Comparison of Simulators for Process and Aqueous Chemistry Modeling

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The capabilities of four commercial simulators to model precipitation processes is discussed via two case studies: copper(II) sulfide and cobalt(II) carbonate precipitation, respectively. Two approaches were adopted in the modeling, using various existing modeling tools or developing simulation models from an independent critical review of the literature. Simulated results were compared with experimental investigations in order to inform and/or refine model predictions. Results were strongly influenced by the nature and the number of thermodynamic data taken into account in the model. The influence of various parameters on controlling metal solubility have been identified and discussed. This study emphasises the importance of selecting comprehensive and reliable thermodynamic data before modeling a process. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 2358-2368, 2005
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Introduction

Precipitation is the most cost-effective method for the removal of metals from industrial wastewaters, and many studies have demonstrated its efficiency in removing various metals (for example, nickel, copper, cobalt, zinc, cadmium and lead) as sulfide or carbonate, instead of hydroxide.[1-9] Besides yield and selectivity, the precipitated product must have good filterability and dewatering characteristics to make the process economically feasible. Considerable effort has been expended to develop more efficient precipitation processes, particularly by combining separation technologies[5,10] or using seeded precipitation.[8,9,11,12]

In all the articles mentioned previously, the methodology and the capability of the processes developed are usually well described. However, the explanations of the precipitation mechanisms and the system chemistry relevant to precipitation technology are relatively limited and comparatively little has been done to improve the understanding of the process, with a view to controlling and optimizing the technology.[7,8,13,14]

In many precipitation systems, the characteristic reaction and nucleation times are very short, of the order of milliseconds or less,[7] and, thus, kinetic considerations are of minor concern compared to thermodynamics. In this case, solubility considerations are especially important for three major reasons:

1. In a system with the potential for more than one solid species to precipitate, the relative solubilities of the solid phases will have an influence,

2. the determination of the remaining metal concentrations in the solution, at equilibrium for batch reactors or at steady state for dynamic reactors, allows the assessment of the precipitation process efficiency as follows:

$$\eta(\%) = \frac{M_{in}^{z+} - M_{out\text{-}total}^{z+}}{M_{in}^{z+}} \times 100,$$

where M^{z+} is the concentration of the metal of interest in solution (kg/m^3), and

3. the sparingly soluble nature of many precipitating spe-

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cies will result in very high supersaturation levels, which in turn determine the characteristics of the precipitate formed.

An understanding of the solution chemistry provides insight into the effects of process variables on the speciation of the metal under the defined operating conditions and on species precipitation. From this information, the behavior of a complex system in aqueous solution can be well defined with a view to controlling the metal removal process. However, analytical measurement limitations, experimental errors, time and/or economic constraints all mean that acquiring experimental information about the behavior of metals in solution is not straightforward. Phase and chemical equilibria calculations can become unmanageable when dealing with a complex system involving a large number of species and simplifications are necessarily made - with the risk of inaccuracies in the modeled results. This "solubility domain" approach has been successfully validated with experiments for some metal/ligand systems,[1,15,16] and to a lesser extent for other systems with an accurate prediction only for a specific range of operating conditions.[8,17] An obvious problem with this approach is that any missing or inaccurate data for the relevant soluble and insoluble species that could be formed in solution might lead to erroneous solubility limits. The consequences can be dramatic when dealing with toxic compounds, such as heavy metals and sulfide. These problems have been previously pointed out[18,19] and methods for estimating unknown or inaccurate thermodynamic data have been proposed and applied successfully to various metal/ligand systems.[18,20-22]

Chemistry and process simulation tools incorporating extensive databases have been developed to simulate aqueous-based chemical systems involving a variety of species over a broad range of temperature, pressure and composition. Minteqa2,[23] Mineql+,[24] OLI Systems, Inc. Stream Analyser and ESP Process,[25,26] Aspen Plus,[27] belong to the most frequently used software in the environmental and industrial fields, respectively. They predict chemical and phase behavior (liquid, solid, gas) and/or process efficiency while incorporating the effect of aqueous chemistry on the process. The incorporated information is usually highly comprehensive and, therefore, potentially allows a more reliable prediction of phase and chemical equilibria than the solubility domain approach does.

This study focuses on the understanding of metal removal as sulfide or carbonate salts by precipitation through coupled theoretical and experimental investigations. Stability and solubility considerations for the metal system are examined in order to assess metal speciation over a range of operating conditions (reagent or metal concentration, ligand/metal ratio, pH). Four commercial chemistry and process simulation tools (Minteqa2, Mineql+, OLI Systems, Inc. ESP Process and Stream Analyser and Aspen Plus) are considered. Their reliability for and applicability to precipitation processes are compared with a solubility domain model and discussed from a critical review of the literature combined with experimental case studies. At best, the software allows specific operating conditions (pH, concentration of reactants, reagent/metal ratio) to be determined to maximize metal removal as metal sulfide or carbonate. At worst, the software may help in improving the understanding of the metal system, by qualitatively and quantitatively predicting the range of predominant solid phases (once precautions have been taken to calculate realistic stability and/or solubility limits).

Thermodynamic Models

Aqueous chemistry and process simulations

The presence of ions in the liquid phase may cause highly nonideal thermodynamic behavior. Consequently, the solution chemistry may affect physical property calculations and equilibrium calculations. Different thermodynamic property methods can be applied depending on the commercial simulation tools used in relation to the characteristics of the solution.

As mentioned by all the authors,[23-27] the four software packages contain very large, in-place thermodynamic databanks allowing users to accurately carry out aqueous chemistry simulation and process modeling. If needed, these databases can be extended. In this work, no attempt is made to incorporate new data in those existing databases as the purpose is to test their existing accuracy and suitability for predicting metal precipitation performance.

OLI Systems Inc (ESP Process, Stream Analyzer) and Aspen Plus Simulations. Liquid phase properties are calculated in OLI Systems, Inc. using the Bromley-Zemaitis activity coefficient model which represents only ion-ion interactions. It is an extension of the Bromley equation[28] that combines the Debye-Huckel term for long-range interactions between the ions and the solvent, a semiempirical expression for short-range electrostatic interactions (cations/anions/solvent) and two new terms with temperature functionalities. For ion-molecule and molecule-molecule interactions, the Pitzer model is used.[29] Liquid phase properties in Aspen Plus are calculated using the Electrolyte Non Random Two Liquid activity coefficient model[30] which accounts for ion-ion, ion-molecule and molecule-molecule interactions.

For both simulators, standard state properties are determined using the Helgeson-Flowers Equation of State, vapor phase fugacity coefficients are calculated from the Redlich-Kwong equation of state (or an extended form for OLI Systems, Inc.) and phase equilibria involving volatile species are calculated using the Henry's Law.

The Stream Analyzer software package making up the OLI Systems, Inc. engine[25] was used to generate solubility curves that predict the residual metal ion concentration in solution as a function of pH, from experimental input conditions (that is, metal and ligand concentrations, temperature, pressure).

The Environmental Simulation Program (ESP),[26] utilizing the OLI Systems, Inc. engine, and Aspen Plus[27] were used to predict the precipitation efficiency of the unit operation, at steady state. The process simulation is done by creating a block flow diagram which illustrates the equipment used, as well as the related input and output streams. The thermodynamically stable species that precipitate under a particular set of operating conditions is predicted, and the simulation generates a graph of mass flow of precipitate as a function of pH or as a function of the precipitating agent mass flow introduced in the system. Specific operating conditions for optimum metal removal as precipitate can, therefore, be determined.

