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PROCEEDINGS

Edited by

Saša Stojadinović

and

Dejan Petrović

November 29th – 30th 2021

Bor, Serbia

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OPTIMIZATION OF CATHODIC MATERIAL LEACHING PROCESS IN ACID-SULPHATE SOLUTION

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Abstract

Lithium cobalt oxide is the first commercialized electrode material with the greatest potential for recycling. In this paper, the influence of different process parameters (leaching agent concentrations, solid phase concentrations and temperatures) on the degree of cobalt leaching was investigated. It was found that the maximum degree of cobalt leaching (about 100%) is achieved at the followingprocess parameters: sulfuric acid concentration was 3 mol/dm^3, solid phase concentration was 33 g/dm^3, volume flow of sulfur dioxide was 2 dm^3/min, temperature was 85°C and leaching process durationwas 60 minutes.

Keywords: *$LiCoO_2$, leaching, sulfur dioxide.*

1. INTRODUCTION

Sony commercialized the production of lithium-ion batteries in 1991, and their use in many electronic devices and electric vehicles has grown since then [1]. Improper disposal of waste batteries enables the release of cobalt into the environment, which presence in water systems can cause intestinal disorders, hearing loss, ischemia of the heart muscle, etc. [2]. Battery recycling technology protects the environment, preserves natural metal resources, and achieve significant economic benefits [1]. The methods that can be applied in the process of battery recycling are: hydrometallurgical, pyrometallurgical and biometallurgical [3,4]. Although the pyrometallurgical process is characterized by high efficiency, its application leads to high energy consumption, material loss and emissions of gaseous pollutants [5]. Compared to the traditional pyrometallurgical process, the hydrometallurgical process requires less energy consumption, emits less harmful gases and provides a high degree of metal valorization [6]. In order to reduce costs and increase process efficiency, biometallurgical processes have been developed in recent years. However, these processes take a very long time due to the difficulties caused by the growth of bacteria [7]. For these reasons, most of the research is focused on the hydrometallurgical process for recycling of valuable metals from lithium-ion batteries.

In this paper, leaching process of cathodic material was optimized in acid sulphate solution with the use of sulfur dioxide, as a reducing agent.

2. EXPERIMENTAL

Seventeen lithium-ion batteries with cathodes made of $LiCoO_2$ were collected and used in the experiments.After the application of pretreatment techniques,the cathode material was obtained and the chemical composition is presented in Table 1. Cobalt and lithium,as basic components of cathode material, were detected by various analytical methods. The presence of aluminum in the cathode material is probably a consequence of pretreatment on spent lithium-ion cells [8,9]. The

total cobalt content was determined using the inductively coupled plasma optical emission spectroscopy (ICP-OES), while the concentration of Co^{2+}in the initial sample of cathode leaching material was determined by UV-VIS spectrophotometric method. The values of the obtained cobalt concentrations, determined with UV-VISmethod, indicated that cobalt in solution was present in the stable ionic form of Co^{2+}, which is confirmed by other authors [10,11].

Table 1 -Chemical composition of the initial cathode material for leaching

Element	Mass content (wt.%)	Analyticmethod
Co	49.81	ICP-OES
Co (Co^{2+})	49.00	UV-VIS
Li	5.98	ICP-OES
Al	0.01	ICP-OES

3. RESULTS

3.1 Optimization of the leaching process

In order to optimize the leaching process of the cathode material in an acid sulphate medium, the influence on the leaching process of various process parameters (leaching agent concentrations, solid phase concentrations and temperature) was examined.

3.1.1 Influence of sulfuric acid concentration on the degree of cobalt leaching

In order to determine the optimal concentration of H_2SO_4 in the process of leaching of the cathode material, in a sulfur dioxide atmosphere, a series of experiments were performed with the different concentrations of H_2SO_4(0.5 mol/dm^3- 3 mol/dm^3). The experiments were performed at a temperature of 35°C, with a solid phase concentration 33 g/dm^3, and with a volume flow of 2 dm^3/min SO_2. Experiment time was 100 min.

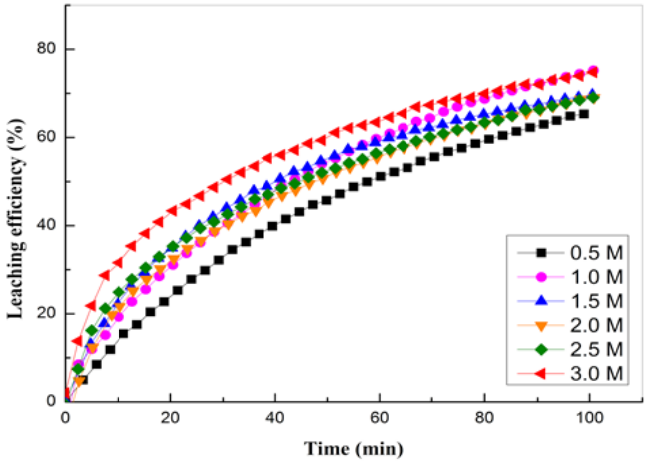

Figure 1 - Influence of H_2SO_4 concentration on the degree of cobalt leaching

The results of the research, shown in Figure 1, indicate that with an increase in the H_2SO_4concentration 0.5 mol/dm^3- 3 mol/dm^3, the degree of cobalt leaching increases from 65.3% to 73.9%. Considering the obtained results, the H_2SO_4concentration of 3 mol/dm^3 can be taken as optimal value and was used in further experimental studies.

