Research Journal of Recent Sciences ISSN 2277-2502
Vol. **2(9),** 1-4, September **(2013)** *Res.J.Recent Sci.*

Precipitation of Lead Species in a Pb – H_2O System

Escudero R.*, Espinoza E. and Tavera F.J.
Instituto de Investigaciones Metalurgicas, Universidad Michoacana de San Nicolas de Hidalgo, Morelia, Michoacán, MÉXICO

Available online at: www.isca.in
Received 17th March 2012, revised 23rd August 2012, accepted 23rd March 2013

Abstract

Precipitation of metallic species in either, liquid-liquid, solid-solid, or liquid-solid systems is a current phenomenon 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 the 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 by adding $Pb(N_O3)_2$*, and open to the atmosphere. The pH of the media was varied from 3 to 13. The proposed mechanism of reaction for the system tested here is:* $Pb(NO_3)_2 + H_2O \rightarrow Pb^{2+} + PbSO_4 \rightarrow Pb_3(CO_3)_2(OH)_2$*. Being the formation of lead carbonate explained by considering the replacement of sulfates or sulfites, to carbonates in a system reacting with the atmospheric air. From the information derived in this work, it is possible to design a process for cleaning water contaminated with heavy metals through the route sedimentation – flotation, and to predict or avoid the formation of certain species on ore particles that reduce the metallurgical efficiency of 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[4-6].

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:

$$I = \frac{1}{2}\sum m_i z_i^2 \tag{1}$$

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 salt $Pb(NO_3)_2$, 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:

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

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 a of given specie I, can be calculated according to:

$$a[i] = \gamma_i m_i \tag{3}$$

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:

$$Eh = E° - \left(\frac{0.05916}{Z}\right)\log Q \tag{4}$$

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:

$$E° = \frac{-\Delta G°}{ZF} \tag{5}$$

Where $\Delta G°$ 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 salt was dissolved in distilled water and physicochemical parameters as ionic strength, activity coefficient, activity, and electrochemical potential were calculated, in a pH ranging from 3 to 13. Lead 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 lead 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 practically re-dissolved at pH 5. Lead crystals are formed again at pH 7, and finally the precipitates are dissolved once more at pH 11. Table 1 shows the chemical analysis results from liquids, and by mass difference the amount of precipitated lead is calculated.

Table-1
Quantitative chemical analysis of lead (dissolved and precipitated), The total lead in the solution is 40 ppm

pH solution	Pb dissolved, ppm	Pb precipitated, ppm
3.0	10.48	29.52
5.0	38.92	1.08
7.0	6.12	33.88
9.0	0.76	39.24
11.0	0.0	40
13.0	40.0	00

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 $Pb_3(CO_3)_2(OH)_2$) or $2PbCO_3Pb(OH)_2$, 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 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 Taylor[12] and Azareño[13]:

$$PbSO_4 + CO_3^- \rightarrow PbCO_3 + SO_4^- \quad (7)$$

In the case of the decomposition of lead sulfate:

$$PbSO_4 + 2H^+ \rightarrow Pb^{2+} + H_2SO_4 \quad (8)$$

From the above reactions it is possible to observe that the dissolution or precipitation of lead species just depends on pH. On the other hand, the calculation of the ionic strength shows that in the range of pH from 3 to 11 there is not a considerable variation of this variable (figure 1); nevertheless, starting at pH 13 the ionic strength observes a noticeable increase due to the fact that large amount of chemical reagent is needed in order to get such value of pH. Beside the former statement, in the same figure there is observed that the concentration of Pb^{2+} in the liquid media decreases because of the presence of lead precipitates at pH higher than 5.

Table 2 shows the calculated values of activity for equations (6), and (8), 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.

