**Precipitation of cobalt salts for recovery in leachates**

N. Djoudi1\*, M. Le Page Mostefa1, H. Muhr1

*1Laboratoire Réactions et Génie des Procédés (LRGP) UMR 7274 CNRS,*

*Université de Lorraine, 1 rue Grandville BP20451, 54001 NANCY,FRANCE*

*\*Corresponding author: neila.djoudi@univ-lorraine.fr*

**Highlights**

* 99.8% of cobalt recovery from batteries leachate by precipitation
* Impact of temperature on cobalt precipitation kinetic
* Impact of temperature on particle size distribution
* Optimum precipitation conditions for cobalt recovery

**1. Introduction**

Fifty metals are considered strategic for industry and essential for global economic and geopolitical issues [1]. It is certain that, due to the communication development, information technologies, and electrical vehicles, demand for strategic metals will become more and more important counting cobalt. Indeed, this metal is present in all the technologies that are becoming essential for the energy and the digital transition. According to the European Commission, cobalt has been recognized as a critical raw material [2]. That is why, it is more important than ever to develop cobalt recovery processes for the coming years. Our current research work focuses on cobalt recovery from Li-ion batteries, by precipitation. After a bibliographical and simulation study, the precipitating agent chosen was the hydroxide ion. Simulation’s result allows to determine cobalt precipitation conditions for a recovery of 99.8%. Experimentally, several operating parameters were varied on a solution containing only cobalt (II), results show the high impact of temperature on cobalt hydroxide precipitation kinetic and on particles size distribution.

**2. Methods**

To perform cobalt (II) precipitation with hydroxide ion: Co2++ 2 OH- = Co (OH )2 (s), the following reactants were used:

- Sodium hydroxide solution: NaOH (1 mol.L-1, VWR Chemicals),

- Cobalt (II) sulfate heptahydrate solution: CoSO4,7H2O (0.131 mol.L-1, Fisher).

The experimental set-up is composed of:

- a double-jacketed reactor of one liter, a thermostatic bath (Julabo F32-EH),

- pH meter (Mettler Toledo)

- Büchner filtration system with 0.45 or 0.22 µm porosity,

- Laser diffraction particle size analyzer (Hydro MS 2000 Malvern)

Experiments were performed at different temperatures: 25°C, 56°C and 60°C. To precipitate 0.0131 mol of Co2+, 0.0262 mol of OH- are needed, which corresponds to a volume of 26.2 mL of soda (1 mol.L-1). The thermostatic bath regulates the experimental media at the desired temperature. After that, all soda volume is rapidly introduced into the cobalt solution. Every 10 minutes, during 3 hours, pH is measured and a sample of the solution is taken for ICP analyses. These analyses allow to determine the cobalt concentration as a function of time and thereby cobalt hydroxide precipitation kinetic. Concerning particle size analyses, samples are analyzed in the same day.

**3. Results and discussion**

3.1 Temperature impact on particle size distribution

Particles size distributions show that the particle size decreased when the temperature increased. It is due to the larger Gibbs free energy; this energy is highly dependent on solution temperature. The increasing temperature (>50°C) lead to a more important supersaturation and thus to a large number of small particles [3]. Consequently, the median diameter is around 25 µm at 25 °C, d50= 14 µm at 56 °C, and d50= 12 µm at 60°C. According to different research studies [3], the kinetic energy of particles gets higher with increasing temperature, which allow to obtain a better precipitation efficiency [3].

**Figure 1.** Particle size distribution in function of temperature.

3.2 Temperature impact on cobalt precipitation kinetic:

Temperature impact on Cobalt recovery were investigated at 25°C and 50°C (Figure 2). It appears that, at 25°C, the highest yield of cobalt recovery is obtained. Indeed, at t=28 minutes, 99. 98% of cobalt is in Co(OH)2 form. In comparison, at 50°C, at t= 8 minutes, 99. 73% of cobalt has precipitated. Also, it can be seen a little dercrease of cobalt yield (0.8%) during time. It can be explained by Co(OH)2 oxidation into Co(OH)3 by oxygen from the air.

First of all, at 25°C, under a very high supersaturation effect, cobalt precipitates as Co(OH)2 and reaches in a few minutes more than 99.9% precipitation. Its stabilization is between 16 and 30 minutes. This nearly stabilization amounts to the dissolution of α-Co(OH)2 polymorph and its precipitation in its most stable form β-Co(OH)2. Indeed, Cobalt hydroxides are known to crystallize in two polymorphic forms α and β. The pink colored ß-Co(OH)2 is the most stable polymorph, with a brucite-like structure [4]. This crystallographic form doesn’t have intercalated species, unlike the alpha form. Indeed, the blue-green α-Co(OH)2 is hydrotalcite-like structure, this ionic lamellar structure contains inorganic anions (e.g., NO3-, CO32-, Cl-…) and water molecules comprised in Co(OH)2-x monolayers charged positively. Experimentally, α-Co(OH)2 appears first, then dissolves, to allow β-Co(OH)2 precipitation. When this transformation process begins, a concentration plateau that lies between the solubilities of the two forms appears. Which can be explained by the growth of the thermodynamically stable phase β-Co(OH)2, compensated by the less stable phase α-Co(OH)2 dissolution. In addition, it is observed that this plateau is absent at 50°C, which means that α-Co(OH)2 appears and disappears very quickly. Its transformation into β-Co(OH)2 occurs in less than 8 minutes. Thus, temperature accelerates the process of phase transformation.

On the other hand, at 25°C, from 36 minutes onwards, cobalt concentration decreases slowly. This is explained by the gradual transformation of Co(OH)2 into Co(OH)3. In comparison to 50°C, where oxidation occurs more quickly, from 8 minutes and more significally. Thus, temperature accelerates phases transition from α-Co(OH)2 to β-Co(OH)2. However, this transition occurs without improving cobalt recovery in solution, especially since the oxidation reaction is accelerated at high temperatures. Therefore, it will be more interesting to work at room temperature, in order to obtain a precipitation rate higher than 99.9% within a few minutes. After that, filter immediately afterwards in order to maintain the same precipitation rate.

****

Figure 2: Cobalt recovery in function of time at 25°C and 50°C

**Conclusions**

This study allows to highlight temperature impact on cobalt hydroxide precipitation kinetic in one hand and to determine optimum precipitation condition in other hand. It was found that temperature increase accelerates phase transition of α-Co(OH)2 into β-Co(OH)2 and the oxidation reaction of Co(OH)2 to Co(OH)3. It has been demonstrated that cobalt recovery is optimal at 25°C with a yield of 99.98%. Therefore, it will be necessary to study synthetic solutions of battery leachate, containing other metals, such as copper, nickel and manganese and to optimize the operating conditions for cobalt recovery, with high efficiency and good purity.

**References**

1. Deloitte Sustainability, British Geological Survey, Bureau de Recherches Géologiques et Minières, Netherlands Organisation for Applied Scientific Research, Study on the review of the list of critical raw materials final report, Publications Office of the European Union, Luxembourg, 2017.
2. J.H. Huang, C. Kargl-Simard, M. Oliazadeh, A.M. Alfantazi, Hydrometallurgy.75 (2004) 77-90
3. GP.Bharat, VP.Dipak, SK.Sanjay, BP.Aniruddha. Chem Eng. (2012) 946–989
4. Z. Liu, R. Ma, M. Osada, K. Takada, T. Sasaki, J. Am. Chem. Soc. 2005, 127 (40), 13869–13874. DOI: https://doi.org/ 10.1021/ja0523338