



A structured approach to thermodynamic modelling of aqueous solutions for nickel processing

by L.R.C. Cairncross, A.C. Dustan, and J.G. Petrie*

Synopsis

In this study, the general case of semi-batch precipitation of nickel hydroxide, $\text{Ni}(\text{OH})_2$, is modelled. In practical terms, this precipitation may occur at high ionic strengths, and therefore the model for solution chemistry requires a thermodynamic model that is applicable for these non-ideal systems. The activity coefficient model used is the ELEC-NRTL. The simulation of the solution chemistry is performed using *AspenPlus*TM, which is a steady-state process simulation program. This allows for rigorous evaluation of the solution speciation, and hence the degree of supersaturation which dictates the precipitation kinetics. The solution chemistry provides the basis for predicting the formation of solids.

The model consists of a solution chemistry part and a solids formation part. The inputs to the model include the initial concentrations of the streams entering the reactor, kinetic parameters for the precipitation processes, and a particle size distribution obtained from experiments. The solids formation part of the model employs the method of moments for the evaluation of the population balance. The population balance accounts for total particle number, and the formation and increase in size of particles across the entire particle size range. This balance requires kinetic parameters for the processes of nucleation, growth and agglomeration. Using optimization routines inherent in *AspenPlus*TM, parameters for the rate of nucleation, growth and agglomeration may be extracted from experimental particle size distributions. These are then used in the model to extrapolate to other conditions.

Once an understanding of the kinetics of the precipitation processes is gained, the model provides a predictive tool for optimization of these kinetics, in order to increase the overall particle size and therefore improve solid-liquid separation.

The work is deemed to be significant as it sheds some light on solids formation processes involved in precipitation—including nucleation, growth and aggregation—and develops a predictive modelling tool applicable to solutions of high ionic strength. We argue that this dewatering of suspensions is affected significantly by particle size distribution and surface properties of the solids formed by precipitation. This modelling tool should facilitate the design of solids formation processes where downstream dewatering is enhanced.

Precipitation of nickel hydroxide

The recovery of metals from waste water streams is motivated often by economic and environmental considerations. A wide range of technologies is available for this recovery including evaporation, ion exchange, membrane separation, electrolysis and precipi-

tation. In the nickel processing industry, hydroxide precipitation has been used extensively for removing nickel from these streams. This technology has been favoured over other methods of metal removal for its low cost and ease of implementation. However, fine precipitates formed as hydroxides are often sparingly soluble. High levels of supersaturation may occur resulting in high nucleation rates. These fine precipitates create difficulties in solid-liquid separation which limits the application of this technology. While supersaturation control techniques such as sludge recycle increase particle size, knowledge of the precipitation kinetics, including nucleation, growth and agglomeration, is required in order to optimize the process with respect to solid-liquid separation.

Nickel was chosen for consideration in this study as it has relatively simple aqueous chemistry compared with other metals such as iron (it exists only in one oxidation state nickel (II)). Nickel is of economic importance, particularly for the minerals processing industries in South Africa. Various industrial activities result in the formation of nickel-bearing waste waters. These include base metal and platinum group metal (PGM) refining, nickel plating operations, stainless steel works and foundries, motor vehicle and printing industries. Suspended particles containing nickel are toxic and can contaminate lakes and streams. An accumulation of heavy metals in streams and lakes can threaten the well-being of aquatic life, such as fish. A build-up of heavy metals in soils can decrease species diversity, as heavy metals, including nickel, are toxic to many plant species even at low concentrations (UNEP, 1993). Vegetation may show signs of heavy metal contamination, such as stunted growth, severe die back of non-tolerant

* Department of Chemical Engineering, University of Cape Town, Private Bag, Rondebosch 7701.

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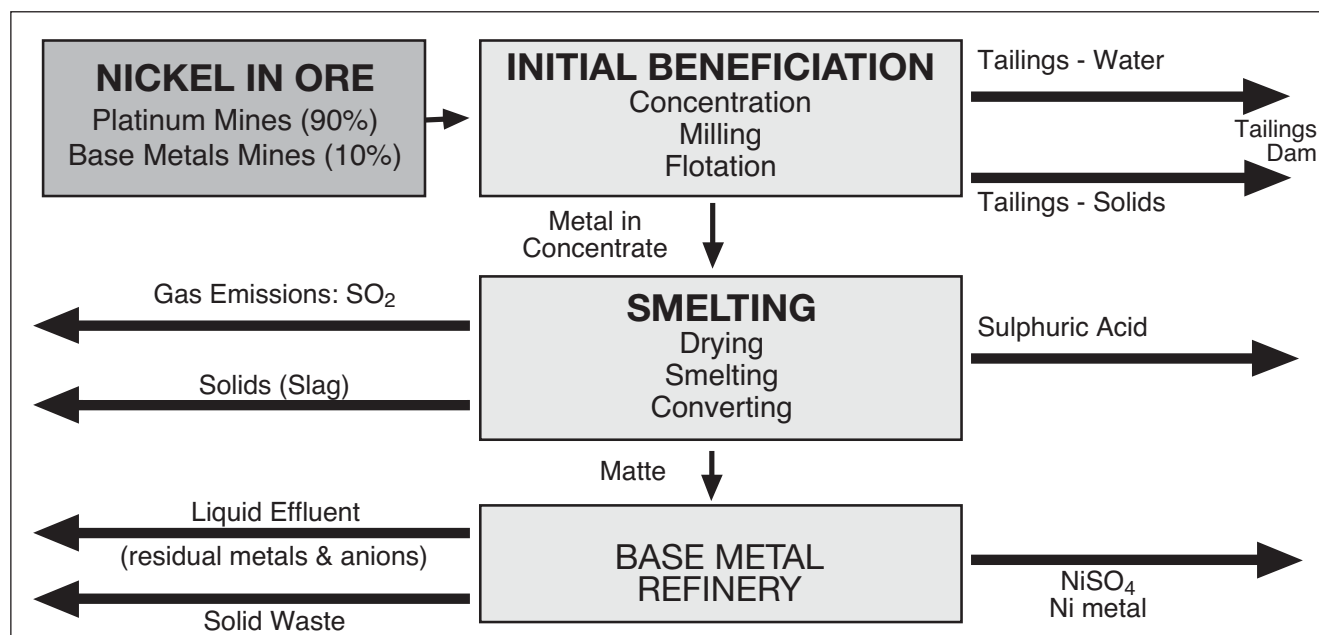


