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Waste Water Treatment by Precipitating Copper, Lead and Nickel Species

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Abstract

Precipitation of metallic species in either, liquid-liquid, solid-solid, or liquid-solid systems is a current phenomenon that is related with the formation and/or deposition of second phases. An example of the above is the deposition of some precipitated species on ore particles during milling, changing their surface properties and affecting the process of capture during flotation. Precipitation of species also occurs during waste water treatment. Despite the fact that several procedures have been designed to clean water contaminated with heavy metals (i.e., activated zeolite and membranes, gas dispersion devices, bird feathers, biological procedures, etc.) the mechanisms describing the formation of such phases or species are not well understood. This work establishes from a thermodynamic point of view the conditions (pH, electrochemical potential, ionic strength, activity coefficient) to predict the formation of certain species (precipitated or dissolved) in distilled water contaminated with lead, copper, and nickel, and open to the atmosphere. The pH of the media was varied from 3 to 13. Experimental results show the feasibility to control selectively the precipitation of given copper, nickel, and lead species from contaminated water, by controlling the pH of the liquid media. From the information derived in this work, it is possible to design a process for cleaning water contaminated with heavy metals by promoting the sedimentation of metallic species, and to predict or avoid the formation of certain species on ore particles that reduce the metallurgical efficiency during the flotation process.

Keywords: Waste water treatment, column flotation, heavy metals, Pourbaix diagrams.

Introduction

The source of heavy metals is given not only by industrial discharge or mine water, now even taken for electronic waste[1]. The heavy metal contamination is a problem that has been detected in rivers and their species[2], some investigations are related to water quality in some effluents contaminated with heavy metals, which, unfortunately, suggest that water sources are unfit for human consumption without being subjected to a pretreatment[3]. The role of heavy metals in reactions involving liquid-liquid and liquid-solid relationships is not enough studied yet. In the case of waste water treatment several research has been done although the mechanisms of precipitation of certain species and the selectivity of their capture in not clear[4,5,6].

On the other hand, there is known the galvanic interaction among species during milling, affecting the surface properties of the ore minerals and then the metallurgical performance of flotation[7,8].

For liquid-liquid, and solid-liquid systems, the interaction between species is ruled by the following expressions:

$$I = \frac{1}{2}\sum m_i z_i^{\,2} \qquad (1)$$

Where I is the ionic strength, which is a measure of the intensity of the electric field in the system[9,10]; m is the molality of i; and z is the charge of the corresponding ion i (i represents every specie involved in a given reaction). In this work the involved species are the salts: $Pb(NO_3)_2$, $CuSO_4$, and $NiSO_4 \cdot 6H_2O$, the water and the pH modifiers, H_2SO_4, and KOH.

The chemical activity is a corrected concentration[11], and physically is the actual amount of reagent that takes part during the reaction; in this case is the concentration of metallic ions in the media that affectively react. The average activity coefficient is calculated as follows:

$$\gamma \pm = 10^{\left(A\left|z+z-\right|\sqrt{I}\right)} \qquad (2)$$

Being A the constant value from Debye –Hückel equation for liquid media and pressure of 1 atmosphere, $|z + z -|$ is the absolute value of the sum of the electric charge of the dissolved ions. The activity α of given i species can be calculated according to:

$$a[i] = \gamma_i m_i \qquad (3)$$

Where m is the molarity of the i species.

In order to calculate the electrochemical potential, Eh, the equation proposed by Garrels[9] was applied:

$$Eh = E^\circ - \left(\frac{0.05916}{Z}\right)\log Q \quad (4)$$

Being E° the standard potential, Z the number of electrons participating during the reaction, and Q is the reaction quotient. E° can be calculated through the following expression:

$$E^\circ = \frac{-\Delta G^\circ}{ZF} \quad (5)$$

Where ΔG° is the Gibbs free energy of the corresponding reaction, and F is the Faraday constant (96487 C/mol = 23 060.9 Cal/Vol•mol).

