

Article

Recovery of Co, Li, and Ni from Spent Li-Ion Batteries by the Inorganic and/or Organic Reducer Assisted Leaching Method

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Abstract: The battery powder (anodic and cathodic mass) manually separated from spent Li-ion batteries used in laptops was subjected to acidic reductive leaching to recover the Co, Li, and Ni contained in it. In the laboratory experiments, 1.5 M sulfuric acid was used as the leaching agent and the reducing agents were 30% H₂O₂ solution or/and glutaric acid. Glutaric acid is a potential new reducing agent in the leaching process of spent lithium-ion batteries (LIBs). The influence of the type of the used reducer on obtained recovery degrees of Co, Li, and Ni as well as the synergism of the two tested reducing compounds were analyzed. As a result, it was determined that it is possible to efficiently hydrometallurgically separate Co, Li, and Ni from battery powder into solutions. The highest recovery degrees of the investigated metals (Co: 87.85%; Li: 99.91%; Ni: 91.46%) were obtained for samples where two reducers, perhydrol and glutaric acid, were added, thus confirming the assumed synergic action of H₂O₂ and C₅H₈O₄ in a given reaction environment.

Keywords: Li-ion batteries; battery-related metals; metal recycling; hydrometallurgy

1. Introduction

Batteries are the basic source of electric current necessary to power various mobile electric and electronic devices. Due to high energy density, long-life, and ease of manufacturing, the most commonly used portable Li-ion batteries are batteries in which the cathode material is LiCoO₂ [1].

The increasingly growing need for this type of power source entails a constantly growing amount of waste. Due to various chemical substances from which Li-ion batteries are composed, spent batteries of this type must be appropriately managed. There are a number of various technologies applied in Li-ion chemical power source processing. However, due to numerous environmental and economic benefits, the strongest interest among scientists has been aroused by the recovery of metals (mainly Li and Co) being part of the cathode mass using hydrometallurgical methods. The chemical composition of a typical Li-ion battery was discussed by Shin et al. in their publication. According to these authors, it contains 5–20% of cobalt, 5–10% of nickel, and 5–7% of lithium [2].

The above-listed metals can be effectively leached from cathode powder to a solution with inorganic acids as well as organic ones used as leaching agents. The most commonly investigated leaching agents, also at the initial stages of hydrometallurgical development of metal recovery from spent Li-ion batteries, are inorganic acids—Mainly sulfuric acid (H₂SO₄), but also hydrochloric acid (HCl), nitric acid (HNO₃), and phosphoric acid (H₃PO₄) [3–7]. The use of strong acids allows high leaching efficiency to be achieved, and hence a high metal recovery degree while maintaining optimal conditions for the process. Apart from technological advantages, inorganic acids are also relatively inexpensive reagents, thus they can be used on an industrial scale. However, very low pH values during leaching may lead to faster wear and tear (corrosion) of the used equipment. Another issue to

be considered is waste management, namely the battery powder contaminated with mineral acids obtained by leaching. Moreover, during inorganic acid leaching, there is a certain probability of the release of gases posing a danger to human health and the environment, particularly, Cl_2 , SO_3 , or NO_x [8,9].

The frequently occurring problems resulting from the application of inorganic acids in the leaching process of spent Li-ion batteries have induced scientists to search for effective alternatives whose application would not lead to such a negative impact on the environment. Therefore, the research on the use of organic acids as leaching agents was commenced. For the last five years, citric acid has been the most frequently investigated acid in this matter [10–14]. Additionally, the results of a number of research papers have shown that the following acids have been tested as the leaching agent: succinic [15], aspartic [15], lactic [16], formic [17], tartaric [18], oxalic [19], acetic [20], malic [21], maleic [22], iminodiacetic [22], adipic [23], and nitrilotriacetic [24]. It has been shown that it is possible to effectively recover metals from battery powder from spent Li-ion batteries using organic compounds as leaching agents, however, the reactions during the process are slower (longer contact time) than in the case of experiments where the leaching agents were inorganic acids. The use of organic acids reduces the corrosion risk to equipment and they are also safer for the people involved in this process. Additionally, during organic compound leaching, secondary contamination hardly ever occurs. However, the price of reagents may pose a problem: they are more expensive than the inorganic acids, hence their use may increase the operating costs of industrial installations. Moreover, in the literature, there are frequent indications that it is difficult to precisely determine chemical reactions taking place during leaching with organic acids, and thus also in determining particular products resulting from these reactions, due to the high probability of forming various compound organic complexes and semi-products in the process.

Most frequently, the acidic leaching of spent Li-ion batteries is supported with the use of additional compounds, the so-called reducers. Their application may cause the metals that are part of battery powder to transform to a divalent form that is soluble in acidic solutions. In the case of a LiCoO_2 cathode, it has been shown that the addition of a reducer has the highest influence on cobalt ions (i.e., during leaching the cobalt valence state changes from Co(III) to Co(II) [9]). In effect, metal recovery may be higher and the concentration of used acids is lower. The most common compound used as a reducer in the process of battery powder acidic leaching is hydrogen peroxide (H_2O_2), which was repeatedly dosed in experiments where it was combined with acids, both inorganic [5,7,25–29] and organic [10–16,20,21] and used as leaching agents. In the literature, there are also examples of other compounds used as reducers in the leaching process of battery powder released from spent Li-ion batteries. Researchers investigated the reducing properties of sodium bisulfite (0.075 M NaHSO_3) [25], ammonium chloride (0.8 M NH_4Cl) [30], sodium thiosulfate (0.25 M $\text{Na}_2\text{S}_2\text{O}_3$) [4], and organic compounds like ascorbic acid (0.11 M $\text{C}_6\text{H}_8\text{O}_6$) [3], glucose, sucrose, and cellulose (0.4 g) [31] combined with sulfuric acid as a leaching agent. In the experiments in which the leaching agent was an organic acid, a commonly used reducer, apart from hydrogen peroxide, was 0.02 M ascorbic acid, whose presence in this process also improved the efficiency of metal recovery, especially cobalt [14,18,22,23].

