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SELECTIVE ELECTRODEPOSITION TO EXTRACT COBALT AND NICKEL FROM LEACHING SOLUTION

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Abstract: *Leaching solutions of complex ore concentrates are reach in different elements, some hindering the extraction of others. Chemically similar elements are difficult to extract using conventional separation methods. Electrochemical techniques are employed for Co and Ni selective extraction out of so-called pregnant leaching solution (PLS). Selective electrodeposition using chronoamperometry (CA) as a tool was used to extract cobalt and /or nickel from the solution. Besides different ions depositing at applied cathodic potential, hydrogen evolution reaction also occurs, which can impede deposition of the desired metals. Previous Linear sweep voltammetry (LSV) analysis of prepared model solutions at different pH values, and upon H_2O_2 addition, was conducted. The removal of metal ions from the solution, can be performed with adjusting the pH and applied potential (E), so their combination in electrochemical hydro-extraction for Ni and Co is investigated. It has been demonstrated that Fe can be separated from Ni and Co through Fe precipitation in the pH range of 3–6, followed by the electrochemical extraction of Ni/Co.*

Keywords: *metal ions extraction; leaching selectivity.*

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1. INTRODUCTION

Cobalt and nickel are now considered critical raw materials. Cobalt plays a vital role in various electrical applications, especially in the fast-growing market of electric vehicles [1]. The demand for nickel is expected to increase significantly in the coming decades, primarily due to the rising need for fast-working and high-tech steels, which have broad industrial applications [2].

The primary source of these metals is lateritic ores [3]. These ores are in an oxidized state and contain high amounts of iron, which is undesirable for the extraction processes of cobalt and nickel. Due to the low content of cobalt and nickel in the ores, a meticulous processing route is essential. The development of new technologies, including advanced precipitation methods, makes processing such ores economically and technically viable.

Generally, iron precipitation occurs at a lower pH, where cobalt and nickel remain stable in the solution. Iron removal is typically achieved by adding bases to adjust the pH of the pregnant leach solution. Precipitation has been challenging due to the overlapping behavior of iron, nickel, and cobalt. This paper aims to delve deeper into this ternary system. It also partially presents a new approach using electrochemical methods for extraction experiments.

2. EXPERIMENTAL

Lateritic ore concentrate leaching was performed in a standard glass cell, employing stirring unit and temperature control. The reaction flask was placed inside of a temperature controlled heating unit (SAF Wärmetechnik GmbH, Germany) and temperature was kept constant at 70 °C for 2 h. The lateritic ore concentrate was leached with 1M H2SO4 at a stirring speed of 300 rpm. Liquid to solid ratio upon the leaching was 5:1. The ore solid residue was filtered off using a centrifuge, and the resulting clear solution was then utilized for further electrochemical investigations.

Electrochemical measurements were performed in a standard three electrode system using potentiostat/galvanostat, model SP-200 (Bio-Logic SAS, France). Glassy carbon electrode served as working electrode, Pt wire as counter electrode and saturated calomel electrode (SCE) as a reference electrode. All measurements were conducted in the as prepared filtered solution (pH 0.5) and in the NaOH-treated filtered solution (pH 3.7). Addition of NaOH was performed under constant stirring at 500 rpm in a separated beaker. Cyclic voltammetry advanced (CVA) was performed with a sweep rate of 10 mV s−1, according to Open circuit potential; -1200 mV to 1200 mV; Cathodic holding time was 2 minutes. Chronoamperometry (CA) was employed

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for the electrodeposition of ions from the solution on the GC electrode.

3. ELECTROCHEMICAL LEACHING APPROACH

Selective electrodeposition using chronoamperometry (CA), by applying a constant potential to the PLS, as a tool was used to extract cobalt and /or nickel from the solution. This leads to the reduction of the cobalt and nickel ions from the solution and their deposition on the working electrode. The value of deposition potential was determined using the Nernst equation (1). This potential then was adjusted to the concentration of the obtained leachate (pH = 0.5).

$$E\ (Co/Co^{2+}) = E_0(Co/Co^{2+}) + \frac{R * T}{z * F} * \ln(\ c(Co^{2+}) \qquad (1)$$

Where: z - number of exchanged electrons, F - Faraday constant, R - ideal gas constant, T - Temperature in K, c - concentration of ion in the solution. Standard potentials were given versus SHE, having in mind that: E (*vs* SCE) = E (*vs* SHE) – 0.244 *V*.

Immersing GC working electrode in the filtered solution applying potential required for Co deposition, can lead to deposition of some other ions from solution, meaning that electrodeposition is not selective. Fe ions present in this solution (5,97g/L) should be in the Fe^{3+} form, according to the Pourbaix diagram. In this case Fe^{3+}/Fe^{2+} reaction could have occurred as well. This transition would have been registered as current peaks, so it would be difficult to differentiate which peak corresponded to which process.

Out of this reason, the only metals that could be deposited at the used potentials are nickel, cobalt and iron. Fe deposition, though, should only take place at lower potentials, according to the calculations. Deposition of other metals should not be possible, since their potential of reduction is more negative to the electrodeposition potentials. Chromium is unlikely to deposit as well, hindered by lower hydrogen overpotential and therefore main reaction is hydrogen evolution (HER), instead of deposition of chromium.