Minteqa2 and Mineql+ Simulations. Minteqa2[23] and Mineql+[24] are equilibrium speciation models both used to calculate the equilibrium composition of dilute electrolyte systems. Liquid-phase properties are determined using the modified Debye-Huckel equation or the Davies equation. Alternatively, users can add extended versions of the Debye-Huckel equation, which include terms to account for ion interactions

occurring in more concentrated solutions (ionic strengths greater than 0.5). With the exception of H_2O, the activity coefficients of neutral species are calculated using the development of Helgeson. They contain the same comprehensive USEPA's Minteqa2 database plus additional data for Mineql+ from the original Mineql program.

Solubility domain approach

The solubility domain approach[1] is used to draw solubility curves. This method can only be applied to infinitely dilute systems (ion activities replaced by ion concentrations) in order to facilitate calculations. On the other hand, the ligand concentration has to be in excess compared to the metal concentration in order to simplify the mass balance for the ligand (metal complexes not taken into account).

Choice of Equilibrium Constants. All equilibrium constants were selected at 25°C and at zero ionic strength. When not available at $I = 0$ mol.L^{-1} (only a few values), data were recalculated using the Davies equation. In this article, all the constants were expressed as global formation constants β. Thus, ligand (sulfide, carbonate, hydroxide, sulfate) protonation constants, metal/ligand complexation constants and solubility products were expressed as follows:

$$K_j = \frac{[H_jL]}{[H^+][H_{j-1}L]} \tag{1}$$

$$\beta_j = \frac{[H_jL]}{[H^+]^j[L]} \tag{2}$$

$$K_{M_iH_jL_k} = \frac{[M_iH_jL_k]}{[M]^i[H^+][H_{j-1}L_k]} \tag{3}$$

$$\beta_{M_iH_jL_k} = \frac{[M_iH_jL_k]}{[M]^i[H^+]^j[L]^k} \tag{4}$$

$$\beta_{M_i(OH)_jL_k} = \frac{[M_i(OH)_jL_k]}{[M]^i[OH^-]^j[L]^k} \tag{5}$$

$$\left.\begin{aligned} K_{sp} &= [M]^i[L]^k \\ K_{sp} &= [M]^i[OH^-]^j[L]^k \\ K_{sp} &= [M]^i[OH^-]^j \end{aligned}\right\} \tag{6}$$

where L is S^{2-}, CO_3^{2-} or SO_4^{2-}.

In the case of metal/ligand complex species, when only conditional constants K were available (Eq. 3), global formation constants (Eq. 4) were recalculated using global protonation constants of the corresponding ligand (Eq. 2).

It is well known that an amorphous precipitate has a higher solubility than the evolved crystalline structure, as is the case for numerous hydroxides and sulfides. When available in the literature, solubility product values used in the model should correspond to the amorphous solid formation, in order to represent at best the behavior of freshly precipitated sparingly soluble compounds in aqueous solutions.

The Copper-Hydroxy-Sulfide System. The solubility was drawn as a function of pH, at a total sulfide concentration of $S_T = 1.57 \times 10^{-3}$ mol.L^{-1}. The sulfide/copper ratio investigated was in the concentration range between 1.5/1 and 10/1.

From a critical review of the literature, thermodynamic constants have been selected and are given in Table 1. These stability constants are compared with those used in OLI Systems, Inc. ESP Process and Minteqa2/Mineql+ thermodynamic databases (see Table 1). Data from Aspen Plus are not directly accessible to users and could, therefore, not be compiled. The most probable values appear in bold characters in Table 1, as motivated later.

All the stability constant values for copper hydroxide and oxide species except the uncharged soluble species $Cu(OH)_2^0$ were chosen from the compilations of Smith and Martell,[31] and agreed well with other compilations previously mentioned.[22] The value for $Cu(OH)_2^0$ was selected from Lacour et al.[22] who used a special correlation[18] (relating the β formation constant of the uncharged soluble species with the solubility product Ks) to refine it due to doubts about its validity. This constant differs from that given in Smith and Martell's compilation and to a lesser extent from the value selected by Minteqa2 and OLI Systems, Inc. ESP Process.

Whereas consistent values of the first acid dissociation constant of hydrogen sulfide ($\log Ka_1 = -7.0$) have been reported in the literature,[31-33] the difference in values given for the second acid dissociation constants can reach six orders of magnitude ($-19 < \log Ka_2 < -13$).[33,34] From a critical review of the literature combined with potentiometric studies, Licht[34] concluded that the most probable value of $\log Ka_2$ is -17.3 ± 0.3 at 25°C, which is in accordance with other UV and Raman spectrophotometric studies cited in the article. This low value indicates that free aqueous sulfide (S^{2-}) exists only in extremely concentrated alkaline solutions.

Shea and Helz[35] estimated the solubility product of a poorly crystalline precipitate $CuS_{(s)}$ (obtained by mixing Cu^{2+} and HS^- solutions) to be about three orders of magnitude greater than that of covellite. Despite its instability, dissolved copper could be controlled by this amorphous phase rather than the covellite phase, at short timescales (a few weeks). From Table 1, this value ($\log K_{sp} = -35.8$ when recalculated with the second acid dissociation constant of hydrogen sulfide evaluated by Licht[34]) is similar to the value estimated by Dyrssen[36] ($\log K_{sp} = -36.0$), and those selected in the OLI Systems, Inc. database ($\log K = -36.3$), and by Bollinger et al.[18] ($\log K_{sp} = -35.1$). The highest difference is observed with the solubility product selected by Minteqa2, which is more than 10 orders of magnitude higher ($\log K_{sp} = -23.0$). Databases used in simulation tools do not provide specific information about original references to individual reactions. The independent literature review allowed the source to be found. This value, apparently taken from Licht,[34] corresponds actually to the K_{sp} equilibrium reaction involving HS^- rather than S^{2-}, implying that there is an error in the datapoint in the Minteqa2 database. Recalculating the $\log K_{sp} = -23.0$ as a function of S^{2-} concentration allows the $\log K_{sp}$ from Licht[34] to be retrieved ($\log K_{sp} = -40.3$).

Dyrssen[36] calculated stability constants for various metal sulfides from the dithizone extraction constants selected in the literature together with already compiled metal sulfide constants. He reported the potential formation of CuS^0, $CuHS^+$ and $Cu(HS)_2^0$ in equilibrium with the CuS solid. Depending on the value of the hydrogen sulfide acidity constants selected,

Table 1. Values of Global Protonation Constants, Complexation Constants and Solubility Products with Sulfide, Hydroxide and Sulfate Ligands, given at $I = 0$ mol . L^{-1} and $T = 25°C$, from Thermodynamic Databases and Independent Literature Review, for the Copper-Hydroxy-Sulfide System