To meet the increasing demand for battery waste treatment, especially the Li-ion ones, and also taking into consideration both the numerous advantages of hydrometallurgical methods used in metal recovery from batteries and the latest research trends, a new concept of laboratory tests has been developed in this respect. A number of laboratory experiments were conducted to test the acidic reductive leaching of the total (anodic and cathodic) powder, obtained as a result of the mechanical processing of collected spent Li-ion batteries, in which 1.5 M sulfuric acid was used as a leaching agent. The process was conducted in the presence or without the presence of reducers (i.e., a 30% solution of hydrogen peroxide and/or a potential new agent, glutaric acid).

2. Materials and Methods

The research material was a waste stream of Li-ion batteries previously used to power laptops. The spent batteries first underwent mechanical processing (i.e., individual battery was manually disassembled). Next, the batteries were discharged by connecting them to resistors (resistor power: 5 W, resistance: 1.5 Ω in the case of weakly or medium charged batteries, and 3.3 Ω if batteries were nearly completely or completely efficient). Discharged batteries were subjected to a series of fragmentation and separation actions. As a result, various fractions of the materials that the batteries were composed of including battery powder and mass were separated and constituted the material used in further research of hydrometallurgical metal recovery. The black mass was composed of both anodic and cathodic mass (in the literature most frequently only the cathodic powder is investigated), and due to this, this part of mechanical processing was significantly simplified (the separation of both types of powder was neglected). Moreover, in the proposed method, before leaching, the separated mass was not subjected to additional chemical and thermal processes for the separation of potential contaminants (e.g., graphite), due to the minimization of technological processes (and their potential cost intensiveness). Such a simple preparation of the research material may significantly facilitate the mechanical processing of the discussed battery waste on an industrial scale.

A homogenous sample of the tested battery mass was subjected to the analysis of x-ray powder diffraction (XRD) to determine the qualitative phase composition. A Philips X'PERT (CuK α) X-ray diffractometer (Philips, Amsterdam, The Netherlands) was applied for the tests. The measuring range of the 2 theta angle was 3–100°, counter speed of 0.05°, single pulse counting time of 2 s, voltage of 40 kV, current of 30 mA. The experimental data were processed using the DHN - Powder Diffraction System computer program. Identification of individual crystalline phases of minerals found in the sample was carried out by comparing the experimental diffraction pattern of the tested sample with the standard diffraction patterns found in the International Centre for Diffraction Data PDF-2 (ICDD PDF-2) database. In addition to this, the battery powder sample was mineralized. The sample (weight of about 0.5 g) was spread wet in an open system (DigiPREP Jr mineralization system (SCP Science, Quebec, QC, Canada) using 10 cm³ of 65% HNO₃ (mineralization time: 5 h, temperature: 120 °C). The resulting solution was evaporated to about 0.5 cm³, quantitatively transferred to a plastic container, and supplemented with deionized water to 50 g. At the same time, the reagent blank was made and included in final results. The analysis was performed in three parallel replicates (n = 3). In the obtained solution Al, Ca, Co, Cr, Cu, Fe, Li, Mg, Na, Ni, Si, and Zn ions were determined using the atomic spectrometry emission method with inductively coupled plasma optical emission spectroscopy (ICP-OES; optical spectrometer with the horizontal position of the plasma torch, Agilent 720, Agilent Technologies, Santa Clara, CA, USA) to determine the qualitative and quantitative composition of the investigated material.

The battery mass leaching tests were divided into three stages. First, the influence of temperature and the addition of an inorganic reducer on the leaching degree of Co, Li, and Ni were examined. Next, based on the obtained results, the same temperature was established for all subsequent experiments and then the influence of the type of the dosed reducer and the synergism of the two reducing compounds were investigated. Finally, the process was optimized by the selection of a suitable dose of 30% H₂O₂ solution (Table 1).

Each time, the battery powder was leached with inorganic sulfuric acid (H₂SO₄) at a 1.5 M concentration. The process was conducted with or without the presence of reducers, both inorganic and organic ones (i.e., 3 cm³ of 30% hydrogen peroxide solution (H₂O₂)—Perhydrol and 5 g of glutaric acid (C₄H₈O₅)). The reducers were dosed individually (H₂O₂ and C₄H₈O₅ separately) or together (H₂O₂ + C₄H₈O₅). The experiments were conducted for 120 min at a solid–liquid phase ratio (s/l) of 1/10 (10 g battery mass /100 cm³ leaching agent). The process temperature was 55 °C or 90 °C, while the mixing rate was 500 revolutions per minute.

After completing the experiments, each sample was drained under reduced pressure. In the obtained solutions, the content of Co, Li, and Ni ions was determined using the inductively coupled plasma optical emission spectroscopy method (ICP-OES).

Table 1. Plan of the experiments.

