

# An Improved Process for Precipitating Cyanide Ions from the Barren Solution at Different pHs

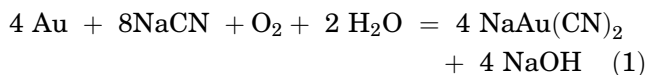
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In recent decades, the use of metal sulfides instead of hydroxide precipitation in hydrometallurgical processes has gained prominence. Some arguments for its preferential use are as follows: a high degree of metal removal at relatively low pH values, the sparingly soluble nature of sulfide precipitates, favorable dewatering characteristics, and the stability of the formed metal sulfides. The Merrill–Crowe zinc-precipitation process has been applied worldwide in a large number of operations for the recovery of gold and silver from cyanide solutions. However, in some larger plants, the quality of this precious precipitate is low because copper, zinc and especially lead are precipitated along with gold and silver. This results in higher consumption of zinc dust and flux during the smelting of the precipitate, the formation of the matte, and a shorter crucible life. The results show that pH has a significant effect on the removal efficiency of zinc and copper cyanide ions. The optimal pH range was determined to be 3–4, and the removal efficiency of zinc and copper cyanide ions was up to 99%.

## INTRODUCTION

Since the 1890s, cyanide has been used to recover gold from gold-bearing ores. Today, over 115 years later, most of the world's gold is recovered, with cyanide still playing a large part in the beneficiation process of the yellow precious metal. Chemically, it is a rather simple reaction:

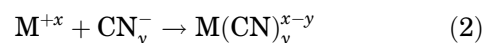


This reaction presumes that the only reactants are the gold, sodium cyanide and water. However, no two ores are the same. In fact, the chemical composition throughout the ore body varies greatly. These “extra” elements in the mineral compounds often disrupt the chemical reaction.

Copper is definitely worth mentioning because copper minerals tend to dissolve in cyanide solutions, causing an increased usage of cyanide. The copper–cyanide complexes formed by this process

tend to inhibit the dissolution of gold in the cyanide solution. Zinc is the element used to precipitate gold from the solution. If present in the ore, it bonds with the cyanide to form zinc cyanide compounds.<sup>1</sup>

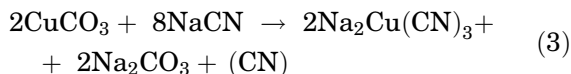
Therefore, the concentration of cyanide used in cyanidation plants to dissolve gold in the ores is typically higher than the stoichiometric ratio because other minerals are also dissolved by cyanide. Free ionic cyanide produces complexes with several metallic species, especially transition metals, which show broad variations in both stability and solubility. This is discussed by Rehman.<sup>2</sup>



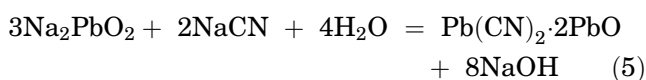
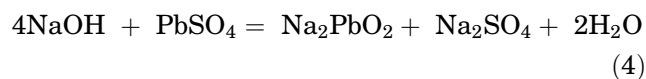
Many common copper minerals, which are typically found in leach conditions during the gold cyanidation process, are soluble in the dilute cyanide solution. Minerals, such as azurite and malaquite (Table I), are fast leached and are soluble in dilute cyanide solutions. Enargite and chalcopyrite minerals leach more slowly but are sufficiently

soluble to cause excessive cyanide losses. Consequently, the leach solutions become contaminated with arsenic.<sup>3</sup>

In the cyanidation of malachite and azurite minerals, the copper carbonate component leaches as shown by Eq. 3.



Lead ores, such as galena and anglesite (Table I), behave similarly toward cyanide. The reactivity of galena depends largely on the ease with which it oxidizes to form the sulfate compound. It is important to use low concentrations of alkali because, in excessive amounts, the mineral plumbite tends to form. Plumbite interacts with cyanide to form basic insoluble lead cyanide. The main reactions are as follows:



At low concentrations of alkali, a less basic lead cyanide ( $\text{Pb}(\text{CN})_2 \cdot 2\text{PbO}$ ) is formed. In the presence of excess alkali, plumbite hydrolyzes with the

liberation of HCN, which forms alkaline cyanide. The hydrometallurgical treatment of these ores by cyanidation exhibits a series of associated difficulties as follows: an increase in the consumption rate of cyanide and oxygen, a decrease in the dissolution rate of gold and silver, and poor precipitation, which contains excess copper and lead in the cementation process.

