Original Research Article

CHEMICAL PRECIPITATION OF NICKEL SPECIES FROM WASTE WATER

ABSTRACT

In the liquid-liquid and solid-liquid systems there is possible to promote the chemical precipitation of certain species by controlling the physical-chemical conditions of the liquid media. In the case of solid-liquid interactions the chemical precipitates can adsorb on the surface of particles modifying their surface properties (i.e. during milling), whereas for the liquid-liquid system this precipitation contributes to clean for instance to wastewater contaminated with heavy metals.

In this work nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$) was dissolved in distilled water, to establish the physicochemical conditions (pH, electrochemical potential, ionic strength, activity coefficient) that enhance the chemical precipitation of nickel species.

The experimental results show that nickel precipitates as nickel hydroxide ($Ni(OH)_2$) starting at pH 3, being more evident at pH 9. Nickel precipitates completely at pH 11. From these results, there is possible to propose a cleaning route of water contaminated with nickel.

Keywords: Wastewater treatment, heavy metals, chemical precipitation, Pourvaix diagrams, amorphous nickel.

1. INTRODUCTION

Many procedures have been designed to process waste water contaminated with heavy metals, for instance, through activated membranes and ores, fungus, bacteria, algae, by means of chemical precipitation by varying the pH of the liquid media, among others, including the technology normally used to concentrate minerals such as flotation columns [1, 2, 3, 4]; although the corresponding thermodynamic analysis is not well understood yet.

In other case, the galvanic interaction among species in the solid-liquid and solid-solid systems during the mineral processing (i.e., milling) alter the surface properties of particles, decreasing the metallurgical performance of the unit operation, for example, during recovery of valuable ore particles [5, 6].

Regarding the physicochemical properties of the liquid media that rule the interaction between solids and liquids (Ionic strength (I), Chemical activity (a), Activity coefficient (γ)), their knowledge allow to calculate the Electrochemical potential (Eh), throughout the equation proposed by Garrels [7], and depicted by Escudero [8] in a previous work.

With all the former parameters known, it is possible to build a thermodynamic stability diagram (Pourvaix diagram) in such a way that reaction (transformation) lines are located, together with the co-existing steady species (solid or liquid), under certain pH and Eh conditions

In this work nickel salt was 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. Nickel precipitates were identified and the corresponding formation reactions were established and located in a Pourbaix diagram.

The obtained information makes possible at first to design a procedure to clean water contaminated with nickel 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.

2. MATERIAL AND METHODS

The experimental work was carried out in a cell with 0.1 m in diameter and 0.3 m high. The cell was constructed with transparent acrylic tube.

2.1. Preparation of diluted solutions of nickel in distilled water

Nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$) was dissolved 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 by centrifugation, dried at room temperature and analyzed through X-ray diffraction (XRD). The remnant nickel in each solution was 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.

2.2. Chemical analysis of precipitates and solutions

The chemical analysis of precipitates was carried out by X-ray diffraction (XRD). The quantitative chemical analysis of liquids was carried out by atomic absorption spectroscopy (AAS).

2.3. 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 line as a function of the pH. The resulting equilibrium diagrams are shown below.

Figure 1 shows the experimental setup to dissolve the salt of nickel and varying the pH. The monitored variables were electrical conductivity, pH, temperature, and ORP

