

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231375315>

Controlled Nickel Sulfide Precipitation Using Gaseous Hydrogen Sulfide

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · JANUARY 2008

Impact Factor: 2.59 · DOI: 10.1021/ie0711224

CITATIONS

13

READS

132

3 AUTHORS, INCLUDING:



Rob Van Hille

The Moss Group, Cape Town, South Africa

70 PUBLICATIONS 895 CITATIONS

SEE PROFILE



Alison Lewis

University of Cape Town

61 PUBLICATIONS 684 CITATIONS

SEE PROFILE

Controlled Nickel Sulfide Precipitation Using Gaseous Hydrogen Sulfide

Nazneen Karbanee, Robert. P. van Hille, and Alison E. Lewis*

Crystallization and Precipitation Research Unit, Chemical Engineering Department, University of Cape Town, Rondebosch, Cape Town, South Africa 7701

In the precipitation of metal sulfides from solution, either aqueous or gaseous sources of sulfide can be used. In this work, batch aqueous and gaseous sulfide experiments confirmed that no precipitation of Ni^{2+} was possible when only the $\text{H}_2\text{S}(\text{aq})$ sulfide species was available for reaction. Gaseous sulfide precipitation of Ni^{2+} using $\text{H}_2\text{S}(\text{g})$ was carried out in a semibatch bubble reactor. Alkalinity was supplied in the form of NaOH to facilitate formation of bisulfide ions and thus precipitate NiS. When NaOH flow rates were an order of magnitude lower than $\text{H}_2\text{S}(\text{g})$ flow rates, the precipitation was controlled at approximately pH 3.5. Dissolution of precipitates was observed and confirmed in batch experiments by monitoring nickel and sulfide concentrations with time at varying Ni:S molar ratios. The molar ratio of NaOH to $\text{H}_2\text{S}(\text{g})$ at which efficient NiS precipitation occurred with no significant reagent wastage was found to be approximately 1.66:1 for the flow rates tested. Sulfide wastage occurred through either accumulation in the reaction solution or being lost as unabsorbed $\text{H}_2\text{S}(\text{g})$. Below this molar ratio, precipitation of $\text{Ni}(\text{OH})_2$ may occur since the hydroxide ion acts as the precipitating agent in the absence of sufficient sulfide.

Introduction

Sulfide precipitation of metals has many possible applications, including removal of base metals in base metal refinery processes^{1,2} and purification of hydrometallurgical effluents.³ The precipitation of Ni(s) in the hydrogen reduction autoclave of the modified Sherritt-Gordon Leach process used at Impala produces an aqueous, sulfate and ammonia rich stream containing significant amounts of Ni (1.25 g/L) and Co (0.2–0.3 g/L). The removal of nickel and cobalt from this stream is desirable, since these are impurities that contaminate the recovered $(\text{NH}_4)_2\text{SO}_4$. Sulfide precipitation of heavy metals is attractive for this purpose due to the low solubilities of metal sulfides over a broad pH range and the rapid precipitation kinetics.⁴ However, in combination, these factors are disadvantageous to the sulfide precipitation process because they lead to rapid generation of extremely high supersaturation, resulting in difficulty in the control of the precipitation process and the formation of fine particles.

The use of a gaseous sulfide source as opposed to an aqueous one has been proposed^{5,6} to decrease the rate of generation of supersaturation by exploiting the mass-transfer resistance to dissolution of $\text{H}_2\text{S}(\text{g})$ and thus to exert a measure of control over the precipitation process.

The dissolution of $\text{H}_2\text{S}(\text{g})$ is followed by the pH-dependent speciation of $\text{H}_2\text{S}(\text{aq})$:



There is good agreement of values for $\text{p}K_1$ in literature, but values for $\text{p}K_2$ vary considerably between 12.9⁹ and 17.6 \pm 0.3.¹⁰ Most calorimetric determinations of $\text{p}K_2$ are found to be between 12 and 14. Stephens and Cobble¹¹ report $\text{p}K_2 = 13.78$, and Wagman et al.¹² report $\text{p}K_2 = 12.92$. The most recent value for $\text{p}K_2$ determined by surface sulfidation of crystalline sulfur is taken in this study, as shown above in eq 2. This value is in

good agreement with other noncalorimetrically determined $\text{p}K_2$ values: $\text{p}K_2 = 17$,¹³ $\text{p}K_2 = 17 \pm 1$,¹⁴ and $\text{p}K_2 = 17.1 \pm 0.3$.¹⁵

Koltoff and Moltzau¹⁶ proposed that sulfide precipitation involves the reaction of bisulfide ions to initially form the metal hydrosulfide which, by secondary loss of hydrogen sulfide, results in the formation of the metal sulfide itself. Lewis and van Hille¹⁷ have also suggested that the principle sulfide species participating in the sulfide precipitation reaction was the bisulfide ion. Thus, the expected reaction for nickel sulfide precipitation is



As the NiS precipitation reaction occurs according to eq 3, the generated protons/ H^+ ions increase acidity and spontaneous precipitation no longer occurs.¹⁸ Supporting evidence is provided by Hammack et al.⁵ who state that the theoretical lower pH limit for precipitation of Ni^{2+} by gaseous sulfide is 5.8. The increasingly acidic environment limits dissolution of $\text{H}_2\text{S}(\text{g})$ and prevents speciation of $\text{H}_2\text{S}(\text{aq})$, thus depressing the bisulfide ion (HS^-) concentration. When the supply of HS^- ions is exhausted, then precipitation is no longer possible.