	Separate Literature Review					Databases	
						OLI Systems Inc.	Minteqa2/Mineql+
	Log β or log K_{sp}					Log β or log K_{sp}	
Hydroxide (OH^-)							
$CuOH^+$			**6.5**[31]			6.7	6.0
$Cu(OH)_2^0$			**15.2**[22]			13.9	14.2
$Cu(OH)_3^-$			**15.1**[31]			15.6	15.0
$Cu(OH)_4^{2-}$			**16.0**[31]			16.5	16.4
$Cu_2(OH)_2^{2+}$			**17.4**[31]			—	17.7
$Cu_3(OH)_4^{2+}$			**35.2**[31]			—	—
$Cu(OH)_{2(s)}$			**−19.3**[31]			−19.1	−19.3
$CuO_{(s)}$			**−20.3**[31]			−21.5	−20.3
Sulfide (S^{2-})							
H_2S			20.9[31]	**24.3**[34]		19.8	19.7
HS^-			13.9[31]	**17.3**[34]		12.9	12.8
CuS^0	**19.5**[18]	26.0[36]	11.9[31,37]		15.3[34,37]	<30.4[39]	—	—
$CuHS^+$			28.0[31,36]	**31.4**[34,36]			—	—
$Cu(HS)_2^0$			49.4[31,36]	**56.2**[34,36]			—	—
$Cu(HS)_3^-$			—				—	64.3
$CuS(HS)^-$			<42.8[31,39]	**<49.6**[34,39]				
$CuS(HS)_2^{2-}$			57.9[31,39]	**68.1**[34,39]				
$CuS(HS)_3^{3-}$			72.3[31,39]	**85.9**[34,39]				
$Cu_2S_3^{2-}$			39.3[31,37]	**49.5**[34,37]			—	—
$CuS_{(s)}$	−40.3[34]	**−35.1**[18]	−36.0[36]		**−35.8**[34,35]	−38.7[34,35]	−36.3	−23.0
					−32.4[31,35]	−35.3[31,35]		
Sulfate (SO_4^{2-})							
$CuSO_4^0$			**2.4**[31]				2.3

global stability constants for these complexes take on different values (Table 1).

Multiple experimental investigations carried out by Luther et al.[37,38] showed the formation of bisulfide complexes with various metal ions but not with Cu(II) or Zn(II). Instead, at the early stage of the reaction of Cu^{2+} with HS^- (a few seconds), copper complexes of three stoichiometries, MS, M_2S_3 and M_4S_5, were found depending on the operating conditions applied. Stability constants for $CuS^0$and $Cu_2S_3^{2-}$ were determined and recalculated according to Eq 4. Acid-base titrations did not provide any evidence for any protonated complexes at pH ≥ 5 without any copper sulfide precipitating. In their most recent article,[38] aqueous copper sulfide clusters (formed from condensation of Cu_3S_3 rings) were well characterized and were found to act as intermediates during copper sulfide solid formation.

Shea and Helz[39] measured experimentally the solubility of covellite in solutions containing various concentrations of either bisulfide (HS^-) or polysulfide (that is, S_3^{2-}, S_4^{2-}, S_5^{2-}) ligand. In the case of bisulfide solutions, they obtained a good fit to the experimental data with equilibria involving two divalent copper polysulfide complexes (that is, $CuS(HS)_2^{2-}$ and $CuS(HS)_3^{3-}$). The reported conditional stability constants were recalculated as the global constants presented in Table 1. At lower HS^-, concentrations ($< 10^{-2}$ mol.L^{-1}), they claimed the potential formation of CuS^0 and $CuS(HS)^-$, but could only establish upper limits of the conditional log K expressed as a function of HS^- (log $K_{cond} \leq -8.3$ and ≤ -6.4, respectively). From these data, global stability constants could be calculated and are listed in Table 1 (log $\beta < 30.4$ for CuS^0 and log $\beta <$ 49.6 for $CuS(HS)^-$ using Ka_2 from Licht[34]). Thompson and Helz[40] also observed the formation of a variety of copper complexes with bisulfide, sulfide, and polysulfide ligands, copper being in its monovalent form. Only one oxidation state of copper is considered in this article and these complexes have therefore not been taken into account in the model.

OLI Systems, Inc. (as well as Aspen Plus) databases do not consider the potential formation of any soluble complexed copper sulfide species. Surprisingly, Minteqa2 (and Mineql+) take into account the potential formation of the $Cu(HS)_3^-$ species. To our knowledge, only one experimental study postulated its formation (cited in Shea and Helz[39]), however doubts about its correctness have been expressed by several authors cited in the article.[39]

Very large discrepancies in the literature data are apparent as regards the formation constant of the sparingly soluble copper sulfide species CuS^0. The most recent data determined experimentally from voltammetric investigations[37] is the lowest stability constant reviewed. They found evidence for the formation of this species only for a low sulfide to copper molar ratio (< 0.4). As soon as the S/Cu ratio exceeded this critical value, aqueous rings and clusters (Cu_3S_3, Cu_4S_5, Cu_4S_6 being the tetrameric structure of $Cu_2S_3^{2-}$ complexes) formed in solution. Bollinger et al.[18] used a special approach for the estimation of the solubilities, and the formation constants of insoluble metal sulfide from well known data of the corresponding insoluble carbonates. They gave a higher stability constant value for the CuS^0 species, but still lower than the value calculated by Dyrssen[36] or that proposed by Shea and Helz.[39] The influence of this species on the amount of residual soluble copper will be discussed in the relevant section.

A copper sulfate complex was considered in the model, as sulfate ions are usually associated with copper metal ion in

Table 2. Values of Global Protonation Constants, Complexation Constants and Solubility Products with Carbonate, Hydroxide and Sulfate Ligands, Given at $I = 0$ mol.L^{-1} and $T = 25$°C, from Thermodynamic Databases and Independent Literature Review, for the Cobalt-Hydroxy-Carbonate System

	Separate Literature Review			Databases	
				OLI Systems Inc.	Minteqa2/Mineql+
	Log β or log K_{sp}			Log β or log K_{sp}	
Hydroxide (OH^-)					
$CoOH^+$		**4.3**[31]		4.3	4.8
$Co(OH)_2^0$		**9.2**[31]		9.2	9.7
$Co(OH)_3^-$		**10.5**[31]		10.5	10.8
$Co(OH)_4^{2-}$		**9.7**[31]		9.7	—
$Co_2(OH)^{3+}$		**3.0**[31]		—	—
$Co_4(OH)_4^{4+}$		**25.5**[31]		—	—
$Co(OH)_{2(s)}$	**−14.9**[31]	−14.0[41]	−15.7[41]	−15.2	−15.9
Carbonate (CO_3^{2-})					
H_2CO_3		**16.7**[31]		16.7	16.7
HCO_3^-		**10.3**[31]		10.3	10.3
$CoCO_3^0$		4.3[31] **5.6**[41]		—	—
$CoHCO_3^+$		11.9[31] **11.8**[41]		—	—
$CoCO_{3(s)}$	**−10.0**[31]	−12.8[41]	**−11.2**[44]	−8.7	−12.8
Hydroxy-carbonate					
$3CoCO_3{\cdot}4Co(OH)_2$		**−87**[45]		—	—
Sulfate (SO_4^{2-})					
$CoSO_4^0$		**2.4**[31,41]		2.4	—

industrial wastewaters. The corresponding stability constant comes from the compilations of Smith and Martell.[31]

Depending on the thermodynamic data selected from literature, various sets of data can be plotted from the solubility domain approach, leading to different modeled solubility limited systems.

