

Supporting information

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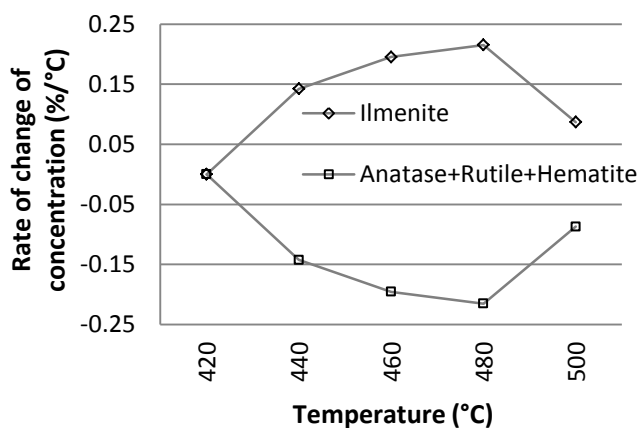


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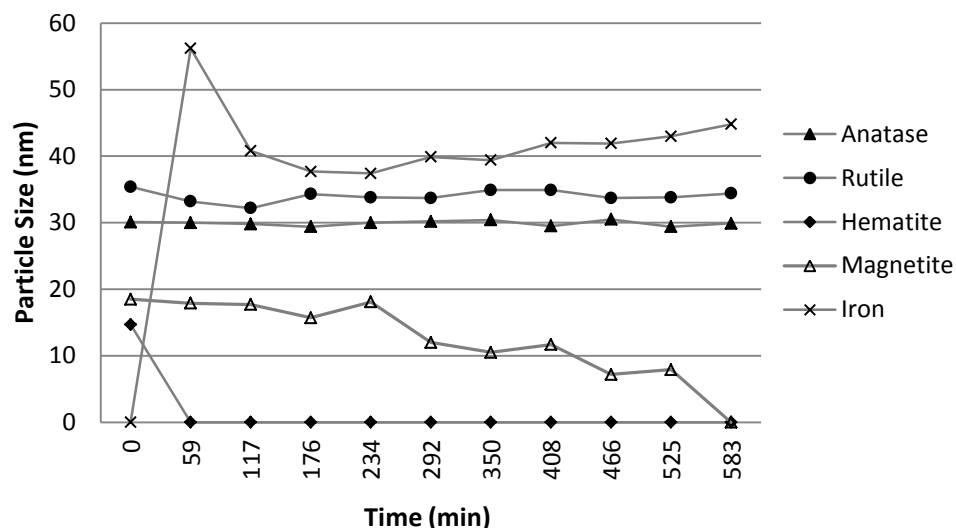


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Derivation of Equations

Although the Rietveld method was initially developed for the refinement of crystal structures and structure solution, some of the non-structural parameters used in the refinement provide non-structural information. The most important of these parameters, for this work, is the Rietveld scale factor, which relates to the amount of a particular phase in a multiphase mixture.

The integrated intensity (I) of an hkl reflection for phase α in a multiphase mixture can be calculated using:

$$I_{(hkl)\alpha} = \frac{I_0 \lambda^3}{32\pi r} \frac{e^4}{m_e^2 c^4} \cdot \frac{M_{hkl}}{2V_\alpha^2} F_{(hkl)\alpha}^2 \frac{1 + \cos^2 2\theta \cos^2 2\theta_m}{\sin^2 \theta \cos \theta} \cdot \frac{W_\alpha}{p_\alpha \mu_m^*} \dots 1$$

where I_0 is the incident beam intensity, e is the charge on an electron, m_e is the mass of an electron, r is the distance from the scattering electron and the detector, c is the speed of light, M is the multiplicity of the hkl reflection, V is the unit cell volume, F is the structure factor of the hkl reflection, θ and θ_m are the diffraction angles for the hkl reflection and monochromator respectively, W_α is the weight fraction, p_α is the density of phase α and μ_m^* is the mass absorption coefficient of the sample (Madsen & Scarlett 2009). The expression in the first square bracket in equation 1 describes the instrumental setup and can, therefore, be reduced to a constant during quantitative phase analysis (QPA). The expression in the second square bracket is a constant for reflection hkl of phase α . Equation 1 can, therefore, be rewritten as:

$$I_{i\alpha} = C_{i\alpha} \frac{W_{\alpha}}{p_{\alpha} \mu_m^*} \dots \mathbf{2}$$

where $I_{i\alpha}$ is the intensity of a reflection, or group of reflections (i), $C_{i\alpha}$ is a constant that combines both the instrumental and reflection expressions for a given reflection. Equation **2** can be rewritten using the fact that the constant C is inversely proportional to V^2 , I is proportional to the Rietveld scale factor (S) and the density of a phase can be calculated using:

$$p_{\alpha} = 1.6604 \cdot \frac{Z M_{\alpha}}{V_{\alpha}} \dots \mathbf{3}$$

where Z is the number of formula units in the unit cell, M_{α} is the molecular mass of the formula unit and 1.6604 is the conversion factor from $\text{AMU} \cdot \text{\AA}^{-3}$ to $\text{g} \cdot \text{cm}^{-3}$ (Hill 1991). The resultant formula for QPA is therefore:

$$W_{\alpha} = \frac{S_{\alpha}(ZMV)_{\alpha} \mu_m^*}{K} \dots \mathbf{4}$$

where K is a scaling factor that is used to present W_{α} on an absolute basis. It has been shown that K is dependant only on the instrumental conditions and not on phase and sample-related parameters (O'Connor & Raven 1988). K is usually determined by performing a single measurement on a standard mixture, referred to as an external standard, where the weight fraction (W) of a particular phase is known. The calculated value for K is then used to determine W_{α} as long as the unknown sample is run under exactly the same instrumental conditions as the external standard.

The need to measure K and μ_m^* can be eliminated by the addition of a known amount, W_s , of an internal standard (also referred to as a spike), s , to the unknown sample, in this case our supports and catalysts. Taking the ratio of W_{α} to W_s eliminates K and μ_m^* to give:

$$W_{\alpha} = W_s \frac{S_{\alpha}(ZMV)_{\alpha}}{S_s(ZMV)_s} \dots \mathbf{5}$$

Hill and Howard (1987) applied Chung's matrix flushing method (Chung 1974 & 1974) to Rietveld analysis and were able to show that W_{α} in a mixture made up of n phases can be given by:

$$W_{\alpha} = W_s \frac{S_{\alpha} ZMV_{\alpha}}{\sum_{k=1}^n S_k ZMV_k} \dots \mathbf{6}$$

This method normalizes the sum of the analyzed weight fractions to 1.0. If the sample contains amorphous phases and/or minor concentrations of unidentified crystalline phases, the analyzed weight fractions will be overestimated. The inclusion of an internal standard allows for the modification of the measured W_{α} 's via:

$$W_{\alpha(\text{abs})} = W_{\alpha} \times \frac{W_{s(\text{known})}}{W_{s(\text{measured})}} \dots \mathbf{7}$$

and:

$$W_{(\text{unkown})} = 1.0 - \sum_{k=1}^n W_{k(\text{abs})} \dots \mathbf{8}$$

giving absolute, rather than relative, phase percentages of all the crystalline phases present in the sample as well as an “amorphous” value for the total amount of amorphous materials and/or unidentified crystalline phases.

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