By applying the former equations there is possible to build Eh – pH diagrams and to use them as tools to understand the conditions under which given ionic or precipitated species are chemically stable.

In this work lead, nickel, and copper salts were dissolved in distilled water and physicochemical parameters such as ionic strength, activity coefficient, activity, and electrochemical potential were calculated, in a pH ranging from 3 to 13. Lead, nickel, and copper precipitates were identified and the corresponding formation reactions were established in order to build a Pourbaix diagram.

The obtained information makes possible at first to design a procedure to clean water contaminated with the heavy metals mentioned here through the route sedimentation-flotation or filtering-flotation.

The experimental results also provide information regards deposited species on mineral surfaces during milling which affect the behavior of collectors during flotation decreasing its metallurgical performance.

Material and Methods

Preparation of diluted solutions of Cu, Ni, and Pb in distilled water: Lead nitrate ($Pb(NO_3)_2$), copper sulphate ($CuSO_4$), and hexahydrated nickel ($NiSO_4 \cdot 6H_2O$) were dissolved separately and simultaneously in distilled water. The pH of the media was varied in 3,5,7,9,11, and 13. After 24 hours the precipitated solids were separated and analyzed through X-ray diffraction (XRD), and scanning electron microscopy (SEM) techniques. The remaining lead, copper, and nickel in every solution were quantified by atomic absorption spectroscopy (AAS) analysis. The pH was modified by adding sulfuric acid (H_2SO_4), and potassium hydroxide (KOH). The initial metal concentration in each solution was 40 ppm.

Chemical analysis of precipitates and solutions: The chemical analysis of precipitates was carried out by X-ray diffraction (XRD), and scanning electron microscopy (SEM). On the other hand, the quantitative chemical analysis from liquids were carried out by atomic absorption spectroscopy (AAS).

Thermodynamic analysis of the system: With the quantitative and qualitative chemical analysis data, the values of activity, activity coefficient, ionic strength, and electrochemical potential were calculated. The former information was used to calculate the corresponding transformation lines as function of the pH. The resulting equilibrium diagrams are shown below.

Results and Discussion

Precipitation of lead species: Visually the formation of lead precipitates starts at pH 3, although these solids are re-dissolved at pH 5. Lead crystals are formed again at pH 7, and finally the precipitates are dissolved once more at pH 11.

From XRD analysis at pH 3 the detected species are the lead sulfate ($PbSO_4$), and hydrated lead nitrite ($Pb(NO_2)_2(H_2O)$), which indicates the decomposition and hydration of the salt originally dissolved. The precipitated solids at pH from 7 to 11 correspond to an hydroxicarbonate $Pb_3(CO_3)_2(OH)_2$), also known as hydrocerusite.

Taking into consideration that hydrocerusite forms under alkaline conditions, and in absence of ionic sulfate, the following reaction is suggested:

$$Pb_3(CO_3)_2(OH)_2 + 6H^+ \rightarrow 3Pb^{2+} + 4H_2O + 2CO_2 \quad (6)$$

The re-dissolution of hydrocerusite is carried out according to the following reaction proposed by Pankow[11], and thermodynamically it occurs at pH 11.2:

$$Pb_3(CO_3)_2(OH)_2 + 5H_2O \rightarrow 3Pb(OH)_3^- + 2CO_2 + 3H^+ \quad (7)$$

On the other hand, the formation of carbonated species is explained by considering the replacement of sulfates or sulfites to carbonates in an open system to air, according the following reaction proposed by Azareño[12]:

$$PbSO_4 + CO_3^- \rightarrow PbCO_3 + SO_4^- \quad (8)$$

In the case of the decomposition of lead sulfate:

$$PbSO_4 + 2H^+ \rightarrow Pb^{2+} + H_2SO_4 \quad (9)$$

From the above reactions it is possible to observe that the dissolution or precipitation of lead species just depends on pH. The Pourbaix diagram built according the calculated variables is shown in figure 1. As known, in the following equilibrium diagrams the dashed lines represent the zone where aqueous species are stable; within these lines both the aqueous and precipitated species co-exist.