NiS precipitation can be facilitated by increasing the solubility of $\text{H}_2\text{S}(\text{g})$ through increase of the temperature, increase of pressure, and/or the use of a catalyst. Increasing the temperature and partial pressure of $\text{H}_2\text{S}(\text{g})$ to 120 °C and 355 kPa causes precipitation of nickel as a sulfide from a solution at pH 3. Precipitation of NiS occurred when the pressure of $\text{H}_2\text{S}(\text{g})$ was increased to 709 kPa at room temperature and nickel powder employed as a catalyst. Increasing the temperature to 120 °C at atmospheric pressure increased the rate of reaction and was fast enough not to require a catalyst.⁷

In this study NiS precipitation was facilitated by providing alkalinity to neutralize the pH lowering effect of generated H^+ ions. The addition of alkalinity simultaneously increased $\text{H}_2\text{S}(\text{g})$ solubility and shifts the equilibrium of eq 1 toward the right, thus providing HS^- ions which were then available to precipitate Ni^{2+} ions. NaOH was fed continuously into the reactor, and the concentrations were varied in order to determine the effect on nickel removal. The threshold NaOH concentration below which $\text{H}_2\text{S}(\text{g})$ dissolution limits the presence of sulfide in

* To whom correspondence should be addressed. Phone: +27 21 650 4091. Fax: +27 21 650 5501. E-mail: Alison.Lewis@uct.ac.za.

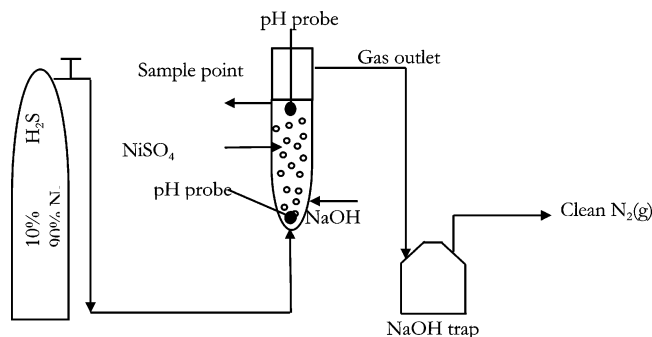


Figure 1. Schematic representation of the semibatch bubble column reactor.

solution but does not limit nickel removal was determined. This is advantageous as it is an initial step toward optimization of the precipitation process by minimizing reagent excesses.

Materials and Methods

Batch Experiments. Batch experiments were conducted in a 750 mL closed reactor, continuously stirred with a Rushton impeller at 330 rpm. The reactor was charged with a 200 ppm Ni^{2+} solution in the form of NiSO_4 . An equimolar aqueous source of sulfide was slug-dosed into the reactor at time $t = 0$ min. Samples of 5 mL each were periodically withdrawn and filtered through a $0.45 \mu\text{m}$ nylon membrane syringe filter and analyzed using atomic absorption spectroscopy (AAS). The pH of the reacting solution was measured continuously throughout the duration of the run (pH meter details).

Bubble Column. The semibatch bubble column reactor (Figure 1) consisted of a cylindrical glass column charged with a 200 ppm Ni^{2+} sulfate solution. The gaseous sulfide source was $10 \pm 3\%$ $\text{H}_2\text{S}(\text{g})$ and 90% $\text{N}_2(\text{g})$. The sulfide gas mixture was sparged into the reactor through a distribution cap fitted to the bottom of the reactor. Unreacted $\text{H}_2\text{S}(\text{g})$ was passed into a 1 L, 0.5 M NaOH trap in order to produce cleaned, sulfide-free $\text{N}_2(\text{g})$. Reaction was facilitated by the addition of NaOH of varying concentrations. The pH was measured at the top and bottom of the bubble column.

Reagents. All reagents ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, NaOH, and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) used in this investigation were analytical grade Merck chemicals. Solutions were made up to required concentrations using distilled water.

Sample Collection and Analysis. Liquid samples were taken from the top of the column at 30 s intervals for the first 5 min and at 1 min intervals between 5 and 10 min. Each sample was filtered through a $0.45 \mu\text{m}$ nylon membrane filter and analyzed to determine nickel in solution (Varian SpectraAA-30 atomic absorption spectrophotometer) and free sulfide (method described below).

Total free sulfide ($\text{H}_2\text{S}(\text{aq})$, HS^- , and S^{2-}) in solution was determined using a spectrophotometric method based on the reaction of sulfide with *p*-phenylenediamine. The assay is only accurate to concentrations of 1.50 mg/L; therefore dilutions of samples were made. The samples were analyzed immediately to prevent sulfide oxidation. A volume of sample, usually 15–50 μL , was transferred to a test tube containing 200 μL of zinc acetate to halt the reaction. The volume was made up to 5 mL by addition of oxygen free distilled water. A 500 μL aliquot of *N,N*-dimethyl-*p*-phenylenediamine hydrochloride solution followed by 500 μL of ferric chloride solution was added to the sample. The sample was mixed and allowed to react completely, about 5 min. The absorbance was read at 665 nm, and the concentration read off a standard curve.

Table 1. Experimental Conditions for Batch Experiments

run	pH _i ^a	$\text{H}_2\text{S}(\text{aq})$, HS^- , or S^{2-} ^b	$[\text{Ni}^{2+}]:$ [sulfide] ^c	$[\text{Ni}^{2+}]$ (mg/L)
B01	11.95 (unadjusted)	HS^-	1: 1	201.10
B02	9.88	HS^-	1: 1	215.45
B03	4.24	$\text{H}_2\text{S}(\text{aq})$	1: 1	238.95

^a Initial pH of $\text{Na}_2\text{S}(\text{aq})$. ^b Theoretical sulfide species available for reaction. Based on $\text{p}K_1 = 6.99$ ⁷ and $\text{p}K_2 = 17.4$.⁸ ^c Molar ratio of reagents.

Table 2. Details of Batch Experiments to Determine the Effect of Metal to Sulfide Ratio on Nickel Removal by Batch Aqueous Sulfide

run	$[\text{Ni}^{2+}]:$ [sulfide] ^a	$[\text{Ni}^{2+}]$ (mg/L)
B04	1: 0.5	198.2
B01	1: 1.0	201.1
B05	1: 1.5	206.8
B06	1: 2.0	179.8

^a Molar ratio of reagents.

