

Cobalt and lithium recovery from active mass of spent Li-ion batteries: Theoretical and experimental approach



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ABSTRACT

The paper is focused on the experimental study of cobalt and lithium recovery from active mass of spent lithium batteries with theoretical explanation of behavior of components in this process. Two leaching agents – H_2SO_4 and HCl were used in order to compare their effects on cobalt and lithium extraction. It follows from the results that using HCl as a leaching reagent is more appropriate than using H_2SO_4 . Optimal conditions for cobalt and lithium recovery were: 2 M HCl , 60–80 °C, leaching time 90 min. The work also explains the influence of temperature on cobalt and lithium extraction from active mass by activation energy in case of both leaching agents. It was found that the cobalt extraction in sulfuric acid occurs in two time periods. In the first time period, in 15 to 20 min from the beginning of leaching, the process is controlled by the rate of a chemical reaction ($E_a(\text{Co}) = 43\text{--}48 \text{ kJ}\cdot\text{mol}^{-1}$). In second time period, the process changes to diffusion controlled, as it is evidenced from the value of $E_a(\text{Co}) = 3\text{--}3.5 \text{ kJ}\cdot\text{mol}^{-1}$. In the case of HCl , cobalt extraction in first time period is controlled by the rate of chemical reaction, $E_a(\text{Co}) = 40\text{--}44 \text{ kJ}\cdot\text{mol}^{-1}$. In the second time period, process is converted to a mixed mechanism, $E_a(\text{Co}) = 20\text{--}26 \text{ kJ}\cdot\text{mol}^{-1}$. Lithium extraction is controlled by the diffusion in both of time periods, or occurs in mixed mode. $E_a(\text{Li})$ is between 2 and 20 $\text{kJ}\cdot\text{mol}^{-1}$ in both of leaching agent. The study of the fine structure confirmed the hypothesis that on the cobalt and lithium extraction affects the internal structure of the active mass, which consists primarily of LiCoO_2 and the cobalt extraction is dependent on lithium extraction from the LiCoO_2 structure.

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1. Introduction

Currently, the lithium ion batteries (LiBs) represent a mobile source of electricity in many electrical devices. Their consumption is constantly increasing because of the expansion of information technologies as well as hybrid and electric vehicles (HEV and EV). It can be concluded that increasing consumption of lithium cells will result in long-term increasing amount of LiBs in waste. From that reason, their successful recycling is highly actual issue.

LiBs belong to secondary electrochemical cells as a chemical reaction inside of LiBs is reversible. They consist of package, electrodes – anode and cathode, electrode active material, electrolyte and separator. Various binders and other additives can be added in order to improve their required properties. A special kind of LiBs is polymer LiBs, which differ from conventional LiBs by used separator and electrolyte (Wakihara, 2011; Linden and Reddy, 2001).

A cathode active material of LiBs is mainly composed of metal oxides based on LiMO_2 , where $\text{M} = \text{Co}, \text{Mn}, \text{Ni}$ etc., which are deposited on an aluminum foil. The most common cathode material is LiCoO_2 (Antolini,

2004). Lithium content in LiBs is in range of 2–5%. Cobalt content in LiBs is up 20% (Miskufova et al., 2009).

A cathode active material is a part of active mass which can be obtained by mechanical pre-treatment using crushing, grinding, sieving, etc. The active mass is a powder mixture of the cathode and anode active material (graphite, carbon) and electrolyte (organic solvent with dissolved lithium salts) usually with a particle size 0.8–0.1 mm. The active mass can be contaminated by residues of the electrode foils and separators, which cannot be mechanically separated. From this reason, the active mass is a mixture of several components – metal, non-metal and metal bearing which have different behavior during leaching.

The possibilities of the cobalt and lithium recovery from active mass can be divided into pyrometallurgical and hydrometallurgical treatment. Current research in laboratory scale focuses mainly on the sophisticated hydrometallurgical processing. It involves leaching of spent LiBs active mass and subsequent extraction of metals from leach liquor.

Research on the leaching of the active mass of spent LiBs focuses on selecting a suitable leaching agent, temperature, L:S ratio and other parameters. The leaching is mostly carried out in an acidic leaching agent such as HCl , H_2SO_4 , HNO_3 (Chen et al., 2011; Kang et al., 2010a; Lee and Rhee, 2003; Paulino et al., 2008; Shin et al., 2005; Meshram et al., 2014, 2015a). The most common leaching agent is H_2SO_4 at various

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concentrations with addition of H_2O_2 as a reducing agent (Dorella and Mansur, 2007; Granata et al., 2012; Ferreira et al., 2009; Chen et al., 2011; Kang et al., 2010a, 2010b; Paulino et al., 2008; Shin et al., 2005; Jha et al., 2013). Another possibility is using of $NaHSO_3$ as reducing agent (Meshram et al., 2015b). The metals from the leach liquor can be obtained by solvent extraction, chemical precipitation, controlled crystallization, etc.

However, despite the high extraction of metals, there are some problems that need to be solved. Active mass from spent LiBs represent a complex system of different materials. The active mass may include in addition to the initial components also new phases that can be produced during their life cycle – for example during discharging or overcharging. The all components have individual behavior during recycling and they can interact with each other.

From this reason a mechanism of main metals (Co, Li) extraction is important to define, but a mechanism of their conversion to the leach liquor has not yet been published. Also determination of rate constants and rate-limiting steps for cobalt and lithium extraction has not yet been published so far.

Moreover, in the current research there is a lack of publications focused on the progress of leaching active mass from spent LiBs by using HCl and H_2SO_4 without addition of a reducing agent. In order to choose the optimum leaching agent it would be useful to compare the leaching of the active mass from LiBs in both of the mentioned leaching agents under the same conditions, and to determine the optimum leaching conditions and parameters.

The main novelty aspects of this work are:

- The study of the thermodynamics of leaching of active mass from spent LiBs;
- The study of kinetics of cobalt and lithium extraction from active mass of spent LiBs during leaching in sulfuric and hydrochloric acid by activation energy based on the shape of kinetic curves;
- The study of fine structure of leaching residue for explanation of mechanism of cobalt and lithium extraction to leach liquor.