For the copper case, the vertical lines correspond to the transformations shown in reactions (6), (7), and (9).

In light of the above, from pH up to 3.9, both ($PbSO_4$), and Pb^{2+} co-exist; whereas from pH 3.9 to 6 the all lead is dissolved. In the pH range from 6.0 to 11.2 the steady species are the Pb^{2+} and the $Pb_3(CO_3)_2(OH)_2$. For pH larger than 11.2 the hydrocerusite is dissolved again and a led hydroxide is formed.

According to information from quantitative chemical analysis, the concentration of Pb^{2+} in the liquid media decreases because of the presence of lead precipitates at pH higher than 5, and the ionic lead increases again for pH higher than 11.

Table 1 shows the calculated values of activity for equations (6), and (9), as well as their Gibbs free energy, and the equilibrium pH. Thermodynamically the lead precipitation starts at pH 3.9 ($PbSO_4$), although visually it is noticed at pH 3. In the case of the $Pb_3(CO_3)_2(OH)_2$, this visually starts at pH 7, whereas according to thermodynamics the precipitation of such specie would initiate at pH 6. Differences between observations and calculations are due to human errors and it suggests the use of another technique (i.e., conductivity measurements[13]) to detect accurately the moment at which the precipitation phenomena take place.

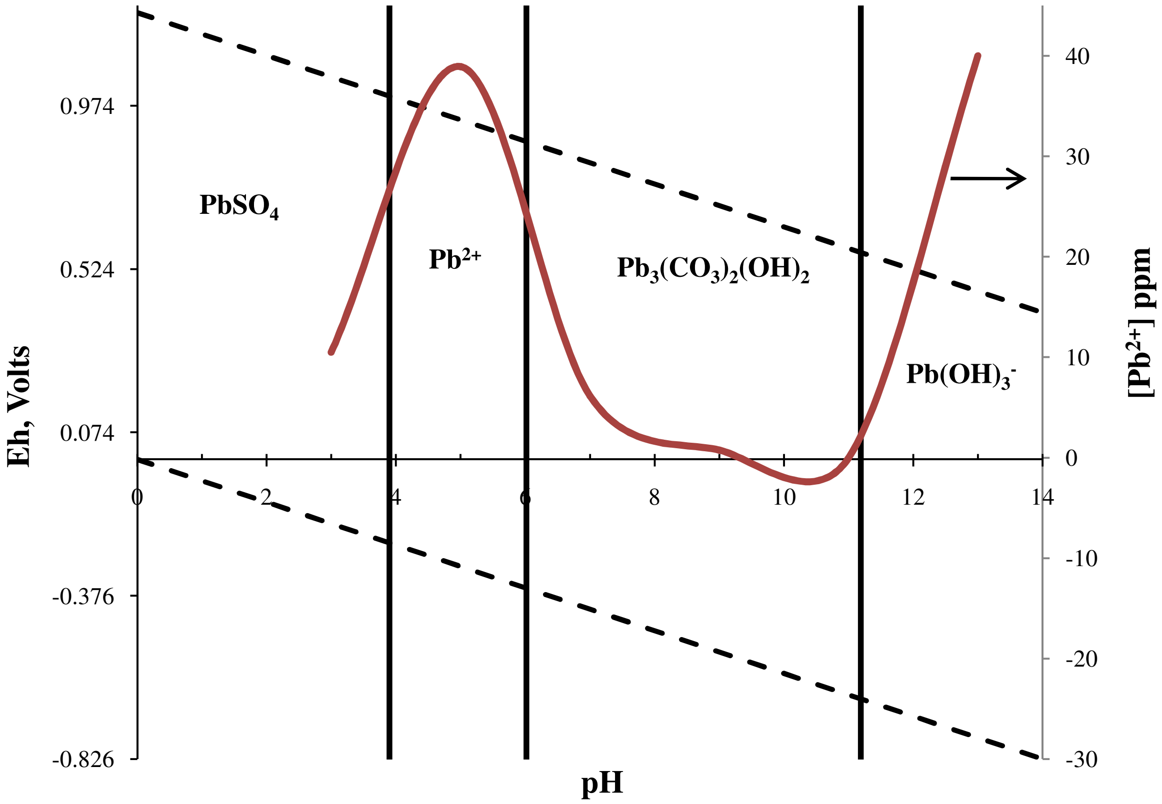

Figure-1
Transformation lines with changes on the metal concentration in the bulk solution. Lead – sulfate - water system

Table-1
Calculated values of activity of Pb^{2+}, Gibbs free energy, and the equilibrium pH for equations (6), and (9)