Table 3. Experimental Conditions for Semibatch Gaseous Bubble Column Reactions

run	10% $\text{H}_2\text{S}(\text{g})$ and 90% N_2 (L/min)	$\text{H}_2\text{S}(\text{g})$ (mmol/min)	NaOH (mmol/min)
L01	0.2	0.893	0.100
L02	0.6	2.68	0.100
L03	0.8	3.57	0.175
L04	0.8	3.57	0.150
L05	0.8	3.57	0.100
L06	0.8	3.57	0
T01	0.8	3.57	2.23
T02	0.5	2.23	2.23
T03	0.3	1.34	2.23
T04	0.1	0.446	2.23
T05	0.8	3.57	1.75
T06	0.5	2.23	1.75
T07	0.3	1.34	1.75
T08	0.1	0.446	1.75
T09	0.3	1.34	1.20
T10	0.2	0.893	1.20
T11	0.1	0.446	1.20

Experimental Design. (a) Batch Aqueous Experiments To Establish the Participating Sulfide Species. Experiments were run to determine the sulfide species participating in the precipitation of NiS . In these batch experiments (Table 1), the initial pH (pH_i) of the sulfide slug dose was adjusted such that only a single sulfide species was present before addition to the NiSO_4 solution.

Various $\text{Ni}:\text{S}$ molar ratios were tested (Table 2) to ascertain the effect of excess or limiting sulfide reagent on the precipitation reaction because, during batch experimentation with low alkalinity flow rates, a dissolution phenomenon was encountered when excess sulfide was present in solution. These batch experiments with varying sulfide dosage were designed to further study the dissolution effect.

(b) Semibatch Gaseous Bubble Column Experiments. Gaseous sulfide experiments were conducted using NaOH flow rates an order of magnitude lower than $\text{H}_2\text{S}(\text{g})$ flow rates; thus, experiments are NaOH limited. At these concentrations of NaOH and $\text{H}_2\text{S}(\text{g})$ the mass-transfer delay of the sulfide source was not apparent.

Bubble column experiments (Table 3) were then conducted to study the efficiency of Ni^{2+} removal by determining the threshold at which $\text{H}_2\text{S}(\text{g})$ mass transfer limits the presence of aqueous sulfide while maintaining the same rate of nickel removal. Thus, wastage of sulfide reagent is minimized without compromising control.

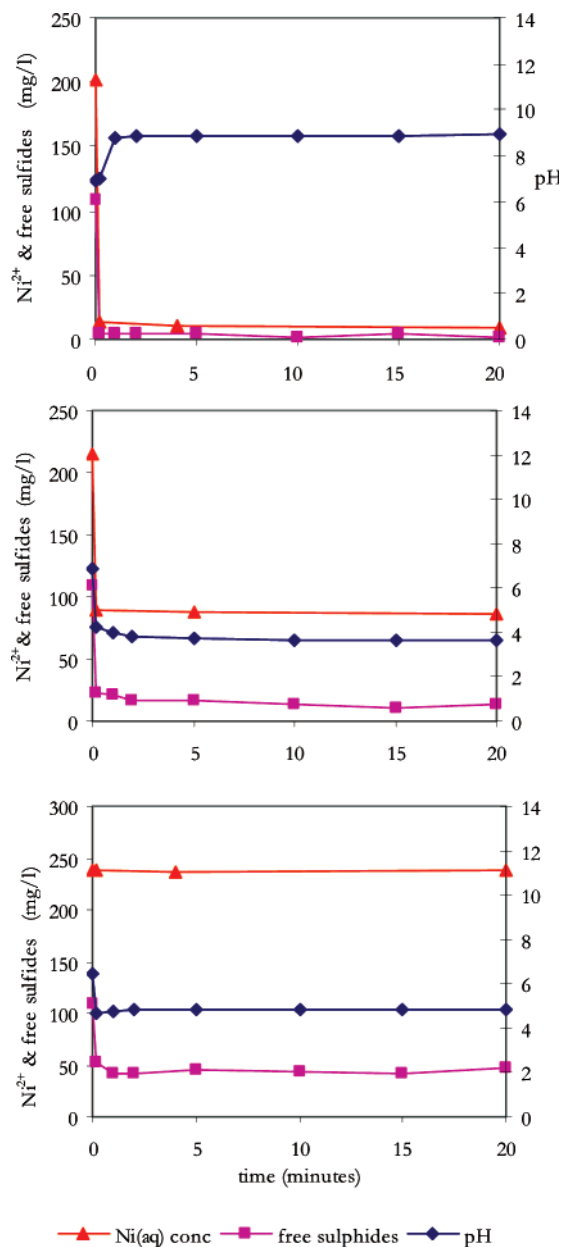


Figure 2. Results of slug dosage of aqueous sulfide to a batch reactor $pH_i = 11.59$ (top) [B01], $pH_i = 9.88$ (middle) [B02], and $pH_i = 4.24$ (bottom) [B03], showing Ni^{2+} concentration, free sulfide concentration, and pH in solution.

Results and Discussion

Participating Sulfide Species. Batch experimental results shown in Figure 2 indicate no Ni^{2+} removal occurs when the pH drops below pH 4, suggesting that precipitation of NiS cannot occur in the presence of only the $H_2S(aq)$ species. When $pH_i = 11.59$ (B01), the major sulfide species initially present was the bisulfide ion and the sulfide removed was stoichiometrically equivalent to the amount of nickel removed, with 11 ppm nickel remaining in solution. The OH^- ions in solution neutralized the H^+ ions released by reaction (eq 3) and speciation (eq 1), and thus the pH did not drop to as great an extent as $pH_i = 9.88$ (B02). The final solution pH was relatively alkaline, leading to the hypothesis that nickel polysulfide ions were responsible for incomplete precipitation of nickel.

At $pH_i = 9.88$, the bisulfide species was at the highest concentration (99.86% HS^-) within the sulfide solution but incomplete conversion of nickel was observed. The pH after

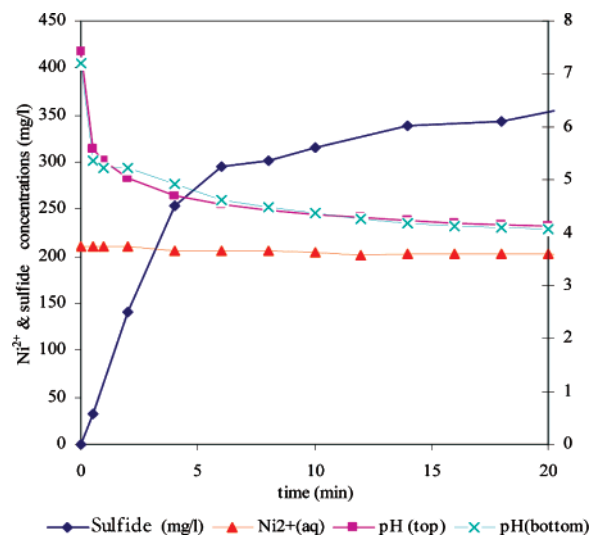


Figure 3. Results of semibatch NiS precipitation using $H_2S(g)$ [L05] showing Ni^{2+} concentration, free sulfide concentration, and pH in solution.