2. Experimental

2.1. Material

A sample of spent portable LiBs from mobile phones and laptops weighing 20 kg was used for the experiments. The sample contained 80 wt.% of LiBs and 20 wt.% of polymer LiBs. The sample was subjected to the mechanical pre-treatment, which consisted of multiple crushing and sieving followed by drying to constant weight. Loss by drying was 3.26 wt.%. Size fraction has been divided into two fractions, one passing through -0.71 mm and other as $+0.71$ mm. Active mass was concentrated in fine fraction ($+0 - 0.71$ mm) and represented 37.88% of the total weight.

Obtained active mass was subjected to analysis of the chemical and phase composition. The chemical analysis of active mass was carried out by the AAS method using Varian Spectrophotometer AA20+. The results are shown in Table 1. Cobalt and lithium content in the sample was 22.43% and 3.65%, respectively. Except metal components, active mass contains oxygen from oxides, carbon and other elements.

According the qualitative XRD analysis (Fig. 1), cobalt and lithium in active mass are present as $LiCoO_2$. Other present phases containing

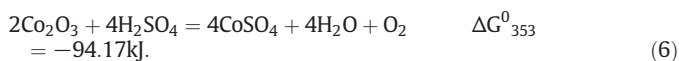
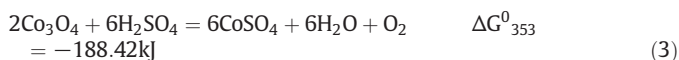
cobalt and lithium that have been identified in the sample are Co_3O_4 and $Li_{0.45}Ni_{1.05}O_2$. These phases confirm the chemical composition of the active mass, which is shown in the Table 1.

2.2. Thermodynamic study

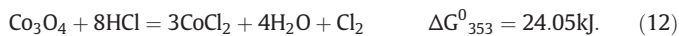
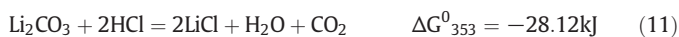
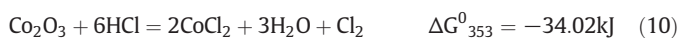
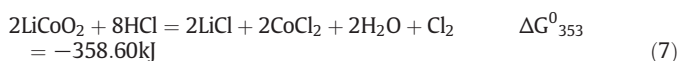
Thermodynamics studies systems in equilibrium state and predicts the probability of reactions in the system, depending on the external conditions. Thermodynamic calculations were carried out using the software HSC Chemistry 6.1 (Roine, 2010).

A thermodynamic study presented in this work was focused on the determination of the values of standard Gibbs free energy change ΔG^0 and study of E-pH diagrams in order to find out the stability areas of cobalt and lithium in the Co-S- H_2O , Co-Cl- H_2O , Li-S- H_2O and Li-Cl- H_2O systems. The values of ΔG^0 were calculated for temperature of 293–353 K (20–80 °C).

The following equations describe the possible reactions of cobalt and lithium in a sulfuric acid solution, with values of ΔG^0_{353} :



The following equations describe the possible reactions of cobalt and lithium in a hydrochloric acid solution, with values of ΔG^0_{353} :



Tables 2 and 3 show the values of ΔG^0 at 293, 313 and 333 K for the estimated chemical reactions during the leaching of active mass in H_2SO_4 as well as HCl.

For sulfuric acid as usable leaching agent results from the thermodynamic values in Table 2 that the reactions (1) to (6) are probable as their values of ΔG^0 are negative at all given temperatures. This means, that all these chemical compounds, present in active mass, are potentially leachable by sulfuric acid.

For hydrochloric acid, all calculated values of ΔG^0 were negative at all range of temperatures (293–353 K), except of the reaction (12). It follows that the reactions occur in the direction of product formation with a high probability. The reaction (12) with a positive value of ΔG^0 probably occurs in the opposite direction.

If only values of ΔG^0 would be taken into account, neglecting other factors (kinetics, system complexity and side effects), probability of

Table 1
Chemical composition of the active mass from spent LiBs.

Active mass (fine fraction +0 – 0.71 mm)	Metal amount [wt.%]						
	Co	Li	Ni	Cu	Al	Mn	Fe
	22.43	3.65	1.54	1.33	0.72	1.49	1.27

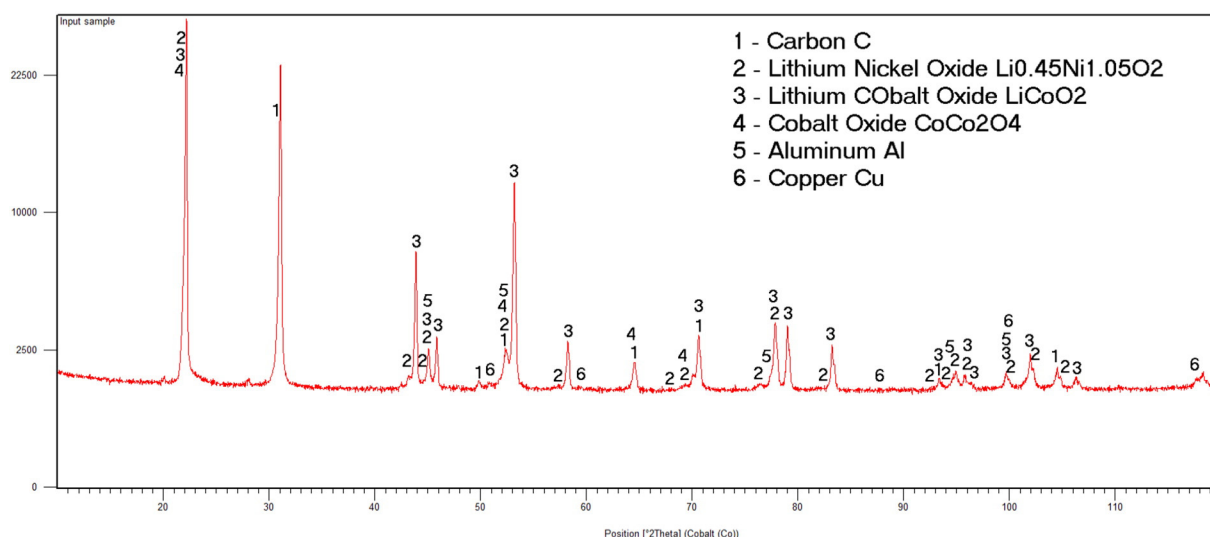


Fig. 1. XRD pattern of the active mass sample.

cobalt and lithium extraction in both of leaching agents increases with increasing temperatures in the following order 293 → 313 → 333 → 353 K.

