# CHEMICAL PRECIPITATION OF NICKEL SPECIES FROM WASTE WATER

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## ABSTRACT

In liquid-liquid and solid-liquid systems, it is possible to promote chemical precipitation of certain species by controlling the physicochemical conditions of the liquid media. In the case of solid-liquid interactions the chemical precipitates can absorb on the surface of particles modifying their surface properties (i.e. during milling), whereas for liquid-liquid system precipitation contributes to the removal (cleaning) of contaminated water (wastewater).

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, it is possible to propose a decontamination mechanism for wastewater containing 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].

Knowing the physicochemical properties of liquid media which governs the interaction between solids and liquids such as: Ionic strength (I), chemical activity (a), activity coefficient ($\gamma$)), facilitate the determination of electrochemical potential (Eh) through the equation proposed by Garrels [7], and reported by Escudero [8] in a previous work.

With the other parameters known, it is possible to plot or design 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

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

## 2. MATERIAL AND METHODS

The experimental works were 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 ($NiSO_4 \cdot 6H_2O$) (MEYER, 99.7 % purity), was dissolved in distilled water. The pH of the media was measured with a pHTestr 10BNC (Cole-Parmer), and varied in 3,5,7,9,11, and 13. After 24 hours the precipitated solids were separated by centrifugation (Centrifuge Sartorius Mod. A14, 4000 rpm), 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 ($H_2SO_4$) (Sigma Aldrich), and potassium hydroxide (KOH) (Sigma Aldrich). 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) (XR Difractor, Siemens, mod. D-5000). The quantitative chemical analysis of liquids was carried out by atomic absorption spectroscopy (AAS) (Spectrometer Perkin-Elmer, mod. 3100).

### 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 (Conductivimetre TACUSSEL Corv. 62), pH, temperature, and ORP (Thermocientific Mod. Orion 3 Star).