Figure 1—Nickel processing in South Africa

species, leaf fall or leaf coloration. People can be affected indirectly through the consumption of crops grown in contaminated areas or from consuming grazing animals that have ingested contaminated vegetation. Nickel and nickel salts are recognised as common skin sensitizers and may result in allergic dermatitis in workers in hydrometallurgical operations (UNEP, 1993). Technologies for the removal of nickel from effluent streams are therefore necessary. An understanding of the factors influencing the formation of nickel hydroxide facilitates the application of techniques to form solid particles that can be easily separated from the carrier fluids.

In order to locate the significance of the precipitation of nickel hydroxide within the nickel processing industry, a generalized flowsheet is given as Figure 1 (Gaylard, 1997). As can be seen from this Figure, liquid effluent streams are produced largely in the initial beneficiation processes and base metal refineries.

Although precipitation is used widely in industry, it is still applied on an empirical basis and is not well understood. There are frequently deviations in the performance of precipitation technology in comparison with chemical theory (Patterson, 1987). The effective treatment of waste waters may also depend on the solids separation efficiency, which is influenced by particle size, and surface properties.

During the precipitation process a wide range of stable and unstable solid phases may form. Kinetic and thermodynamic factors as well as the particular ions present in solution will influence the solids which may form (Patterson, 1987). Precipitation involves the induction of supersaturation, nucleation, growth, aggregation, ageing and transformation. In considering precipitation kinetics, the following mechanisms are taken into account by the model proposed in this paper: nucleation, growth and aggregation. These rates are dependent largely on the degree of supersaturation. As solids are formed, the degree of supersaturation of the

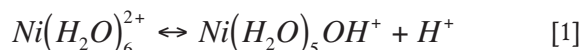
solution decreases and thus the nucleation, growth and aggregation are time-dependent within the semi-batch process considered in this study. The model takes these effects into account explicitly.

Nickel chemistry

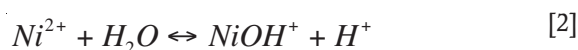
Water is a natural solvent and can behave either as a solvent or as a pure liquid. Water has a distinct polar charge distribution, which allows each water molecule to participate in strong polar interactions (Israelachvili and Wennerström, 1996). This is important particularly in a consideration of metal ion solvation.

The properties of electrolytes are affected by the interactions between ions and water molecules in solution. These interactions are not fully understood, especially in concentrated solutions. Each nickel ion, Ni²⁺, has six molecules of water attached to it by co-ordination bonds, in a fairly ordered manner. These water molecules are attached as a sphere and form what is known as an inner sphere hydration (Bryson, 1996). An outer sphere has a larger number of water molecules attached more loosely, in a much less orderly manner. These attached molecules are less organized the further one moves from the central ion. The chemistry of ions in solution is dependent largely on changes in the solution environment that affect the degree of solvation.

The first stage of hydrolysis occurs when a hydrogen atom is removed from the inner hydration sphere. For the inner sphere species, the reaction can be written as:



Conventionally, however, the water molecules in the inner sphere are ignored and Equation [1] becomes:



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The second stage of hydrolysis is a similar process:



Another mechanism involves the loss of a proton directly from this oxy-cation. This reaction can be represented as:



The complexity of the solution chemistry of nickel hydroxide precipitation, where the solid phase is formed by reaction, can be illustrated by considering a relatively simple system with nickel sulphate, NiSO₄, and sodium hydroxide, NaOH, in solution. A number of possible species and complexes may occur in solution, as shown in Table I (Baes and Mesmer, 1976).

Typical concentration ranges for nickel are 0.46 to 3.4 mg/l (0.0078 to 0.058 mmol/l) for acid mine drainage, and up to 900 mg/l (0.015 mol/l) for plating plant rinse waters (Sittig, 1975). For waste waters and process streams from nickel refining, the solution ionic strength is likely to be high; for example, concentrations of up to 50 g/l (0.85 mol/l) have been reported for a base metals refining process stream entering the precipitation reaction vessels. When modelling the thermodynamics of solutions with high metal concentrations, thermodynamic models applicable at these ionic strengths are needed in order to represent the real solution chemistry as accurately as possible. Some resultant complexities are discussed in the following section.

Complexities of solution chemistry

From precipitation thermodynamics, a solid forms when

$$\Delta G = \pm RT \ln(a/a^{eq}) < 0 \quad [5]$$

where ΔG is the change in Gibbs energy, R is the universal gas constant, T is the temperature, a is the activity of the solute in the solution and a^{eq} is that of the saturated solution. The supersaturation ratio, S is given by:

$$S = \frac{a}{a^{eq}} \quad [6]$$

For a reaction, $A + B \rightarrow C$, supersaturation, S , can be defined as:

$$S = \frac{a_A \cdot a_B}{a_A^{eq} \cdot a_B^{eq}} = \frac{\gamma_A m_A \gamma_B m_B}{\gamma_A^{eq} m_A^{eq} \gamma_B^{eq} m_B^{eq}} \quad [7]$$

where for component i , a_i is defined as the activity, γ_i is the activity coefficient, m_i is the concentration in terms of molality, and the superscript *eq* refers to equilibrium conditions. The activity of a component i is related to the activity coefficient by $a_i = \gamma_i m_i$. The solution is said to be supersaturated when $S = a/a^{eq} > 1$ and $\Delta G < 1$. Thus supersaturation is the driving force for precipitation and 'the supreme governing parameter' (Demopoulos, 1993).