Reaction	**aPb^{2+}**	**ΔG° Reaction (Kcal/mol)**	**Equilibrium pH**
$PbSO_4 + 2H^+ \rightarrow Pb^{2+} + H_2SO_4$	3.84E-04	-5975.14	3.9
$Pb_3(CO_3)_2(OH)_2 + 6H^+ \rightarrow 3Pb^{2+} + 4H_2O + 2CO_2$	2.14E-04	-24617.8	6.0

Precipitation of copper species: From qualitative DRX analysis the detected crystalline species are the hydrated copper hydroxisulphate ($Cu_4SO_4(OH)_6H_2O$), cupric hydroxide ($Cu(OH)_2$), and cupric oxide (CuO). In the pH range from 3 to 5.5 there is not precipitation of any copper specie, whereas among pH 7.5 and 10.5 the three former species co-exist. From pH 5.5 to 7.5, and 10.5 to 13, the precipitated species are the hydrated copper hydroxisulphate, and the cupric oxide, respectively.

The solid, $Cu_4(SO_4)(OH)_6.H_2O$, in a given pH transforms itself and co-exist with both the cupric hydroxide and the cupric oxide, and finally the cupric hydroxide transforms to cupric oxide at pH 10.5.

In the case of formation of the hexahydrated copper hydroxisulphate :

$$Cu_4SO_4(OH)_6 \cdot H_2O + 6H^+ \rightarrow 4Cu^{2+} + SO_4{}^{2-} + 7H_2O \qquad (10)$$

For the precipitation of the cupric hydroxide:

$$4Cu(OH)_2 + 2H^+ + CuSO_4 \rightarrow CuSO_4(OH)_6 \cdot H_2O + Cu^{2+} + H_2O \quad (11)$$

Being the formation of the cupric oxide defined by the following reaction:

$$4CuO + CuSO_4 + 3H_2O + 2H^+ \rightarrow Cu_4SO_4(OH)_6 \cdot H_2O + Cu^{2+} \qquad (12)$$

The Pourvaix diagram for the Cu – SO_4 – H_2O system is shown in figure 2, and table 2 shows the Gibbs free energy values for reactions (10), (11), and (12).