Given values describe the situation in the equilibrium state and relate only to individual phases. However, the real system consists of more than one phase, so it is necessary to verify how the system will behave under specified conditions. For this purpose, thermodynamic study through E-pH diagrams was carried out. E-pH diagrams indicate possible stable phases of an aqueous electrochemical system. Predominant ion boundaries are represented by lines. Calculated E-pH diagrams reflect real values of metal concentrations in solution.

The resulting E-pH diagrams for the systems Co-S-H₂O and Co-Cl-H₂O at 353 K are shown in Fig. 2a–b, where can be seen the stability of ions in an aqueous medium of sulfuric acid and hydrochloric acid. In sulfuric acid, cobalt is present in soluble compounds as Co²⁺ which is stable to pH ~5.3. In hydrochloric acid cobalt is present in the form of chlorine complexes which are stable to pH ~5.7. Increasing the pH value causes hydrolytic precipitation of cobalt from both of leaching agents. Practically, it means that after leaching out cobalt and lithium into the solution, free acid can be partially consumed what can lead to increasing pH and subsequent hydrolytic precipitation of cobalt from the solution. Lithium remains in a soluble form as Li⁺ in whole acidic pH range (Ferreira et al., 2009; Meshram et al., 2014). Precipitation of cobalt should be avoided by choosing suitable leaching conditions.

Thermodynamic study showed that cobalt and lithium extraction is theoretically possible in both of considered leaching agents. It was base for experiment condition design which was aimed to ensure cobalt and lithium extraction into solution and determine the optimum conditions.

2.3. Leaching experiment conditions

Leaching experiments were carried out in standard laboratory leaching apparatus. The concentration of leaching agents (0.1, 0.5, 1 and 2 M H₂SO₄ and HCl) and temperature (20, 40, 60 and 80 °C) were investigated for cobalt and lithium extraction from active mass of LiBs.

Table 2

The values of ΔG^0 for chemical reaction in H₂SO₄ at 293–333 K.

T [K]	The value of ΔG^0 for the reactions (1)–(6) [kJ]					
	(1)	(2)	(3)	(4)	(5)	(6)
293	–612.24	–307.32	–185.65	–122.553	–115.55	–99.65
313	–610.72	–307.11	–186.35	–123.73	–115.09	–97.42
333	–609.63	–306.90	–187.28	–125.09	–114.61	–95.59

The following constant leaching conditions were used: L:S = 50, 300 rpm, the leaching time of 90 min. All experiments were carried out at atmospheric pressure. Liquid samples of 10 ml were taken at the fixed time intervals after 1, 5, 10, 15, 30, 60 and 90 min from each experiment. The all liquid samples were analyzed by AAS on Varian AA-240 to determine concentration of cobalt and lithium in the solution. All results were recalculated due to the change of the pulp volume caused by sampling and evaporation.

2.4. Results and discussion

2.4.1. Behavior of cobalt

The kinetic curves of cobalt extraction in the both of the leaching agents at marginal temperatures (20 and 80 °C) are shown in Fig. 3a–d. The results show that the leaching in H₂SO₄ leads to lower cobalt extraction (50–60%) and the kinetic curves have tendency to decay. On the contrary, the kinetic curves of leaching in HCl have progressive character and at appropriate leaching temperature (80 °C) almost 100% of cobalt extraction can be achieved. There is a premise that the process will proceed much faster with further increasing temperature to a level close to the boiling point.

2.4.2. Behavior of lithium

Comparison of the effect of the used leaching agent and its concentration on the lithium extraction at marginal temperatures (20 and 80 °C) is shown in Fig. 4a–d. Unlike cobalt, lithium leaching proceeds relatively progressive with higher extractions. At lower acid concentration, 0.1 M and 0.5 M H₂SO₄ seems to be more effective leaching agent than 0.1 M and 0.5 M HCl at the same temperature (20 °C). At higher concentrations (1–2 M) and temperature (60–80 °C), the lithium extraction is similar in both of the leaching agents.

In the case of cobalt, during the leaching in H₂SO₄ (Fig. 3), in a short time, up to 15 min, 40–60% of cobalt extraction was achieved. The amount of cobalt passing into the solution is dependent on temperature and/or concentration of leaching agent. After 15 min, the process of

Table 3

The values of ΔG^0 for chemical reaction in HCl at 293–333 K.

T [K]	The value of ΔG^0 for the reactions (7)–(12) [kJ]					
	(7)	(8)	(9)	(10)	(11)	(12)
293	–337.16	–188.97	–37.61	–19.51	–11.57	58.31
313	–344.77	–191.41	–39.56	–24.68	–17.24	46.29
333	–351.90	–193.71	–41.33	–29.51	–22.75	34.89

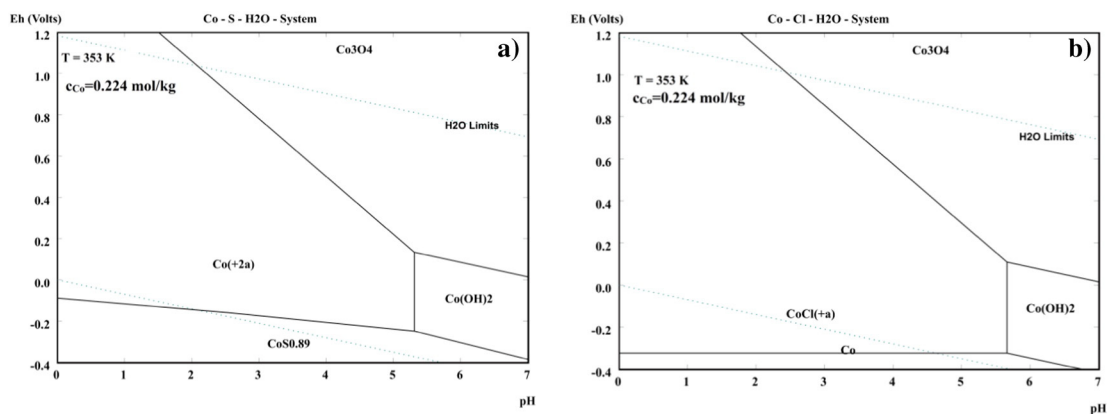


Fig. 2. E-pH diagrams at 353 K for the system a) Co-S-H₂O b) Co-Cl-H₂O.

cobalt extraction significantly slows down or stops. In the case of HCl, cobalt is leached continuously until its practically complete extraction from active mass depending on temperature (80 °C) and concentration (2 M HCl). Also in this case the process is very fast at the beginning, later is slowing down, but continues until complete extraction of cobalt.