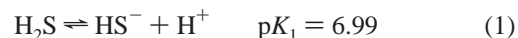
reaction was lower (pH 3.95) when $pH_i = 9.88$ (B02) because the initial hydroxide ions in solution were insufficient to neutralize the H^+ ions generated by the precipitation reaction. As a result of the pH decrease to below pH 4, bisulfide ions were unavailable and the reaction was unable to continue; thus, nickel in solution could not be completely precipitated. When $pH_i = 4.24$ (B03), there was $H_2S(aq) = 99.76\%$ in solution initially and no significant precipitation of nickel occurred. The acidic pH remained constant throughout the run, and sulfide in solution decreased due to $H_2S(g)$ release.

Therefore, these results suggest that sulfide species other than $H_2S(aq)$ must be made available in order to precipitate Ni^{2+} .

Precipitation Using $H_2S(g)$. When $H_2S(g)$ was bubbled through the nickel sulfate solution, the pH dropped rapidly (within 1 min) to an acidic value of pH 5.53 and remained acidic for the duration of the run. At these acidic pH values the precipitation of nickel was negligible, with the nickel concentration decreasing by only 10 ppm over the 30 min duration of the experimental run. Jackson⁷ states that, kinetically, NiS precipitation at standard conditions does not occur below pH 3. Hammack et al.⁵ state that the theoretical lower pH limit for precipitation of Ni^{2+} by gaseous sulfide is 5.8. This supports data generated from the batch experiments which indicates that $H_2S(aq)$ is unable to precipitate nickel.

The sulfide concentration increased rapidly between 0 and 6 min as the pH decreased to acidic values. After this, the sulfide concentration increased more slowly, approaching a saturation concentration at the constant pH = 4 attained in the solution. The abundance of protons present in solution at these acidic pH values prevented the speciation of the $H_2S(aq)$ into HS^- , and thus NiS precipitation was not possible.

Therefore, to precipitate nickel from solution using $H_2S(g)$, the bisulfide ion must be made available. This was achieved by shifting the equilibrium speciation of $H_2S(aq)$ toward HS^- (eq 1) through manipulation of the pH.



Since the pH becomes acidic during reaction (Figure 3), an alkali source was added to facilitate the precipitation of NiS.

In most existing sulfide treatment systems, an alkaline agent such as lime is first added to raise the pH to between 6 and 8 after which the sulfide precipitating agent is introduced to the system. Hammack et al.⁶ and Bhattacharyya et al.⁴ investigated

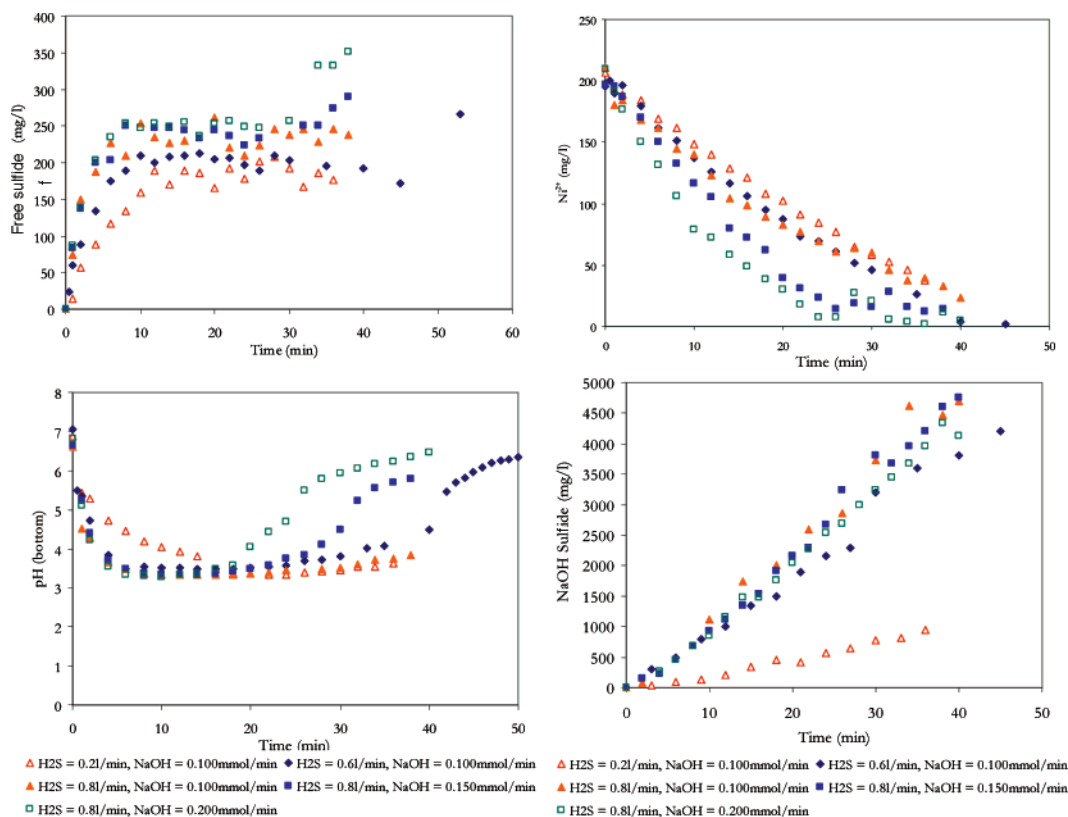


Figure 4. Results of semibatch NiS precipitation using H₂S(g) with low flow rates of NaOH [L1–L6] showing Ni²⁺ concentration, free sulfide concentration, pH in solution, and sulfide concentration in the sulfide trap with time (NaOH sulfide).

the combined effects of (a) sulfide–hydroxide precipitation and (b) sulfide followed by lime as precipitating agents. By the addition of lime or hydroxide ions (alkaline sources), pH manipulation was possible, leading to the complete precipitation of all metals present, and, further, selective precipitation of metals was possible at different pH values. Bryson and Bijsterveld¹ utilized ammonium sulfide to precipitate manganese and cobalt, thus combining the alkali source with the sulfide precipitation agent. Esposito et al.¹⁹ make use of independent addition of NaHCO₃ as well as sensitive sulfide control to precipitate ZnS using Na₂S and biogenic sulfide.