Besides different ions depositing at applied cathodic potential, hydrogen evolution reaction also occurred. This reaction can impede deposition of the desired metals, so applied potential was negative enough for the metal deposition to happen, but not too negative to have hydrogen evolution. The addition of oxidizing agent H_2O_2 enables the onset of Fe^{3+}/Fe^{2+} reaction at altered potentials, what benefits the selectivity of extraction process. In order to reach maximum selectivity and minimum hydrogen evolution, potentials of -680 mV and -900 mV were chosen for the electrodeposition using CA in these experiments.

3.1. Linear Sweep Voltammetry analysis

Linear sweep analysis of prepared solution at different pH and upon treatment with H_2O_2 are shown, but for comparison the LSV curves of non-H_2O_2-treated solution are presented as well. The removal of metal ions from the solution, especially iron, chromium and aluminum, can be performed with adjusting the pH. The LSV curves focus on anodic dissolution of the deposit from leachate with addition of hydrogen peroxide into the leachate and different potential applied in for preceding electrodeposition.

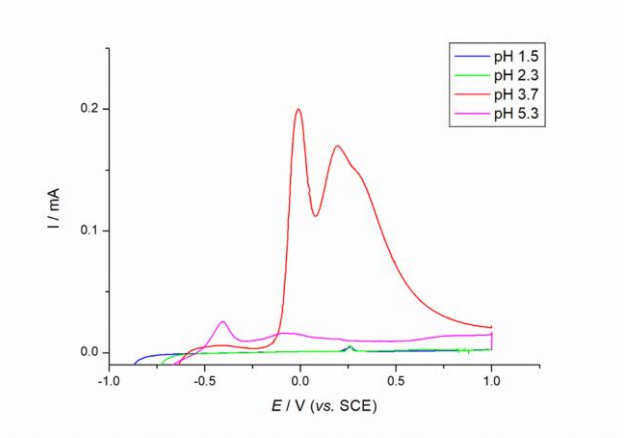

Figure 1. LSV curves, potential of -900 mV, without H_2O_2, varying pH, v =10 mV s-1

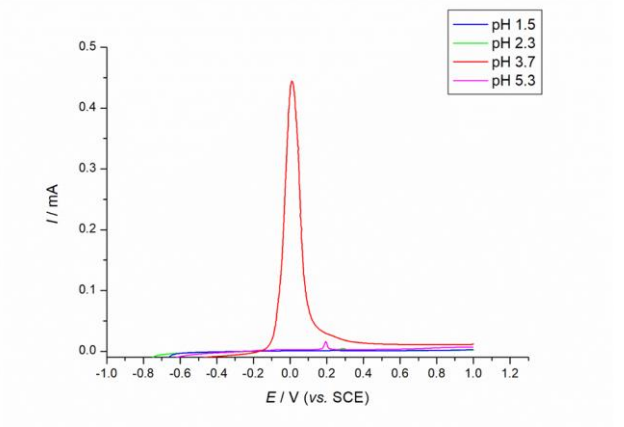

Figure 2. LSV curves, potential of -680 mV, without H_2O_2, varying pH, *v* =10 mV s^{-1}

Figures 1 and 2 show the same LSV at different pH, but with different electrodeposition potential, Fig. 1 presents results with potential of -900 mV, while Fig.2 presents LSV with -680 mV, which is preferable for Fe deposition. At pH 1.5 and 2.3 only one peak can be found at the potential of 0.2 V. Intensity of the peaks are considerably lower with respect to pH 3.7, reaching a maximum of 0.01 mA. At pH 3.7 one major peak can be found at the anodic potential of 0 V. The intensity reaches a maximum of 0.45 mA. At pH 5.3, one anodic peak is visible at the potential of 0.2 V.

Figure 3 shows a comparison of the hydrogen-peroxide treated solution at different pH; while potential of electrodeposition for both trials is -680 mV. Anodic peaks at both pH are at similar positions, indicating the deposition of similar phases. Peaks are registered at -0.4 V (only for pH 1.5), 0 V, 0.2 V and 0.3 V. The current of

the maximum, though, is higher for the solution with higher pH, being around 0.3 mA at most. The similarity of the LSV curves for both pH at the same potential of -680 mV indicate the same metal deposition on the electrode surface.