Stage	Sample	Leaching Agent	Reducer	Duration of the Process	s/l Ratio	Temperature	Mixing Rate
First leaching stage	1.1	1.5 M H ₂ SO ₄	-	120 min	1/10	55 °C	500 rpm
	1.2		-			55 °C	
	2.1		-			90 °C	
	2.2		-			90 °C	
	3.1		H ₂ O ₂ (3 mL)			55 °C	
	3.2		H ₂ O ₂ (3 mL)			55 °C	
	4.1		H ₂ O ₂ (3 mL)			90 °C	
	4.2		H ₂ O ₂ (3 mL)			90 °C	
Second leaching stage	5.1	1.5 M H ₂ SO ₄	C ₅ H ₈ O ₄ (5 g)	120 min	1/10	90 °C	500 rpm
	5.2		C ₅ H ₈ O ₄ (5 g)				
	6.1		H ₂ O ₂ (3 mL) + C ₅ H ₈ O ₄ (5 g)				
	6.2		H ₂ O ₂ (3 mL) + C ₅ H ₈ O ₄ (5 g)				
Process optimization	7.1	1.5 M H ₂ SO ₄	H ₂ O ₂ (5 mL) + C ₅ H ₈ O ₄ (5 g)	120 min	1/10	90 °C	500 rpm
	7.2		H ₂ O ₂ (5 mL) + C ₅ H ₈ O ₄ (5 g)				
	8.1		H ₂ O ₂ (10 mL) + C ₅ H ₈ O ₄ (5 g)				
	8.2		H ₂ O ₂ (10 mL) + C ₅ H ₈ O ₄ (5 g)				
	9.1		H ₂ O ₂ (15 mL) + C ₅ H ₈ O ₄ (5 g)				
	9.2		H ₂ O ₂ (15 mL) + C ₅ H ₈ O ₄ (5 g)				

3. Results

3.1. Qualitative and Quantitative Analysis of the Investigated Material

It was shown that in the phase composition of the tested spent Li-ion batteries, the prevalent components were lithium and cobalt, occurring in the form of lithium cobalt oxide (LiCoO_2). The conducted XRD analysis (Figure 1) confirmed the data available in the literature sources, where the subject of the research was battery mass obtained from spent Li-ion batteries, initially used to power mobile devices [14,23,32–35]. Carbon present in the diffractogram originated from anodic (graphite) mass included in battery powder.

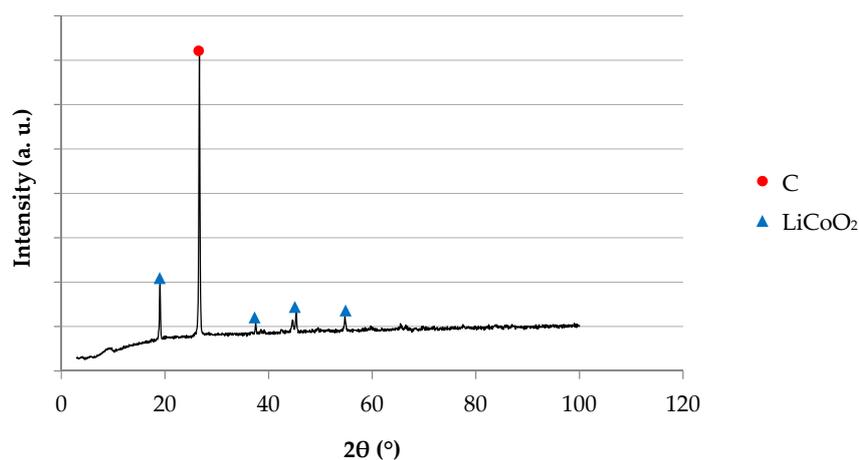


Figure 1. X-ray diffraction (XRD) analysis results for the battery mass formed after the mechanical processing of spent Li-ion batteries.

In the subsequent step, the tested fraction was subjected to mineralization. On the basis of the obtained results (Table 2), it can be concluded that the composition of the spent Li-ion battery resulting from the experiment closely matched the data published in the primary sources [2–5,10,15,36]. Moreover, the investigated battery mass contained various metals. The highest concentrations were obtained for cobalt, lithium, and nickel, which were recovered at the next stage of the experiment: acidic leaching. The high nickel concentration was most likely due to its presence in the chemical composition of battery powder, which has already been indicated in the literature, (e.g., by Golmohammadzadeh et al. [10]). It can also be caused by the inaccuracy of manual processing (contamination from the dismantling of the steel casing). In this case, it can be assumed that the nickel is in metallic form. In addition, it should be emphasized that the research material comes from spent batteries, which are often stored in inappropriate conditions and thus damaged, which can affect the change in the form of this metal (e.g., into oxides).

Table 2. Quantitative–qualitative composition of paramagnetic fraction originating from spent Li-ion batteries.

Metal	Al	Ca	Co	Cr	Cu	Fe	Li	Mg	Na	Ni	Si	Zn
C (mg/kg)	931	403	256,000	5.47	3599	273	33,200	560	302	14,400	3765	76.4

3.2. Acidic Leaching: Inorganic Reducer (H_2O_2)

The experimental research results (Figure 2) showed that high yield nickel leaching was obtained for sample 4.2 (reducer 30% H_2O_2 , temperature 90 °C) of 89.70%, however, it was not possible to obtain an identical result for the second sample in the same series. The most similar effects in terms of nickel recovery were obtained from samples 3.1 and 3.2 in the reducer assisted leaching process of 30% H_2O_2 at a temperature of 55 °C: 80.91% and 82.60%, respectively. The smallest amount of nickel (i.e., 35.01%

and 34.97%) was leached during experiments in which no reducer was dosed, and the process was conducted at a temperature of 55 °C (samples 1.1 and 1.2). In contrast, in the case of lithium ions, in practically every experiment, high leaching degrees were obtained: at the minimum level it was 70.80% for sample 1.1. The largest nickel yield (i.e., 80.97%, 83.60%, 84.19%, and 82.77%) was reported for samples 3.1 and 3.2 of leaching with the addition of 30% H₂O₂, T = 55 °C and for samples 4.1 and 4.2 of leaching with the addition of 30% H₂O₂, T = 90 °C. Hence, it was demonstrated that there was no dependence between the temperature of the process and the Li recovery degree. Moreover, in these two experimental series (3.1–4.2), the obtained nickel and lithium concentrations were very high, while in the case of cobalt, the leaching degree was very low (1.62–1.95%), which indicates a high process selectiveness. The largest amount of Co was obtained by leaching in solutions without a reducer, where the recovery level was on average 30%.