In this study, alkalinity in the form of NaOH, was supplied to the reactor at a constant rate in order to promote the speciation of H₂S(aq) toward HS[−] (eq 1) and thus facilitate NiS precipitation. The alkali source was provided during, as opposed to prior to, the sulfide precipitation and independent of the sulfide source in order to harness the speciation of HS[−] in a controlled manner. Therefore, the effect of various alkali feed rates on the rate of nickel removal and efficiency of sulfide usage.

Low NaOH Flow Rates. Figure 4 shows the effects of varying NaOH and H₂S(g) flow rates. The NaOH concentrations are all approximately an order of magnitude lower than the H₂S(g) concentrations (Table 2).

At the same NaOH concentration and varying H₂S(g) flow rates (0.2, 0.6, and 0.8 L/min) the rates of nickel removal from solution were very similar, and as the NaOH concentration increased (0.100, 0.150, and 0.200 mmol/min), the rates of nickel removal increased, suggesting that the alkalinity is controlling the rate of precipitation. For the former set of experiments, where NaOH = 0.100 mmol/min, 98.9% removal is achieved for H₂S(g) = 0.6 L/min, which would be expected for H₂S(g) = 0.2 and 0.8 L/min at the same alkalinity rate.

However, complete removal of nickel from solution was not achieved for the runs H₂S(g) = 0.8 L/min and NaOH = 0.150

and 0.200 mmol/min. Figure 4 shows that after approximately 93 and 97% nickel removal at 24 and 26 min, respectively, the nickel concentration in solution increased. The reintroduction of nickel into solution suggests that dissolution of precipitates occurred. The same phenomenon of re-dissolution of metal sulfide precipitates in the presence of excess sulfide was observed by van Hille et al.³ when copper precipitation was carried out in a fluidized bed reactor using Na₂S.

The concentrations of sulfide in solution were very high during reaction, ranging between 150 and 275 ppm as NaOH and H₂S(g) flow rates increased, leading to wastage of sulfide reagent within the reaction solution. Associated disadvantages of excess sulfide within the mother liquor after precipitation include safety as well as odor problems and recycling difficulties. Wastage of sulfide was also apparent in the large quantities of unabsorbed, unreacted sulfide present in the NaOH sulfide trap.

After the initial decrease in pH, the pH during the reaction was acidic pH (3.35–3.60). The acidic pH shown was a global effect resulting from the instantaneous speciation of H₂S(aq) to HS[−] (eq 1), facilitated by the alkalinity, followed by the instantaneous reaction of Ni²⁺ and HS[−] to form NiS, generating protons (eq 3) which reduced the pH. Around the region of the alkalinity entry point into the reactor local volume elements of higher pH occurred. However, since the rate of reaction was greater than the rate of macromixing, global acidic pH values were recorded and the pH values at the top and the bottom of the reactor were equivalent.

The constant acidic pH at which the reaction occurred allowed for only H₂S(aq) species to persist in solution, with HS[−] ions provided solely by the alkalinity supplied. The alkalinity added to the reactor was insufficient to raise the pH above acidic values during reaction but did facilitate the reaction, by promoting speciation of a portion of sulfide to HS[−], which kept the pH

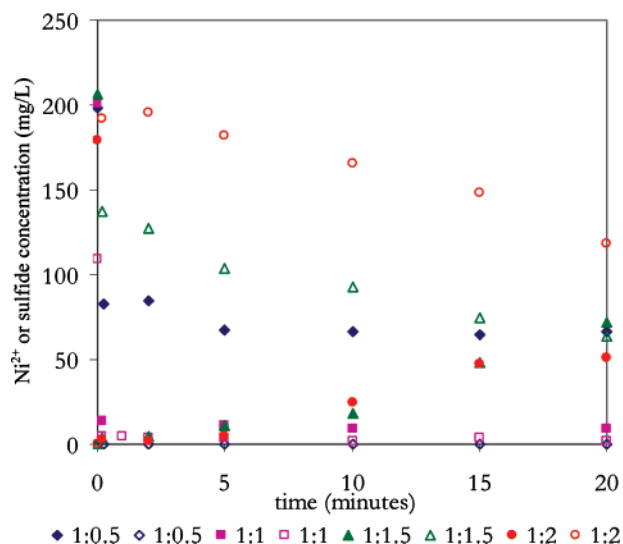


Figure 5. Change in nickel and sulfide concentrations (mg/L) for batch precipitation of nickel from NiSO_4 using Na_2S with varying ratios of Ni:S [B04, B01, B05, and B06]. Closed symbols = nickel; open symbols = sulfide.

Table 4. pH after Batch Precipitation of Nickel from NiSO_4 Using Na_2S for Various Ratios of Ni:S

run	ratio Ni:S	initial Ni^{2+} (ppm)	pH after reaction
B04	1:0.5	198.2	8.27 ± 0.02
B01	1:1.0	201.1	8.86 ± 0.05
B05	1:1.5	206.7	11.23 ± 0.05
B06	1:2.0	179.5	11.47 ± 0.04

acidic due to the generation of protons from NiS precipitation. The alkalinity was used to neutralize the protons released by speciation and not those released during reaction.

