

Modelling a semi-batch reactive precipitation of ferrihydrite

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ABSTRACT

The reactive precipitation of ferrihydrite was studied in a laboratory semi-batch precipitator, where a highly concentrated sodium hydroxide solution was fed into an iron nitrate solution. Instantaneous hydrolysis of iron[III] takes place when the two reagents are mixed generating supersaturation, and leading to immediate precipitation of ferrihydrite via a primary nucleation mechanism then followed by limited crystallite growth to 3 to 7nm. A mathematical model of the semi-batch laboratory precipitator was used to simulate the pH responses during the precipitation of ferrihydrite at different reagent feed rates. The model comprised of interconnected compartments of averaged hydrodynamic conditions, incorporating physically meaningful turbulent mixing time constants. The precipitation process is described by the solute concentration conservation equation incorporating a postulated ferrihydrite primary nucleation model. It was found that the semi-batch precipitator model predicted the experimental pH response reasonably well. The experimental results demonstrated that the reagent feed rate has a critical effect on the course of the precipitation of ferrihydrite, i.e. it is a rate determining step given the fast hydrolysis and precipitation kinetics.



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INTRODUCTION

Processes involving mixing, fast chemical reaction and precipitation of sparingly soluble materials in a turbulently stirred vessel have many industrial applications (1-3). One example is the reactive precipitation of ferrihydrite in hydrometallurgical processes for removing iron from process liquors. The hydrolysis of iron[III] is usually driven by the addition of a base to raise the pH, thereby increasing the supersaturation and followed by instantaneous precipitation of ferrihydrite.

As the reaction and precipitation times are generally short compared to mixing times, e.g. the acid-base neutralisation, the time scale is in the order of nanoseconds and the time required to mix two aqueous reagents is hardly less than 1 ms (3). Hence, mixing has a great influence on these reactive precipitation processes. In this fast reactive precipitation process, mesomixing, i.e. the coarse scale turbulent mixing between the fresh feed and the bulk solution, plays a critical role in dispersing and breaking down the unmixed reagent blobs in the precipitator prior to micromixing taking control of contacting reagents at molecular level. Micromixing directly influences the course of the chemical reaction and the distribution of supersaturation, and hence the precipitated product phase, product yield and morphology.

In this work, a compartmental semi-batch model incorporating the physically meaningful mesomixing and micromixing time scales, similar to the segregated feed model (4-6), was adopted to simulate the dynamic pH responses during the semi-batch precipitation of ferrihydrite at different reagent feed rates.

PRECIPITATION OF FERRIHYDRITE IN ACIDIC SOLUTION

The hydrous iron oxyhydroxide phase known as ferrihydrite is usually the first phase to precipitate in the hydrolysis of aqueous iron[III] solutions. Ferrihydrite is a poorly ordered nanocrystalline phase, and its structure and aggregation characteristics are to some extent dependent on the conditions of supersaturation, i.e. temperature and pH, under which it is precipitated (7). Ferrihydrite is often given the nominal formula $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$, but defining the precise stoichiometry of this phase has proved difficult, because the water content of laboratory samples is highly variable, and the formula cannot be constrained on the basis of known crystal structure. Although a number of formulae have been proposed (7,8) in most case the Fe:O ratio is close to 1:3, hence the hydrolysis of iron[III] is approximated as the precipitation of $\text{Fe}(\text{OH})_3$ as shown below, which is a simplification of a number of steps involving olation, oxolation and dehydration reactions.



The rapid ferrihydrite primary nucleation is a consequence of very high supersaturations, due to the very low equilibrium solubility of ferrihydrite. Measurement of the ferrihydrite equilibrium solubility is difficult, particularly at high temperature, as the ultrafine ferrihydrite particles pass through conventional filter papers and their metastable nature tends towards formation of less soluble and more stable phases such as goethite and hematite during extended equilibration times. The variations in ferrihydrite solubility with pH are well understood, with lowest solubility occurring at neutral pH, and higher solubility observed under acidic or basic conditions (8).

EXPERIMENTAL SEMI-BATCH FERRIHYDRITE PRECIPITATION

The semi-batch precipitation of ferrihydrite was carried out isothermally at 25°C in a 350 mL jacketed cylindrical glass precipitator, agitated at 400 rpm with an angled-blade impeller. In a typical precipitation experiment, 300 mL of 0.112M Fe[III] nitrate solution was placed in the precipitator followed by the addition of approximately 12 mL of 8M NaOH solution. The feed was delivered continuously through a 1mm Teflon tube placed near the impeller via a peristaltic pump over the nominated feed times of either 1 minute or 10 minutes.