Traditionally, supersaturation calculations have used simplifications and correlations appropriate for dilute solutions to account for the influence of ionic strength on the activity coefficients. Correlations for activity coefficients that assume infinite dilution as a basis are inadequate for solutions with high concentrations (above 0.1 molal) and errors may well be introduced when extrapolating outside of the concentrations for which the thermodynamic models are reported to hold (Zemaitis *et al.*, 1986).

Thermodynamic models

A number of thermodynamic models are available for calculating the activity coefficients of components in solution. Many of these are not applicable to solutions of high ionic strength and using them would introduce significant errors into any simulation of the solution chemistry (Zemaitis *et al.*, 1986).

In dilute solutions, long range interactions of interionic electrostatic forces dominate over short range interactions. In concentrated solutions, short range interactions (molecule-molecule interactions and ion-molecule interactions) are of greater significance. Using the background provided by Zemaitis *et al.* (1986), the Electrolyte-NRTL (ELEC-NRTL) activity coefficient model, developed by Chen *et al.* (1982) was chosen for this work, as it is applicable to multi-component solutions. It takes into account both long and short range interactions and is therefore applicable at high ionic strengths.

Precipitation kinetics

The precipitation kinetics considered in this study are the rates of nucleation, growth and aggregation. These mechanisms are dependent on the solution supersaturation although aggregation may also be dependent on hydrodynamic parameters, such as solution mixing characteristics. Very high nucleation rates may be a consequence of localized regions of very high supersaturation, due in part, to mixing behaviour (for further discussion refer to Dustan and Petrie, 1997).

The formation of a solid phase by nucleation can result from primary or secondary mechanisms. Primary nucleation can be homogeneous, in which new crystals form directly from solution, and are a result of supersaturation only. Heterogeneous nucleation on the other hand, requires foreign insoluble material to catalyse the formation of a new particle. Secondary nucleation is initiated by the presence of the solid

Table I

Equilibria formed from a solution of NiSO₄ and NaOH

	Equilibrium	Constant	Equilibrium	Constant
H_2O	$\leftrightarrow H^+ + OH^-$	K_W	$NiSO_4 \leftrightarrow Ni^{2+} + SO_4^{2-}$	K_7
$Ni^{2+} + (OH)^-$	$\leftrightarrow NiOH^+$	K_1	$H^+ + SO_4^{2-} \leftrightarrow HSO_4^-$	K_8
$Ni^{2+} + 2(OH)^-$	$\leftrightarrow Ni(OH)_{2(m)}$	K_2	$H^+ + HSO_4^- \leftrightarrow H_2SO_4$	K_9
$Ni^{2+} + 3(OH)^-$	$\leftrightarrow Ni(OH)_3^{\pm}$	K_3		
$Ni^{2+} + 4(OH)^-$	$\leftrightarrow Ni(OH)_4^{2\pm}$	K_4	$NaOH \leftrightarrow Na^+ + OH^-$	K_{10}
$2Ni^{2+} + (OH)^-$	$\leftrightarrow Ni_2(OH)^{3\pm}$	K_5	$Na^+ + SO_4^{2-} \leftrightarrow NaSO_4^-$	K_{11}
$4Ni^{2+} + 4(OH)^-$	$\leftrightarrow Ni_4(OH)_4^{4\pm}$	K_6	$Na^+ + NaSO_4^- \leftrightarrow Na_2SO_4$	K_{12}

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phase of the crystallizing material itself. For a more complete description of possible nucleation mechanisms both primary and secondary nucleation for both seeded and unseeded systems, should be considered. However, the scope of this study is limited to primary nucleation in an unseeded system.

Growth of a particle occurs when non-particulate material is deposited on its surface. This non-particulate material is normally an ion diffusing to and reacting on the surface of a crystal. Since it is not usually possible to determine accurately the linear dimensions of a crystal, an overall linear growth rate is defined as $G=dL/dt$. In the model discussed in this paper, a size-independent growth rate, referred to as the McCabe 'ΔL law', is used as suggested by McCabe (1929).

Aggregation occurs when two particles collide and adhere to one another to form a new larger particle. The rate of aggregation $r_{agg}(L,\lambda)$, of particles of size $[L,L+dL]$ with particles of size $[\lambda,\lambda+d\lambda]$ in a multiparticulate system is characterized by the aggregation kernel, $\beta(L,\lambda)$. This rate is given by:

$$r_{agg}(L,\lambda) = \beta(L,\lambda)dN_LdN_\lambda \quad [8]$$

The aggregation kernel is a measure of the frequency with which a particle of size L aggregates with one of size λ . Sastry (1975) proposed that the aggregation kernel is the product of two factors:

$$\beta(L,\lambda) = \beta_0 \times f(L,\lambda) \quad [9]$$

The first factor, β_0 , is independent of size and depends on operating conditions such as supersaturation and stirrer speed, and affects the rate at which the aggregation takes place. The second factor, $f(L,\lambda)$, is some function of particle size and often reflects the mechanism thought to have caused the aggregation. This factor affects the shape of the resulting particle size distribution. A number of different functional forms of the kernel have been proposed. Some of these are shown in Table II.

An aggregation kernel has to be chosen for a particular system and this problem is typically approached by finding the kernel that provides the best fit to the experimental data (Smit *et al.*, 1994). This is the method that was used in our study.

