

3.9. QUANTITATIVE PHASE ANALYSIS

rearranged equation (3.9.21). For this determination, the goethite scale factor from the first few data sets, prior to the start of the reaction, was averaged to minimize any errors that may be introduced by counting statistics. The value of the sample mass absorption coefficient μ_m^* was set to an arbitrary value of unity for both the determination of K and all subsequent analyses, since the overall chemical content of the capillary, and hence the attenuation of the X-ray beam, does not change during the reaction.

This experimental work was conducted at the Australian Synchrotron where the storage-ring current was boosted every 12 h. Between these times the current, and hence the incident-beam intensity, decays, resulting in what amounts to a change in the ‘instrument configuration’. This requires a modification of the K value and subsequent calculation of concentration to compensate for the changing incident intensity using equation (3.9.22).

Fig. 3.9.7 now shows the results of QPA derived from equation (3.9.22). In this case the concentrations of the $\text{Al}(\text{OH})_3$ polymorphs are similar to those in Fig. 3.9.6. However, since the phase abundances are derived using an external standard approach, any changes in the apparent goethite concentration can now be monitored. Fig. 3.9.7 shows that the goethite concentration did not change significantly in the early stages of the experiment ($t < 10$ min) before $\text{Al}(\text{OH})_3$ crystallization was observed but there is a small, systematic decrease in the apparent goethite concentration as the experiment progresses. At the end of the experiment, the goethite concentration appears to be lower by about 1% relative to the concentration at the start.

This apparent decrease could be due to a number of causes including (i) poor correction for beam-intensity changes or (ii) solid material moving about in the capillary with some movement out of the X-ray beam. Alternatively, the decrease could be attributed to the ‘shielding’ of the goethite from the X-ray beam by the $\text{Al}(\text{OH})_3$ phases as they form and coat the goethite particles. This decrease could then be used to obtain an average thickness of the $\text{Al}(\text{OH})_3$ phases on the seed particles. This layer was calculated to be about $5.5 \mu\text{m}$ (assuming a linear absorption coefficient of 9.5 cm^{-1} for gibbsite at 0.826 \AA) resulting in an overall particle size of about $11 \mu\text{m}$ at the end of the run (the goethite particles are about $0.2 \times 2 \mu\text{m}$ and hence do not contribute significantly to the overall particle size). These values are in good agreement with independent studies (Webster *et al.*, 2010) where the gibbsite was examined using scanning electron microscopy (SEM) techniques (Fig. 3.9.8) following crystallization under similar conditions to those used here.

3.9.5. Alternative methods for determination of calibration constants

3.9.5.1. Standardless determination of the phase constant C

In order to determine the phase calibration constant C , it is common to obtain (i) a pure sample of the phase of interest that accurately reflects the form of the phase in the samples to be analysed, or (ii) a multiphase sample in which the phase concentration is known by other means (for example, chemical analysis or point counting). In some systems, there may be insufficient sample available to risk ‘contaminating’ it with an internal standard, especially if the material needs to be analysed using other techniques. The addition of an internal standard may also introduce microabsorption problems or increase the complexity of patterns that are already highly overlapped. For

other situations, the time frame demanded for the analysis may prohibit the time-consuming procedures of standard addition, data collection and separate determination of the phase calibration constant.

Zevin & Kimmel (1995) have described an approach to the derivation of phase constants which relies on having a suite of samples to be analysed that (i) have the same phases present in all samples and (ii) exhibit a wide range of composition of these phases in various samples in order to stabilize the analysis. If we reconsider the relationship between the weight fraction W_α and the observed intensity [equation (3.9.3)],

$$W_\alpha = \frac{I_\alpha \mu_m^*}{C_\alpha}, \quad (3.9.34)$$

and assume that all phases in the system are known and included in the analysis, we can introduce the additional constraint that the sum of all W_α 's is unity (or at least a known value):

$$\sum_{j=1}^n W_j = 1.0. \quad (3.9.35)$$

In a system of n samples containing m phases, we can explicitly write the relationships expressed in equations (3.9.34) and (3.9.35) as a set of simultaneous equations:

$$\begin{aligned} 1.0 &= \frac{1}{C_1} I_{11} \mu_1^* + \frac{1}{C_2} I_{12} \mu_1^* + \dots + \frac{1}{C_m} I_{1m} \mu_1^*, \\ 1.0 &= \frac{1}{C_1} I_{21} \mu_2^* + \frac{1}{C_2} I_{22} \mu_2^* + \dots + \frac{1}{C_m} I_{2m} \mu_2^*, \\ 1.0 &= \frac{1}{C_1} I_{n1} \mu_n^* + \frac{1}{C_2} I_{n2} \mu_n^* + \dots + \frac{1}{C_m} I_{nm} \mu_n^*, \end{aligned} \quad (3.9.36)$$

where μ_n^* is the mass absorption coefficient for the n th sample.