The objective of this study is to obtain fundamental information on the mechanism of sulfide precipitation for the removal of copper, zinc, iron and lead hydroxides from barren cyanide solutions. This process involves the use of sodium sulfide ( $\text{Na}_2\text{S}$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). A better quality Doré will be yielded when all these ions are removed from the barren cyanide solution.

### PRECIPITATION PROCESS FOR CLEANING THE BARREN SOLUTION OF CYANIDE IONS

Metals existing in wastewater are usually removed by precipitation. Other unit operations such as coagulation, flocculation, ion exchange, solvent extraction, cementation, complexation, electrochemical operations, biological operations, adsorption, evaporation, filtration, and membrane processes are also used. Seventy percent of electroplating facilities use some form of precipitation treatment.<sup>4</sup> Three types of precipitation treatments are utilized in industries, namely sulfide precipitation, hydroxide precipitation and carbonate precipitation.<sup>5</sup> Such techniques take considerable time and require an extensive setup. Each step takes place in a separate tank. The entire treatment process requires several adjustments of pH, as well as the addition of acid, coagulant lime or flocculants (caustic and polymeric). In addition, this process generates large volumes of sludge/waste, which requires disposal. Hydroxide precipitation is the most commonly used precipitation method due to its relative simplicity, low cost, and ease of automatic pH control. However, most heavy metal hydroxides have similar solubilities. Other metals can be

**Table I. Mineral formulas**

Copper minerals	
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
Malaquite	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
Enargite	$\text{Cu}_3\text{AsS}_4$
Chalcopyrite	$\text{CuFeS}_2$
Lead minerals	
Galena	$\text{PbS}$
Anglesite	$\text{PbSO}_4$
Plumbite	$\text{PbO}_2$

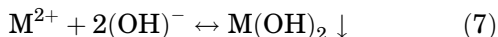
**Table II. Solubility of sulfides and hydroxides of heavy metals and pH precipitation concentrations of metal ions, mg/l<sup>5,6</sup>**

Metal (ion)	Kinetic constants		pH precipitation range	
	Sulfide	Hydroxide	Sulfide	Hydroxide
Cadmium ( $\text{Cd}^{2+}$ )	$6.7 \times 10^{-10}$	$2.3 \times 10^{-5}$	3.0–4.0	9.0–11.0
Chromium ( $\text{Cr}^{3+}$ )	No ppt	$8.4 \times 10^{-4}$	–	6.5–11.0
Copper ( $\text{Cu}^{2+}$ )	$5.8 \times 10^{-18}$	$2.2 \times 10^{-2}$	1.0–2.0	7.0–7.5
Iron ( $\text{Fe}^{2+}$ )	$3.4 \times 10^{-5}$	$8.9 \times 10^{-1}$	1–3	8–11
Iron ( $\text{Fe}^{3+}$ )	No ppt	$1.0 \times 10^{-4}$	1–3	5.0–5.5
Lead ( $\text{Pb}^{2+}$ )	$3.8 \times 10^{-9}$	2.1	3.0–6.0	8.5–9.0
Mercury ( $\text{Hg}^{2+}$ )	$9.0 \times 10^{-20}$	$3.0 \times 10^{-4}$	2.0–4.0	–
Nickel ( $\text{Ni}^{2+}$ )	$6.9 \times 10^{-8}$	$6.9 \times 10^{-3}$	2.0–8.0	9.0–11.0
Silver ( $\text{Ag}^+$ )	$7.4 \times 10^{-12}$	13.3	3.0–11.0	9.0–12.0
Zinc ( $\text{Zn}^{2+}$ )	$2.3 \times 10^{-25}$	$3.4 \times 10^{-17}$	1.0–6.0	8.0–8.5