Table II Aggregation kernels used to model aggregation during precipitation	
Mechanism	Kernel $\beta(L,\lambda)$
Size-independent	β_0
Brownian motion	$\beta_0(L+\lambda)(L^{\pm 1} + \lambda^{\pm 1})$
Gravitational	$\beta_0(L+\lambda)^2 L \pm \lambda $
Shear	$\beta(L+\lambda)^3$
Particle inertia	$\beta_0(L+\lambda)^2 L^2 \pm \lambda^2 $
Thompson kernel	$\beta_0 \frac{(L^3 \pm \lambda^3)^2}{(L^3 + \lambda^3)}$

Source: Bramley, Hounslow and Ryall (1996)

Solving the population balance

In precipitating systems where both growth and aggregation occur simultaneously, difficulties are encountered when attempting to determine the rates of both size-enlargement mechanisms. The differential equations which describe such systems are virtually impossible to solve analytically except in highly idealized situations. It is therefore necessary to employ numerical methods in which the particle size distribution is divided into a large number of intervals. Direct integration may be achieved by a variety of methods. However, this procedure is likely to be computationally intensive and discretization is the preferred method for solution of the population balance equations.

The population balance

The population balance is the statement of continuity for particulate systems. Randolph and Larson (1971) give the population balance for a well-mixed batch system of constant volume as

$$\frac{\partial n}{\partial t} + \frac{\partial(G_r n)}{\partial L} = B \pm D \quad [10]$$

where n is the number-density function, L is the particle size, G_r is the growth rate, and B and D are the birth and death rates respectively. The particle length, L , is used as the internal coordinate (with respect to the particle itself) to describe the particle. For a system where there are dN particles per unit volume of suspension, in the size range L to $L+dL$ then at that size and time the density function is:

$$n(L) = \frac{dN}{dL} \quad [11]$$

Equation (11) gives the rate of change of the number of particles in the differential size range L to $L+dL$ to the rates of growth into and out of that size class and the rates of birth and death in the size range. The birth and death terms for the aggregation rate were developed by Hulburt and Katz (1964) using volume as an internal coordinate and given by Hounslow *et al.* (1988) using length as an internal coordinate:

$$B(L) = \frac{L^2}{2} \int_0^L \frac{\beta \left[(L^3 - \lambda^3)^{1/2}, \lambda \right] n \left[(L^3 - \lambda^3)^{1/2} \right] n(\lambda) d\lambda}{(L^3 - \lambda^3)^{3/2}} \quad [12]$$

$$D(L) = n(L) \int_0^\infty \beta(L,\lambda) n(\lambda) d\lambda \quad [13]$$

Moment transformation of the population balance

In most instances where growth and aggregation occur simultaneously, as is the case with the precipitation of nickel hydroxide, a complete analytical solution of the population balance is not possible. Moment transformations are used to convert the population balance equations into a set of solvable ordinary differential equations, as outlined by Randolph and Larson (1971). The j th moment of the number density function $n(L)$, with respect to particle size L , is defined as

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$$m_j = \int_0^{\infty} L^j n(L) dL \quad [14]$$

The first four moments of the particle size distribution (PSD) provide useful overall properties, with length as the internal coordinate. The zeroth moment is equal to the total number of particles, the first, second and third moments are proportional to the length, area and volume of particles, respectively.

Transforming the population balance into its moment form, Randolph and Larson (1988), Equation [10] becomes:

$$\frac{dm_j}{dt} + jG_r m_{j\pm 1} = \bar{B}_j + \bar{D}_j \quad [15]$$

where the birth and death terms on the right are defined as:

$$\bar{B}_j = \int_0^{\infty} L^j B dL \quad [16]$$

$$\bar{D}_j = \int_0^{\infty} L^j D dL \quad [17]$$

Once the population balance has been transformed into moment form, it may be discretized to facilitate numerical solution.

Discretized population balance

Various numerical methods are available for solving the population balance and these may be classified as classical numerical methods (such as finite elements), cubic spline methods and discretized population balances (DPBs). A discretized population balance is applied in our current work, using the method of Hounslow and Marshall (1988). In this method, the size domain is discretized into intervals, and some form for $n(L)$ is assumed. By using the DPB, the population balance equation is transformed into a set of ordinary differential equations, which may be solved more readily.

The method developed by Hounslow and Marshall (1988) ensures that the correct particle number and volume for the aggregation terms and the first three moments are predicted. The particle size distribution (PSD) is divided into particle size classes in a geometric series such that the lower and upper bounds of each size interval are in a ratio, r , of $\sqrt[3]{2}$. A set of equations for each size class can be formulated. These equations relate the changes in the particle number within each size class to the processes of nucleation, growth and aggregation.

The rate of change of the particle number due to nucleation in the first size class is given by:

$$\frac{dN_1}{dt} = \dot{N}_1|_{nuc} = B_0 \quad [18]$$

where $\dot{N}_1|_{nuc}$ is the rate of change in particle number in the first size class due to nucleation and B_0 is the nucleation rate parameter, distinct from the birth term, B referred to in Equation [10] in the population balance of Randolph and Larson (1971). Nucleation is only considered in the first size class and therefore the first size class has three mechanisms that influence the particle number: nucleation, growth and

aggregation, whereas the rest of the size classes are influenced by growth and aggregation only.

For growth in the first size class:

$$\dot{N}_1|_g = \frac{2G_r}{(1+r)L_1} \left(\left(1 \pm \frac{r^2}{r^2 \pm 1} \right) N_1 \pm \frac{r}{r^2 \pm 1} N_2 \right) \quad [19]$$

where G_r is the growth rate parameter.