Knudsen (1981) has described a modification to this approach by including an internal standard in each of the samples to be analysed and using the ratio of intensities of the analyte and internal standard phases in place of the I_{nm} in equation (3.9.36). While this eliminates the need to determine and use the mass absorption coefficient, the tedious procedure of adding and mixing an internal standard is required for each sample and for reasons described above may not be appropriate.

The relationships embodied in equations (3.9.36) can be expressed more simply in matrix notation as

$$\mathbf{L}' = \mathbf{I}'\mathbf{C}', \quad (3.9.37)$$

where \mathbf{L}' is a column vector (dimensions $1 \times n$) containing the known (or assumed) sum of weight fractions for each sample (unity in this case), \mathbf{C}' is a column vector (dimensions $1 \times m$) containing the calibration constants for each phase and \mathbf{I}' is a rectangular matrix (dimensions n rows \times m columns) containing the measured peak intensities (or scale factors) for each phase multiplied by the sample mass absorption coefficient.

A least-squares solution of equation (3.9.37) to derive the value for C for each phase can be calculated using matrix-manipulation methods (Knudsen, 1981):

$$\mathbf{C}' = (\mathbf{I}'^T \mathbf{I}')^{-1} \mathbf{I}'^T \mathbf{L}', \quad (3.9.38)$$

where the superscripts T and -1 represent the transpose and inverse matrix functions, respectively.

Accuracy in the calculation of the individual values of C is improved by having (i) phases of the same or similar composition in all samples and (ii) a wide range of concentrations of each phase across the sample suite. These conditions may be met in,

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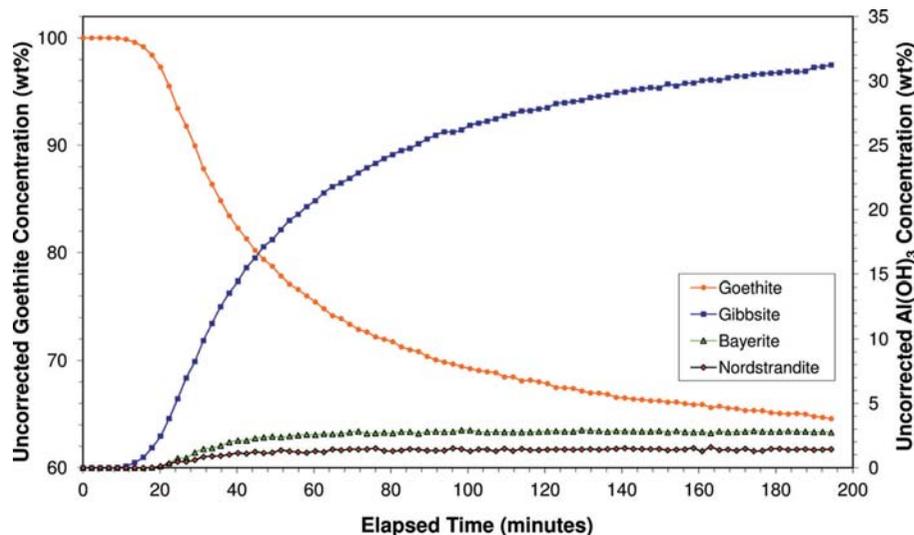


Figure 3.9.5

The results of QPA of the *in situ* XRD data collected during the seeding experiments of Webster *et al.* (2010). The values were derived using the Hill/Howard (Hill & Howard, 1987) relationship in equation (3.9.26). Note the decrease in apparent goethite concentration (left axis) as the polymorphs of $\text{Al}(\text{OH})_3$ (right axis) crystallize from solution.