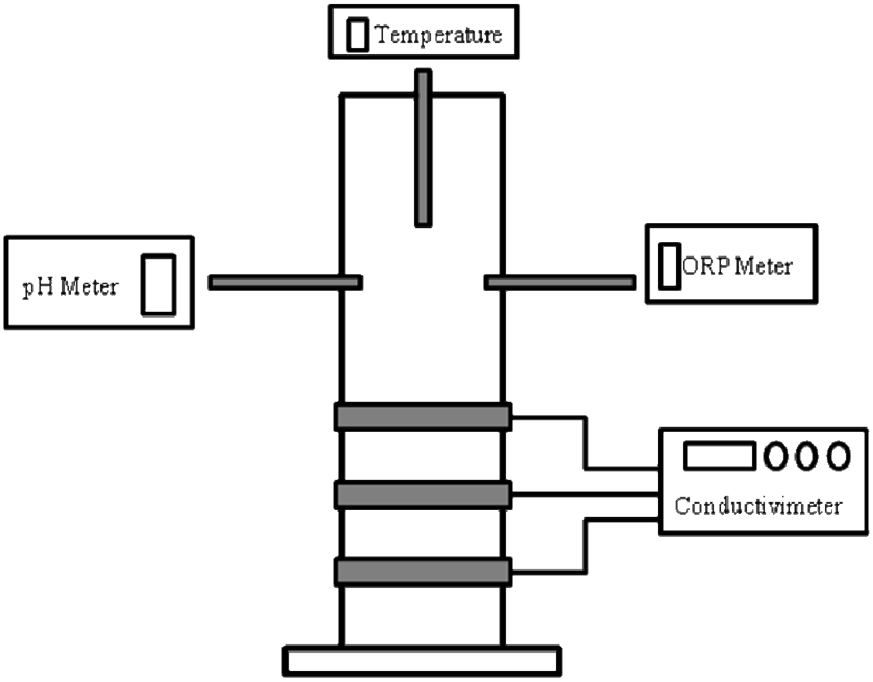

**Figure 1.- Experimental setup to monitor the dissolution and chemical precipitation of nickel.**

## 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.

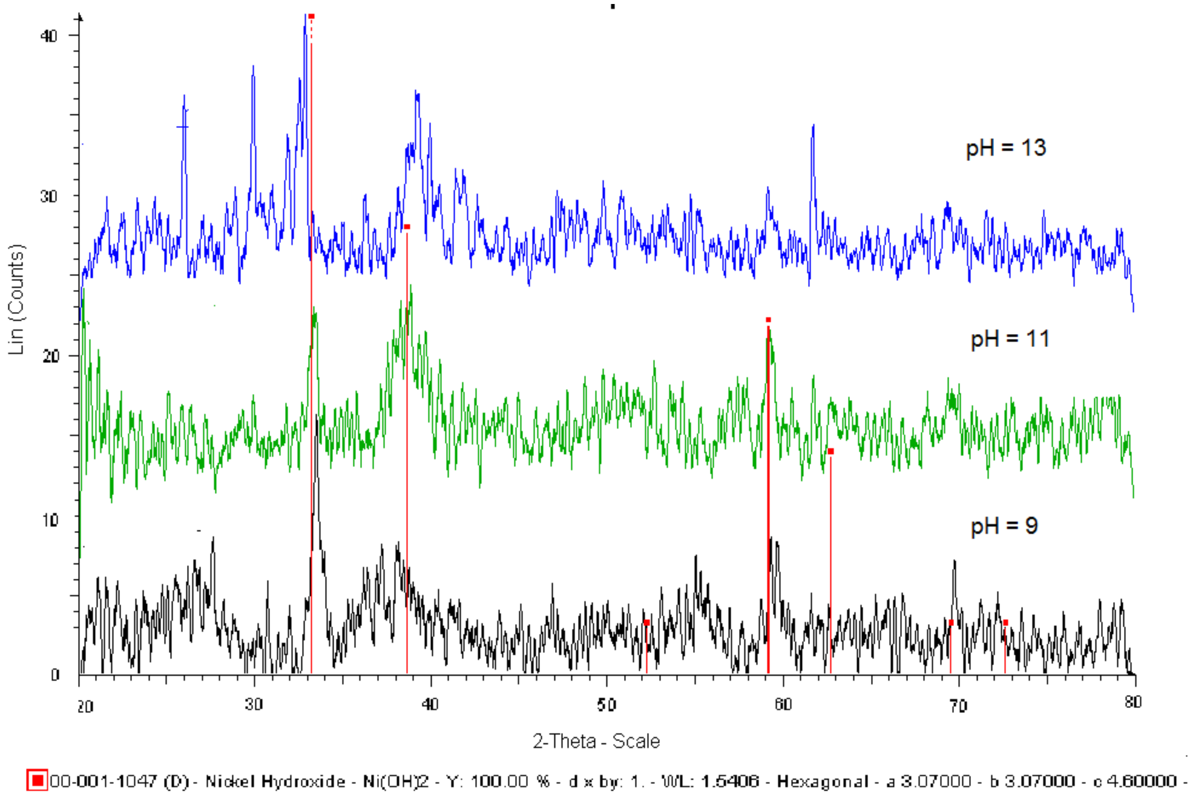

**Figure 2.- X-ray diffraction results for nickel precipitates at pH 9, 11, and 13.**

The literature agrees with the identification of $Ni(OH)_2$ and differentiates this phase as $\alpha$-$Ni(OH)_2$ and $\beta$-$Ni(OH)_2$, [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.

**Table 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:

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

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** | ***aN+2*** | ***ΔG°*** ***(Kcal/mol)*** | ***K*** | ***pH*** |
|---|---|---|---|---|
| $Ni(OH)_2 + 2H^+ \rightarrow Ni^{+2} + 2H_2O$ | 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.