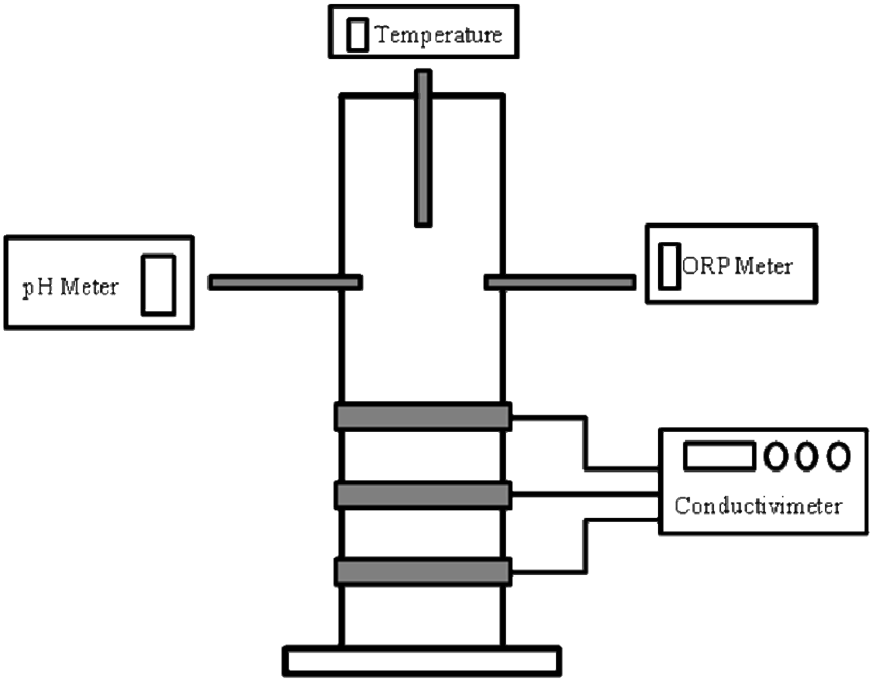

Figure 1.- Experimental setup to monitor the dissolution and chemical precipitation of nickel.

3. RESULTS AND DISCUSSION

From the qualitative chemical analysis by X-ray diffraction, the only detected crystalline specie was the nickel hydroxide within the pH from 7 to 13; although, the precipitation of $Ni(OH)_2$ starts at pH 9 as shown in Figure 2.

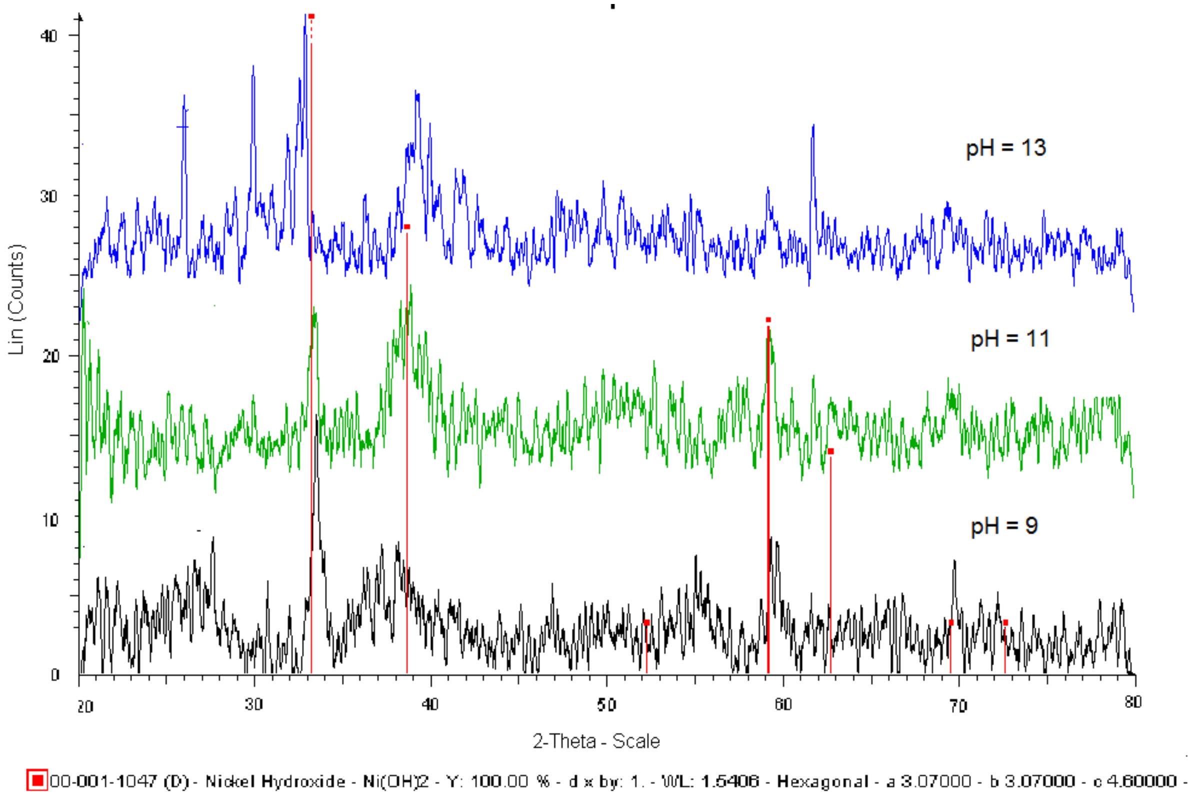

Figure 2.- X-ray diffraction results for nickel precipitates at pH 9, 11, and 13.

The literature agrees with the identification of $Ni(OH)_2$ and differentiates this phase as α-$Ni(OH)_2$ and β-$Ni(OH)_2$, [9, 10, 11, 12, 13, 14, 15]. The alpha phase appears at angles 12.52, 23.68, and 35.16; whereas the beta specie is shown at 19.2, 38.7, and 52.0.