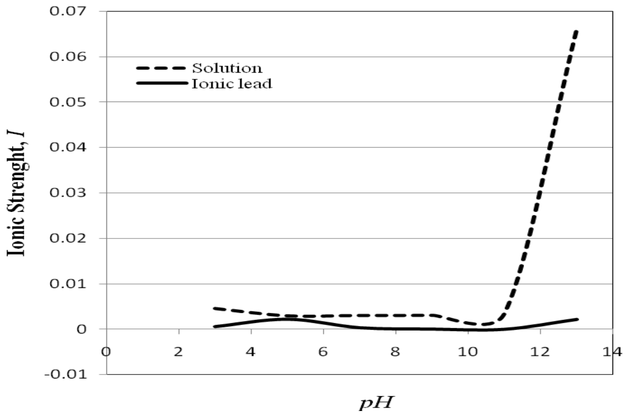


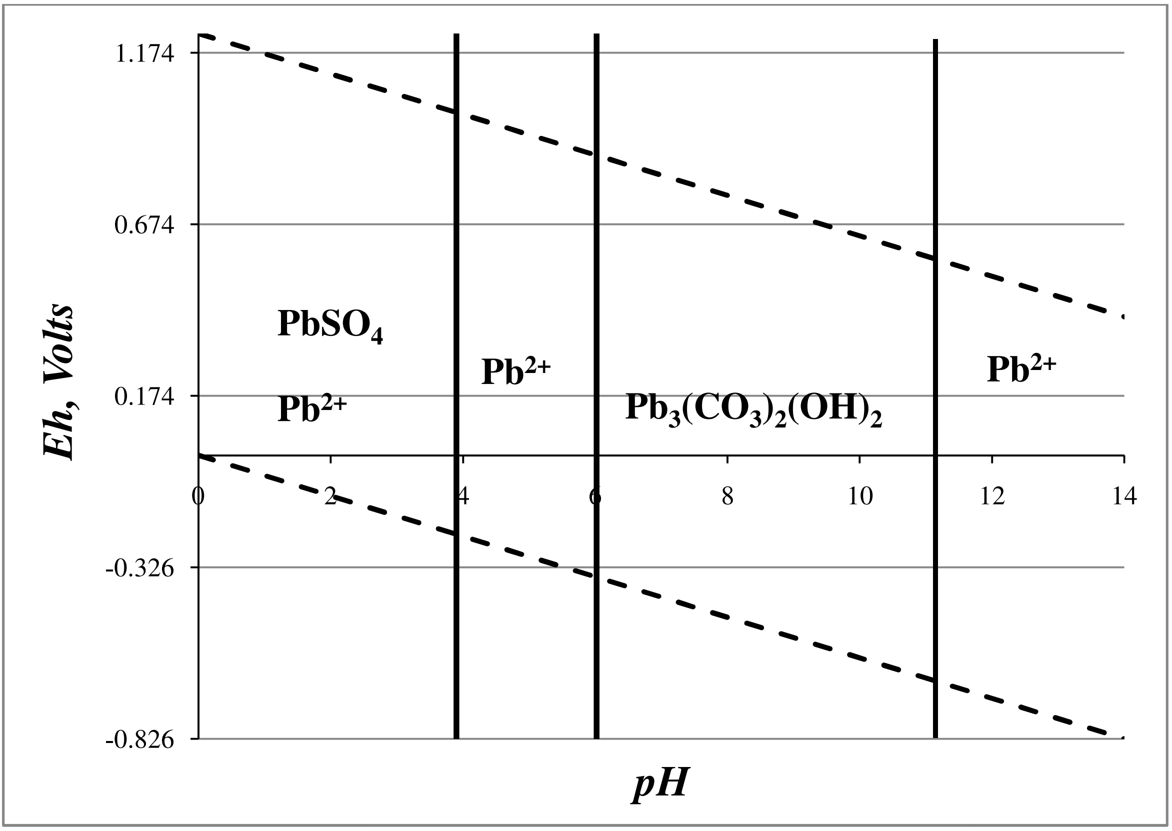
Figure-1
Changes on the ionic strength (I) with the pH of both, the ionic lead and the bulk solution

Thermodynamically and according to Pankow[14] this reaction occurs at pH 11.2. Differences between observations and calculations are due to human errors and it suggests the use of another technique (i.e., conductivity measurements[15,16]) to detect accurately the moment at which the precipitation phenomena take place.

The Pourvaix diagram built according the calculated variables is shown in figure 2. The dashed lines represent the zone where aqueous species are stable; within these lines both the aqueous and precipitated species co-exist. The vertical lines, on the other hand, correspond to the transformations shown in reactions (6) and (8).

Table-2
Calculated values of activity of Pb^{2+}, Gibbs free energy, and the equilibrium pH for equations (6), and (8)

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



\

Figure-2
Transformation lines for reactions (6), and (8) in a *Eh* vs *pH* equilibrium diagram for the Pb – SO_4 - H_2O system

In light of the above, from pH 0 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 range of pH from 6.0 to 11.2 the steady species are the Pb^{2+} and the $Pb_3(CO_3)_2(OH)_2$.