3.1.2 Influence of solid phase concentration on the degree of cobalt leaching

The influence of solid phase concentration (in the range of 10 g/dm^3 to 67 g/dm^3) on the degree of cobalt leaching was examined under the following conditions: H_2SO_4 concentration was 3

mol/dm^3, volume flow sulfur dioxide was 2 dm^3/min, temperature was 35°C,and time of leaching was 100 min. The obtained results, shown in Figure 2, indicate that with the increase of the solid phase concentration, the degree of cobalt leaching decreases. The highest degree of cobalt leaching was recorded at a solid phase concentration of 10 g/dm^3. From the industrial point of view, in the process of material leaching, it is desirable to use a higher solid-liquid phase ratio, regardless of the achieved lower degree of metal leaching [12,13]. For this reason, a solid phase concentration of 33 g/dm^3 was taken as the optimal concentration and used in further experimental studies.

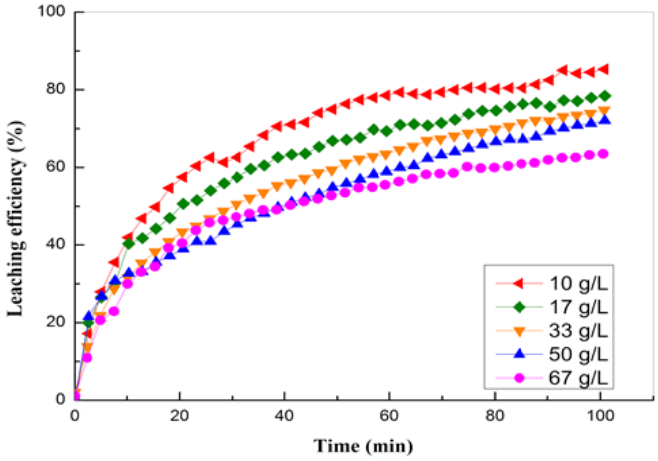

Figure 2 -Influence of solid phase concentration on the degree of cobalt leaching

3.1.3 Influence of temperature on the degree of cobalt leaching

In order to examine the kinetic laws of the process, the influence of the temperature of the cathode material on the degree of cobalt leaching was examined under the following conditions: acid concentration was 3 mol/dm^3, volume flow $SO_2$was 2 dm^3/min and solid phase concentration was 33 g/dm^3. The results of the research, shown in Figure 3, indicate that temperature has a positive effect on the degree of cobalt leaching. It was concluded that with an increase of the leaching temperature 35°C to 85°C, the degree of cobalt leaching increases from 74.8% to 99.4%.

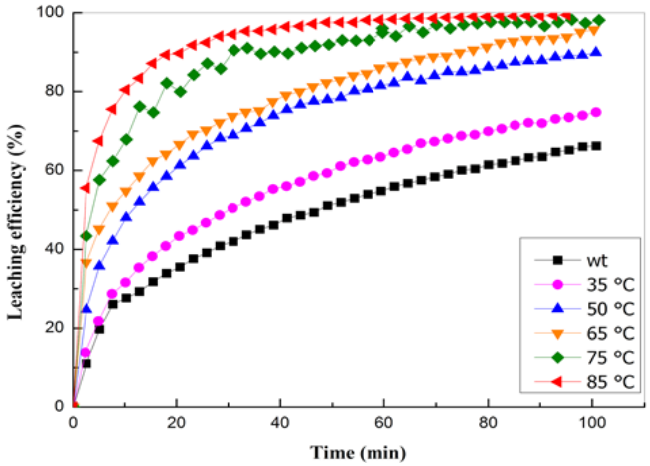

Figure 3 -Influence of temperature on the degree of cobalt leaching

4. CONCLUSION

Based on the results of leaching of the cathode material in a sulfur dioxide atmosphere, it can be concluded that the temperature and duration of the process have the greatest influence on the

leaching process. Also, the shape of the kinetic curves of leachingindicated that the concentration of sulfuric acid and the concentration of the solid phase, slightly influence the leaching of cobalt from the cathode material of spent lithium-ion batteries. The maximum degree of cobalt leaching (about 100%) was achieved at a sulfuric acid concentration of 3 mol/dm^3, a solid phase concentration of 33 g/dm^3, a volume flow of sulfur dioxide of 2 dm^3/min, temperature of 85°C and leaching process duration of 60 minutes.

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