The Cobalt-Hydroxy-Carbonate System. The solubility was drawn as a function of pH, at a total carbonate species concentration of $C_T = 4.22 \times 10^{-3}$ mol.L^{-1}. A closed precipitation system was considered. The carbonate/cobalt ratio investigated was in the concentration range between 1.5/1 and 10/1. Thermodynamic constants selected from the independent literature review, and those used in OLI Systems, Inc. and Minteqa2/Mineql+ databases are given in Table 2. As for the copper sulfide system, the most probable values appear in bold in Table 2.

The data for soluble cobalt hydroxide species and carbonate ligand selected from the compilations made by Smith and Martell[31] are in fairly good agreement with those from other literature sources as well as those used in OLI Systems, Inc., Minteqa2 and Mineql+ databases. The $CoCO_3^0$ and $CoHCO_3^+$ constants come from the compilations of either Smith and Martell[31] or Pettit and Powell.[41] A discrepancy is observed only for the $CoCO_3^0$ constant. All databases do not take into account the potential formation of soluble complexed cobalt carbonate species, such as $C°CO_3^0$ and $CoHCO_3^+$.

The values for log K_{sp} of $Co(OH)_{2(s)}$ collected from literature data are within the range $-15.9 <$ log $K_{sp} < -14.0$. Precipitating Co(II) from alkaline solutions (sodium hydroxide) leads to the formation of a blue ($\alpha-Co(OH)_2$) or a pink ($\beta-Co(OH)_2$) polymorph, as observed by Gaunand and Lim.[42] Only the pink precipitate remains stable in aged solutions (from several minutes to a few hours) at room-temperature. The lowest values of log K_{sp} (from -15.9 to −14.9) are, therefore, attributed to the pink precipitate. If we use the correlation relating the β formation constant of the uncharged soluble species $Co(OH)_2^0$ with the solubility product K_{sp},[18,22] the value of log $K_{sp} = -14.9$[31] best fits the linear relationship with log $\beta = 9.2$.[31]

The solubility behavior of cobalt(II) oxide in deoxygenated (N_2 medium) sodium hydroxide solutions has previously been investigated at various temperatures (from 22 to 288°C).[43] Co(II) ion activity in aqueous solutions was shown to be controlled by the hydrous Co(II) oxide ($\beta-Co(OH)_2$) rather than metallic cobalt ($Co_{(s)}$) or anhydrous Co(II) oxide ($CoO_{(s)}$). Taking into account these observations, only the cobalt(II) hydroxide form was considered in this study.

Discrepancies of more than 4 orders of magnitude are apparent for the solubility product values for $CoCO_{3(s)}$. All the separate literature data reviewed gave log K_{sp} between −10.0 and −12.8. OLI Systems, Inc. database uses a very low solubility product value that could not be traced to a reliable original source. Grauer[44] made a critical review on solubility products of M(II)−carbonates and proposed that the most probable value of log K_{sp} for $CoCO_{3(s)}$ is -11.2 ± 0.2. In this case, the constant value for the formation of the $CoCO_3^0$ species from Pettit and Powell[41] (log $\beta = 5.6$) best fits the linear relationship[18,22] between log K_{sp} and log β.

The formation of the pure cobalt water-free carbonate is expected to occur at temperatures above 160°C[44] and hydroxy-carbonates are preferentially formed at room temperature. However, solubility data for these compounds are severely limited: Only one reference could be found and this deals with an estimation of the solubility product of $3CoCO_3.4Co(OH)_2.6H_2O$, at ambient temperature.[45] In the process of estimating K_{sp}, the authors neglected the presence of the molecular form $3CoCO_3.4Co(OH)_2^0$ in solution. No data was, therefore, available to include this species in the model. It was, thus, assumed that this species contributed negligibly to the enhancement of cobalt solubility, compared with the $Co(OH)_2^0$ and $CoCO_3^0$ species.

Cobalt forms several other mixed salts (such as hydroxy-

chloride and -sulfate) for which solubility data is scarce. Gaunand and Lim[42] studied the precipitation, and the transformation of $\alpha-Co(OH)_{2(s)}$ by mixing a $CoSO_4$ solution with NaOH (molar ratio of reagents = 1/1.9). They proposed that sulfate ion adsorption occurs on the internal and lateral surfaces of the $\alpha-Co(OH)_{2(s)}$ and $\beta-Co(OH)_{2(s)}$ particles, respectively, leading to two kinds of precipitates $\alpha-Co(OH)_{2(1-0.08)}(SO_4)_{0.08}$ and $\beta-Co(OH)_{2(1-0.05)}(SO_4)_{0.05}$. However, they gave no value of the corresponding solubility constants.

The formation of a soluble cobalt sulfate complex ($CoSO_4^0$) is taken into account by OLI Systems, Inc., unlike the other databases, and may originate from the compilations made by Smith and Martell or Pettit and Powell.[31,41]

The cobaltous ion (Co^{2+}) was considered in this study to be the most stable valence in aqueous solution at 25°C, the +3 or +4 state dominating under stronger oxidizing conditions and/or in the presence of some particular ligands not considered in this study.

Experimental Methods

Batch experiments (controlled solubility measurements)

All chemicals were analytical grade reagents dissolved in ultra-pure water (Milli-Q Plus system). Samples were taken under high purity nitrogen purging, then filtered through 0.22μm cellulose nitrate membrane (Sartorius) and acidified at pH < 2. Sample analysis was performed using graphite furnace or flame Atomic Absorption Spectrometry AAS (Varian). pH measurements were made with a combination pH probe (Eutech Instruments, pH 310 Series) calibrated against three standard buffers, at 25°C.

Copper sulfide or cobalt carbonate suspensions were prepared by adding a N_2-purged sulfide or carbonate solution (Na_2S, $9H_2O$ from Acros Organics or Na_2CO_3, 10 H_2O from Fluka Biochemika, respectively) to a N_2-purged copper ($CuSO_4$, $5H_2O$, Sigma Aldrich) or cobalt solution ($CoSO_4$, 7 H_2O, Sigma Aldrich). Ionic strength was fixed at 0.1 M with Na_2SO_4 (Merk) or $NaNO_3$ (Fluka) and temperature at 25 $\pm$ 1°C. A S/Cu ratio equal to 10/1 was investigated with an initial copper concentration in the mixture equal to 1.57 x 10^{-4} mol.L^{-1}. The CO_3/Co ratio equal to 10/1 corresponded to an initial cobalt concentration of 4.22 x 10^{-4} mol.L^{-1}. pH was adjusted (by adding concentrated HNO_3 or NaOH from Prolabo) to the desired value before and immediately after the sulfide or carbonate solution addition, then regularly controlled during the course of the experiments.

For the copper sulfide system, the complete reversibility of the equilibrium has previously been well demonstrated experimentally using two different techniques.[35,39] The preliminary precipitation experiment was done in duplicate without any pH adjustment. Equilibrium could be achieved within 50 h. In the other experiments, controlling pH at a constant value was a very difficult task, as it changed significantly with time depending on the initial pH value imposed (from 7 to 11). Therefore, samples for copper analysis were taken just before the regulation of pH at a given time, and at least 50 h after. The maximum uncertainty in the copper concentration calculated from triplicate AAS analyses did not exceed 3%. Experiments were conducted over a 13 day period.