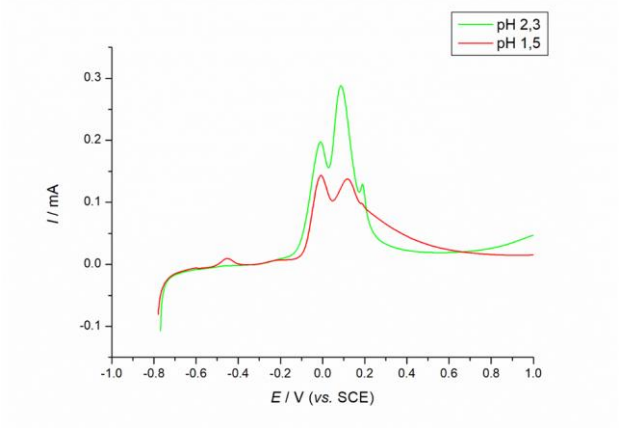

Figure 3. Comparison of LSV, potential of -680 mV, with 10 ml H_2O_2, pH 1.5 and 2.3, v =10 mV s^{-1}

Main difference of both pH is the amount of metallic compound on the surface, resulting in higher peaks for pH 2.3 and different resolution of the peaks. Reason for this is the suppressed initial evolution of hydrogen as a side reaction during electrodeposition at higher pH. The activity of H^+ ions appear to play a major role for the presence of different phases, indicating improved formation of Ni and Co with increasing pH.

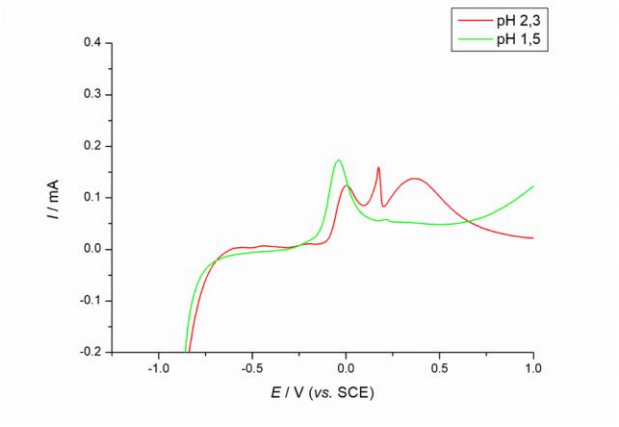

Figure 4. Comparison LSV, potential of -900 mV, with 10 ml H_2O_2, pH 1.5 and 2.3, v =10 mV s^{-1}

When the solutions treated with H_2O_2 at different pH (1.5 and 2.3), but at higher deposition potential of -900 mV, a complex variation of anodic peaks is observed. The comparing curves are shown in Figure 4. The major peak is present around 0 V for both curves, indicating the same phase is present at both pH. The anodic peaks of 0.2 V and 0.4 V for the solution of pH 2.3 indicate the presence of a more complex deposition at the electrode. Especially the anodic peak at 0.4 V shows the presence of Fe at the electrode surface, since it is unique for all LSV curves for the investigated H_2O_2 treated solutions. The higher pH of 2.3 enhance the formation of iron during electrodeposition. At lower pH of 1.5, the formation of iron is hindered by hydrogen evolution.

3.2 Chronoamperometry

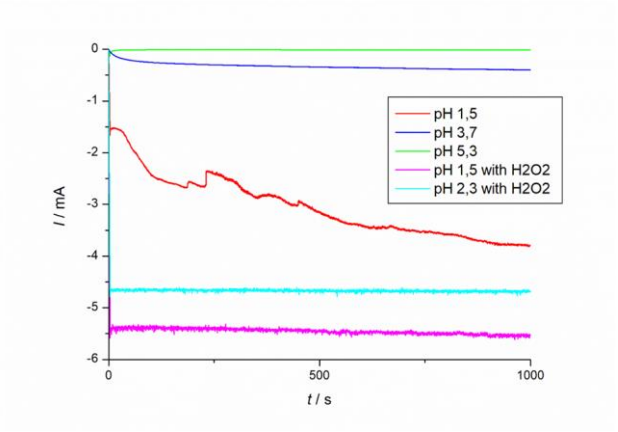

Figure 5. CA diagram registered during electrodeposition of different leachates, with and without H_2O_2, potential of -900 mV, N_2 saturated, 1000 rpm.

CA curves for the leaching solutions at different pH, with and without addition of H_2O_2 are presented in Fig.5. It can be seen that with pH increasing, the currents are lower and more stable, indicating metal deposition on the surface of the working electrode competing with HER that dominates at lower pH of 1.5. On the other hand, LSV curves show only minor peaks for low pH values due to onset of HER.

4. CONCLUSION

It is demonstrated that selective removal of undesired metal ions from a PLS of lateritic ore can be achieved. Nevertheless, the precipitation behavior in the lateritic ore system deviates from the Pourbaix diagrams of the particular metals. Further studies should be conducted using measurements of redox potential to gain more parameters of this complex system, such as PLS.

References

[1] Deetman, S.; Pauliuk, S.; van Vuuren, D. P.; van der Voet, E.; Tukker, A.: Scenarios for demand growth of metals in electricity generation technologies, cars, and electronic appliances, Environmental science & technology 52 (2018), no. 8, pp 4950–4959

[2] Davis, J. R. (ed.): Nickel, cobalt, and their alloys, 1. ed., Materials Park, Ohio: ASM International, 2000. (ASM specialty handbook)

[3] Slack, J. F.; Kimball, B. E.; Shedd, K. B.; Schulz, K. J.; DeYoung, J. H.; Seal, R. R.; Bradley, D. C.: Critical Mineral Resources of the United States—Economic and Environmental Geology and Prospects for Future Supply, 2017.

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