The following experimental results show the effect of varying the ratio of the nickel to sulfide ion concentrations, demonstrating the dissolution of NiS precipitates when excess sulfide ion was present in solution at neutral to alkaline pH values. Synthetic NiSO_4 solution was used with a concentration of 200 ppm Ni^{2+} (Figure 5). The proposed mechanism for dissolution is the formation of aqueous polysulfide ions complexed to the NiS precipitate molecules. Luther et al.²⁰ reported on stable sulfide complexes of nickel and other metals. The polysulfide complexes of nickel reported were NiHS^+ , $\text{Ni}_2(\text{HS})^{3+}$, and $\text{Ni}(\text{HS})_5^{5+}$ as no complexes with S^{2-} were possible. All complexes dissociated below pH = 7, releasing $\text{H}_2\text{S}(\text{g})$ from solution.²⁰

When Ni:S = 1:1 (B01), the sulfide and nickel concentrations in solution were completely depleted due to the formation of NiS precipitate (Table 4). When the Ni:S was 1:0.5 (B04), the sulfide concentration was completely depleted upon reaction but nickel ions remained in solution because there was insufficient sulfide to precipitate the nickel ions completely. The final pH values obtained after reaction for experiments where NiS = 1:0.5 and 1:1 were approximately 8.27 and 8.86, respectively.

When the ratio of Ni:S was increased to 1:1.5 (B05) and 1:2 (B06), the sulfide concentrations were initially depleted to the stoichiometric requirement for the reacted nickel but then, as the runs progressed, continued decreasing although no further reagents were added to the solutions. Initially, the nickel ions in solution for both reagent ratios were completely precipitated as NiS and thus were no longer present in solution. However, as the runs continued, the nickel concentration increased steadily, until at 20 min 34 and 28% of the nickel initially precipitated had reappeared in solution, for Ni:S = 1:1.5 and 1:2. The pH values for these runs were 11.23 and 11.47 for Ni:S = 1:1.5

and 1:2, respectively, which are more alkaline values than Ni:S = 0.5:1 (B04) and 1:1 (B01).

During runs B05 (Ni:S = 1:1.5) and B06 (Ni:S = 1:2) the nickel ions in solution increased while the sulfide ions in solution decreased with time. This evidence suggests that when there is excess bisulfide in solution, there is dissolution of nickel sulfide precipitates due to the formation of polysulfide complexes. The semibatch data show that $\text{H}_2\text{S}(\text{aq})$ can be present at a concentration of 200 ppm without effecting the NiS precipitation reaction. The pH values of these solutions after reaction were above pH 7, and thus the formation of stable nickel polysulfide complexes with the bisulfide ion was possible.²⁰

Determination of the Threshold at Which $\text{H}_2\text{S}(\text{g})$ Dissolution Becomes Significant. Figure 6 compares the effects of three different alkalinity flow rates (NaOH = 1.20, 1.75, and 2.23 mmol/min) at the same $\text{H}_2\text{S}(\text{g})$ flow rate (0.3 L/min). Thus, when the alkalinity flow rate was lower, the pH was lower and there was a greater concentration of sulfide in solution present as the unreactive $\text{H}_2\text{S}(\text{aq})$. When the rate of alkalinity provided was sufficient to convert the incoming sulfide to the reactive HS^- , then there was no aqueous sulfide present during reaction. This represents efficient use of the added sulfide.

The diagram in Figure 7 shows the threshold above which excess sulfide was present in solution during reaction, leading to sulfide reagent wastage and thus process inefficiency. The threshold is the boundary below which the rate at which NaOH enters solution was sufficient to shift the speciation to the formation of HS^- at a rate comparable to the entering $\text{H}_2\text{S}(\text{g})$ flow rate. The threshold at which $\text{H}_2\text{S}(\text{g})$ dissolution becomes apparent is significant for purposes of process optimization. Above this threshold there is significant reagent wastage, either accumulating in the reacting solution or lost as unabsorbed $\text{H}_2\text{S}(\text{g})$ to be collected in the NaOH trap.

For the experiments where $\text{H}_2\text{S}(\text{g})$ = 0.1 L/min and NaOH = 1.20, 1.75, and 2.23 mmol/min and $\text{H}_2\text{S}(\text{g})$ = 0.3 L/min and NaOH = 1.75 and 2.23 mmol/min, no sulfide was present in solution during reaction and therefore these points lie below the sulfide usage efficiency threshold. The other experiments showed significant unused sulfide in solution during reaction and are therefore points which lie above the threshold. A possibility of operating below the sulfide usage efficiency threshold is that when sulfide is limiting, $\text{Ni}(\text{OH})_2$ precipitation may occur ($K_{\text{SP},\text{Ni}(\text{OH})_2} = 10^{-10.4}$).

Conclusions

Batch experiments were inconclusive in determining whether HS^- or S^{2-} species were responsible for the precipitation of NiS, but sufficient evidence exists to confirm that the $\text{H}_2\text{S}(\text{aq})$ sulfide species cannot precipitate Ni^{2+} at ambient conditions. The most recent $\text{p}K_2$ value of 17.4,⁸ used in this study, suggests that the bisulfide ion (HS^-) was responsible for NiS precipitation because the sulfide ion (S^{2-}) was not present at significant concentrations for the extent of the real pH scale (0–14). It was found that sulfide precipitation of Ni^{2+} using $\text{H}_2\text{S}(\text{g})$ decreased the pH and limited the extent of reaction as the supply of reactive sulfide ions (HS^-) was exhausted.