For the cobalt carbonate system, the reversibility of the equilibrium was checked with both precipitation and dissolution experiments carried out in duplicate. When pH fluctuations were higher than 0.1 unit pH, uncertainties in cobalt concentration were determined from an identical experiment, taking at least three data points at pseudoequilibrium. The maximum uncertainty did not exceed 10%. As far as dissolution experiments are concerned, precipitates were initially prepared from solutions at a 10/1 CO_3/Co molar ratio. These were filtered on 0.22 μm cellulose nitrate filters (Sartorius) and rinsed with deionized water. The recovered solids were dried for 48 h at 40°C. Known precipitate amounts were then placed in solutions at fixed ionic strength (0.1 M), temperature (25°C) and desired pH value (from 8 to 11). Precipitation and dissolution experiments lasted about 30 and 40 days, respectively.

Continuous reactor experiments (uncontrolled solubility measurements)

A laboratory scale fluidized-bed reactor was used in order to investigate copper-sulfide precipitation. Detailed descriptions of the reactor and of the experimental procedure have been previously published.[9,46] Briefly, the reactor consists of a column sealed from the atmosphere, filled with sand (95–97% SiO_2) (250–500 μm) as a seed material onto which precipitate crystallizes. The fluidization is achieved mainly through a recirculation flow, which involves efficient mixing of the reactants (copper sulfate and sodium sulfide solutions) while preventing pellet cementation. Copper inlet stream is pumped from the bottom of the reactor and mixed with the precipitating agent (inlets located on one side of the column). The outlet stream (treated water) is recovered at the top of the reactor. A number of sampling points (other side of the column) are used for removing coated sand particles (for further analysis) and/or for establishing copper concentration and pH profile within the bed (intermediate outlet streams). The temperature of the bed (sand) and solution was 24 $\pm$ 3 °C. H_2SO_4 and NaOH (0.1mol/L) were used to control pH. For every sample drawn from the column (outlet stream), half was filtered using 0.45μm nylon membrane filters with the other half being left as drawn, then analyzed using AAS. pH measurements were carried out using a combination pH probe (HI 1332, Hanna) calibrated against standard buffers, at 25°C.

Steady state was reached in the reactor within 25 min of operation, after which fluctuations in residual aqueous copper concentration did not exceed 5%. Kinetics were found to be very rapid with a significant decrease in copper concentration in the outlet stream within 5 min. A copper conversion (dissolved copper removal) of 99.6% could be achieved at S/Cu molar ratios above 1/1. The formation of fine particles during the precipitation process was observed by analyzing both the total (not filtered) and dissolved (filtered) copper concentrations in the outlet stream. A total removal efficiency of 95.8% (when considering the fines as part of the outlet metal concentration) could be achieved. Under various operating conditions (copper and sulfide concentrations, S/Cu ratio), residual dissolved copper concentrations in the outlet stream, at steady state, were measured under pH control and compared to modeling results (referred as FBR experiments in Figure 3). The stoichiometry of the precipitate was determined from SEM/EDAX (Leica S440) analysis (atomic percentages) and was close to 1/1, irrespective of the operating conditions.

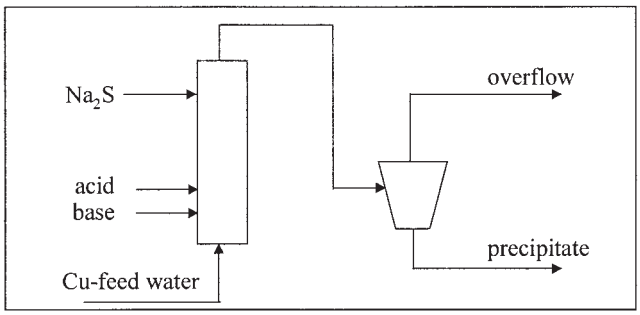

Figure 1. Simulation flowsheet developed with OLI Systems, Inc. ESP Process and Aspen Plus.

Results and Discussion

Thermodynamic modeling of copper precipitation as sulfide

Process simulation: The removal of copper from aqueous solution by sulfide precipitation was simulated with Aspen Plus and OLI Systems, Inc. ESP Process. The simulation flowsheet illustrated in Figure 1 is composed of a mixer block and a liquid/solid separator. Different sulfide/copper molar ratios were investigated and varied from 1/1 to 10/1, sulfide and copper flow rates being equal. Sulfide feed water had a constant concentration equal to 1.57×10^{-3} mol.L^{-1} (copper concentration varied between 1.57×10^{-4} mol.L^{-1} and 1.57×10^{-3} mol.L^{-1}). Acid and base streams were introduced into the mixer block for pH control. The effect of the change in pH on metal salt precipitation could also be examined. The simulation was carried out at 25°C.

Species considered in Aspen Plus and OLI Systems, Inc. ESP Process simulations were identical: Cu^{2+}, $CuOH^{+}$, $Cu(OH)_2^0$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, $CuSO_4^0$, $CuSO_{4(s)}$, CuS(s), $Cu(OH)_2$(s).

Both simulations predicted a total copper precipitation as sulfide over the entire pH (1 to 14) and S/Cu ratio (1/1 to 10/1) ranges investigated. No soluble copper was present in the overflow as the mass flow of the recovered precipitate was exactly equal to the inlet mass flow of copper stream.

Solubility Domain Approach Results. Figure 2 was drawn for the copper-sulfide system using the solubility domain approach described previously, at a total sulfide concentration of $S_T = 1.57 \times 10^{-3}$ mol/L, for a sulfide/copper ratio in solution above 1/1. The figure was determined from a superimposition of the hydroxide, sulfide and oxide solubility diagrams.[1,33] To examine the effect of the discrepancies observed in the thermodynamic data, various sets were plotted depending on the values of the constants used in the model. In these cases, the following aqueous species were taken into account: Cu^{2+}, CuS^0, $CuHS^{+}$, $Cu(HS)_2^0$, $Cu_2S_3^{2-}$, $CuS(HS)^{-}$, $CuS(HS)_2^{2-}$, $CuS(HS)_3^{3-}$, $CuOH^{+}$, $Cu(OH)_2^0$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$, $Cu_2(OH)_2^{2+}$, $Cu_3(OH)_4^{2+}$ and $CuSO_4^0$; the composition of the solid phases being CuS(s), $Cu(OH)_2$(s) and CuO(s).

For all the data sets presented, the $CuS_{(s)}$ precipitate dominates over $Cu(OH)_{2(s)}$ or $CuO_{(s)}$ precipitates, for the entire pH range investigated.

Large differences can be observed between the predicted theoretical solubility limits of the $CuS_{(s)}$ solid, depending on the values of the constants used in the model for the hydrogen sulfide ligand, and for the CuS^0 species, as well as depending on the presence of polysulfide complexes. The largest difference is 4 to about 10 orders of magnitude at acidic and basic pH, respectively. As far as the acidity constant values of hydrogen sulfide are concerned, Licht[34] proposed that the most probable value for the second acidity constant is log Ka_2 = -17.3 ($\pm$ 0.3). Therefore, data sets 1 and 3 should be excluded.

The difference between data sets 2, 4 and 5 at pH $<$ 11 can be attributed to the change in the $CuS_{(s)}$ solubility product value. At basic pH (pH $>$ 11), the solubility limit is affected by the CuS^0 formation constant value (data sets 2 and 4).

When all the polysulfide species are taken into account in the model (data sets 6 and 7), the solubility of copper controlled by the CuS precipitate is highly enhanced (comparison between data sets 2 and 6 as an example). From data set 6, $CuHS^{+}$ and $Cu(HS)_2^0$ dominate as aqueous species at $1 \leq$ pH ≤ 6 (no dissociation of copper sulfide complexes at acidic pH, as previously observed[37]). Then, $CuS(HS)^{-}$ becomes the major aqueous species in equilibrium with the CuS precipitate at $7 \leq$ pH ≤ 14.