**Table III. Methods of ionic precipitation<sup>7</sup>**

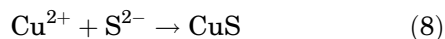
	Precipitating agent	Examples
Sulfides	H <sub>2</sub> S	CuS
Sulfides	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub>	CuS, NiS, CoS, ZnS Copper ammonium sulfites Cu <sub>2</sub> SO <sub>3</sub> ·7(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub> ·10H <sub>2</sub> O Cu <sub>2</sub> SO <sub>3</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub> Cu <sub>2</sub> SO <sub>3</sub> ·CuSO <sub>3</sub> ·2H <sub>2</sub> O (Chevreul's salt)
Hydroxides	OH <sup>-</sup>	Mg(OH) <sub>2</sub> , Co(OH) <sub>2</sub>
Carbonates	CO <sub>3</sub> <sup>2-</sup>	Li <sub>2</sub> CO <sub>3</sub>
Cyanides	HCN	CuCN

separated from zinc by carbonate precipitation, because, unlike zinc, other metals can be selectively precipitated. Table II shows the solubilities of metal sulfides and hydroxides. Both methods involve a reaction of the metal cation with either OH<sup>-</sup> or S to form the corresponding insoluble metal hydroxide or sulfide, as shown below:



Multiple metals are present at high levels in wastewater from metal finishing and metallurgical operations. Therefore, the most effective pH must be determined prior to treatment.

Ionic precipitation is based on the addition of a reagent to a solution containing metal ions. Under these conditions, a compound with very low solubility is formed, and precipitation takes place immediately. For example, when H<sub>2</sub>S is bubbled through a CuSO<sub>4</sub> solution, CuS is immediately precipitated because Cu<sup>2+</sup> ions and S<sup>2-</sup> ions react to form a compound of very low solubility. This is shown by reaction 8:



This reaction is different from crystallization, where the compound precipitated has a high solubility. Proper conditions of temperature and concentration must be present for crystallization to occur. The general process of precipitation can be represented as follows:



A number of precipitants are shown in Table III, and most are applied industrially.

Sulfide precipitation has been demonstrated to be an effective alternative to hydroxide precipitation for removing various heavy metals from industrial wastewaters. The high reactivity of sulfides (S<sup>2-</sup>, HS<sup>-</sup>) with heavy metal ions and the insolubility of heavy metal sulfides over a broad pH range are attractive features compared with the hydroxide

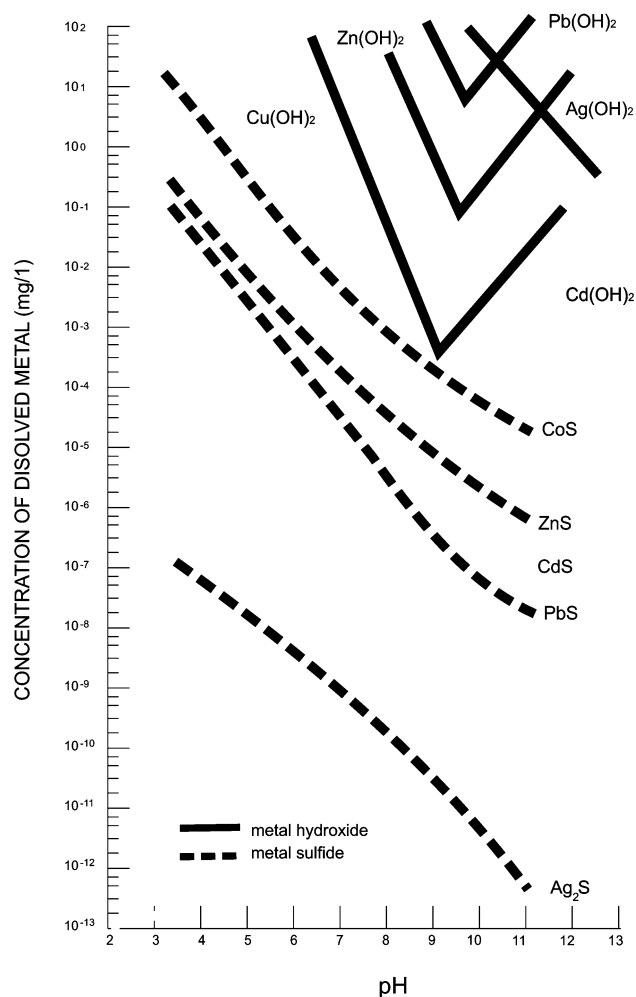


Fig. 1. Solubilities for metal hydroxides are taken from curves.<sup>8</sup>

precipitation process (Fig. 1). Sulfide precipitation can also achieve low metal solubilities in the presence of certain complexing and chelating agents.<sup>8</sup>

The main difference between the two processes that currently use sulfide precipitation is the means of introducing the sulfide ion into the wastewater. In the soluble sulfide precipitation (SSP) process, the sulfide is added in the form of a water soluble sulfide reagent, such as sodium sulfide (Na<sub>2</sub>S) or sodium hydrosulfide (NaHS). In the other process, a slightly soluble ferrous sulfide (FeS) slurry is added to wastewater in order to supply the needed sulfide ions required to precipitate the heavy metals. Because most of the heavy metals have solubilities less soluble than ferrous sulfide, that will precipitate as metal sulfide.