During addition of the base, hydrolysis of Fe[III] takes place instantly generating supersaturation, and followed by primary nucleation and limited crystallites growth (10). The very low solubility and negligible mass contents in this system make it difficult to obtain representative and accurate measurements of solute concentration and precipitated solids. Nevertheless, the temperature and pH responses during the precipitation process were monitored, logged at 5 s intervals. This experimental procedure often encounters problems in reproducing the same pH condition for precipitation, because of the extremely fast hydrolysis of Fe[III] and ferrihydrite nucleation.

SEMI-BATCH FERRIHYDRITE PRECIPITATOR MODEL

Compartmental Semi-Batch Mixing Model

The compartmental mixing model employed here has a similar structure to the segregated feed model reported in the literature (4-6). A schematic of the model is shown in Figure 1; the precipitator volume is divided into a reagent feed zone and a bulk zone. The reagent feed plume introduced into the precipitator will disintegrate through convective mixing and exchanges of mass with the bulk solution via diffusion mixing. These processes are governed by their characteristic time constants.

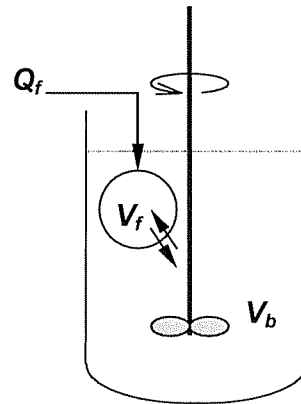


Figure 1 – Schematic of the semi-batch precipitator compartmental model

The compartmental mixing model assumes the following;

1. The reaction between reagents is instantaneous as soon as they are mixed;
2. Homogeneous conditions exist within each zone; and
3. Feed plumes are small compared to the bulk volume.

The governing equations of the above model consist of the volume and solute conservation equations. The total precipitator volume, V_T , is made up of a feed volume, V_f , and a bulk volume, V_b , as

$$V_T = V_f + V_b \quad (2)$$

The change in feed volume with time is

$$\frac{dV_f}{dt} = Q_f - \frac{V_f}{t_s} \quad (3)$$

where Q_f is the reagent feed rate and t_s is the mesomixing time constant.

The change in the bulk volume with time is

$$\frac{dV_b}{dt} = \frac{V_f}{t_s} \quad (4)$$

The change in the concentration of reagent i in the feed zone, $C_{i,f}$, is described by

$$V_f \frac{dC_{i,f}}{dt} = Q_f C_{i0,f} - \frac{V_f C_{i,f}}{t_s} - \frac{V_f (C_{i,f} - C_{i,b})}{t_E} - C_{i,f} \frac{dV_f}{dt} - V_f r_{i,f} \quad (5)$$

and similarly, the change in concentration in the bulk zone is

$$V_b \frac{dC_{i,b}}{dt} = \frac{V_f C_{i,b}}{t_s} + \frac{V_f (C_{i,f} - C_{i,b})}{t_E} - C_{i,b} \frac{dV_b}{dt} - V_b r_{i,b} \quad (6)$$

where $C_{i0,f}$ is the feed concentration of reagent i , and $r_{i,f}$ and $r_{i,b}$ are the reaction rate in the feed and bulk zones, respectively.

Characteristic Mixing Time Constants

Two mesomixing mechanisms are reported in the turbulent mixing literature - turbulent diffusion and disintegration of large eddies (1-2). Turbulent diffusion describes the spreading of a feed stream as it flows. The time constant, τ_D , for turbulent diffusion and dispersion can be approximated by

$$\tau_D = \frac{Q_f}{u D_T} \quad (7)$$

where Q_f is the feed addition rate, u is the relative velocity close to the feed point, and D_T is the turbulent diffusivity. Estimation of the relative velocity and turbulent diffusivity can be complex, requiring detailed hydrodynamic characterisation of the vessel.

The disintegration of large eddies describes the gradual breakdown of a feed stream in a turbulent environment from an initial scale, L_s , towards the kolmogorov scale where micromixing can occur, and its time constant, τ_s , is defined as

$$\tau_s \approx \left(\frac{L_s^2}{\varepsilon} \right)^{\frac{1}{3}} \quad (8)$$

where ε is the energy dissipation rate. Estimation of the initial eddy scale requires knowledge of the feed velocity, feed concentration and vessel hydrodynamics.

Micromixing involves the deformation of fluid elements and molecular diffusion. The characteristic time scale for this fine scale mixing, τ_E , is known as the engulfment time constant (1-2),

$$\tau_E = 17.3 \left(\frac{\nu}{\varepsilon} \right)^{\frac{1}{2}} \quad (9)$$

where ν is the kinematic viscosity.