For growth in all other size classes:

$$\dot{N}_i|_g = \frac{2G_r}{(1+r)L_i} \quad [20]$$

$$\left(\frac{r}{r^2 \pm 1} N_{i\pm 1} + N_i \pm \frac{r}{r^2 \pm 1} N_{i+1} \right), i \neq 1.$$

The rate of change in the particle number due to aggregation in the i th interval for any size class:

$$\begin{aligned} \dot{N}_i|_{agg} = & N_{i\pm 1} \sum_{j=1}^{i\pm 1} 2^{j\pm i+1} \beta_{i\pm 1,j} N_j + \frac{1}{2} \beta_{i\pm 1,i\pm 1} N_{i\pm 1}^2 \\ & \pm N_i \sum_{j=1}^{i\pm 1} 2^{j\pm 1} \beta_{i,j} N_j \pm N_i \sum_{j=i}^{n_{eq}} \beta_{i,j} N_j \end{aligned} \quad [21]$$

where $\beta_{i,j}$ is the aggregation parameter with respect to size classes i and j .

Thus, the change in the number of particles in the first size class, \dot{N}_1 , is given by the sum of the changes in particle number due to nucleation, growth and aggregation:

$$\dot{N}_1 = \dot{N}_1|_{nuc} + \dot{N}_1|_g + \dot{N}_1|_{agg} \quad [22]$$

For the size intervals $i = 2$ to the last size interval, $i = n_{eq}$, the change in the number of particles in the size class is given by:

$$\dot{N}_i = \dot{N}_i|_g + \dot{N}_i|_{agg} \quad [23]$$

From Equations [22] and [23], the change in the number of crystals in each size class and the population balance for the system can be established. The kinetic parameters required for these equations need to be extracted from existing experimental data. The method followed here is that presented by Bramley *et al.* (1996).

Extracting the kinetic parameters

The parameters for nucleation, growth and aggregation required for the population balance equations (B_0 , G_r , β_0), outlined in the previous section, may be extracted from experimental data. The kinetic parameters, B_0 , G_r , β_0 , can be related to changes in solution supersaturation. Power law expressions have been used by Tavare and Garside (1990) to relate nucleation and growth to supersaturation:

$$B_0 = k_n (S \pm 1)^n \quad [24]$$

$$G_r = k_g (S \pm 1)^g \quad [25]$$

$$\beta = k_{agg} (S \pm 1)^\beta \quad [26]$$

It has been found it is possible to obtain a unique solution for these parameters. Different aggregation kernels can be used in the population balance, as mentioned previously, and a comparison between the simulated PSDs

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and those obtained experimentally would give an indication of which aggregation mechanism is most likely to have resulted in the PSDs obtained experimentally.

Simulation model

The application of simulation software for prediction of solution speciation depends on the availability of reliable thermodynamic data that describe solution behaviour over a range of conditions. A large number of correlations are available. However, no one correlation is consistent and precise for all thermodynamic properties under various conditions for any multi-component system (Renon, 1996). Bassett and Melchior (1990) give an overview of some of the simulation packages available for the modelling of aqueous systems. *AspenPlus*TM was chosen as it handles solution chemistry, has data regression capabilities and allows for user-defined add-on modules. In addition, its particulate processing capability is attractive for the study of reactive crystallization.

*AspenPlus*TM provides data for ionic species, binary interactions and ionic reactions. The thermodynamic databases and methods available in *AspenPlus*TM are capable of handling solutions of high concentration (in particular the Electrolyte-NRTL), the significance of which was discussed earlier. While the ELEC-NRTL method is adequate for describing the solution chemistry of solutions with high ionic strength, the database may not have parameters for particular systems. As a result, users may encounter difficulties in obtaining the required parameters. For the nickel system, the *AspenPlus*TM database contains a number

of nickel salts and species but not all the equilibria required. The missing equilibria were obtained from Baes and Mesmer (1976)—with reference to Table I, the reactions with equilibrium constants K_4 , K_5 , K_6 .

Data regression tools are available within *AspenPlus*TM to regress electrolyte system data from experimental data provided by the user. This tool may be useful when the required parameters are not present within the software's databases or when the user's data are preferred. As a simulation tool *AspenPlus*TM provides rigorous and robust flowsheet modelling and all the unit operations can handle electrolytes. Thus it is a suitable environment for design purposes.

The module available within *AspenPlus*TM for crystallization is for a continuous steady-state crystallizer whereas the system under consideration required a semi-batch crystallizer. It was therefore necessary to write a user-defined subroutine in FORTRAN to account for the solids formation processes. This block was attached to the batch reactor module available within *AspenPlus*TM. A schematic representation of the different blocks in module can be seen in Figure 2.

The inputs to the simulation model, including the initial component concentrations, C_A^0 , C_B^0 , the initial concentration of solids, W_0 , the kinetic parameters discussed in the preceding section, and the initial experimental particle size distribution, can be seen in Figure 3, which shows the details of the simulation. Looking at the discretized population balance (DPB) then, at the beginning of each time increment, the solution speciation and the activities of the various species are calculated for the semi-batch reactor. This information is passed into the solids formation block where