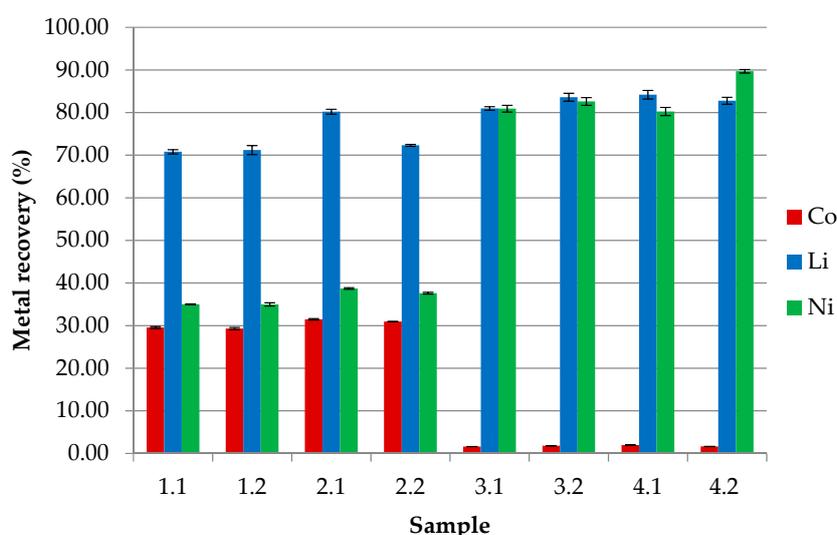


Figure 2. Recovery degrees for Co, Li, and Ni from solutions obtained by leaching with 1.5 M sulfuric acid with or without the presence of 3 mL perhydrol.

The comparison of the obtained results related to metal yield, especially cobalt and lithium (research publications on battery powder leaching from spent Li-ion batteries with a LiCoO₂ cathode do not refer to the nickel recovery degree), with literature data indicating certain differences. Gao et al. [37] in their work argued that it was possible to recover even 99.54% lithium and 54.40% of cobalt from battery powder (LiCoO₂ cathode) in the leaching process, in which the leaching agent was 1 M H₂SO₄ (s/l = 20 g/L, T = 80 °C, t ≤ 5 min) and no reducer was dosed. The addition of 4% of H₂O₂ as a reducer resulted in the recovery of a great deal more cobalt (99.76%), and simultaneously, lithium recovery efficiency was only insignificantly lower (99.05%). Zhu et al. [38] conducted similar research (the same leaching agent of H₂SO₄ and reducer of H₂O₂), however, the conditions of the process were different, (i.e., 2 M H₂SO₄, 2% volume H₂O₂, T = 60 °C, s/l = 33 g/L, t = 120 min). As a result, 96.3% of cobalt and 87.5% of lithium were leached. On the other hand, Sun et al. [29] obtained nearly 100% recovery of cobalt and lithium in solutions obtained by leaching (similarly to Zhu et al. [38]) when the leaching agent and reducer were 2 M sulfuric acid, and hydrogen peroxide, respectively, in addition to this, its dose was increased to 5% vol. (the remaining process parameters were T = 80 °C, s/l = 50 g/L, t = 60 min). Very similar experiments to those conducted by Sun's team [29] were performed by Bertuol et al. [26]. The only differences in the set process parameters were related to temperature (it was lower, 75 °C) and the volume of the used hydrogen peroxide (8% vol.). In the designed experiments, 98% of cobalt was leached. Kang et al. [9] demonstrated that leaching battery powder for one hour in the presence of 2 M H₂SO₄ and 6% vol. of H₂O₂ allowed for the recovery of 98% of cobalt and 97% of lithium at a lower temperature (i.e., 60 °C), however, the solid/liquid ratio was significantly increased, and it was as much as 100 g/L.

The presented results of scientific publications [26,29,37–39] were significantly higher than the effects of the experiments conducted in the present work (Figure 2). In addition to this, they confirmed the influence of the presence of hydrogen peroxide used as a reducer on the obtained degrees of cobalt ion leaching [9], which could not be replicated in the discussed laboratory works. Most certainly, such discrepancies result from differences in the initial preparation of the research material (it contained an anode and electrolyte residues, the components of which may influence the reductive effect of hydrogen peroxide) and the assumed parameters of the leaching process of the tested battery powder (which also indicates the high sensitivity of the process in terms of the changes of particular agents). Some of the main parameters that influence the obtained results certainly encompass an insufficient volume of H_2O_2 used as a reducer in samples, and due to this, the obtained cobalt recovery degrees were too low. An attempt was made to prove this hypothesis by entering the set experimental data to a computer database supporting research design and the interpretation of the obtained results on MiniTab 18 software. In effect, the essential factors (in the context of the recovery of particular metals Co, Li, and Ni) influencing the process (Pareto Charts–Figure 3a,c,e) and their direct impact of process efficiency (evaluated also in terms of Co, Li, and Ni leaching degrees–Figure 3b,d,f) were determined. The results obtained in the MiniTab software are presented in Figure 3.