Hydrolysis Reaction and Ferrihydrite Precipitation Kinetics

The reaction and precipitation of ferrihydrite is postulated to follow Equation (1). This simplistic scheme is based on the fact that the solubility of ferrihydrite is extremely low, and the intermediate phase generated by the reaction between Fe^{3+} and OH^- species is precipitated very rapidly to form the ferrihydrite. The supersaturation generated during the chemical reaction is approximated as

$$S_j = \left(\frac{c_{A,j}^{\nu_A} c_{B,j}^{\nu_B}}{K_{sp}} \right)^{\frac{1}{\nu_A + \nu_B}} \quad (10)$$

where $C_A = [\text{Fe}^{3+}]$, $C_B = [\text{OH}^-]$, $\nu_A = 1$ and $\nu_B = 3$, and K_{sp} the solubility product of ferrihydrite. For the modelling purposes, the $K_{sp} = 10^{-37.5}$ at 25 °C reported by Yu et al. (9) will be used.

It has been reported that precipitation of ferrihydrite involves primary nucleation followed by limited crystallite growth to 7 nm and then agglomeration into larger sizes (10, 11). Due to the lack of understanding of these mechanisms and the absence of any published kinetics models of these processes for this system, the model presented here treats the crystallite growth and primary nucleation together and ignores agglomeration. The justification for this is the low growth reported for this system. The model used for primary nucleation is

$$B_j^o = k_b \exp\left(-\frac{16\pi\gamma^3\nu^2}{3(kT)^3 \ln^2 S_j}\right) \quad (11)$$

where k_b is the rate constant, γ is the surface energy of solids, ν is molecular volume and S is the supersaturation ratio. The reaction terms in equations (5) and (6) are given by

$$r_{i,z} = \frac{k_v \rho_c L_o^3 B_z^o}{M_c} \quad (12)$$

where k_v is the volume shape factor, ρ_c is the crystal density, M_c is the molecular weight and L_o is the primary crystallite size. The subscript z refers to the zones in the compartmental mixing model.

RESULTS AND DISCUSSIONS

Dynamic pH measurements, taken during ferrihydrite precipitation experiments at feed rates of 12 mL/min and 1.2 mL/min, are showed in figures 2 and 3. In both experiments the pH remains at the initial pH value of 1.82 until the addition of OH^- after which the pH starts to rise steadily until reaching a maximum value coinciding with the end OH^- addition and then drops to a final pH value of 2.72. This indicates that the reaction takes place instantaneously upon OH^- addition and is completed shortly after feed addition is stopped, with both Fe^{3+} and OH^- eventually reaching their equilibrium concentrations.

The pH rises more steeply for the higher feed rate of 12 mL/min than for the lower feed rate of 1.2 mL/min, suggesting that the reaction is controlled by the supply of OH^- with time. The scatter in the experimental pH readings during the experiments may indicate interference of the hydrodynamics on the pH probe.

Based on the experimental conditions employed, the characteristic mixing time constants and supersaturation are approximated using equations (8), (9) and (10), prior to being fed into the model equations (2)-(6). It should be noted that the nucleation rate constant is selected by adjustment until the predicted pH matches the experimental data. The predicted pH is determined from the model predicted Fe[III] concentration according to

$$\text{pH} = \frac{1}{3} (\log(K_{sp}^*) - \log(\text{Fe}^{3+})) \quad (13)$$

where $K_{sp}^* = K_{sp} K_w^3$ and K_w is the solubility product of water.

Figures 2 and 3 show that the compartmental mixing model employed here can reasonably reproduce the dynamic pH changes during this precipitation process. However, the model does not fully capture all the dynamic pH changes, in particular the peaks observed in the experimental pH response. The discrepancies between the measured and model predicted pH values could be a result of uncertainties in the parameters estimates used in the model such as the mixing time constants. However, some of the discrepancy may be due limitations in the models and assumptions adopted, e.g. the primary nucleation model; solubility product of ferrihydrite; and simple reactive precipitation of ferrihydrite scheme used.

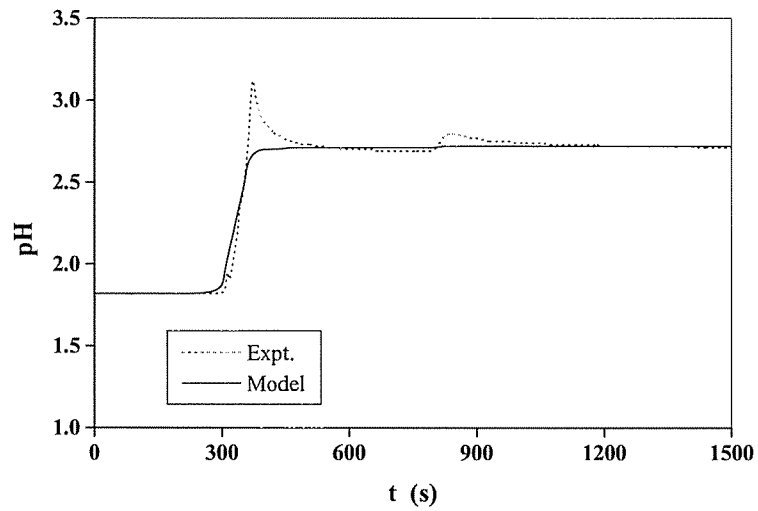


Figure 2 – Comparison of the experimentally measured and model predicted pH at high feed rate of 12 mL/min