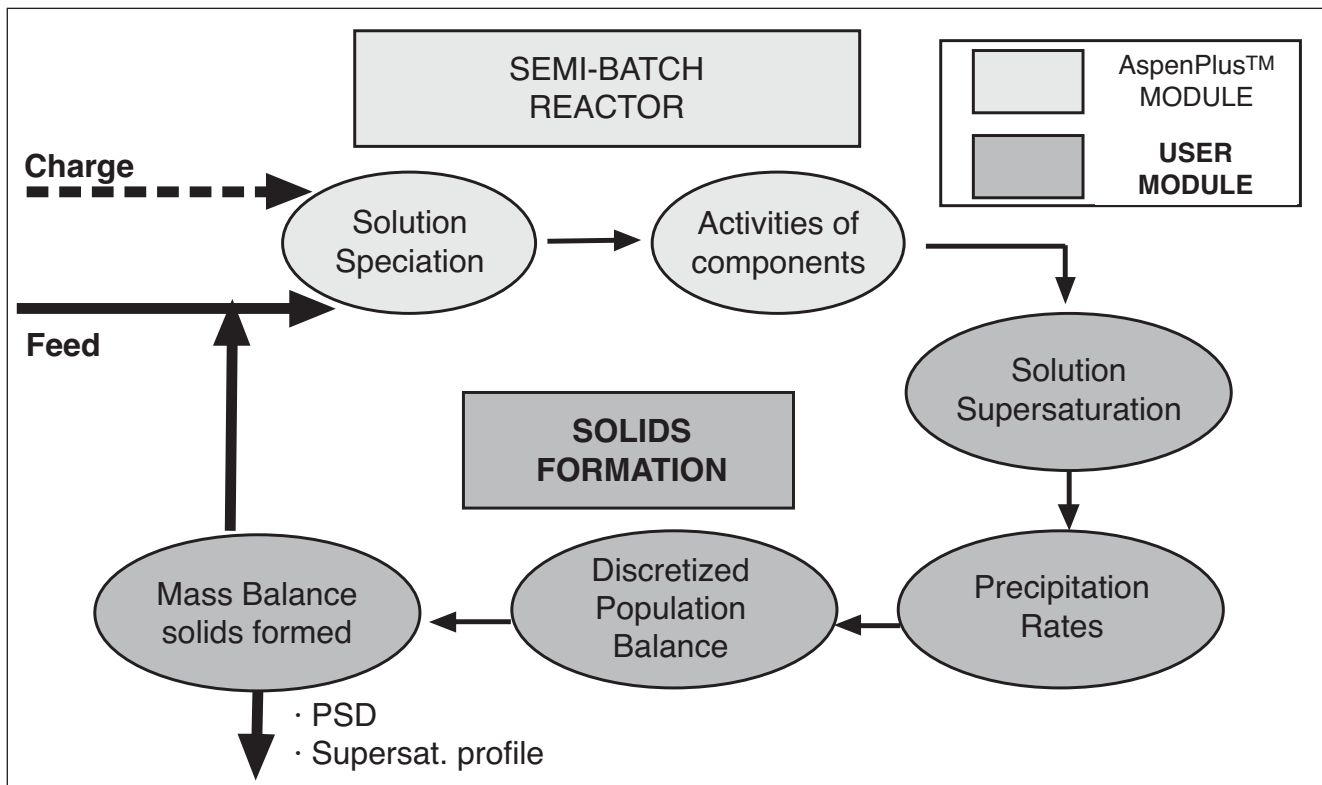


Figure 2—Schematic for simulation of precipitation

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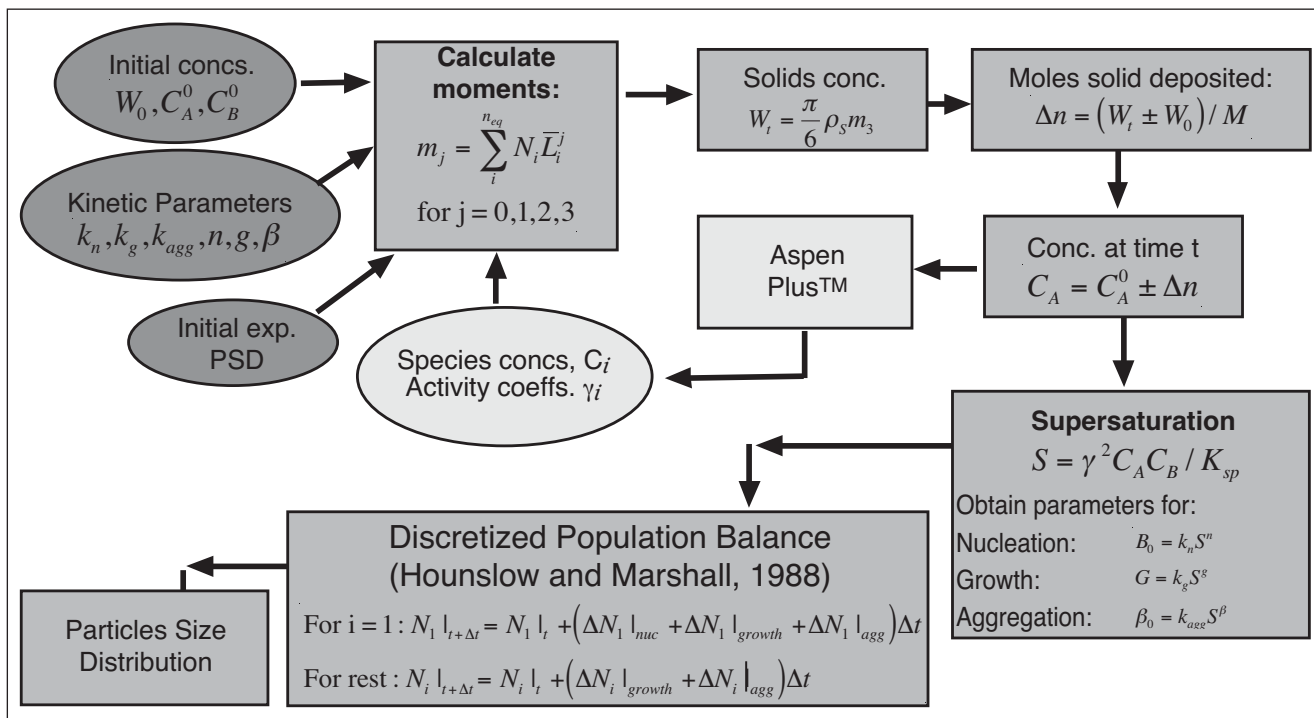


Figure 3—Details of simulation

the moments are calculated, from which the solids concentration can be determined, including the number of moles of solid deposited and the new concentrations for the relevant components. The supersaturation is calculated from the activities of the species involved in the formation of $\text{Ni}(\text{OH})_2$, Ni^{2+} and hydroxide ions (of similar form to Equation [7], see Table I). The kinetic precipitation relationships in conjunction with the supersaturation (outlined in the previous section, Equations [24], [25] and [26]) are used to determine the nucleation, growth and aggregation rates. These rates are used in the DPB to describe the change in the particle size distribution (PSD) for each time increment (Equations [22] and [23]). A mass balance is performed and the new solution concentrations are calculated taking into account the amount of solute deposited as precipitate.