Conclusion

From the thermodynamic analysis of the Pb-H_2O system, and experimental data after dissolving lead salt ($Pb(NO_3)_2$) in distilled water, and varying the pH from 3 to 13, the following conclusions are drawn: Thermodynamically and from experimental data, both the Pb^{2+} and $PbSO_4$ are stable up to pH 3.9. From pH 3.9 to 6.0 the present species are the Pb^{2+} and the $Pb_3(CO_3)_2(OH)_2$; although visually is not evident the $Pb_3(CO_3)_2(OH)_2$. The proposed mechanism of reaction for the system tested here is: $Pb(NO_3)_2$ in water transforms to Pb^{2+} plus $PbSO_4$ and finally the precipitated compound is $Pb_3(CO_3)_2(OH)^2$

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.

References

1. Sharma Pramila, Fulekar M.H. and Pathak Bhawana., E-Waste- A Challenge for Tomorrow, *Research Journal of Recent Sciences,* **1(3)**, 86-93 **(2012)**
2. Aremu M.O., Gav B.L., Opaluwa O.D., Atolaiye B.O., Madu P.C. and Sangari D.U., Assessment of Physicochemical Contaminants in Waters and Fishes from Selected Rivers in Nasarawa State, Nigeria, *Research Journal of Chemical Sciences,* **1(4)**, 6-17 **(2011)**
3. Vaishnav M.M. and Dewangan S., Assessment of Water Quality Status in Reference to Statistical Parameters in Different Aquifers of Balco Industrial Area, Korba, C.G. INDIA, *Research Journal of Chemical Sciences,* **1(9)**, 67-72 **(2011)**
4. Doyle F.M., Ion flotation, Its potential for hydrometallurgical operations, *International Journal of Mineral Processing,* **72,** 387-399 **(2003)**
5. Reyes Pérez M., Tratamiento continuo, de aguas contaminadas con Cu y Pb, por flotación iónica en celdas con dispersores porosos; efecto de las propiedades de la dispersión aire-líquido en la separación, Tesis de maestría, IIM, UMSNH, **(2005)**
6. Barakat M.A., Removal of Cu (II), Ni (III) and Cr(III) Ions from Wastewater Using Complexation - Ultrafiltration Technique, *Journal of Environmental Science and Technology,* **1(3),** 151-156 **(2008)**
7. Yoon R.H., The Role of Surface Forces in Flotation Kinetics, Flotation- Kinetics and Modelling, Proceedings of the XXI International Mineral Processing Congress, **Vol. B**, oral sessions, P. Massacci, Elsevier, Rome, Italy, July 23-27, **(2000)**
8. Manouchheri H.R., Hanumantha Rao K., Forssberg K.S.E., Correlation between the Electrical Properties of Quartz, feldspar and Wollastonite Minerals and their Tribo-Electric Separation Potential, Physical separation Processing, Proceedings of the XXI International Mineral Processing Congress, **Vol. B**, oral sessions, P. Massacci, *Elsevier,* Rome, Italy, July 23-27 **(2000)**
9. Garrels R.M. and Christ C.L., Minerals, Solutions, and Equilibria, Harper & Rowe, N. Y. 450 **(1965)**
10. Cisternas L.A., Diagramas de fases y su aplicación, Reverte, **(2009)**
11. López F.Y., Relaciones hídricas en el continuo agua-suelo-planta-atmósfera, Univ, Nacional de Colombia, **(2000)**
12. Taylor P. and Lopata V.J., Stability relationships between some solids in the system PbO-CO_2-H_2O, Research Chemistry Branch, Atomic Energy of Canada Limited, Whiteshell Nuclear Research Establishment, Pinawa, Man., Canada ROE ILO, Received May 9, 1983, *Can. J. Chem.*, **62**, 395 **(1984)**
13. Azareño O.A., Núñez J.P., Figueroa L.A., León D.E., Fernández S.S., Orihuela S.R., Caballero R.M., Bazán R.R., and Yi Choy A.S., Flotación de Minerales Oxidados de Plomo. Revista del Instituto de Investigación de la Facultad de Ingeniería Geológica, Minera, *Metalúrgica y Geográfica*, **5(10)** 34-43 **(2002)**
14. Pankow J.F., Aquatic chemistry concepts, CRC Press **(1991)**
15. Tavera F.J., Colwell D., Escudero R., and Finch J., Estimation of Gas Holdup in Froths by Electrical Conductivity: Aplication of the Standard Addition Method. Revista de Química Teórica y Aplicada AFINIDAD, Barcelona, **57(486)**, 139-142 **(2000)**
16. Ortiz A.A., Nuñez J.A.A., Figueroa L.A., León D.E., Fernández S.S., Orihuela S. R., Caballero R. M., Bazán R.R., Choy A.S.Y. Notas del Curso “Flotación de Minerales Oxidados de Plomo”. Departamento de Ingeniería Metalúrgica, Universidad Nacional Mayor de San Marcos, Peru, 34-43 **(2012)**