Eliminating sulfide reagent overdose can prevent odor problems, which are commonly associated with these systems. In current soluble sulfide systems that do not automatically adjust reagent dosage to match demand, the process tanks must be enclosed and vacuum evacuated to minimize sulfide odor problems in the work area.

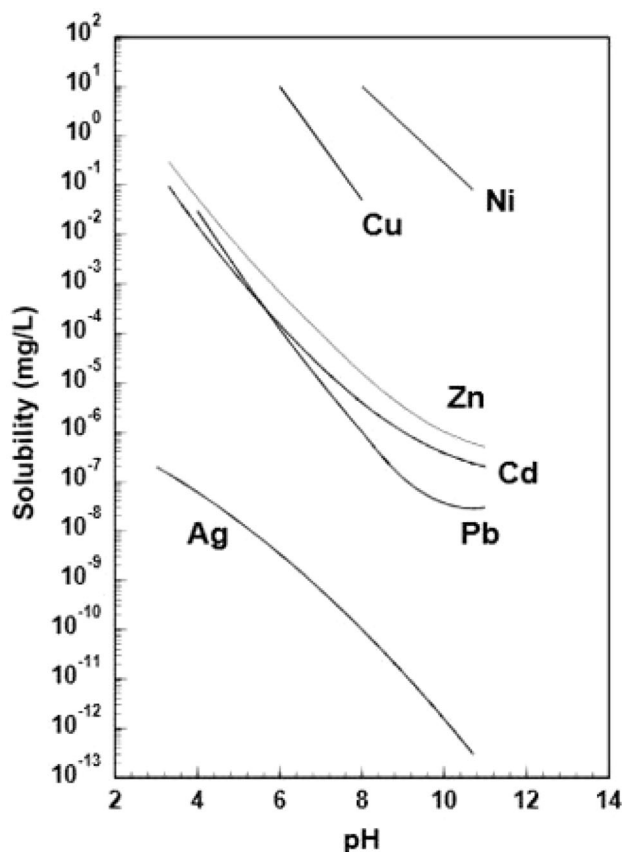


Fig. 2. Solubility of metals sulfides as a function of pH.<sup>11</sup>

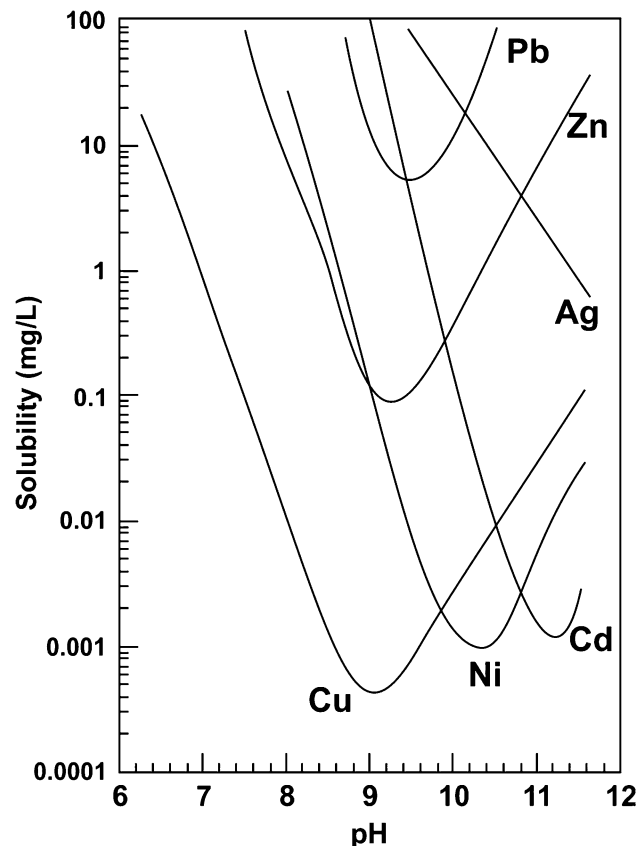


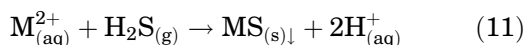
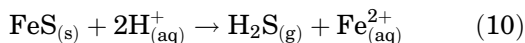
Fig. 3. Solubility of metal hydroxides as a function of pH.<sup>12</sup>