In the case of lithium, during leaching in both of leaching agent almost 100% Li extraction was achieved, depending on used leaching agent and its concentration (2 M H₂SO₄ and HCl) and temperature (60–80 °C).

It results from Fig. 3 that hydrochloric acid is more appropriate leaching agent for LiBs active mass leaching with respect to achieving higher extraction of cobalt. Almost 100% cobalt extraction is possible to achieve by hydrochloric acid depending on its concentration and temperature. Optimal conditions for cobalt and lithium extraction from LiBs active mass during leaching in hydrochloric acid were following: 2 M HCl, 60–80 °C.

2.5. Two-stage leaching

Two-stage leaching in H₂SO₄ was carried out in order to increase cobalt extraction and to confirm the assumption about sufficient amount of free acid during leaching in first stage. Two-stage leaching experiments were carried out at following conditions: 1 M H₂SO₄, 90 min at 60 °C. Solid residue from first stage was leached in the second stage with fresh sulfuric acid as leaching agent. Cobalt and lithium extractions in the two-stage leaching are shown in Fig. 5.

By two-stage leaching the hypothesis about consumption of available free acid during leaching was rejected, because in the second stage with fresh acid Co and Li extraction had been not significantly increased – for cobalt from 58% to 63% of extraction. From the external factors, influence of temperature on metal extractions was mainly recorded. For explanation of temperature influence the rate constants

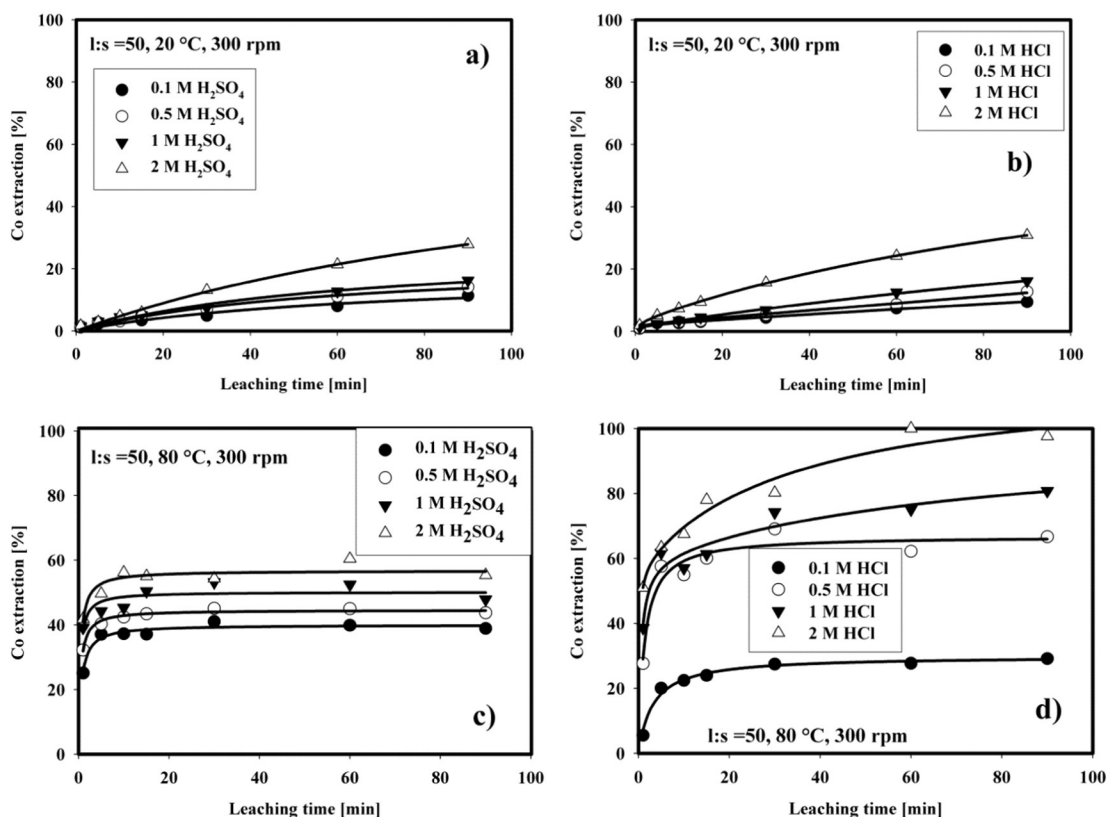


Fig. 3a–d. Kinetic curves of Co extraction — comparison between used leaching agent at temperature 20 and 80 °C.