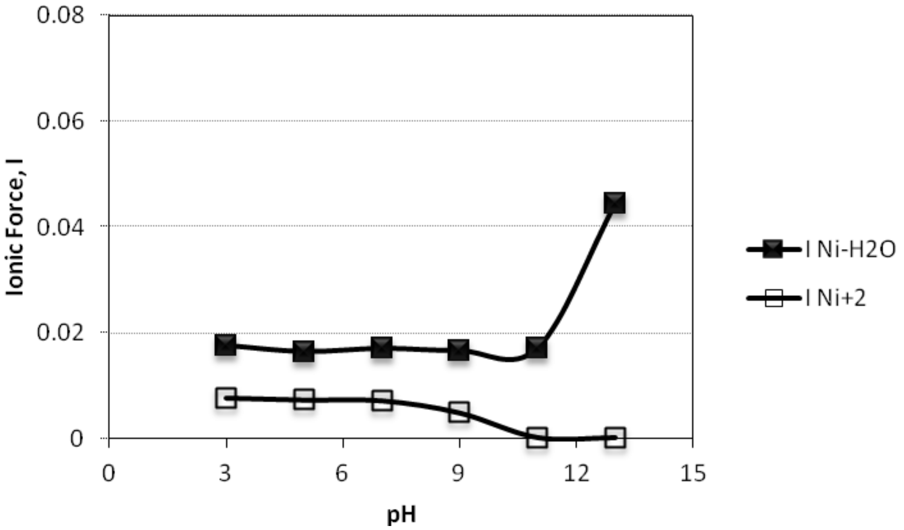

**Figure 3.- Ionic force (I), calculated for the Ni-$H_2O$ system in the pH range from 3 to 13.**

**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).

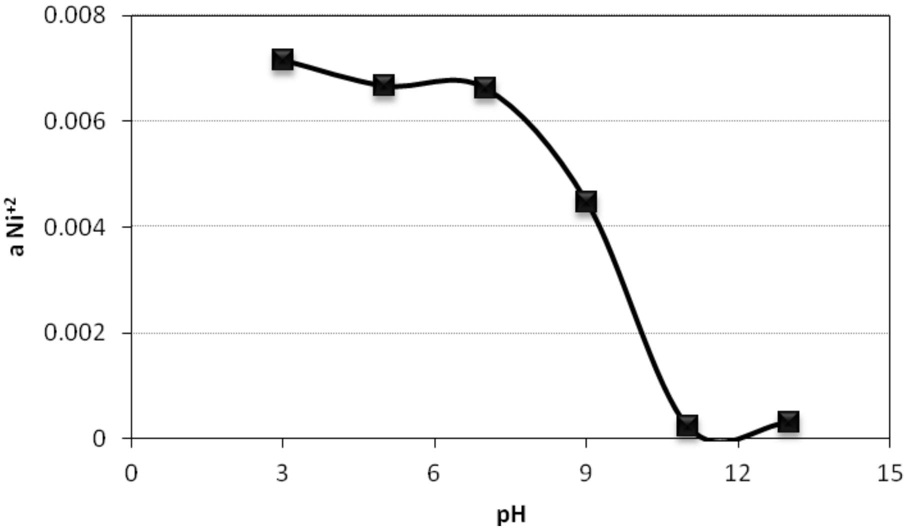

**Figure 4.- Changes in the calculated activity of $Ni^{+2}$ with the pH of the liquid for the Ni-H2O system.**

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

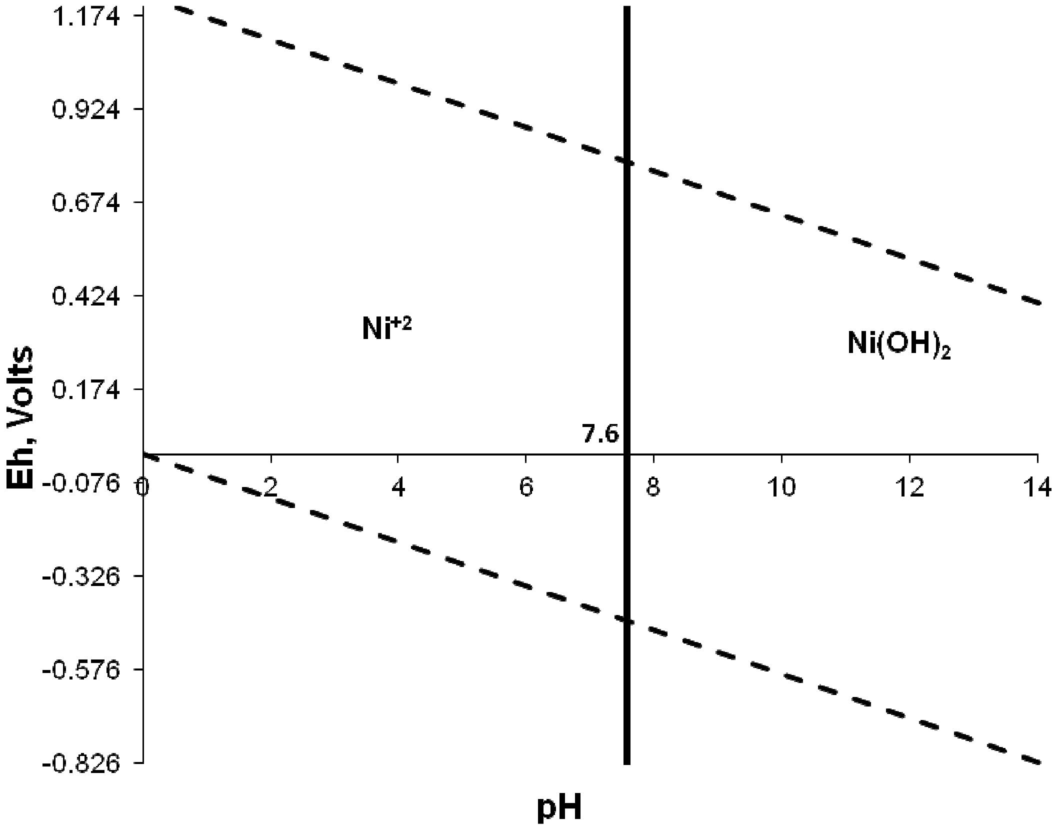

**Figure 5.- Transformation line of reaction (1) in the Eh-pH diagram for the system Ni-$H_2O$.**

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:

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

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, the following conclusions are drawn:

In this system (Ni-$H_2O$) the $Ni^{+2}$ transforms in only one crystalline specie, $Ni(OH)_2$. This transformation depends only of the pH of the liquid.

The physicochemical properties of the liquid media: ionic strength, $Ni^{+2}$ activity, and activity coefficient decrease above pH 7.6 since the nickel precipitation proceeds.

The experimental results show a great concordance with the thermodynamic calculations in such a way that it is possible to design a cleaning procedure for water contaminated with $Ni^{+2}$, trough the route chemical precipitation, crystallization, and sedimentation.

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## COMPETING INTERESTS

The authors of this work declare that that no competing interests exist.

## AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration between all authors. Authors EEE and REG designed and ran the experimental work, whereas authors REG and FR were very valuable members during the discussion of the results. All authors managed the literature searches and produced the initial draft. All authors read and approved the final manuscript.

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