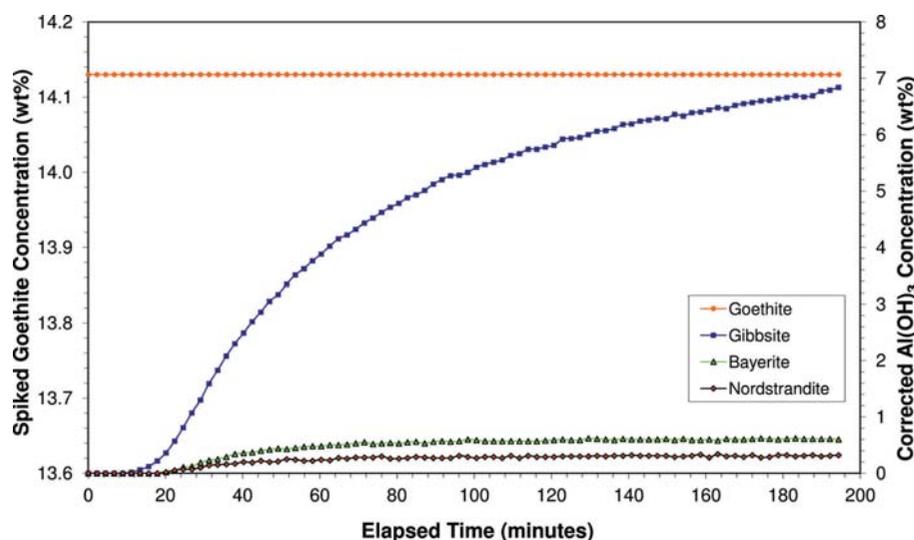


Figure 3.9.6

The results of QPA of the *in situ* XRD data collected during the seeding experiments of Webster *et al.* (2010). The values are absolute phase abundances derived using the internal standard relationship in equation (3.9.25).

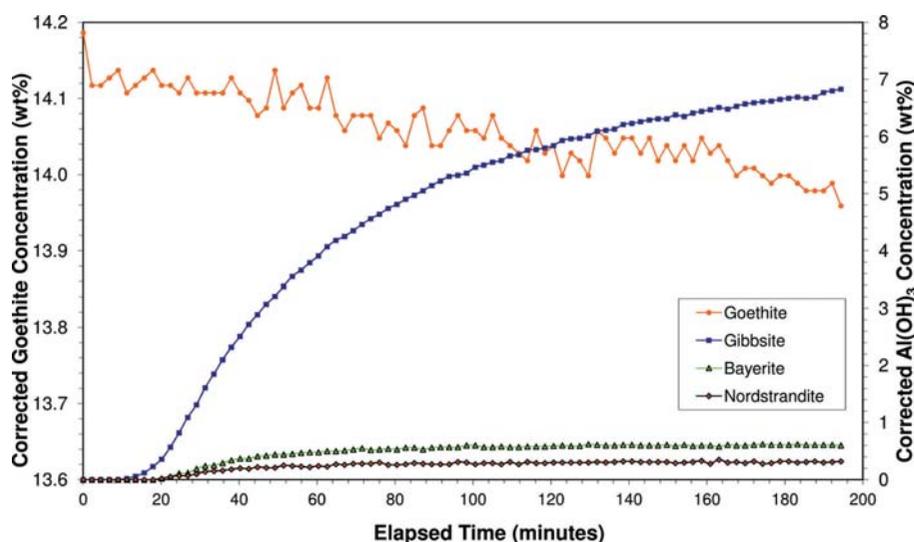


Figure 3.9.7

The results of QPA of the *in situ* XRD data collected during the seeding experiments of Webster *et al.* (2010). The values are absolute phase abundances derived using the external standard relationship in equation (3.9.22). Note the slight decrease in the goethite concentration (left axis) during the run.

for example, mineral exploration samples where a limited number of phases are present in a drill core but their abundance varies as a function of depth. In mineral processing or industrially based material manufacture, the goal is usually to control the system to minimize compositional variation in the product. The side effect of this is that the values of intensity in matrix **I** have too little variation, resulting in large errors in the derived values for **C**. In the limiting case, the system may become indeterminate with no unique solution available. To overcome this, forced or accidental changes to processing conditions may introduce sufficient compositional variation to stabilize the determination of the **C** values through equation (3.9.38). Alternatively, physical or chemical separation of selected components may be sufficient to provide the required compositional variation. Knudsen (1981) provides a detailed statistical analysis used in the determination of the errors in the phase constants.

While Zevin (Zevin & Kimmel, 1995) and Knudsen (1981) have demonstrated the application of this approach for single-peak methods, it is equally applicable if scale factors derived from whole-pattern fitting or Rietveld-based methods are used.

3.9.5.2. Demonstration of the Zevin approach

The sample 1 suite from the IUCr CPD round robin on QPA again provides an ideal platform for demonstrating the applicability of this method due to the wide variation of concentration of the constituent phases. A measure of intensity was derived using an *hkl*_phase (see Section 3.9.6) in which the peak positions were constrained to the space group and unit-cell parameters but the individual peak intensities were refined to empirical values using a pure sub-sample of each of the three phases. For the analysis of the samples, the relative peak intensities were fixed and an overall scale factor *S* for each phase in each sample (eight samples, three replicates, three phases), multiplied by the mass absorption coefficient calculated from the XRF-determined composition, was used as the measure of intensity. These $S\mu_m^*$ values then formed the intensity matrix **I** in equations (3.9.37) and (3.9.38) while all values in the vector **L** were assumed to be 1.0 (*i.e.* all samples were assumed to be fully crystalline). Microsoft Excel provides a useful platform for these calculations since it contains all of the matrix-manipulation functions required by equation (3.9.38). The determined values for **C** for the three phases are given in Table 3.9.3. The values in the C/C_{corundum} column should be compared with the values derived in Section 3.9.4.3 above.