It should be noted that for data set 7, the log β for CuS^0 was selected at 27.5 ($<$ 30.4 as seen in Table 1) to satisfy the upper limits of the log $K_{cond} \leq -8.3$ ($CuS_{(s)} \leftrightarrow CuS^0$) established by Shea and Helz.[39] From data set 7, the major aqueous species in equilibrium with the CuS solid are identical to those calculated from data set 6. Changing the value of the CuS^0 constant in data set 7 does not affect the solubility limit or the nature of aqueous dominant species.

Comparison between Solubility Domain Approach, Commercial Simulators and Experimental Data. In Figure 3, several sets of data collected from the solubility domain approach (S/Cu ratio $>$ 1/1) are compared with solubility curves obtained with three commercial modeling tools (OLI Systems,

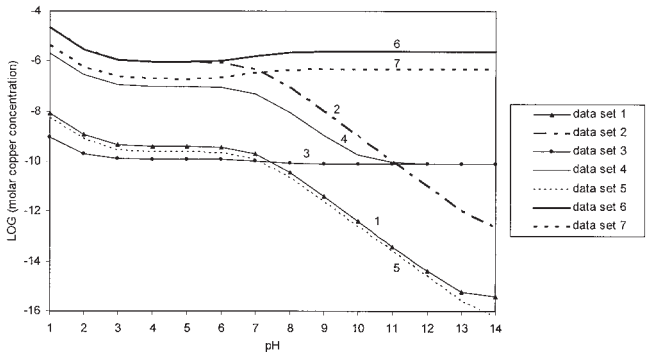

Figure 2. Theoretical solubility limits for the copper-sulfide system calculated using the solubility domain approach, from different literature sources. S/Cu ratio > 1/1.

Data set 1: $CuS_{(s)}$ and CuS^0 from Bollinger et al.[18]; $CuHS^{+}$ and $Cu(HS)_2^0$ from Dyrssen[36]; $Cu_2S_3^{2-}$ from Luther et al.[37]; HS^{-} and S^{2-} from Smith and Martell[31]. *Data set 2*: Data set 1 except HS^{-} and S^{2-} from Licht[34]. *Data set 3*: Data set 1 except $CuS_{(s)}$, CuS^0 from Dyrssen[36]. *Data set 4*: Data set 3 except HS^{-} and S^{2-} from Licht[34]. *Data set 5*: Data set 2 except $CuS_{(s)}$ (covellite) from Shea and Helz[35]. *Data set 6*: Data set 2 plus $CuS(HS)^{-}$, $CuS(HS)_2^{2-}$ and $CuS(HS)_3^{3-}$ from Shea and Helz[39]. *Data set 7*: $CuS_{(s)}$ (poorly crystalline solid) from Shea and Helz[35]; $CuHS^{+}$ and $Cu(HS)_2^0$ from Dyrssen[36]; CuS^0, $CuS(HS)^{-}$, $CuS(HS)_2^{2-}$ and $CuS(HS)_3^{3-}$ from Shea and Helz[39]; $Cu_2S_3^{2-}$ from Luther et al.[37]; HS^{-} and S^{2-} from Licht[34].

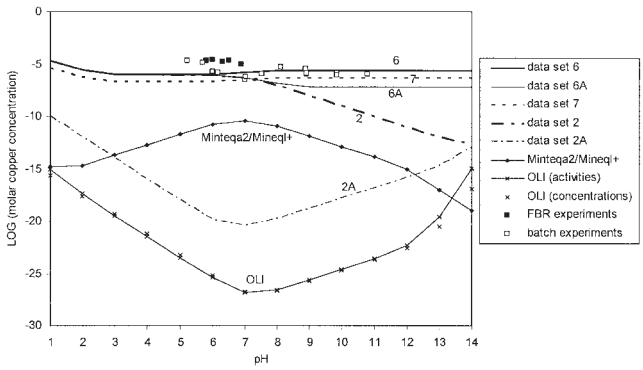

Figure 3. Theoretical solubility limits for the copper-sulfide system calculated from the solubility domain approach, and from OLI Systems, Inc. ESP Process and Minteqa2/Mineql+ (influence of the nature of the species taken into account in the model, on the solubility limit; comparison with experimental results (this study; Peterson[46]); S/Cu ratio > 1/1.)

Data set 6: $CuS_{(s)}$ and CuS^0 from Bollinger et al.[18]; $CuHS^+$ and $Cu(HS)_2^0$ from Dyrssen[36]; $CuS(HS)^-$ $CuS(HS)_2^{2-}$ and $CuS(HS)_3^{3-}$ from Shea and Helz[39]; $Cu_2S_3^{2-}$ from Luther et al.[37]; HS^- and S^{2-} from Licht[34]. *Data set 6A*: Data set 6 without $CuS(HS)^-$. *Data set 7*: $CuS_{(s)}$ (poorly crystalline solid) from Shea and Helz[35]; $CuHS^+$ and $Cu(HS)_2^0$ from Dyrssen[36]; CuS^0, $CuS(HS)^-$, $CuS(HS)_2^{2-}$ and $CuS(HS)_3^{3-}$ from Shea and Helz[39]; $Cu_2S_3^{2-}$ from Luther et al.[37]; HS^- and S^{2-} from Licht[34]. *Data set 2*: $CuS_{(s)}$ and CuS^0 from Bollinger et al.[18]; $CuHS^+$ and $Cu(HS)_2^0$ from Dyrssen[36]; $Cu_2S_3^{2-}$ from Luther et al.[37]; HS^- and S^{2-} from Licht[34]. *Data set 2A*: Data set 2 without CuS^0, $CuHS^+$, $Cu(HS)_2^0$ and $Cu_2S_3^{2-}$. *OLI Systems Inc. ESP Process* does not take into account neither aqueous sulfide complexes, nor $Cu_2(OH)_2^{2+}$, $Cu_3(OH)_4^{2+}$. *Minteqa2/Mineql+* take into account only one aqueous sulfide complex as $Cu(HS)_3^-$; $Cu_2(OH)_2^{2+}$ not present.

Inc. ESP Process, Minteqa2 and Mineql+), as well as experimental results (this work; van Hille et al.[46]). The solubility of copper simulated with Mineql+ is identical to that given by Minteqa2. The Aspen Plus simulation did not reveal concentrations lower than 10^{-15} mol.L^{-1} and reported a residual aqueous copper concentration as 0, irrespective of the pH. No results from Aspen could, therefore, be compiled in Figure 3.

The OLI Systems, Inc. ESP Process solubility curve calculated from activities is in good agreement with that calculated from concentrations with the solubility domain approach using OLI Systems, Inc. constant values, up to pH 13. In highly basic solutions, the approximation made with the solubility domain approach becomes less reliable.