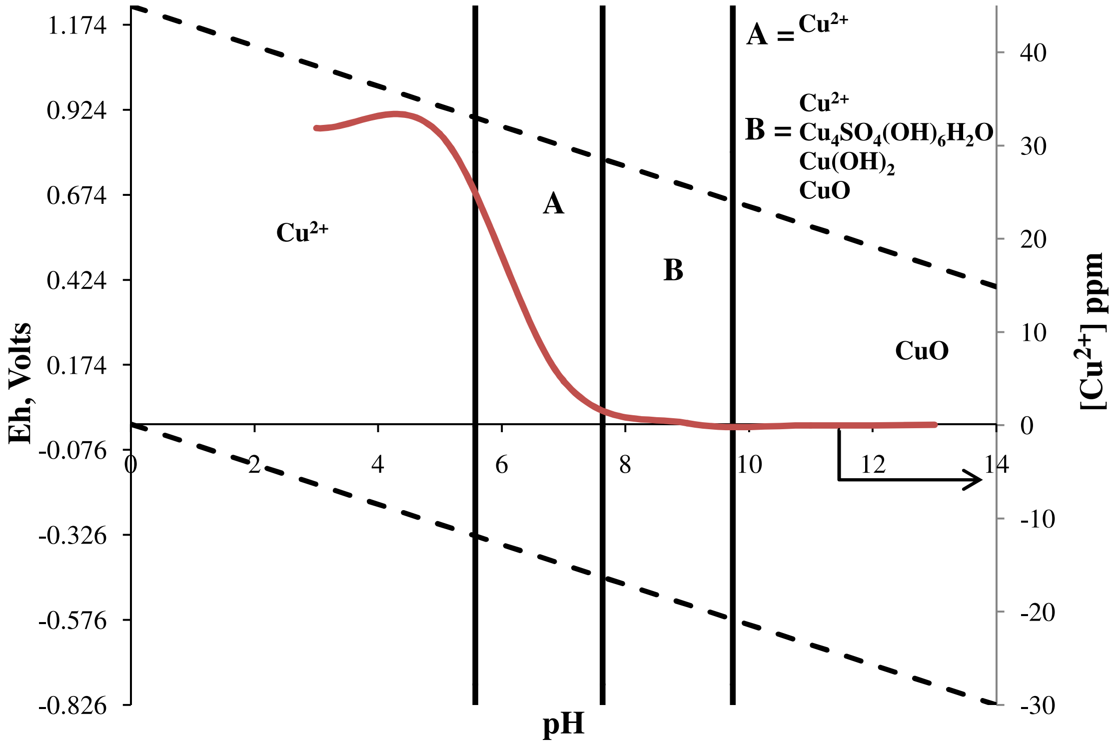

Figure-2
Pourvaix diagram for the Cu-SO_4-H_2O system. A and B means the liquid and solid species that co-exist in a respective region

Table-2
Activity, Gibbs free energy, and equilibrium pH values for reactions (10), 11), and (12)

Reaction	**aCu^{2+}**	**ΔG° Reaction (Kcal/mol)**	**Equilibrium pH**
$Cu_4SO_4(OH)_6 \cdot H_2O + 6H^+ \rightarrow 4Cu^{2+} + SO_4{}^{2-} + 7H_2O$	8.00E-04	193.6	5.6
$4Cu(OH)_2 + 2H^+ + CuSO_4 \rightarrow CuSO_4(OH)_6 \cdot H_2O + Cu^{2+} + H_2O$	4.08E-05	176.37	7.6
$4CuO + CuSO_4 + 3H_2O + 2H^+ \rightarrow Cu_4SO_4(OH)_6 \cdot H_2O + Cu^{2+}$	4.08E-05	143.4	9.7

Precipitation of nickel species: In this case and according the DRX analysis the only detected specie was the nickel hydroxide ($Ni(OH)_2$). Visually the precipitation of such specie is detected at pH 9; although, thermodynamically the nickel hydroxide starts forming at pH 7.6. Figure 3 shows the Eh-pH diagram for the $Ni\text{-}SO_4\text{-}H_2O$ system.

From the above information the proposed reaction is as follows:

$$Ni(OH)_2 + 2H^+ \rightarrow Ni^{2+} + H_2O \qquad (13)$$

The corresponding thermodynamic values are shown in table 3.

Sean et al[14]., Chanturiya, et al[15]., Liu[16], Shigehito et al[17]., and Guo-riu Fu[18], reported the precipitation of two Nickel phases named α – Nickel hydroxide, and β – Nickel hydroxide, within the pH range established in this work. These species were detected by using a IR analysis technique.

