of Cu^{2+} was found to enhance the initial rate of iron(II) oxidation, however it is believed that surface oxide redox couples formed on the carbon control the iron(II)/ iron(III) ratio in solution, and prevent complete iron(II) oxidation. The production of iron oxide pigments under the controlled conditions afforded by the Summit Process, resulted in superior quality pigments than are presently attainable from the Becher Process. However, controlled ageing and crystal growth using waste lepidocrocite from the Becher Process would result in similar quality pigments being produced.

I declare that this thesis is my own account of my research and contains work which has not previously been submitted for a degree at any University.

Christopher Ward

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