Significant differences can be observed between theoretical and experimental residual aqueous copper concentrations, depending on the modeling method used and the nature of species taken into account in the model. The greatest difference between two curves can reach about 20 orders of magnitude. The best agreement between theoretical and experimental solubility was found with data sets 6 and 7, when all the readily and sparingly soluble species are considered. Note that only near-equilibrium conditions were reached in the fluidized-bed reactor,[46] whereas the model assumes that the system is at complete equilibrium. Nonetheless, although these experimental results cannot be compared with those at complete thermodynamic equilibrium, they do reflect realistic industrial operating conditions corresponding to the residual soluble copper concentration found in the outlet stream. Controlled solubility measurements carried out in batch reactors at different pH values confirm the highest values of copper solubility obtained both from thermodynamic modeling (with data sets 6 and 7), and from the experimental study in the fluidized-bed reactor. Eliminating the $CuS(HS)^-$ thermodynamic data from the model (data set 6A), due to its approximate determination,[39] moves away the solubility limit from experimental data at pH $>$ 7. The best agreement between the model (data set 6 or 7), and the experiments is found at $6 < pH < 11$. From the model, $CuHS^+$ and $Cu(HS)_2^0$ dominate in solution until pH 6; from pH 7, $CuS(HS)^-$ is the major aqueous species in equilibrium with the CuS solid (taken as a poorly crystalline precipitate).

Soluble copper sulfide and polysulfide complexes ($CuHS^+$, $Cu(HS)_2^0$, $CuS(HS)^-$) have been identified as the major species in equilibrium with the copper sulfide precipitate (data set 6 or 7). When these species are not taken into account in the model (such as data sets 2, 2A and OLI Systems, Inc.), the copper solubility is severely underestimated. The drastic change in copper solubility observed while using the OLI Systems, Inc. and Minteqa2 commercial simulators is ascribed to the species $Cu(HS)_3^-$ taken into account in Minteqa2 only. A personal databank has to be created when using OLI Systems, Inc., Aspen Plus, Minteqa2 or Mineql+ modeling tools for assessing copper sulfide speciation. The best fit obtained with both controlled and uncontrolled solubility measurements was found with thermodynamic data listed in Table 1 in bold characters.

From Figure 3, the measured solubility varied from log [Cu] $= -4.7$ to -6.5 in the investigated (5 – 11) pH range. From both modeling and experimental results, no specific pH value for optimal precipitation can be deduced although a pH slightly below 7 should be chosen to minimize post-neutralization costs. Under these conditions, aqueous copper will persist in solution mainly as $Cu(HS)_2^0$ and $CuS(HS)^-$ with residual aqueous copper concentrations (about 0.1 ppm) complying with drinking water regulations (1 ppm,[47] 1.3 ppm[48]). Experimentally, a more compact CuS precipitate could be obtained at acidic pH rather than basic pH.[46] More recently, the concentration of free HS^- ions in solution was found to play an important role in the precipitation efficiency in the fluidized-bed reactor,[49] significantly changing the morphology of the precipitate. Under certain operating conditions which modified the sulfide speciation (and, thus, the concentration of free HS^- in solution), either a compact CuS precipitate (low bisulfide to copper ratio) was formed or a very fine precipitate (high bisulfide to copper ratio) which could not be removed through 0.22 μm filtration. High local supersaturation levels (through the influence of chemical speciation as well as mixing conditions) were also responsible for fines formation. All these results show that a thorough knowledge of the complex reaction chemistry of the copper sulfide system, as well as hydrodynamics is needed to control the precipitation process efficiency.

Thermodynamic modeling of cobalt precipitation as carbonate

Process simulation: The efficiency of cobalt removal from aqueous solution by a carbonate precipitation technique at 25°C was simulated using OLI Systems, Inc. ESP Process. The

simulation flowsheet was similar to that illustrated in Figure 1. Different molar ratios of carbonate/cobalt were investigated and varied from 1/1 to 10/1, carbonate and cobalt flow rates being equal. The carbonate feed water had a constant concentration equal to 4.22×10^{-3} mol.L^{-1} (the cobalt concentration varied between 4.22×10^{-4} mol.L^{-1} and 4.22×10^{-3} mol.L^{-1}). Species considered in the model are presented in Table 2.

At a CO_3/Co ratio = 1/1, the $CoCO_{3(s)}$ solid phase dominates in the pH range 7.0-8.5, $Co(OH)_{2(s)}$ dominating at more basic pH values. Maximum removal of cobalt as carbonate solid (73.5%) is expected at pH = 8.0. Residual cobalt species in solution are Co^{2+} (18.3%), $CoSO_4^0$ (8.1%) and $Co(OH)^+$ (0.1%). Increasing the CO_3/Co ratio up to 5/1 enhances $CoCO_3$ precipitation to a maximum of 88.4% at CO_3/Co ratio = 5/1, but restricts the pH range (7.75-8.50) of $CoCO_3$(s) stability. The $CoCO_3$ precipitation efficiency then decreases in the range of ratios from 5/1 to 10/1, $Co(OH)_{2(s)}$ becoming the most stable solid species at pH > 8.5. From the OLI Systems, Inc. ESP Process simulation, the best conditions for cobalt-carbonate precipitation were found to be at pH 8.25, with a slight excess of carbonate compared to aqueous cobalt stream. Under these conditions, the maximum national legislative limit on concentration of cobalt remaining in solution is exceeded (1 ppm = 1.70×10^{-5} mol.L^{-1}).[47] Thus, according to the OLI Systems, Inc. ESP Process simulation, precipitation is not a viable technique to remove cobalt as carbonate to below regulatory levels.

Comparison between the Solubility Domain Approach, Commercial Simulators and Experimental Data. The solubility of the cobalt precipitate was measured as a function of time from both precipitation and dissolution experiments, at different pH values. Figure 4 shows that, at identical controlled pH (8.80 ± 0.05) and temperature (25 ± 1 °C), a metastable equilibrium from both oversaturated and undersaturated solutions is reached within about 13 days.

Figure 5 illustrates the dominance of the different solid phases ($CoCO_{3(s)}$, $Co(OH)_{2(s)}$, $3CoCO_3 \cdot 4Co(OH)_{2(s)}$) as a function of pH, for the solubility domain approach, taking into account all the soluble cobaltous species (free Co^{2+}, cobalt hydroxide, carbonate and sulfate complexes) or only the free Co^{2+} species. When all the soluble complexes are accounted for, $CoCO_3$(s) and $Co(OH)_{2(s)}$ seem to be the most stable solids at pH <11 and pH ≥ 11, respectively.

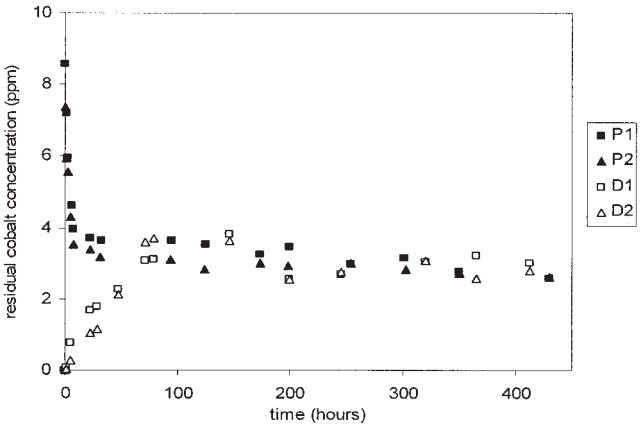

Figure 4. Residual aqueous cobalt concentration as a function of time from replicated precipitation (P1 and P2) and dissolution (D1 and D2) experiments.

pH = 8.80 ± 0.05; T = 25 ± 1 °C. For P1 and P2: $[Co(II)]_{initial}$ = 24.8 ppm (4.22×10^{-4} mol.L^{-1}).