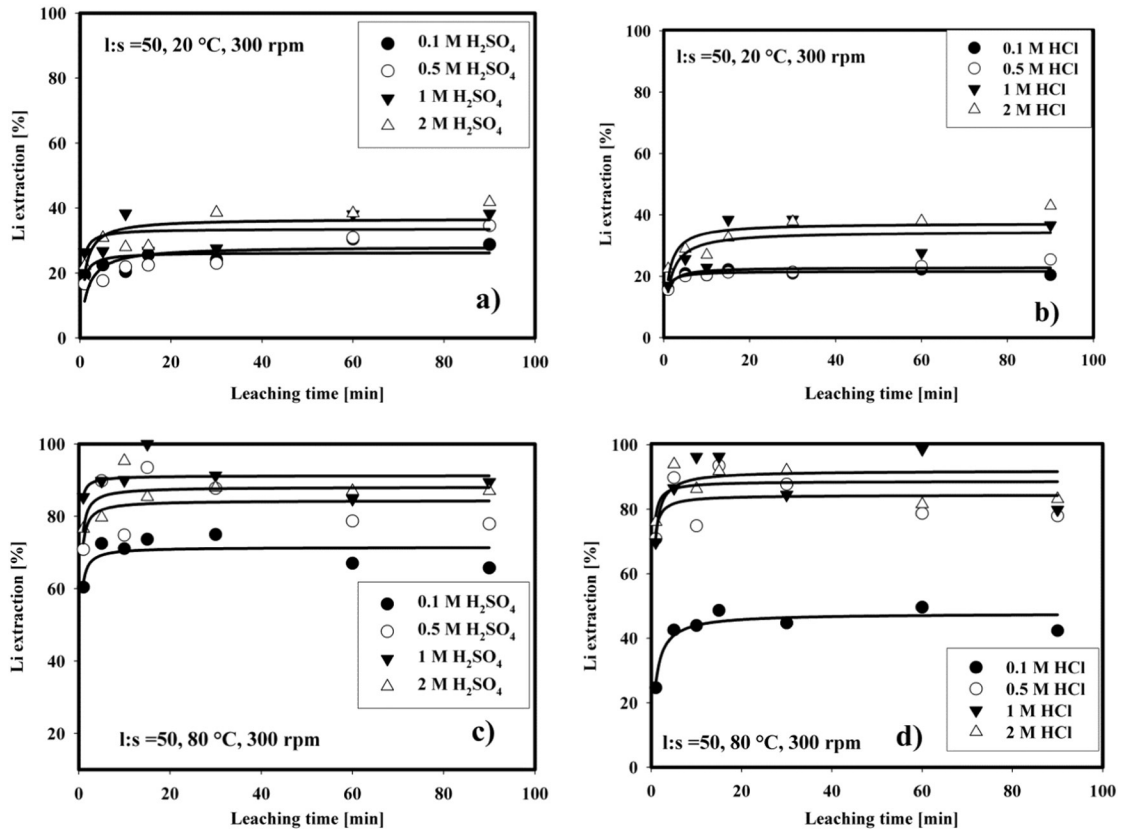


Fig. 4a–d. Kinetic curves of Li extraction – comparison between used leaching agent at temperature 20 and 80 °C.

and rate-limiting steps for leaching were determined by activation energy.

2.6. Kinetic study of cobalt and lithium extraction

The shape of kinetic curves of cobalt and lithium extraction during leaching of the active mass from spent LIBs demonstrates the positive effect of increasing temperature on the extraction of metals. The influence of temperature on cobalt and lithium extraction can be expressed by Arrhenius equation. In order to determine the rate-limiting step of cobalt and lithium leaching, a calculation of the activation energy E_a was carried out. In the first step, a rate constant was determined at

various temperatures from the shape of the kinetic curves. Subsequently, the value of the activation energy was determined through the logarithmic form of the Arrhenius equation (Havlik, 2008). These calculations were carried out for 0.5 M and 2 M sulfuric acid and hydrochloric acid. The shape of kinetic curves of cobalt and lithium extraction indicates that they are composite curves. Therefore, the rate constants were determined for each of the two sections of the kinetic curves according to the model in Fig. 6. Activation energy E_a for cobalt and lithium leaching are shown in Table 4.

In the case of using sulfuric acid as a leaching agent, the diffusion of lithium and cobalt ions on interphase surface occurs in the first section of leaching. This process is very fast, especially in the case of lithium because of very weak bonds of intercalated ions and a small atomic radius of lithium as well. The cobalt ions are considerably more stable than

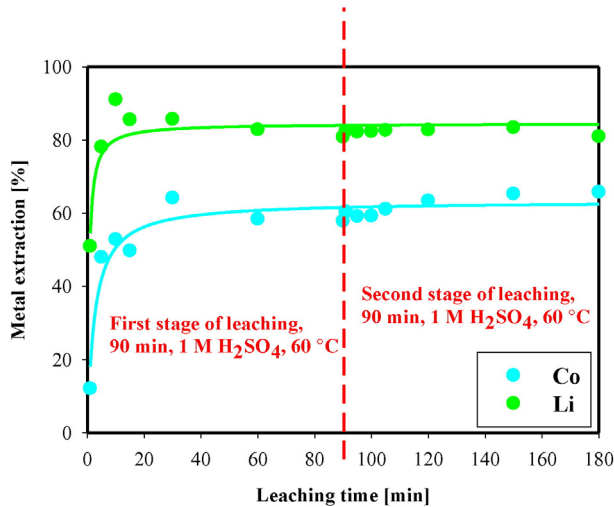


Fig. 5. Kinetic curves of Co and Li extraction during two-stage leaching.

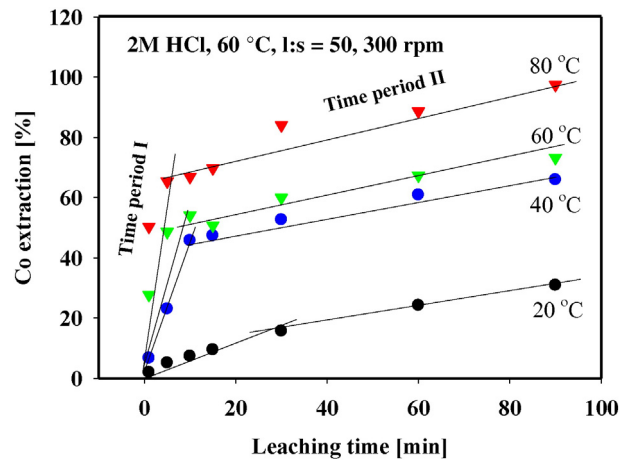


Fig. 6. Model for determination of rate constants.

Table 4
Values of activation energy E_a for cobalt and lithium extraction.