The use of gaseous sulfide to precipitate Ni^{2+} from an aqueous solution was facilitated by the addition of alkalinity, in the form of an independent NaOH source, to provide the bisulfide ions necessary for the reaction. Gaseous sulfide slowed the rate of the precipitation due to the mass-transfer delay of sulfide entering solution. Provided sufficient sulfide has diffused into solution, the control of nickel precipitation by gaseous sulfide was dictated by the rate at which HS^- species were made

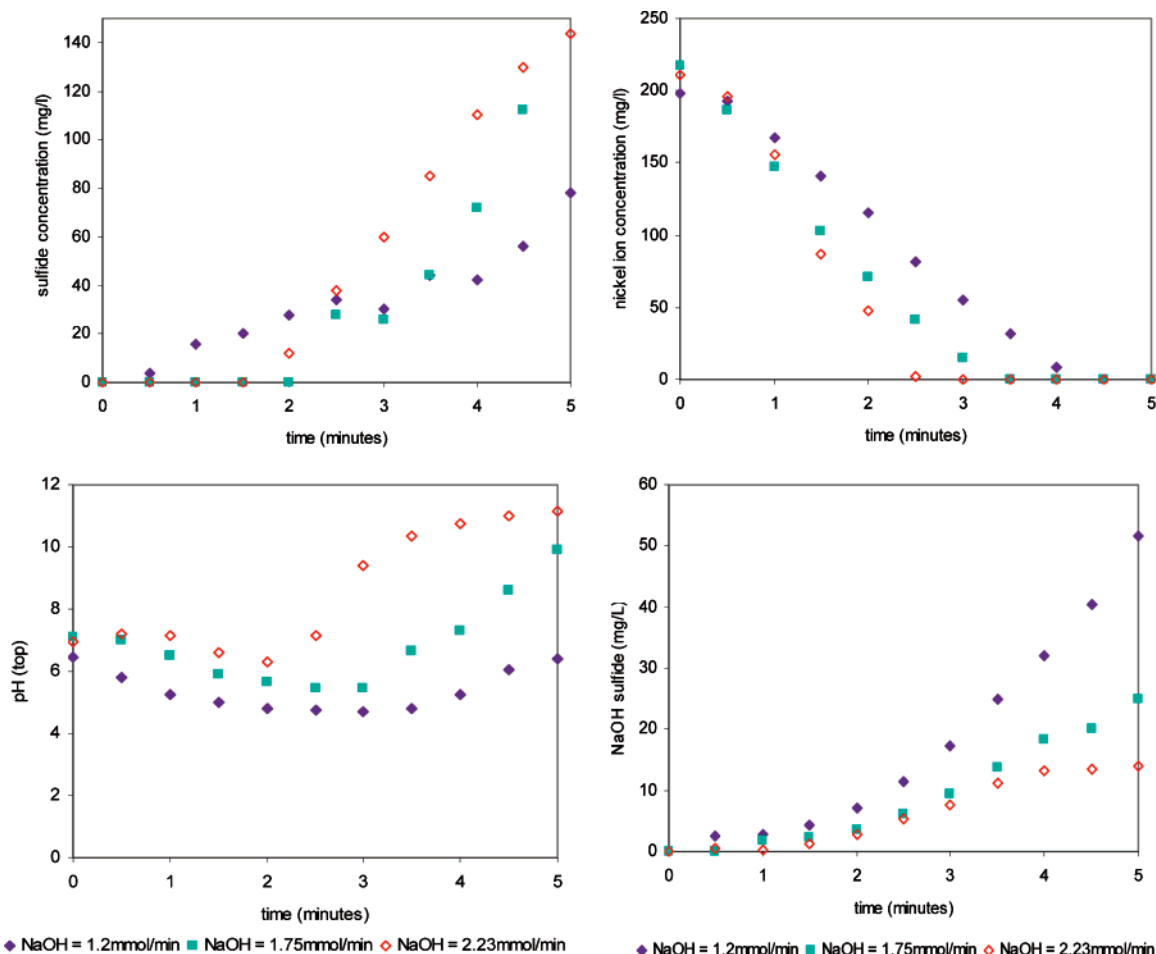


Figure 6. Results of semibatch precipitation using $\text{H}_2\text{S}(\text{g}) = 0.3 \text{ L/min}$. NaOH = 1.20, 1.75, and 2.23 mmol/min [T03, T07, T09] showing Ni^{2+} concentration, free sulfide concentration, and pH in solution.

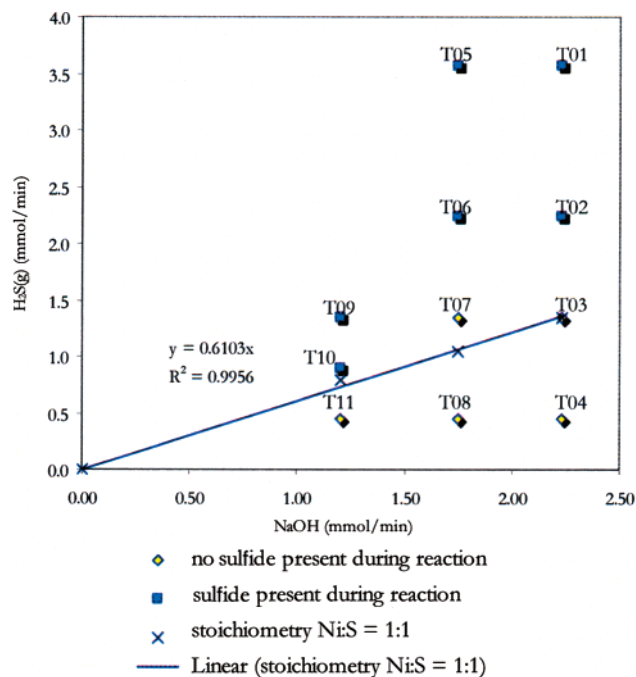


Figure 7. Sulfide usage efficiency threshold: comparing experimental and modeled regions of $\text{H}_2\text{S}(\text{g})$ mass-transfer resistance.

available. In this study, this was controlled by the rate at which NaOH (alkalinity) was supplied.

When the flow rates of NaOH and $\text{H}_2\text{S}(\text{g})$ were such that the supplied alkalinity was an order of magnitude lower than the

sulfide, nickel precipitation occurred at a linear rate and was complete after 25–40 min. In this case, the rate of precipitation was not dependent on the sulfide flow rate but rather on the rate of NaOH addition. Aqueous sulfide accumulated in the system during the precipitation phase and increased as the $\text{H}_2\text{S}(\text{g})$ increased. In all cases, the pH reached a relatively stable value of approximately 3.5 during the precipitation phase, indicating that the accumulated sulfide was the $\text{H}_2\text{S}(\text{aq})$ species. Thus, sulfide was supplied in excess and did not limit the reaction. Previously precipitated nickel was observed to reenter solution during this period. This was attributed to the formation of nickel polysulfide complexes.