### DIFFERENT TYPES OF PRECIPITATION

#### Sulfide Precipitation

Metal sulfides are typically very insoluble in water (Fig. 2). Therefore, metals can be precipitated by adding sulfide ions ( $S^{2-}$ ). Metal sulfides have much lower solubilities than the corresponding metal hydroxides, thus allowing lower residual metal concentrations in the treated wastewater.

Ozverdi and Erdem investigated the use of pyrite and synthetic iron sulfide to remove  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Pb^{2+}$ . The mechanisms governing the metal removal processes were determined as follows: chemical precipitation at low pH ( $<3$ ) due to  $H_2S$  generation (Eqs. 10 and 11), and adsorption at high pH (in the range of 10).<sup>9</sup>



The most widely used process for treating wastewater involves hydroxide precipitation due to its relative simplicity, low cost and automatic pH control. However, sulfide precipitation is superior to hydroxide precipitation for the following reasons: (1) effluent concentrations after treatment are orders of magnitude lower ( $\mu g l^{-1}$  versus  $mg l^{-1}$ ); (2) the interference of chelating agents in wastewater is less

Table IV. Chemical analyses results of the pregnant solution

Parameters	Unit	Sample
Aspect	-	Clean
Color	-	Yellow
Odor	-	Foul smelling
pH	Unit of pH	10.7
Conductivity	$\mu S/cm$	89,000
TDS	mg/l	80-20
DQO	mg/l	6000
Chlorides	mg/l	50,600
Density	g/ml	1.156
Cyanides	mg/l	7000
Copper	mg/l	7.085
Lead	mg/l	8.86
Zinc	mg/l	8.491
Iron	mg/l	4.774
Silver	mg/l	0.1
$Na_2S$	gr/l	5

problematic; (3) selective metal removal is possible; (4) high reaction rates result in low hydraulic retention times; (5) metal sulfides (compared with the corresponding hydroxide sludge) exhibit better thickening and dewatering characteristics; and (6) sulfide precipitates can be processed by existing smelters for metal recovery.<sup>7</sup>