Leaching agent	$E_a(\text{Co}) \text{ kJ} \cdot \text{mol}^{-1}$				$E_a(\text{Li}) \text{ kJ} \cdot \text{mol}^{-1}$			
	Time period I		Time period II		Time period I		Time period II	
H_2SO_4								
0.5 M H_2SO_4	48.73	$R^2 = 0.9894$	3.10	$R^2 = 0.9894$	18.78	$R^2 = 0.9922$	4.71	$R^2 = 0.9933$
2 M H_2SO_4	43.4	$R^2 = 0.9959$	3.66	$R^2 = 0.9761$	16.72	$R^2 = 0.9963$	6.08	$R^2 = 0.9918$
HCl								
0.5 M HCl	44.9	$R^2 = 0.9940$	26.4	$R^2 = 0.9897$	21.2	$R^2 = 0.9989$	3.8	$R^2 = 0.9634$
2 M HCl	40.4	$R^2 = 0.9984$	20.5	$R^2 = 0.9927$	17.4	$R^2 = 0.9681$	9.3	$R^2 = 0.9967$

lithium ions, so that the reaction of cobalt ions is slower and therefore it is the rate-limiting step ($E_a(\text{Co}) = 43\text{--}48 \text{ kJ} \cdot \text{mol}^{-1}$, $R^2 = 0.9894\text{--}0.9959$, depending on the acid concentration). In the second stage, the process proceeds in a typical diffusion mode and depends on the acid concentration and temperature ($E_a(\text{Co}) = 3\text{--}5 \text{ kJ} \cdot \text{mol}^{-1}$, $R^2 = 0.9761\text{--}0.9894$; $E_a(\text{Li}) = 4\text{--}6 \text{ kJ} \cdot \text{mol}^{-1}$, $R^2 = 0.9918\text{--}0.9933$). The cobalt and lithium extractions are increased by increasing concentration of leaching agent and temperature.

In the case of using hydrochloric acid as a leaching agent, in the first section similar situation occurs – diffusion of lithium and cobalt ions in the crystal structure as in the previous case. This process is very fast, so lithium ions on the interface boundary react with hydrochloric acid to form LiCl . The cobalt ions are more stable and the reaction of cobalt ions is slower and hence it is the rate-limiting step ($E_a(\text{Co}) = 40\text{--}45 \text{ kJ} \cdot \text{mol}^{-1}$, $R^2 = 0.9984\text{--}0.9940$, depending on the acid concentration). Unlike the previous case, the cobalt extraction is constantly rising during leaching time and it does not slow down or stop. Cl^- ions react with present lithium and cobalt ions. At the same time, Cl^- ions react with each other to form chlorine gas. Chlorine can be released in the reaction (7), (10), (12). Chlorine is a strong oxidizing agent, and its presence ensures oxidative leaching of cobalt to form soluble chlorine complexes. In this section, the value of activation energy ($E_a(\text{Co}) = 20\text{--}26 \text{ kJ} \cdot \text{mol}^{-1}$, $R^2 = 0.9897\text{--}0.9927$) is seven times higher than in sulfuric acid. The rate-limiting step in the second section is closer to the process controlled by a chemical reaction. Diffusion of chlorine from solution to interphase boundary and subsequent chemical reaction of chlorine gas with cobalt is the most likely rate-limiting step.

The existing results showed that the process of cobalt and lithium extraction from LIBs active mass occurs at least in two time periods. The process is very fast in the first minutes and for both leaching agents, rate limiting step is a chemical reaction. In the case of sulfuric acid, rate-limiting step of cobalt leaching is changed to diffusion with increasing time, in about 15–20 min. In the case of hydrochloric acid, in second time period the process continued in a mixed mode.

In order to confirm the controlling step of the leaching process of cobalt in first time period (0–15 min), the experiments were analyzed using the various model kinetic equations for chemically controlled processes. It was shown, that shrinking core model was successful and it seems to be good fit. The shrinking core model is presented as (13):

$$\tau = 1 - (1 - x)^{1/3} \quad (13)$$

where τ = reaction time (min), x = fractional conversion of the active mass.

Fig. 7 shows plot of $1 - (1 - x)^{1/3}$ vs time at different temperature for Co extraction in sulfuric acid during first time period of leaching.

Fig. 8 shows plot of $1 - (1 - x)^{1/3}$ vs time at different temperature for Co extraction in hydrochloric acid during first time period of leaching.

Based on these facts, a new hypothesis was adopted that the two-time periods leaching of metals is the result of internal changes of active mass structure during leaching. In order to confirm or reject this hypothesis, study of the fine structure of leaching residues was realized, where the mechanism of cobalt and lithium extraction was studied by XRD.

2.7. Study of fine structure of leaching residues

The study of the fine structure by XRD were carried out in order to confirm the hypothesis that the shape of kinetic curves is not affected by external factors (temperature, concentration and type of leaching agents), but their shape is an consequence of the internal influences and changes in active mass structure during leaching. It was assumed that extraction of one metal from the active mass structure depends on the extraction of the second metal and vice versa.

The main phase in active mass with cobalt and lithium content is an oxide binary phase LiCoO_2 . Its presence was confirmed by the XRD in the input sample (Fig. 1), as well as in the leaching residue (Fig. 9).

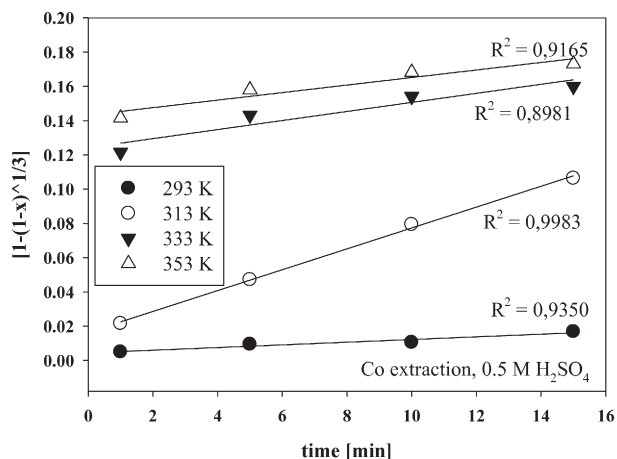


Fig. 7. Plot of $1 - (1 - x)^{1/3}$ vs time at 293–353 K for Co extraction in H_2SO_4 during first time period.

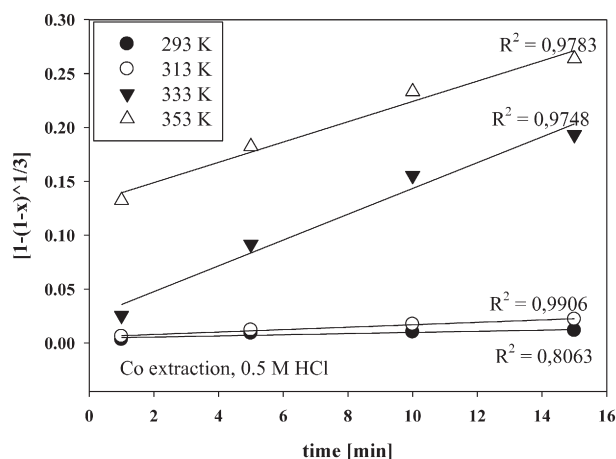


Fig. 8. Plot of $1 - (1 - x)^{1/3}$ vs time at 293–353 K for Co extraction in HCl during first time period.