3.1. Quantification of nickel in solution

The quantitative chemical analysis data of nickel in solution indicate that practically at pH 3 all the nickel is in solution. Between pH 5 and 9 coexist both the precipitated and dissolved species, and from pH 11 the nickel in solution is close to zero. The above behavior is shown in Table I.

Tabla I.- Results of the quantitative chemical analysis by spectrophotometry of atomic absorption of the aqueous media at different pH.

	pH 3	pH 5	pH 7	pH 9	pH 11	pH 13
Ni total (ppm)=	40	40	40	40	40	40
Ni^{2+} in solution (ppm)=	38.5	38.5	35.2	24	0.2	0.1
Ni precipitated (ppm)=	1.5	1.5	4.8	16	39.8	39.9

3.2. Thermodynamic analysis of the reaction system Ni-H_2O

The proposed mechanism of reaction is as follows:

$$\mathrm{Ni(OH)_2 + 2H^+ \rightarrow Ni^{2+} + 2H_2O} \qquad \Delta G° = -17447.1 \text{ cal/mol} \qquad (1)$$

From reaction (1) the precipitation depends only on the activity of hydrogen ions and specifically on the pH of the medium. Calculation of the equilibrium pH indicates that precipitation of nickel takes place at pH greater than 7.6, as indicated in Table II.

Table II.- Reaction-free energy values and equilibrium constant for the proposed reaction (1)

Reaction	aNi^{2+} aNi^{2+}	*ΔG°* *(Kcal/mol)*	*K*	*Ph*
$\mathrm{Ni(OH)_2 + 2H^+ \rightarrow Ni^{2+} + 2H_2O}$	4.476E-03	-17.4471	6.26E12	7.57

From the calculation of the ionic strength for changes on the pH of the system, it is observed from Figure 3 that at the equilibrium pH, the ionic strength of Ni $^{2+}$ decreases as the nickel hydroxide precipitation proceeds, as predicted by thermodynamics. Results of calculations of ionic force, activity coefficient, and activity for reaction (1) are included in Table III.

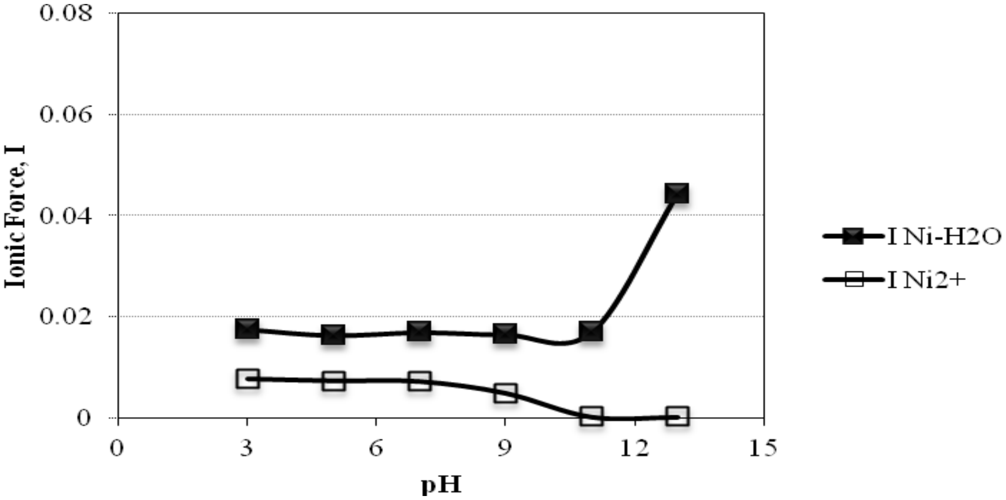

Figure 3.- Ionic force (I), calculated for the Ni-H_2O system in the pH range from 3 to 13.

Table III.- Calculated values of ionic force (I), activity coefficient (γ), and activity (a) for reaction (1).

	pH 3	pH 5	pH 7	pH 9	pH 11	pH 13
I, liquid	0.0175	0.0163	0.0169	0.0165	0.0170	0.0443

I, Ni^{2+}	0.0077	0.0073	0.0072	0.0049	0.00024	0.0002
γ± NI^{2+}	1.8594	1.8209	1.8408	1.8261	1.8424	2.6822
aNi^{2+}	0.0071	0.0066	0.0066	0.0044	0.0002	0.0002

In agreement with the ionic strength behavior, the ionic nickel activity decreases with the activity coefficient, due to the decrease in Ni^{2+} concentration in the liquid, because of the increase in pH (see Figure 4).