Batch experiments in which excess sulfide was provided relative to the stoichiometric dosage of Ni:S (1:1) demonstrated the dissolution of precipitates. In the well-mixed system the amount of resolubilized nickel exceeded 10 ppm after 10 min and then continued to increase linearly with time. This phenomenon was observed to a lesser extent where the Ni:S molar ratio was 1:1 and could most likely be attributed to local HS^- excess during the precipitation reaction.

Where the $\text{H}_2\text{S}(\text{g})$ flowrate was significantly greater than the rate of NaOH addition, it was observed that the majority of added sulfide did not dissolve and accumulated in the sulfide trap. In an industrial precipitation context process economics dictate efficient reagent utilization, and this was not achieved under conditions of low alkalinity addition. Increasing the alkalinity flow rate such that the flow rates of NaOH and $\text{H}_2\text{S}(\text{g})$ were of equal magnitude resulted in significantly faster removal of nickel and decreased sulfide wastage. The molar

ratio of $\text{H}_2\text{S}(\text{g})$ and NaOH addition at which mass-transfer limitations ensured minimal sulfide in solution and no excess $\text{H}_2\text{S}(\text{g})$ passing through the solution, but at which HS^- availability still controlled the rate of nickel removal was determined to be 1:1.66. When experiments were performed at sulfide to hydroxide ratios below this threshold value, the precipitation of nickel as $\text{Ni}(\text{OH})_2$, as well as NiS , occurred because in the absence of sulfide the hydroxide ions accumulated to the point where the solution became supersaturated with respect to $\text{Ni}(\text{OH})_2$.

Literature Cited

- (1) Bryson, A. W.; Bijsterveld, C. H. Kinetics of the precipitation of manganese and cobalt sulphides in the purification of a manganese sulphate electrolyte. *Hydrometallurgy* **1991**, 27, 75–84.
- (2) Lewis, A. E.; Swartbooi, A. Factors affecting metal removal in mixed sulphide precipitation. *Chem. Eng. Technol.* **2006**, 29, 277–280.
- (3) van Hille, R. P.; Petersen, K. A.; Lewis, A. E. Copper sulfide precipitation in a fluidised bed reactor. *Chem. Eng. Sci.* **2005**, 60, 2571–2578.
- (4) Bhattacharyya, D.; Jumawan, A. B.; Sun, G. Precipitation of heavy metals with sodium sulfide: Bench-scale and full-scale experimental results. *Water-1980*, Vol. 77, no. 209, pp 31–38, American Institute of Chemical Engineers, New York.
- (5) Hammack, R. W.; Dvorak, D. H.; Edenborn, H. M. In *The use of biogenic sulfide to selectively recover copper and zinc from severely contaminated mine drainage*; In Torma, A. E.; Wey, J. E.; Lakshmanan, V. L., Eds.; The Minerals, Metals & Materials Society: Warrendale, PA, 1993.
- (6) Hammack, R.; Edenborn, H.; Dvorak, D. Treatment of waste from an open-pit copper mine using biogenic sulfide and limestone: a feasibility study. *Water Res.* **1994**, 28, 2321–2329.
- (7) Jackson, E. *Hydrometallurgical Extraction and Reclamation*; Ellis Horwood and Sons: Chichester, U.K., 1986.
- (8) Migdisov, A.; Williams-Jones, A.; Lakshtanov, L.; Alekhin, Y. Estimates of the second dissociation constant of H_2S from the surface sulfidation of crystalline sulfur. *Geochim. Cosmochim. Acta* **2001**, 66, 1713–1725.
- (9) Garrels, R.; Naeser, C. Equilibrium distribution of dissolved sulphur species in water at 25°C and 1 atm total pressure. *Geochim. Cosmochim. Acta* **1958**, 15, 113–130.
- (10) Licht, S.; Manassen, J. The second dissociation constant of H_2S . *J. Electrochem. Soc.* **1987**, 134, 918–921.
- (11) Stephens, H.; Cobble, J. Thermodynamic properties of the aqueous sulfide and bisulfide ions and the second ionization constant of hydrogen sulfide over extended temperatures. *Inorg. Chem.* **1971**, 10, 619–625.
- (12) Wagman, D.; Evans, W.; Parker, V.; Halow, L.; Bailey, S.; Schumm, R. *Selected Values of Chemical Thermodynamic Properties*; U.S. Government Printing Office: Washington, D.C., 1968.
- (13) Giggenbach, W. Optical spectra of highly alkaline sulfide solutions and the second dissociation constant of hydrogen sulfide. *Inorg. Chem.* **1971**, 10, 1333–1338.
- (14) Meyer, B.; Ward, K.; Koshlap, K.; Peter, L. Second dissociation constant of hydrogen sulfide. *Inorg. Chem.* **1983**, 22.
- (15) Licht, S.; Forouzan, F.; Longo, K. Differential densometric analysis of equilibria in highly concentration media: Determination of the aqueous second dissociation constant of H_2S . *J. Chem. Phys.* **1990**, 56, 202–213.
- (16) Kolthoff, L.; Moltzau, D. Induced precipitation and properties of metal sulfides. *Chem. Rev.* **1935**, 17, 293–325.
- (17) Lewis, A.; van Hille, R. An exploration into the sulphide precipitation method and its effect on metal sulphide removal. *Hydrometallurgy* **2006**, 3, 81, 197–204.
- (18) Simons, C. Hydrogen Sulfide as a hydrometallurgical reagent. In *Unit Processes in Hydrometallurgy*; Wadsworth, M.; Davids, F., Eds.; Gordon and Breach: New York, 1963.
- (19) Esposito, G.; Veeken, A.; Weijma, J.; Lens, P. N. L. Use of biogenic sulfide for ZnS precipitation. *Sep. Purif. Technol.* **2006**, 51, 31–39.
- (20) Luther, G. W.; Rickard, D.; Theberge, S.; Olroyd, A. Determination of Metal (Bi)Sulfide Stability Constants of Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} by Voltammetric Methods. *Environ. Sci. Technol.* **1996**, 30, 671–679.

Received for review August 16, 2007
Revised manuscript received October 9, 2007
Accepted October 19, 2007

IE0711224