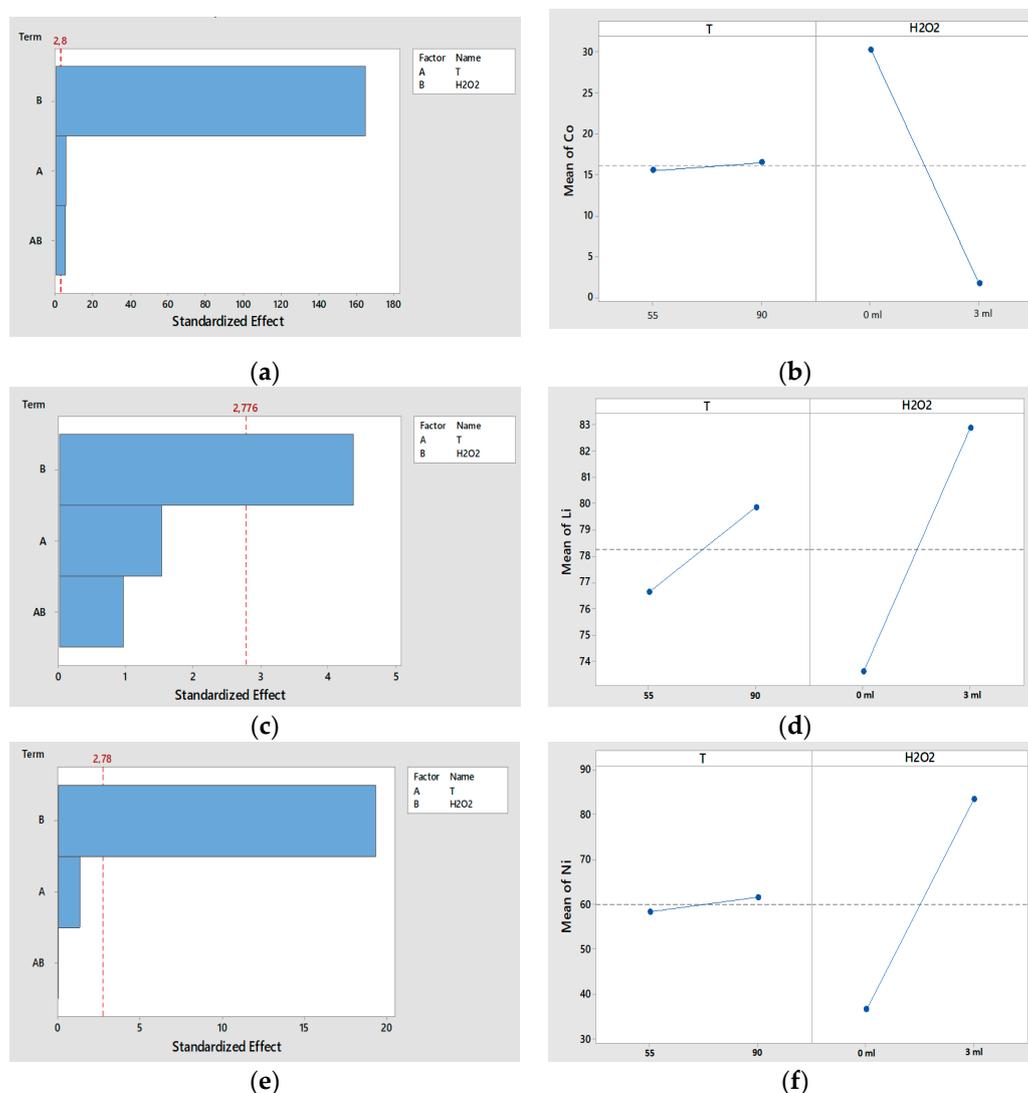


Figure 3. Factors influencing the conducted leaching process. (a) Pareto Chart of the standardized effects–Co; (b) main effects plot–Co; (c) Pareto Chart of the standardized effects–Li; (d) main effects plot–Li; (e) Pareto Chart of the standardized effects–Ni; (f) main effects plot–Ni.

The above-presented analysis confirms the earlier assumption that the addition of a reducer has a significant influence on cobalt leaching degree (Figure 3a, bar B indicating that H_2O_2 dose significantly exceeds the red dashed line, the reference line, which confirms a profound influence of the given factor on the obtained research results), however, in the case of the conducted experiments, hydrogen peroxide had an inhibiting effect on these ions as very low recovery degrees were obtained (Figure 3b), contrary to numerous literature indications claiming it had an assisting effect. Moreover, the computer analysis (Figure 3a) indicates the low dependency of process efficiency on temperature height (at higher temperatures, more cobalt was leached, however, the difference was not significant, which was indicated by the low angle of inclination in the chart). The smallest effect was observed when both parameters (temperature and the addition of H_2O_2 reducer) were combined.

Aside from the dependencies related to cobalt recovery in the leaching process in 1.5 M H_2SO_4 , the parameters influencing leaching lithium and nickel were also analyzed. Pareto charts, plotted for both of these metals (Figure 3c,e), indicate that the recovery degree is influenced only by the presence of hydrogen peroxide in the process, whereas the change of process temperature and the combination of both of the analyzed parameters was of nearly no significance in this context. Figure 3d,f show that a larger amount of lithium and nickel was leached at a higher temperature and in the presence of 3 mL H_2O_2 , which confirms the earlier formulated conclusions and is also reflected in the discussed literature examples [26,29,38,39].