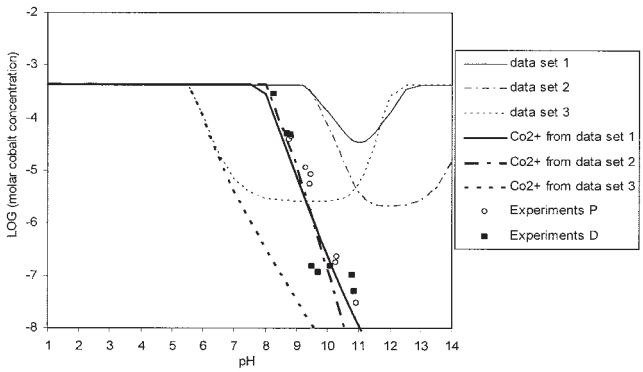

Figure 5. Theoretical solubility limits for the cobalt-carbonate system calculated from the solubility domain approach (influence of the nature of the species taken into account in the model, on the solubility limit; comparison with experimental results (P: precipitation experiments and D: dissolution experiments); CO_3/Co ratio =10/1.)

Data set 1:$3CoCO_3 \cdot 4Co(OH)_{2(s)}$ from Mostafa et al.[45]; all soluble species from Table 2 taken into account. *Data set 2*: $Co(OH)_{2(s)}$ from Smith and Martell[31]; all soluble species from Table 2 taken into account. *Data set 3*: $CoCO_{3(s)}$ from Grauer[44]; all soluble complexes from Table 2 taken into account.

However, residual aqueous cobalt concentrations determined experimentally at different pH values follow the simulated free Co^{2+} ion concentration controlled either by the hydroxide or the hydroxy-carbonate solid. Therefore, it appears that neither the soluble complexes are stable in solution nor the $CoCO_{3(s)}$ precipitate, under our experimental conditions.

Figure 6 gives the predictions obtained with commercial simulators (OLI Systems, Inc., Minteqa2, Mineql+), for a CO_3/Co ratio greater than 1/1 (10/1 as an example).

Minteqa2 (as well as Mineql+) do not reflect a realistic solubility limit and under-estimates it at 4.5 < pH < 10.5. Differences observed with the experimental results can be attributed to the value selected for the $CoCO_{3(s)}$ formation constant at pH < 9.

With OLI Systems, Inc. simulation, the free Co^{2+} ion (and $CoSO_4^0$ as minor soluble species) is in equilibrium with the $CoCO_{3(s)}$ solid at 8.0 < pH < 8.5 which has the lowest formation constant value selected from the literature. In this case, the model fits the experimental data well. At pH > 8.5, $Co(OH)_{2(s)}$ dominates, in equilibrium with soluble hydroxide complexes and the modeled solubility limit appears over-estimated at pH > 9.5. Modeling the solubility with only Co^{2+} as the soluble form (in equilibrium with either $CoCO_{3(s)}$ or $Co(OH)_{2(s)}$ solid from OLI Systems, Inc. database) leads to a better prediction compared to the experimental data. However, the best prediction is obtained while taking into account the formation of the hydroxy-carbonate solid (Co^{2+} from data set 1) at 10 < pH < 11.

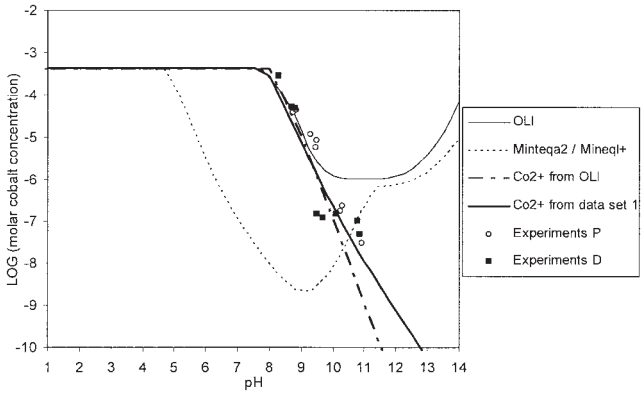

Figure 6. Theoretical solubility limits for the cobalt-carbonate system calculated from the solubility domain approach and from OLI Systems, Inc. ESP Process, Minteqa2 and Mineql+; comparison with experimental results (P precipitation and D dissolution experiments); CO_3/Co ratio =10/1.

Data set 1: $3CoCO_3$. $4Co(OH)_{2(s)}$ from Mostafa et al.[45]. *OLI Systems Inc. ESP Process* does not take into account $C°CO_3^0$, $Co(HCO_3)^+$, $Co_2(OH)^{3+}$, $Co_4(OH)_4^{4+}$, $3CoCO_3$. $4Co(OH)_{2(s)}$. *Minteqa2* and *Mineql+* do not take into account $CoCO_3^0$, $Co(HCO_3)^+$, $Co(OH)_4^{2-}$, $Co_2(OH)^{3+}$, $Co_4(OH)_4^{4+}$, $3CoCO_3$. $4Co(OH)_{2(s)}$.

From a critical review of the literature combined with an experimental study, efficient precipitation of cobalt can be obtained at pH $>$ 9.0, with a residual aqueous cobalt concentration ($<$ 0.015 ppm at pH = 10) complying with drinking water regulations (1 ppm).[47] The simulated solubility limit suggests the formation of a mixed cobalt hydroxy-carbonate phase rather than a simple hydroxide or a carbonate solid, as previously pointed out.[44,45] Soluble hydroxide and carbonate complexes might not be stable in solution, thus limiting the solubility of the mixed precipitate.

Conclusion and further considerations

In this article, the importance of critically evaluating any simulated precipitation results obtained from commercial software tools containing thermodynamic databases is stressed. It is essential to select both comprehensive and reliable thermodynamic data for adequately modeling aqueous chemistry in precipitation processes, and in particular to account for the potential formation of soluble complexes. These species may significantly increase residual aqueous metal concentrations in solution. This aspect is especially important when dealing with toxic metals. However, experimental investigation is still needed to assess the nature of the aqueous species formed in solution that govern the solubility limit.

In addition to the factors outlined earlier, prediction and control of precipitation processes are very difficult tasks. Besides the many parameters that can influence the solid stability (pH, redox potential, reagents concentration, molar ratio and aging), particle size and morphology are significantly influenced by hydrodynamic parameters. Both the local and global supersaturations may control precipitation processes, such as nucleation and growth and ultimately the efficiency of the process. The validity of the model can, therefore, be compromised if it does not take into account mechanisms such as fines formation, and other key parameters defining solid stability conditions, as previously pointed out.[8,46,50] Therefore, thermodynamically based simulators, such as OLI Systems, Inc. ESP Process and Aspen Plus cannot be used to model precipitation process efficiency but are very useful in examining the aqueous chemistry. Moreover, if data relating to hydrodynamic parameters, reaction models and kinetic parameters (depending on the industrial process investigated) can be integrated into the simulators,[51-54] their usefulness in process simulation can be greatly enhanced. The great improvement that some aqueous chemistry simulators (such as Mineql+) now offer to users is that their data are readily accessible, which provides a way for modelers to change any questionable data or to add extra information. Their major drawback is that the original source of individual model parameters is not known, and, thus, prevents users from easily checking data reliability.

Acknowledgments

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