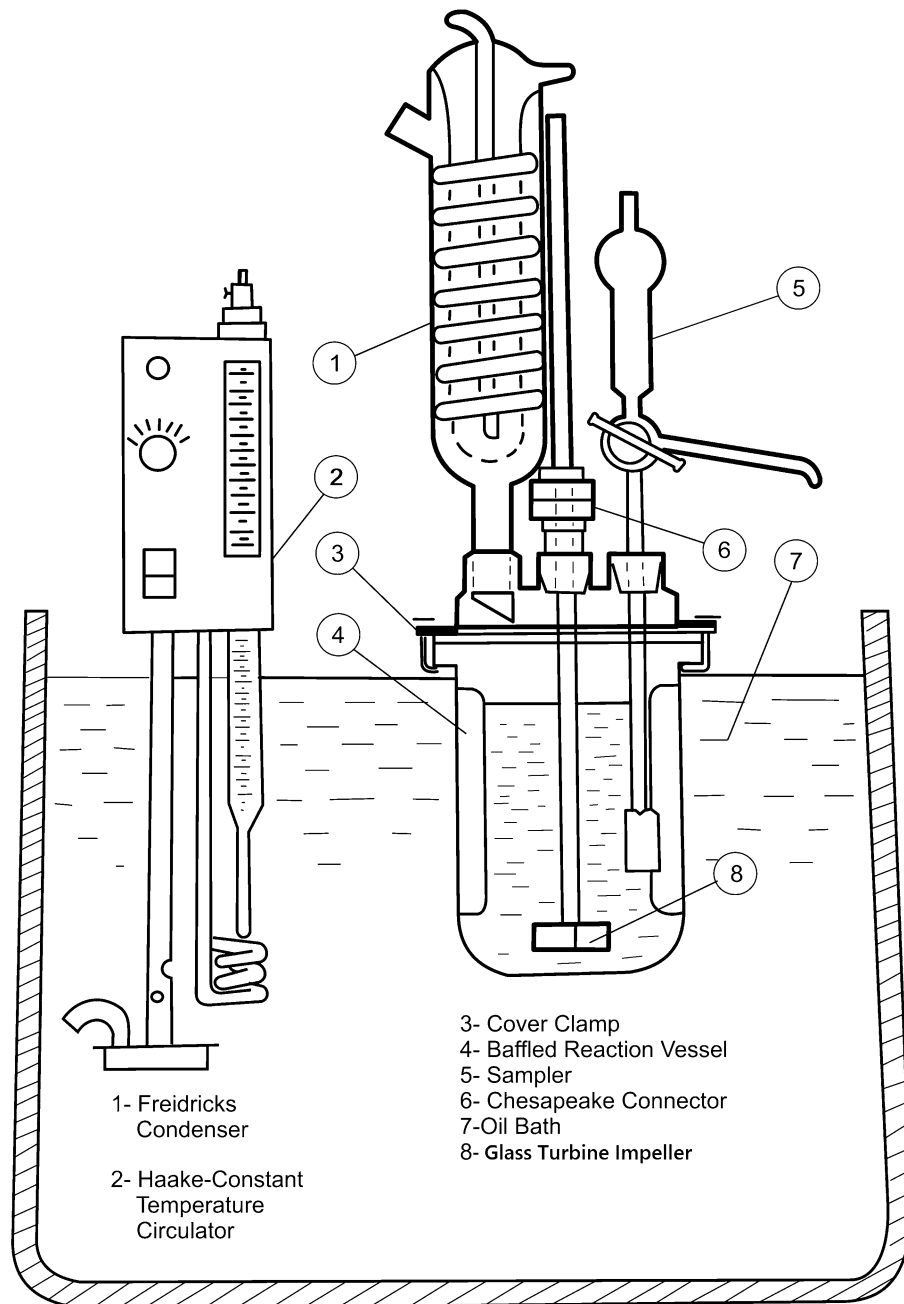
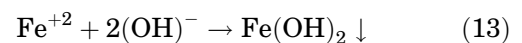
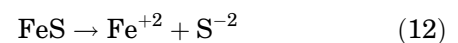


Fig. 4. Schematic diagram of the experimental apparatus used for precipitation.

However, there are potential dangers in using the sulfide precipitation process. Heavy metal ions are often exposed to acidic conditions; however, sulfide precipitants in these conditions can result in the evolution of toxic  $\text{H}_2\text{S}$  fumes. It is essential that this precipitation process be performed in a neutral or basic medium. Moreover, metal sulfides tend to form colloidal precipitates, which can cause some separation problems during either the settling or filtration processes.<sup>10</sup>

### Hydroxide Precipitation

The most common heavy metal precipitation method is by hydroxide formation. The following reactions occur when  $\text{FeS}$  is introduced into a solution containing dissolved metals and metal hydroxides:



**Table V. Results of copper, silver, zinc and iron sulfide precipitates at different pHs**

	<u>Ag</u>	<u>Zn</u>	<u>Cu</u>	<u>Pb</u>	<u>Fe</u>	<u>Na<sub>2</sub>S</u>	<u>pH</u>
Initial solution	0.1	8491	7485	8.86	4774	0	10.7
Solution 1, ppm	0	22	31	1.1	2	1	8
Solid 1, %	114	21.9	121.7	4.4	21.0	–	–
Solution 2, ppm	0	73	389	0.9	2	0.5	7
Solid 2, %	124	17.6	94.9	2.4	11.2	–	–
Solution 3, ppm	0	73	391	0	2	0.5	6
Solid 3, %	121	11.4	80.7	1.07	6.0	–	–
Solution 4, ppm	0	154	0	0	0	1	5
Solid 4, %	78	1.5	62.7	0.2	3.1	–	–
Solution 5, ppm	0	140	0	0	0	1.5	4
Solid 5, %	49	0.4	42.2	0.1	1.1	–	–
Solution 5, ppm	0	134	0	0	0	2.0	3
Solid 5, %	36	1.2	36.6	0.1	0.9	–	–
Solution 6, ppm	0	98	0	0	0	1.5	2
Solid 6, %	29	0.4	23.4	0.01	0.5	–	–