On the basis of the above discussed analyses, it was ascertained that in the subsequent series of research, the process parameters would be maintained, and the temperature would be constant for each sample at 90°C , which is the reason why this temperature allowed the best recovery degrees to be obtained, especially for Li and Ni, at the first stage of leaching. The reducing agents at the second stage of the experiments were organic glutaric acid (5 g) or two reducers (i.e., inorganic perhydrol (3 cm^3) and 5 g of glutaric acid). Both compounds were dosed together to test their synergic effect on the obtained leaching degrees of the investigated metals (the method has not been described in the primary sources as yet).

3.3. Acidic Leaching: Organic and Inorganic Reducer, and a Combination of Two Reducers

The total recovery of nickel was obtained for sample 6.2, where except for the leaching agent of 1.5 M sulfuric acid, two reducers were also dosed, namely a 30% solution of H_2O_2 and glutaric acid. Unfortunately, in an identical sample (i.e., 6.1), the same result was not replicated where a comparison with its twin experiment showed that it was lower by 81.75% (Figure 4).

The addition of the glutaric acid as a metal bond reducer (samples 5.1 and 5.2) resulted in an increase in the level of cobalt leaching (32.30% and 32.03%) with only a slight decrease in lithium recovery degree (75.86% and 74.10%) and significantly lower nickel ion leaching degree (38.77% and 32.88%). To the contrary, the introduction of two reducers to the process (i.e., 30% hydrogen peroxide and glutaric acid (samples 6.1 and 6.2)) enabled the highest cobalt release (59.37% and 59.24%) in the whole series of experiments with a simultaneous high recovery degree of the remaining two metals, (i.e., lithium: 79.81% and 82.18%, nickel: 81.75% and 100% (Figure 4)). Therefore, it was confirmed that both of these compounds acted in synergy in the used method, and their combination led to an increase in the obtained recovery degrees for Co, Li, and Ni.

Scientific publications are increasingly frequently presenting the results of experiments in which the leaching agent was inorganic sulfuric acid, while the reducer was an organic compound. Peng et al. [3] used 2 M H_2SO_4 to leach mixed battery powder from spent Li-ion batteries (mainly LiCoO_2 cathodes with some $\text{LiCo}_{0.25}\text{Ni}_{0.65}\text{Mn}_{0.1}\text{O}_2$ cathodes) and 0.11 M ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) as a reducer. The process was continued for 90 minutes at a temperature of 80°C with quite high solid/liquid ratio of 200 g/L. As a result, the cobalt and lithium recovery degree was 93.8% and 95.7%, respectively. Another example of an experiment in which the leaching agent was H_2SO_4 ($C = 3\text{ M}$), and the reducer was an organic compound (0.4 g cellulose, sucrose, or glucose) was a study by Chen et al. [31] where the process parameters were: $T = 95^\circ\text{C}$, $s/l = 25\text{ g/L}$, $t = 120\text{ min}$. It was shown that when sucrose was used as the

reducer, it was possible to obtain even 100% lithium recovery, with simultaneous 96% cobalt recovery. Total lithium recovery is also possible, however, when the used reducer is cellulose. Nonetheless, the leaching level of cobalt was significantly lower at 54%. On the other hand, it is possible to achieve a higher cobalt recovery level (98%) by adding glucose to the process (lithium recovery degree was 96%).

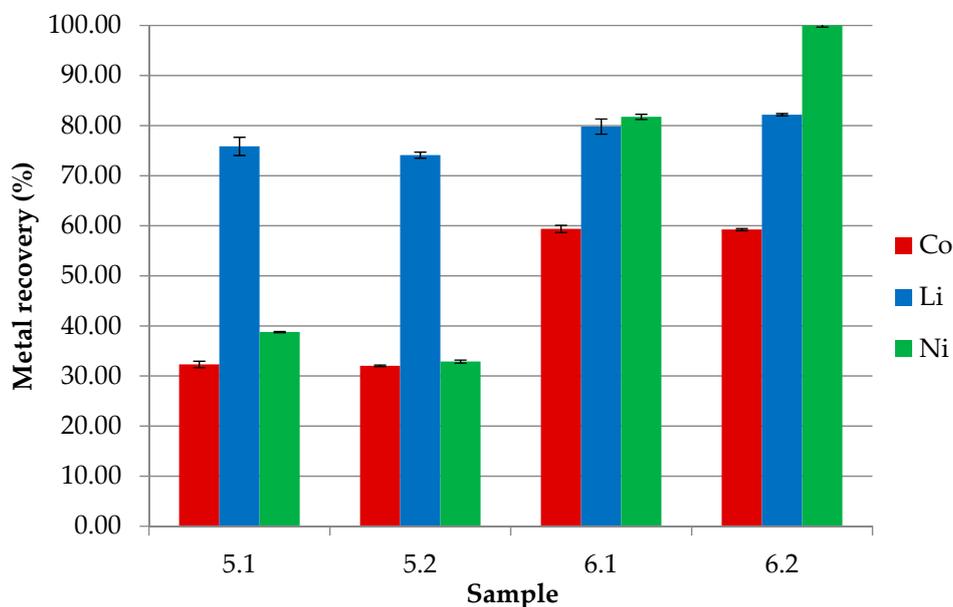


Figure 4. Recovery degrees for Co, Li, and Ni from solutions obtained by leaching with 1.5 M sulfuric acid with or without the presence of 5 g of glutaric acid and/or 3 cm³ perhydrol.