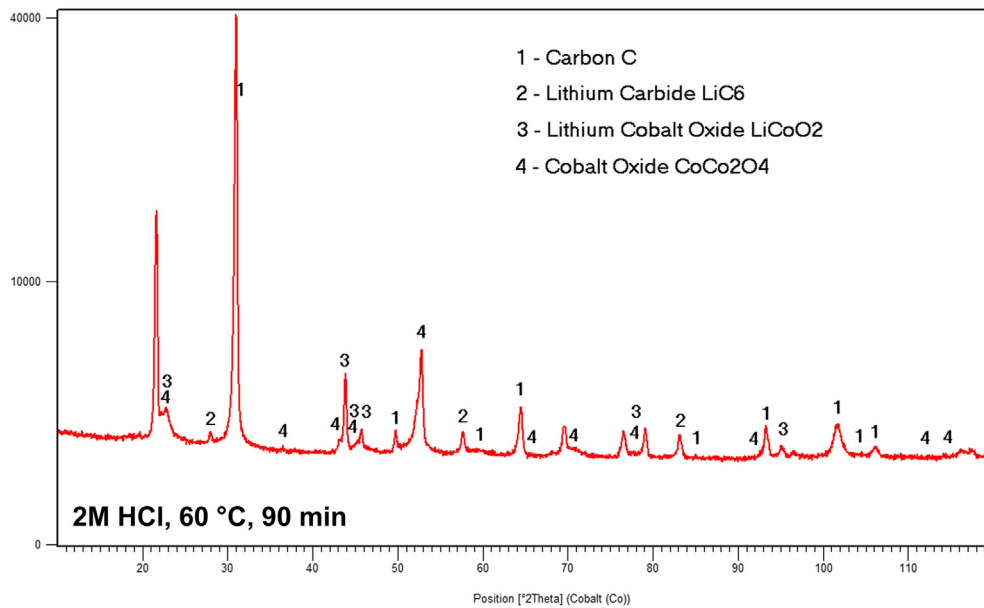


Fig. 9. XRD pattern of the leaching residue.

For these reasons, the phase LiCoO_2 was subjected to study of the fine structure and sample of leaching residue, taken every minute, was investigated.

From comparison of XRD pattern of input sample (Fig. 1) and leaching residue (Fig. 9), the changes in the phase composition of active mass occur during leaching. The amount of carbon was relatively increased, since carbon is inert during leaching and the amount of LiCoO_2 was decreased. In the same time, metallic copper and aluminum amount was reduced as well and the new complex oxide phases of $\text{Li}_x\text{M}_y\text{O}_z$ type were identified, where M is Cu, Al, and Co. It was identified a presence of $\text{Li}_{0.62}\text{CoO}_2$, $\text{Li}_{1.5}\text{CuO}_2$, $\text{Li}_{0.49}\text{CoO}_2$, LiAlO_2 and others, Fig. 10.

These phases are typical solid solution with variable content of components, indicating the possibility of changing values of spacing d depending on non-stoichiometry of the phases. For basic observed phase LiCoO_2 , several minerals were published with variable content of lithium in their structure. In Fig. 11 is shown the position $d(003)$ of LiCoO_2 calculated from the crystal lattice parameters of lithium-

depleted monocrystal Li_xCoO_2 depending on the content of lithium in the structure.

From Fig. 11 it results that $d(003)$ spacing value is proportional to lithium content in the structure of LiCoO_2 . The change of $d(003)$ spacing value indicates a release of lithium from the structure during leaching. By XRD analysis $d(003)$ spacing of LiCoO_2 was established in leaching residues from the active mass leaching in the 1st, 5th, 10th, 15th, 30th and 60th minutes at 60°C in 2 M HCl. The established values $d(003)$ LiCoO_2 was specified to graphite diffraction position $d(002)$ using standard methods. Obtained dependence of the established and specified values of the $d(003)$ spacing LiCoO_2 is shown in Fig. 12.

Depending on the leaching time, diffraction $d(003)$ of LiCoO_2 is shifted to higher values. The processes in the structure of LiCoO_2 during leaching can be described as follows: The first time the structure enlarges its volume by contact with a leaching agent and enhanced temperature. Subsequently, lithium is gradually released from the structure. The structure is deformed because of the vacancies, which

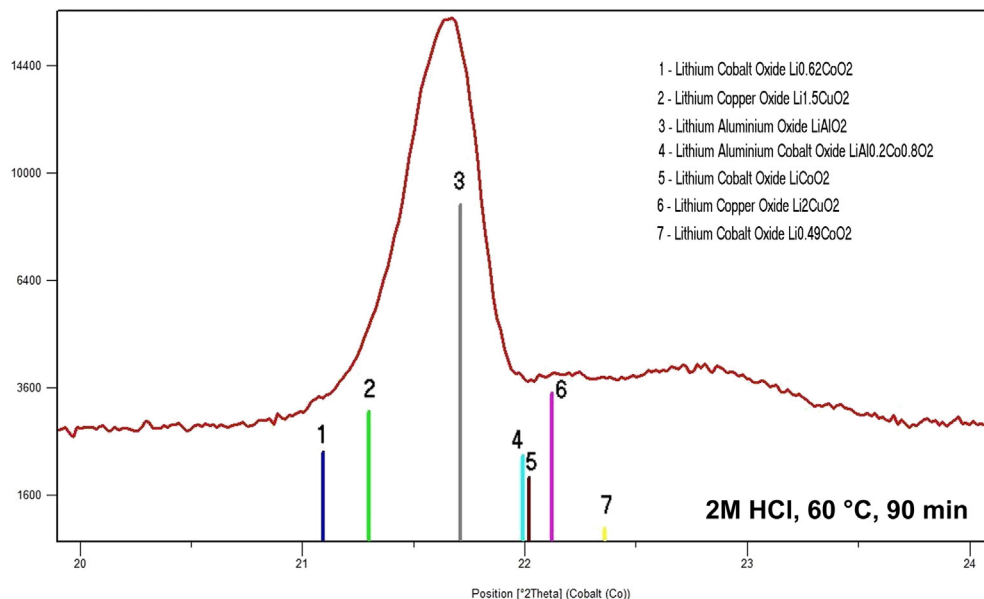


Fig. 10. Detail of XRD pattern of leaching residue.