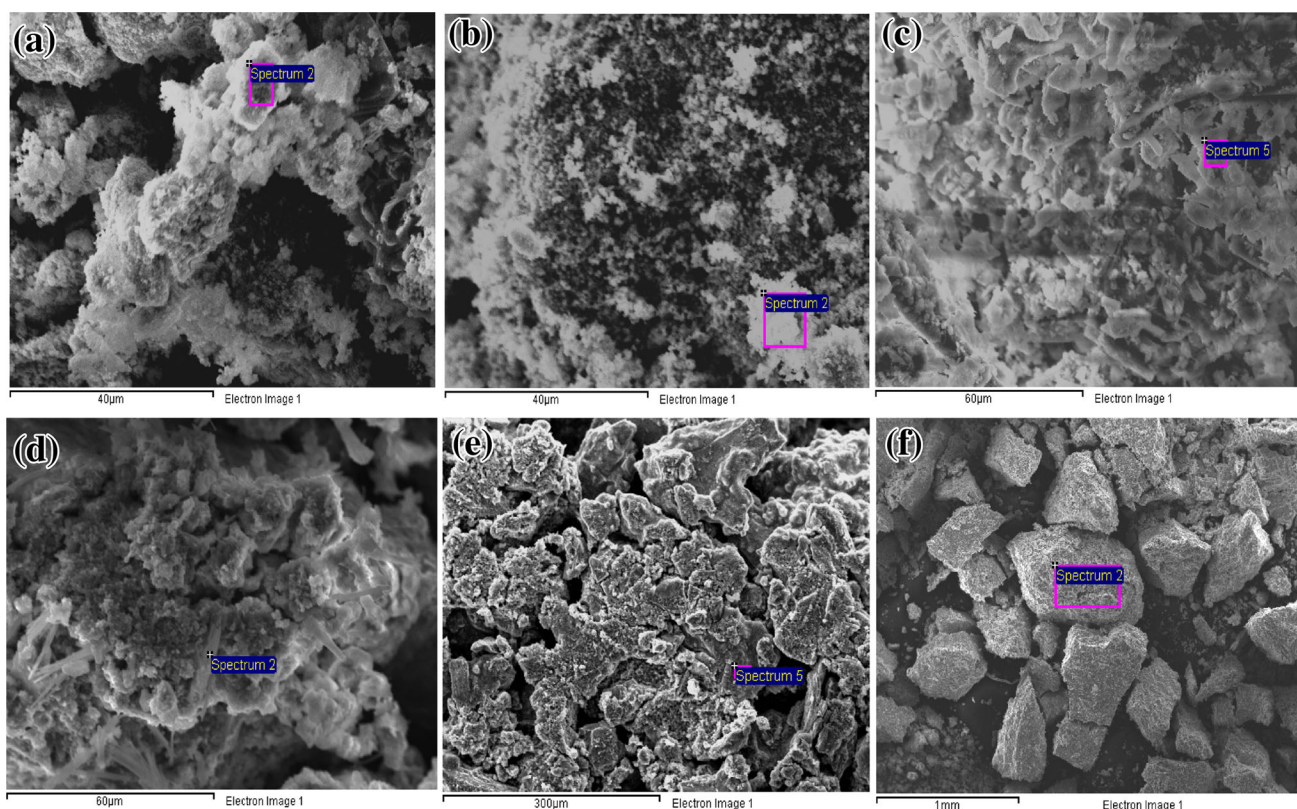
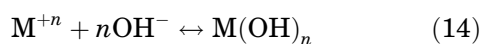


Fig. 5. Morphology of the solids from the pH value experiments: (a) pH 2; (b) pH 3; (c) pH 4; (d) pH 5; (e) pH 6; (f) pH 7.