The presented results [3,31] unequivocally indicate that it is possible to achieve high cobalt and lithium recovery from the leaching solutions with sulfuric acid and an organic dopant used to process battery powder from spent Li-ion batteries, whereby the recovery degree of the investigated metals depends on the use of this organic dopant. The experimental research described in the present paper, similar to the cited publications, allowed us to obtain a relatively high lithium recovery degree (Figure 4, samples 5.1–5.2, about 75%), with still a rather low level of cobalt recovery (Figure 4, samples 5.1–5.2, about 30%), which corresponds to the research on the use of cellulose as a reducer conducted by Chen et al. [31]. This may constitute yet more proof that the process is characterized by very high sensitivity, depending on the preparation of waste material for leaching, the adjustment of experiment parameters each time before the process as well as the chemical reactions occurring in a different way during battery powder leaching (this in turn, depends mainly on the type and concentration of the used chemical agents). The primary sources do not indicate cases when during the inorganic acid leaching of battery mass from spent batteries, two reducers—an organic and inorganic one—were doped (samples 6.1–6.2).

Based on the results obtained in the second series of the experiments, it was finally decided that the highest recovery degrees for all three metals (Co, Li, and Ni) simultaneously were obtained for samples 6.1 and 6.2 (Figure 4). As a result, in further research work, the leaching process with 1.5 M sulfuric acid of battery powder from spent Li-ion batteries was optimized by adjusting the inorganic reducer dose, namely hydrogen peroxide (Table 1). It was also decided to investigate the influence of an increased addition of H₂O₂ solution (5 cm³, 10 cm³, and 15 cm³) on the leaching degree of the tested metals, especially Co, which has also been previously reported in the literature [2] as it is the recovery of this metal that is the most influenced by the presence of a reducer in the process.

3.4. Leaching Process Optimization by Adjusting 30% the H₂O₂ Dose

In the solutions obtained by leaching the investigated spent Li-ion battery powder where the leaching agent was 1.5 M H₂SO₄, and the reducers were 5 g C₅H₈O₄ and 5 cm³ or 10 cm³ or 15 cm³ of 30% H₂O₂ solution, the concentrations of Co, Li, and Ni were determined. Similar to the previously analyzed experiments, they were expressed in the percentage of their recovery (Figure 5, samples 7.1–9.2).

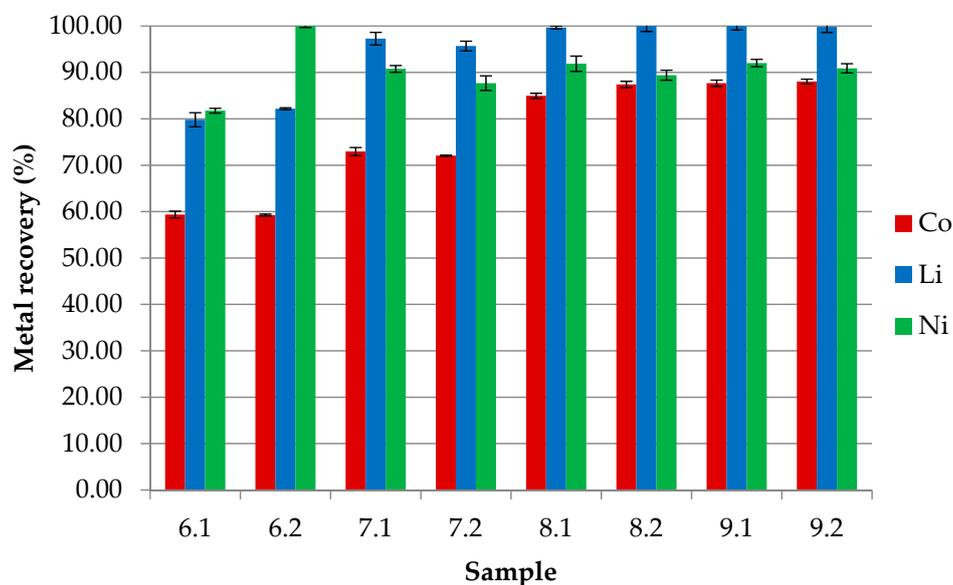


Figure 5. Co, Li, and Ni recovery degrees after battery powder leaching in 1.5 M H₂SO₄ in the presence of reducers of 5 g C₅H₈O₄ and 3 cm³/5 cm³/10 cm³/15 cm³ perhydrol.

As a result of the conducted experiments, high recovery degrees of the tested metals were obtained (Figure 5). The highest cobalt leaching occurred in samples 9.1 and 9.2 (87.66% and 88.03%, respectively), where apart from glutaric acid, 15 cm³ of 30% hydrogen peroxide was also added. In the solutions obtained by leaching, the examined battery powder in the presence of a smaller amount of 30% H₂O₂ (i.e., 10 cm³), the cobalt content was a few percent lower (84.95% and 87.41%). In this series of experiments, the smallest amount of cobalt was obtained in sample 7.1 of 72.94% and sample 7.2 of 72.06% (perhydrol dose of 5 cm³). In the same solutions, the lowest lithium recovery degree was also obtained, however, it was still much higher than the recovery degree for cobalt, (i.e., 97.27% and 95.69%, respectively). In samples 8.2 (10 cm³ of perhydrol) and 9.1 (15 cm³ perhydrol), the total lithium release was obtained (in the corresponding replication tests, over 99% of lithium was leached). In the case of nickel recovery, it was observed that in all solutions, the concentration of this metal was determined at a similar level, however, similar to cobalt and lithium, the best results were obtained for solutions 9.1 and 9.2 by leaching in the presence of 15 cm³ 30% H₂O₂ (92.02% and 90.89%, respectively).