Selective precipitation of metals: With all the above information it is possible to design a cleaning route for water contaminated with lead, copper and nickel. By adjusting the pH of the media selectively any of the metals can be precipitated and then separated by filtration or sedimentation. The proposed procedure is described as follows:

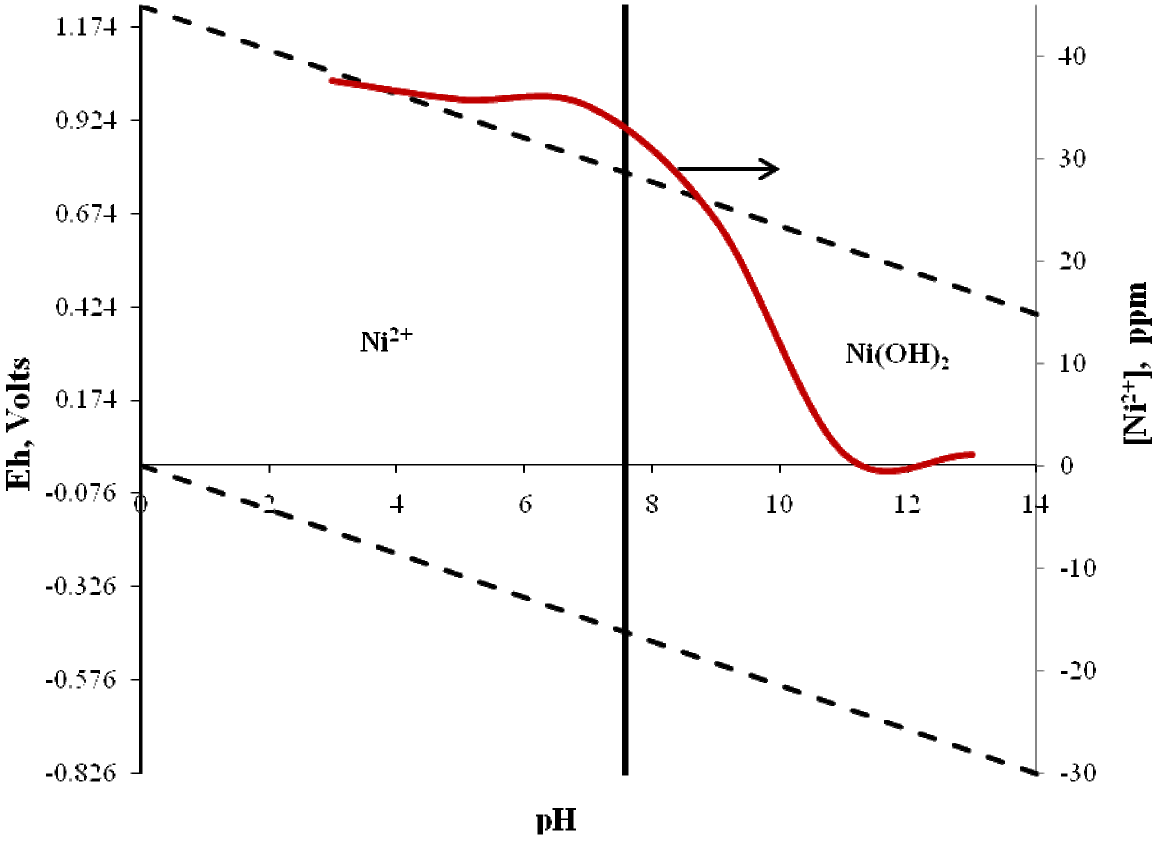

Figure-3
Pourbaix diagram for the Ni – SO_4 – H_2O system. Changes on dissolved nickel is included

Table-3
Activity coefficient, Gibbs free energy, and equilibrium pH for reaction (13)

Reaction	**aCu^{2+}**	**ΔG° Reaction (Kcal/mol)**	**Equilibrium pH**
$Ni(OH)_2 + 2H^+ \rightarrow Ni^{2+} + H_2O$	4.47E-03	-17447.1	7.57

Conclusion

Being the reactions only dependant on the pH of the liquid media. The experimental results converge well enough with the thermodynamic calculations for dissolved or precipitated lead species. With the information from this work it is possible to design a process to clean water contaminated with lead through a sedimentation-flotation route.

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