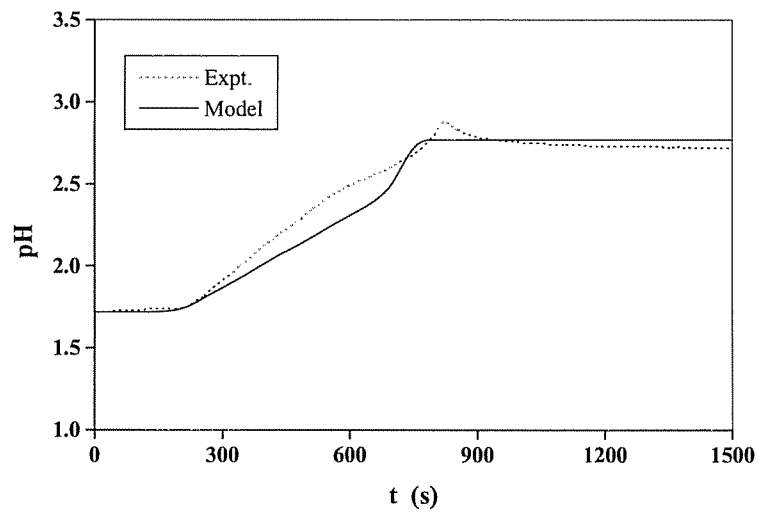


Figure 3 – Comparison of the experimentally measured and model predicted pH at slow feed rate of 1.2 mL/min

CONCLUSIONS

A compartmental precipitator model was employed to simulate the laboratory scale reactive precipitation of ferrihydrite. It was found that the model predictions match the experimental dynamic pH, but do not fully capture details in such as the observed peaks in the experimentally measured pH. Possible causes for the difference are the uncertainties in the approximation of the model parameters and possible limitations in the model formulation.

The experimental and modelling results showed that the reagent feed has a critical role in controlling the reaction and the precipitation of ferrihydrite.

REFERENCES

1. L. Vicum, S. Ottiger, M. Mazzotti, L. Makowski and J. Baldyga, "Multi-scale Modelling of a Reactive Mixing Process in a Semibatch Stirred Tank," Chemical Engineering Science, Vol. 59, 2004, 1761-1781.
2. R. Phillips, S. Rohani and J. Baldyga, "Micromixing in a Single-Feed Semibatch Precipitation Process," AIChE Journal, Vol. 45, 1999, 82-92.
3. R. Pohorecki and J. Baldyga, "The use of a New Model of Micromixing for Determination of Crystal Size in Precipitation," Chemical Engineering Science, Vol. 38, 1983, pp79-83.
4. R. Zauner and A.G. Jones, "Mixing Effects on Product Particle Characteristics from Semi-Batch Crystal Precipitation," Transaction of IChemE, Vol. 78, 2000, 894-902.
5. R. Zauner and A.G. Jones, "On the Influence of Mixing on Crystal Precipitation Processes- Application of the Segregated Feed Model," Chemical Engineering Science, Vol. 57, 2002, 821-831.
6. G. Tosun, "A Mathematical Model of Mixing and Polymerization in a Semibatch Stirred Tank Reactor," AIChE Journal, Vol. 38, 1992, 425-437.
7. J.L. Jambor and J.E. Dutrizac, "Occurrence and Constitution of Natural and Synthetic Ferrihydrite, a Widespread Iron Oxyhydroxide," Chemical Reviews, Vol. 98, 1998, 2549-2585.
8. R.M. Cornell and U. Schwertmann, The Iron Oxides, VCH Publishers, New York, USA, 1996, 189-206.

9. J.Y. Yu, M. Park and J. Kim, "Solubilities of Synthetic Schwertmannite and Ferrihydrite," Geochemical Journal, Vol. 36, 2002, 119-132.
10. M. Loan, G. Parkinson, M. Newman and J. Farrow, "Iron Oxy-hydroxide Crystallisation in a Hydrometallurgical Residue," Journal of Crystal Growth, Vol. 253, 2002, 482-488.
11. B. Lo and T.D. Waite, "Structure of Hydrous Ferric Oxide Aggregates" Journal of Colloid and Interface Science, Vol. 222, 2000, 83-89.