For the purpose of determining the optimal dose of an inorganic reducer (i.e., hydrogen peroxide) in the examined acidic leaching process of spent Li-ion batteries, the cobalt, lithium, and nickel recovery degrees obtained in earlier experiments (6.1 and 6.2) with the smallest addition of perhydrol (3% vol. of 3 cm³) were compared. The obtained leaching levels of these metals in samples 7.1–9.2 are presented in Figure 5. An increase in the amount of hydrogen peroxide in the leaching process of battery powder with 1.5 M sulfuric acid in the presence of two reducers influenced the recovery degrees of the examined metals (Co, Li, and Ni). The application of more than 3 cm³ of 30% H₂O₂ allowed us to increase the leaching process effectiveness, especially for cobalt, but also for lithium and nickel. It was observed that in solutions obtained by leaching in the presence of 5 cm³ H₂O₂, significantly more cobalt was determined (72.94% and 72.06%, respectively) than in the case of samples 6.1 and 6.2 (3 cm³ H₂O₂, 59.37% and 59.24%, respectively). The subsequent increase in the hydrogen peroxide dose (to 10 cm³) resulted in an even higher release Co of 84.95% and 87.41%. Cobalt release degrees in

the solutions obtained by leaching with 15 cm³ 30% H₂O₂ were also examined. In samples 9.1 and 9.2, the highest leaching level of Co (87.66% and 88.03%, respectively) was obtained; in addition to this, in comparison with tests 8.1 and 8.2, the increase was not so high as in the case of the differences observed (e.g., between solutions 6.1–6.2 and 7.1–7.2). The highest cobalt recovery (on average 88%) was obtained with an increased dose of hydrogen peroxide (15 cm³), which confirms the literature data referred to several times in this paper, on the reducing effect of perhydrol on Co ions and its positive influence on the release degrees of this metal. It was also observed that increasing the reducer dose above 10 cm³ had a positive impact on the obtained cobalt leaching; the recovery degrees were higher, however, their growth was estimated at the level of maximum as a few percentage points. Therefore, it can be concluded that a further increase in the dose of 30% H₂O₂ solution in the examined acidic leaching process can slightly improve the obtained cobalt release. As previously mentioned, Co must be in the required form (Co(III)), so the addition of perhydrol effectively supports the recovery process of this metal (i.e., there was a reduction to the form of Co(II)). Moreover, the modification of the set parameters will have an impact on the cost intensiveness of this method (e.g., a larger amount of the used chemical agent) with a simultaneous but only slight improvement of the recovery efficiency of the discussed metal.

The solutions obtained by leaching battery powder with 1.5 M sulfuric acid in the presence of two reducers (glutaric acid and 30% hydrogen peroxide solution) were analyzed also concerning lithium recovery. It was indicated that increasing the H₂O₂ dose to 5 cm³ resulted in a significant rise in the leaching degree of this metal (97.27%, 95.69%) in comparison with the degrees obtained for samples 6.1 and 6.2. In the subsequent experiments, with an increasing dose of hydrogen peroxide (10 cm³ and 15 cm³), the obtained results for lithium leaching were even higher (as much as 100%) in solutions 7.1 and 7.2, however, the observed changes (increase) in the recovery degree of this metal were significantly smaller than between the samples where the amount of dosed 30% H₂O₂ was 3 cm³ and 5 cm³. Similar dependencies were observed for the obtained nickel leaching degrees. With an increase in the hydrogen peroxide dose, the recovery degrees for this metal also grew, and the highest results (i.e., 92.02% and 90.89%), were obtained for solutions 9.1 and 9.2, which were obtained by leaching in the presence of 15 cm³ perhydrol.

4. Conclusions

The analysis of the results of the conducted research work, presented and discussed in this paper, allowed us to formulate the following conclusions:

(1) Battery powder obtained as a result of mechanical processing of spent Li-ion batteries, previously used to power laptops contains various precious metals, primarily Co, Li, and Ni, which can be successfully recovered in an appropriately designed acidic leaching process;

(2) It was determined at the initial phase of the experiment that the best Co, Li, and Ni recovery levels were obtained for samples 6.1 and 6.2 leached with 1.5 M H₂SO₄ in the presence of two reducers: 3 cm³ 30% H₂O₂ and 5 g C₅H₈O₄;

(3) After the research on the optimization of the perhydrol dose, it has been finally determined that it is possible to efficiently recover Co (on average 87.85%), Li (on average 99.91%), and Ni (on average 91.46%) from battery powder as a result of the mechanical processing of spent Li-ion batteries using acidic leaching, where the leaching agent is 1.5 M sulfuric acid, and the reducers are two compounds: 5 g of glutaric acid and 15 cm³ of perhydrol, which confirms the assumed synergic action of C₅H₈O₄ and 30% H₂O₂ solution (the method has not been described in the primary sources as yet); the other process parameters were T = 90 °C, s/l = 1/10, t = 120 min, v_m = 500 rpm);

(4) The obtained results of all the conducted experiments and analyses are the basis for the continuation of laboratory research on the selective recovery of the investigated metals (Co, Li, and Ni) with hydrometallurgical methods (e.g., based on literature information using solvent extraction for selective cobalt and nickel recovery and lithium ion precipitation) to obtain a product that offers both technological and economic benefits.

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