These concentrations are then passed back to the semi-batch module where new feed is also being added. The new solution speciation, activities and concentrations within the semi-batch reactor is calculated. The process is then repeated for the next time increment.

Experimental considerations

From the preceding discussion it is evident that the solution supersaturation controls the precipitation process. The high order dependencies of nucleation rates, in particular, highlight the importance of the calculated supersaturation value. This impacts on both the accuracy of extracted kinetic parameters and on subsequent simulation of solids formation. Such accuracy is essential for extension of the current approach, which is both limited and purely empirical, to a more fundamental description with broader application. The issues of supersaturation calculation in non-ideal situations is of increased importance in the case of the

precipitation of sparingly soluble components (metal hydroxides in this example) where high order supersaturations are typical, resulting in a high order dependence of nucleation rate on these values. These non-idealities accompanying high supersaturations are exacerbated by mixing effects, where, as a result of the relative rates of micromixing and nucleation, localized pockets of extremely high saturation occur which dominate the precipitation behaviour.

While these mixing effects are not dealt with specifically here, their role is recognised particularly for its possible effect on the equilibrium speciation calculations. The nickel hydroxide system, selected for example in this study, exhibits extremely fast precipitation rates (predominantly nucleation and agglomeration). As a result, batch and semi-batch operation of these systems makes evaluation of the kinetics almost impossible. For this study, to slow the kinetics down to a rate which does allow time-dependent measurement, an inhibiting agent is employed. The use of citrates as an inhibiting agent is discussed and demonstrated by Patterson *et al.* (1990). The mechanism of inhibition is thought to be one of surface adsorption and subsequent retardation of surface integration of solute. This, for various theoretical reasons, is preferred to the alternative of metal complexation by the citrate. The range of citrate to nickel ratios investigated in these studies (0.14–0.5) demonstrates significant reduction in precipitation times even for ratios at the low end of this range.

The current experimental setup makes use of the semi-batch precipitation from nickel chloride or nickel sulphate solution by the slow controlled addition of sodium hydroxide. A marine impeller agitates the solution, in a baffled reactor of standard geometry. In the absence of an inhibiting agent, the effects of mixing limitations are evident from the formation

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of a plume of solids immediately following introduction of the hydroxide into the vessel. Under these conditions, measurement of the precipitation kinetics is impossible using current techniques. When citrate is added to the initial nickel charge solution at a citrate-to-metal ratio of 0.2, kinetics are slowed down such that mixing effects are not immediately obvious and suspension characterization allows the extraction of nucleation, growth and agglomeration rates by the methods outlined above.

During the course of an experiment, the pH and conductivity are continuously recorded. Online particle size analysis is made possible by the use of a Malvern Mastersizer S placed in a recycle loop. This allows analysis of particle sizes down to 0.05 microns. During these light-scattering measurements, the light obscuration can be related to the volume concentration of solids in the suspension and allows the total deposited solids volume to be tracked with time. In addition to this, discrete suspension samples are taken, filtered through 0.2 micron membranes and analysed for total dissolved nickel using atomic adsorption spectrophotometry. These nickel levels are used to check those calculated from a mass balance accounting for the amount of nickel hydroxide precipitated. The recorded pH is used to fix the equilibrium nickel activity, following which the solution supersaturation can be calculated.

Concluding remarks

Our purpose here has been to develop a framework for elucidating the kinetics of formation of nickel hydroxide by ionic precipitation. It has not been our express purpose to explore the use of experimental data to validate our model approach. This will be looked at specifically as part of a subsequent paper.

That point aside, we have shown that the solution chemistry may be modelled using the databases contained within *AspenPlus*TM and the thermodynamics embodied in the ELEC-NRTL for calculating the activity coefficients on components in solutions with high ionic strengths, in order to represent the solution speciation. From this speciation, the degree of supersaturation can be obtained. This influences the rates of nucleation, growth and aggregation. The model for the solids formation uses a population balance to determine the particle size distribution. A sensitivity analysis of the system with respect to the conditions in the solution environment that may be varied on the industrial scale, is then possible. These conditions may include variations in feed to the reactor where the precipitation occurs and variations in the pH of the solution. These conditions can then be optimized to form large particles and thus improve solid-liquid separation. It is our hope that this model will prove a valuable tool for designers of industrial precipitation operations.

Nomenclature

a_i	Activity of component i
a_i^{eq}	Activity of component i at equilibrium
B	Birth rate, $m^{-1}.m^{-3}.s^{-1}$
B_0	Nucleation rate, no. $m^{-3}.s^{-1}$
D	Death rate, $m^{-1}.m^{-3}.s^{-1}$

G_r	Growth rate, $m.s^{-1}$
ΔG	Change in Gibbs energy
L	Particle size, m
L_i	Particle size in the i th size interval, m
\bar{L}_i	Average particle size in the i th size interval, m
m_j	j th moment, $m_j.m^{-3}$
\dot{m}_j	Rate of change of the j th moment, $m_j.m^{-3}.s^{-1}$
n	Population density function, $m^{-1}.m^{-3}$
N	Number of particles, no. m^{-3}
N_i	Number of particles in the i th size interval, no. m^{-3}
\dot{N}_i	Rate of change of particle number in the i th size interval, no. $m^{-3}.s^{-1}$
R	Ratio of the upper and lower bounds of a size interval
r_{agg}	Rate of aggregation, $m^{-3}.s^{-1}$
S	Supersaturation
T	Time, s

Greek symbols

β	Aggregation kernel, $m^{-3}.s^{-1}$
β_0	Size independent part of the aggregation kernel, $m^{-3}.s^{-1}$
λ	Particle size, m

Superscripts and subscripts

<i>agg</i>	Aggregation
<i>g</i>	Growth
<i>i</i>	Size interval
<i>j</i>	An integer, for example the j th moment or j th size interval
<i>nuc</i>	Nucleation

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Richards Bay Minerals (RBM) to proceed with additional mining plant*

Richards Bay Minerals' (RBM) board of directors has approved further funds for the continuation of the project to construct an additional mining plant, which will be larger than existing plants operated by RBM. Total expenditure on the project will be in excess of R900 million which includes updating existing plants and infrastructure.