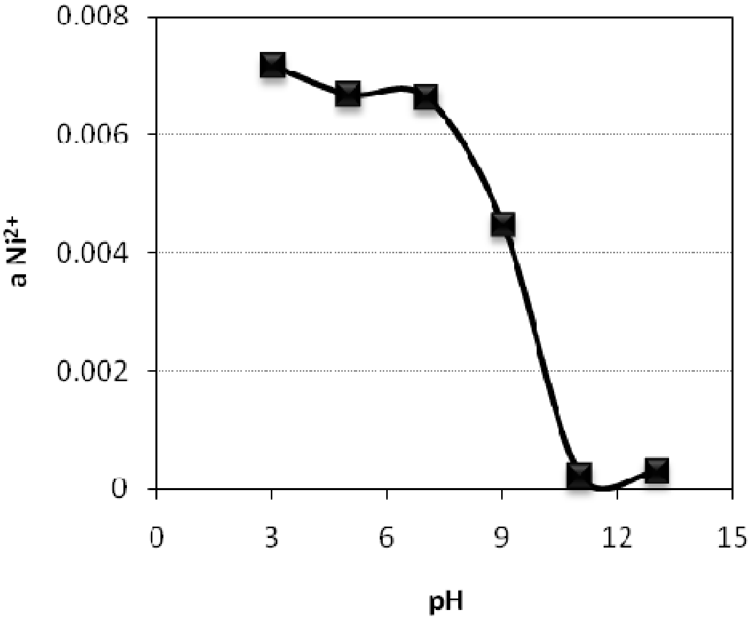

Figure 4.- Changes in the calculated activity of Ni2+ with the pH of the liquid for the Ni-H2O system.

On the other hand, the location of the transformation line (reaction (1)) in the Pourvaix diagram is shown in Figure 5.

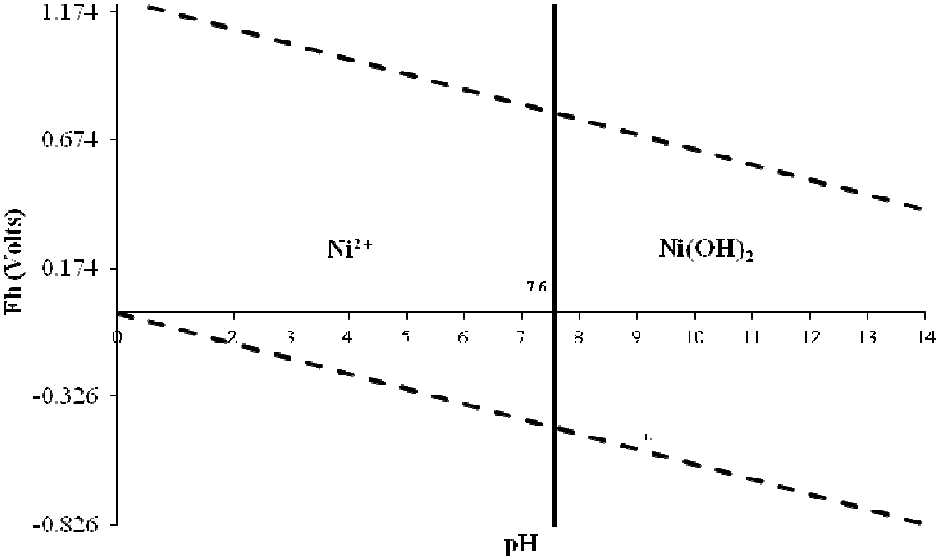

Figure 5.- Transformation line of reaction (1) in the Eh-pH diagram for the system Ni-H_2O.

The dashed lines indicate the stability zone of the aqueous species and within them co-exist both the crystalline and in solution phases, whereas the vertical line represents the transformation reaction. According to reaction (1) the transformation only depends on the pH of the liquid; nevertheless, with the physicochemical calculated information, there is possible to propose another reaction, which limits the stability zone of reaction 1 in terms of dependence of both Eh and pH. This reaction could be the following:

$$\mathrm{Ni(OH)_2 + H_2O \rightarrow Ni^{2+} + 4H^+ + \frac{3}{2}O_2 + 6e^-} \tag{2}$$

Reaction (2) depends on Eh and pH; nonetheless, in order to locate properly this line in the Pourvaix diagram, additional experimentation must be run, by controlling and measuring all the variables such as concentration, pressure drop, temperature, and pH.

4. CONCLUSION

From the experimental work after dissolving $NiSO_4$▪H_2O in distilled water and changing the pH of the liquid media, de following conclusions are drawn:

In this system (Ni-H_2O) the Ni2+ transforms in only one crystalline specie, $Ni(OH)_2$. This transformation depends only of the pH of the liquid.

The experimental results show a great concordance with the thermodynamic calculations, in such a way that it is possible to design a cleaning procedure of water contaminated with Ni2+, trough the route chemical crystallization and sedimentation.

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