The solubilities of the various metal hydroxides are minimized in the pH range from 8 to 11 (Fig. 3). The metal hydroxides can be removed by flocculation or sedimentation. A variety of hydroxides have been used to precipitate metals from wastewater

because of the low cost and ease of handling. In industry, lime is the preferred base of choice used for hydroxide precipitation.<sup>11</sup>

Many heavy metals are amphoteric. Therefore, their solubility, which is different for each metal, reaches a minimum at specific pH values. The hydroxide precipitation process uses Ca(OH)<sub>2</sub> and NaOH to remove Cu(II) and Zn(II) ions from

**Table VI. Chemical composition as determined by EDX for different pH values**

Element	Wt.%						
	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8
C K	10.5	21.5	7.6	22.2	19.1	19.4	16.9
N K	6.9	31.2	30.7	23.1	24.9	21.5	14.3
O K	13.5	13.4	10.7	17.3	10.3	4.1	2.8
S K	14.3	13.8	20.8	7.1	6.4	4.13	0.7
Fe k	12.3	7.6	8.6	6.4	9.3	1.9	5.7
Cu L	11.2	7.5	12.6	11.7	8.6	6.4	2.7
Zn L	31.4	27.2	23.9	11.9	20.9	42.6	56.5
Totals	100	100	100	100	100	100	100

wastewater. The addition of coagulants such as aluminum sulfate, ferrous sulfate, and organic polymers can further enhance the removal of heavy metals from wastewater.

### EXPERIMENTAL PROCEDURE

The precipitation experiments were performed in a 1000-ml glass reactor. The initial solution for all the tests was from the same batch (shown in Table III). The temperature was fixed at 25°C. The solution pH was varied using H<sub>2</sub>SO<sub>4</sub> with 5 g/L Na<sub>2</sub>S. Labry and Bacis mining group provided the pregnant cyanide solution. Table IV lists the chemical analyses results of the solution.

A condenser, stirrer, nitrogen dispersion tube, and sampling device were placed into the reactor through openings in the lid. A Teflon stirrer was attached to the center port by means of a Chesapeake stirrer connection. The solution was stirred with a variable speed motor, and the rotation speed was measured with a stroboscope. An isothermal heater was used to heat the solution and control the temperature.

The pH was measured with a VWR brand scientific 8005-pH meter. Labry and Bacis Mining Group provided the solutions. Inductively coupled plasma (ICP)/atomic emission spectrometry analyses were performed. The conductivity of the pregnant cyanide solutions was adjusted by adding 1 g of NaCl per liter (Fisher; 99.8% lot #995007). The pH was adjusted using a solution of sulfuric acid 0.1 M and sodium hydroxide 0.1 M.

A schematic of the experimental apparatus is shown in Fig. 4.

### RESULTS AND DISCUSSION

The experiments were carried out in the glass reactor at room temperature. The pH was varied. In all the tests, the barren initial solution was from the same batch from the Merrill-Crowe plant (0.1 Ag ppm, 155 Zn ppm, 590 Cu ppm, 4 Fe ppm). The following conditions were also fixed: temperature at 25°C, stirring speed at 200 rpm, 5 g/l Na<sub>2</sub>S, and use different concentrations of sulfuric acid to adjust the pH. The reaction time was 90–600 s.

The experimental results of silver, zinc, copper and iron precipitation at different pH levels are presented in Table V.

The results show that pH has a great effect on the removal efficiency of copper cyanide. The optimum pH was approximately 3–4, and the copper cyanide removal efficiency reached above 99%.

Scanning electronic microscopy (SEM) determined the size, energy dispersive x-ray (EDX) and morphology of the solids from the pH experiments. The results are shown in Fig. 5. The solids in the precipitates are spherical and approximately 100 nm in diameter. The chemical composition of the solid sulfide particles (as determined by EDX) shows the presence of copper, sulfur, zinc and iron (Table VI).

The EDX pattern of the precipitates at different pH values is shown in Table VI. The results indicate that the best pH conditions for sulfide precipitation are between 3 and 4 for copper and between 6 and 8 for zinc.

According to the SEM pictures, the high concentration of dissolved sulfides in the water causes rapid precipitation of the metals as metal sulfides. This often results in the generation of small fines and hydrated colloidal particles. Additionally, the rapid precipitation reaction tends more toward discrete particles rather than nucleation precipitation.

### CONCLUSION

The results for eliminating silver, zinc, copper and iron ions from the barren solution indicate that the best pH conditions for sulfide precipitation are between 3 and 4 for copper and between 6 and 8 for zinc.

This investigated process indicates great potential for eliminating copper, zinc and iron cyanide ions from the barren solution. According to these results, a better Doré will be produced when all of these ions are removed from the barren cyanide solution.

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