Keith Rumble, RBM managing director said that the capital now available would allow for the design phase to proceed, tenders to be issued and the awarding of early contracts. He added that the request for the final capital vote would be submitted to the board of directors in February 1998.

'The project will enable the company to meet its annual production and marketing demands of one million tons of titanium dioxide slag into the next century. RBM is already one of the world's largest producers of its kind, providing more than 25% of the world's demand for titanium dioxide slag, rutile, high-purity pig iron and zircon.

'RBM is keen that local industry should benefit, and with a relatively low imported content this will be possible. Local small and medium sized enterprises will continue to be given the opportunity to participate, and local

communities will benefit from employment. It is anticipated that approximately 900 contractor staff will be employed on-site over a two-year period.

'Dudley Fraser who previously headed up RBM's projects group has been appointed project director, and Hatch Africa has been engaged as consultants and project managers. Hatch Africa acquired Gencor Engineering and Technologies (GET), who were originally responsible for the design and construction of RBM's four existing mining plants.

'The new mining plant will be situated north of existing operations in the company's Zulti North mining lease area. As is common practice, environmental, health and safety aspects are paramount and special precautions will be taken to ensure that the integrity of environmentally sensitive areas are not compromised,' said Rumble. ◆

* Issued by: The Sussens Group, Contact: Piet Maré
Head of Public Relations, Richards Bay Minerals
Tel: (0351) 901 3440 Fax: (0351) 901 3442.

Request for Back Issues of SAIMM Journals

The SAIMM need copies of the July/August 1996 Journals.

Members who have copies available are requested to please send them to:

Ms Mél Varéla

The Institute of Mining & Metallurgy

P.O. Box 61127, Marshalltown 2017

Mineral Resource Classification: Quo Vadis?

International Mineral Classification: the South African Perspective (Hammerbeck 1996) although published in 1996, was produced by the Working Group of the Geological Society in Draft 6 form in 1994 (and subsequently endorsed by the S.A. Institute of Mining and Metallurgy). Since 1994, South Africa in general and the mineral economy in particular have opened up to the outside world. Mineral resources are the basis of mineral property valuations and it is desirable that all role players (including industry, government and foreign entrants to the South African market) have a similar understanding of mineral resource classification.

In an attempt to revive the debate on mineral resource classification, an *ad hoc* meeting was held at the University of the Witwatersrand on the 22nd of August 1997. Seventeen practitioners discussed the issue at length and concluded that *International Mineral Resource Classification: the South African Perspective* (Hammerbeck 1996) should be used as a point of departure with additional reference to the Australasian (JORC) Code (1996). The meeting appointed a smaller *ad hoc* committee with the responsibility of continuing with the South African classification process with the aim of producing a comprehensive guide for mineral resource practitioners in South Africa.

The committee is as follows:

Danie Krige
Jonathan Vieler
Andy Clay
Dick Minnitt
Mike O'Brien (chairman)

The Australasian JORC is regarded as a useful model for the Classification code as it has been successfully implemented and regularly updated. Several reasons for the success of JORC have been advanced (Stephenson, P.R. and Miskelly, N., 1997) and should be considered in the development of a South African equivalent:

- Simplicity
- Developed by industry, not imposed from outside
- Regulatory backing (Stock Exchanges)
- Avoidance of being too prescriptive
- Allow professional judgement to be used
- Industry's ability and willingness to discipline competent persons
- Obligatory membership of national professional body
- Permanent committee
- Communication & regular revisions.

Paraphrasing Stephenson, P.R., (1997), with reference to JORC, but equally applicable to other codes, a mineral resource classification code should:

- ▶ Establish minimum standards for public reporting
- ▶ Set out a system of classification
- ▶ Describe competent persons and their responsibilities
- ▶ Supply a summary list of criteria to be considered

when preparing estimates.

Should not:

- ▶ Seek to regulate the estimation and classification procedures used by competent persons
- ▶ Seek to regulate companies' internal reporting/classification.

Items suggested as important for inclusion in a South African code are:

- ▶ Guidelines for classification applied to deposits of unique interest (Witwatersrand-type gold and Bushveld-type platinum)
- ▶ Standards of minimum disclosure (including scale of mining units, critical for estimating proportions of resource above certain cutoff grades)
- ▶ Definitions of 'competent persons' (not restrictive but effective for disciplinary sanction).

The *ad hoc* committee are conscious of the need to consider submissions from as many role players as possible in the development of a South African code. The following schedule has been provisionally drawn up:

- ▶ 31st January 1998 Initial SA submissions
- ▶ 31st March 1998 Draft Code
- ▶ 31st May 1998 Official 1998 Code.

It is hoped that the 1998 code will be periodically revised as circumstances demand (as per the Australasian JORC code).

Submissions from interested parties are invited to be sent:

by e-mail: mob@db.za
or by post
'Min. Res. Classification'
P. O. Box 62285
Marshalltown 2107
or by Fax
'Min. Res. Classification'
Attention M.F. O'Brien
Tel: (011) 638 4729.

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