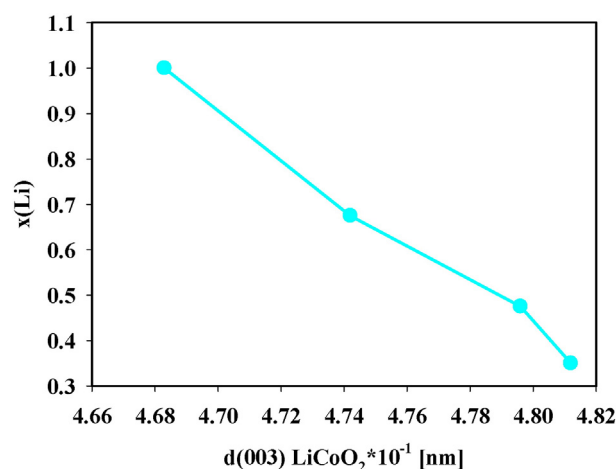


Fig. 11. The dependence of $d(003)$ spacing LiCoO₂ from the lithium amount in the structure.

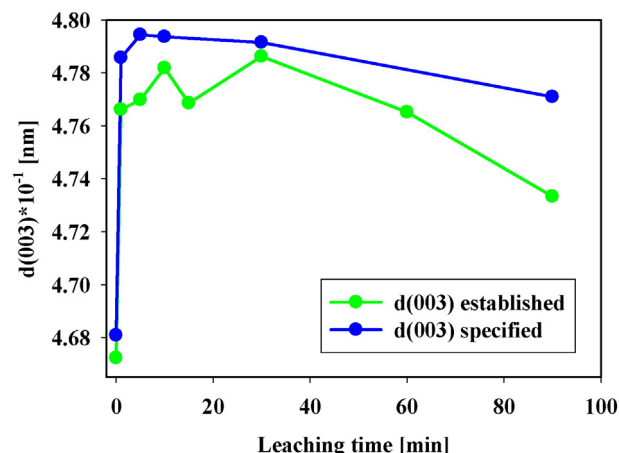


Fig. 12. The dependence of $d(003)$ spacing LiCoO₂ from leaching time.

are a result of lithium extraction. This is reflected by repeated reducing the value of spacings. Cobalt leaves the structure of LiCoO₂ as well, while lithium extraction is close to 100%, cobalt extraction is approximately 50% at same time (in the case of sulfuric acid as the leaching agent). This leads to the stress and deformation of LiCoO₂ structure. On the other hand, defect structure accelerates the leaching. Compilation of kinetic curves of cobalt and lithium extraction and changes of spacings $d(003)$ LiCoO₂ is shown in Fig. 13. Fig. 13 shows a relationship between lithium vacation from the LiCoO₂ structure and subsequent cobalt extraction into solution. The processes of ion migration within the crystal structure are very fast diffusion processes, in this case, particularly with regard to small atomic radius of lithium.

3. Conclusion

This paper focuses on the theoretical and experimental study of cobalt and lithium recovery from active mass of LiBs. It was found that:

- Optimal conditions for almost 100% of Co and Li extraction from the active mass of spent LiBs were established as follows: 2 M HCl, 60–80 °C, leaching time 90 min.
- Co extraction occurs in two time periods. Time period I – Co extraction is controlled by chemical reaction in both of leaching agents ($E_a(\text{Co}) = 40\text{--}48 \text{ kJ} \cdot \text{mol}^{-1}$). Time period II in H₂SO₄ – rate limiting

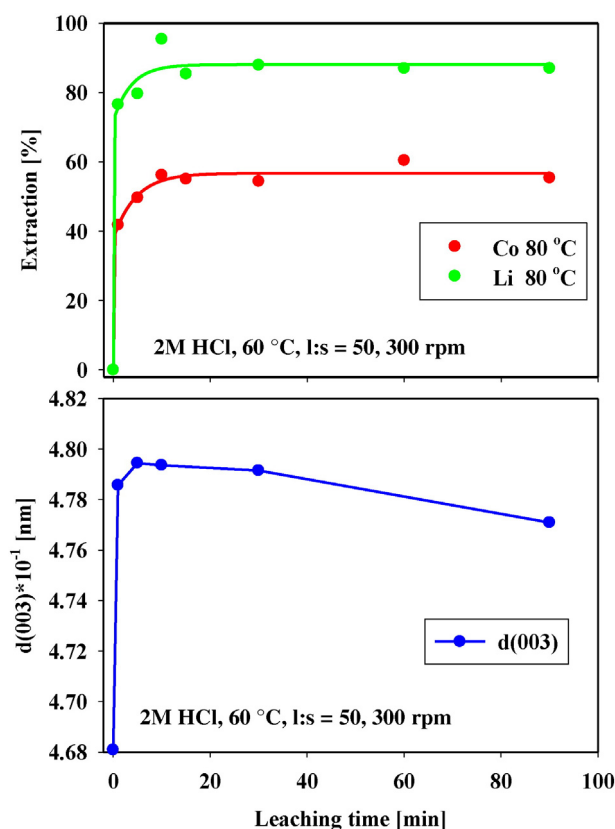


Fig. 13. Comparison between kinetic curves of Co and Li extraction and $d(003)$ LiCoO₂ during leaching.

step is diffusion ($E_a(\text{Co}) = 3 \text{ kJ} \cdot \text{mol}^{-1}$); in HCl – the process is controlled by diffusion of the chlorine from solution to interphase boundary and chemical reaction of chlorides formation ($E_a(\text{Co}) = 20\text{--}26 \text{ kJ} \cdot \text{mol}^{-1}$).

- Li extraction occurs in mixed mode in first time period, in second time period occurs in diffusion mode.
- By study of the fine structure by determining the $d(003)$ spacing of LiCoO₂ in leaching residues was found that lithium vacation from the LiCoO₂ structure, directly affects cobalt extraction during leaching. This means that lithium is extracted first and subsequently a way for cobalt extraction from crystal lattice is opened. The resulting defect structure accelerates the leaching.

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