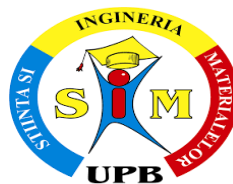


**POLITEHNICA UNIVERSITY of BUCHAREST**  
**Doctoral School of Materials Science and Engineering**



**PHD THESIS SUMMARY**  
**THEORETICAL AND EXPERIMENTAL RESEARCHES**  
**REGARDING THE RECOVERY AND CAPITALIZATION OF**  
**COBALT FROM ACTIVE PASTE OF SPENT Li-ion /LCO**  
**BATTERIES**

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**BUCHAREST**  
**2020**

## Introduction

The increase demand for electronic devices on the market, an effect of technological progress in recent years and population growth, has influenced the increase in the price of metals used in these devices, which has led to their recycling becoming an increasingly interesting topic in the field of materials science, with effects on environmental protection and economic implications. The recycling methods of spent batteries from mobile phones need to focus on large-scale practical technologies with little impact on the environment and the possibility of reusing materials obtained in other industrial fields. This paper focuses mainly on the recovery of cobalt from the cathode of spent Li-ion batteries from mobile phones.

The doctoral thesis is divided into 4 chapters and organized into 2 parts: the study of literature and experimental research.

The first chapter presents EU legislation on the collection and sorting of spent Li-ion batteries with its transposition into national law, along with a classification of Li-ion batteries.

The second chapter focuses on the classification of recycling techniques for spent Li-ion batteries and the need to recover cobalt from these batteries.

The third chapter presents the laboratory equipment used and the steps followed in recovering cobalt from the cathode of used Li-ion batteries. It also presents the experimental results obtained, which were corroborated with the results obtained from mathematical modeling.

The last chapter presents the conclusions related to the theoretical study and experimental results, personal contributions and future research perspectives.

The research carried out throughout the doctoral internship took into account the fulfillment of the following objectives:

- Theoretical study on the recycling technologies of spent Li-ion batteries from mobile phones.
- Establish the research direction on cobalt recovery, taking into account the regulations imposed by the European Union in the field of recycled waste batteries.
- Carrying out experiments related to cobalt recovery. Determining and interpreting the factors influencing the recovery process (time, power, acid concentration) on the leaching yield, in order to recover cobalt.
- Mathematical modeling of the obtained values
- The study of cobalt capitalization
- Proposals to improve the recovery process of active cathode material from spent Li-ion batteries.

The experimental researches and the processing of the obtained data were carried out in the Hydrometallurgy Laboratory of the Department of Engineering and Management of Metallic Materials within the Faculty of Materials Science and Engineering.

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### **Keywords:**

- **Spent Li-ion batteries**
- **Ultrasonic bath**
- **Cathode material**
- **Cobalt blue**
- **Leaching**
- **Acetic acid**
- **Citric acid**

# **1. Choice justification of research topic for the doctoral thesis entitled: „Theoretical and experimental researches regarding the recovery and capitalization of cobalt from active paste of spent Li-ion/LCO batteries”**

Cobalt, alongside lithium are two strategic metals used in making lithium-ion batteries that power mobile phones, laptops and electric cars produced by companies such as Apple, Samsung and major automakers; However, cobalt is five times more expensive than lithium (\$ 80,000 / t -2018). Demand for cobalt has tripled globally over the past five years and it is estimated that this growth rate will continue in the future, mainly due to the acceleration of electric cars production.

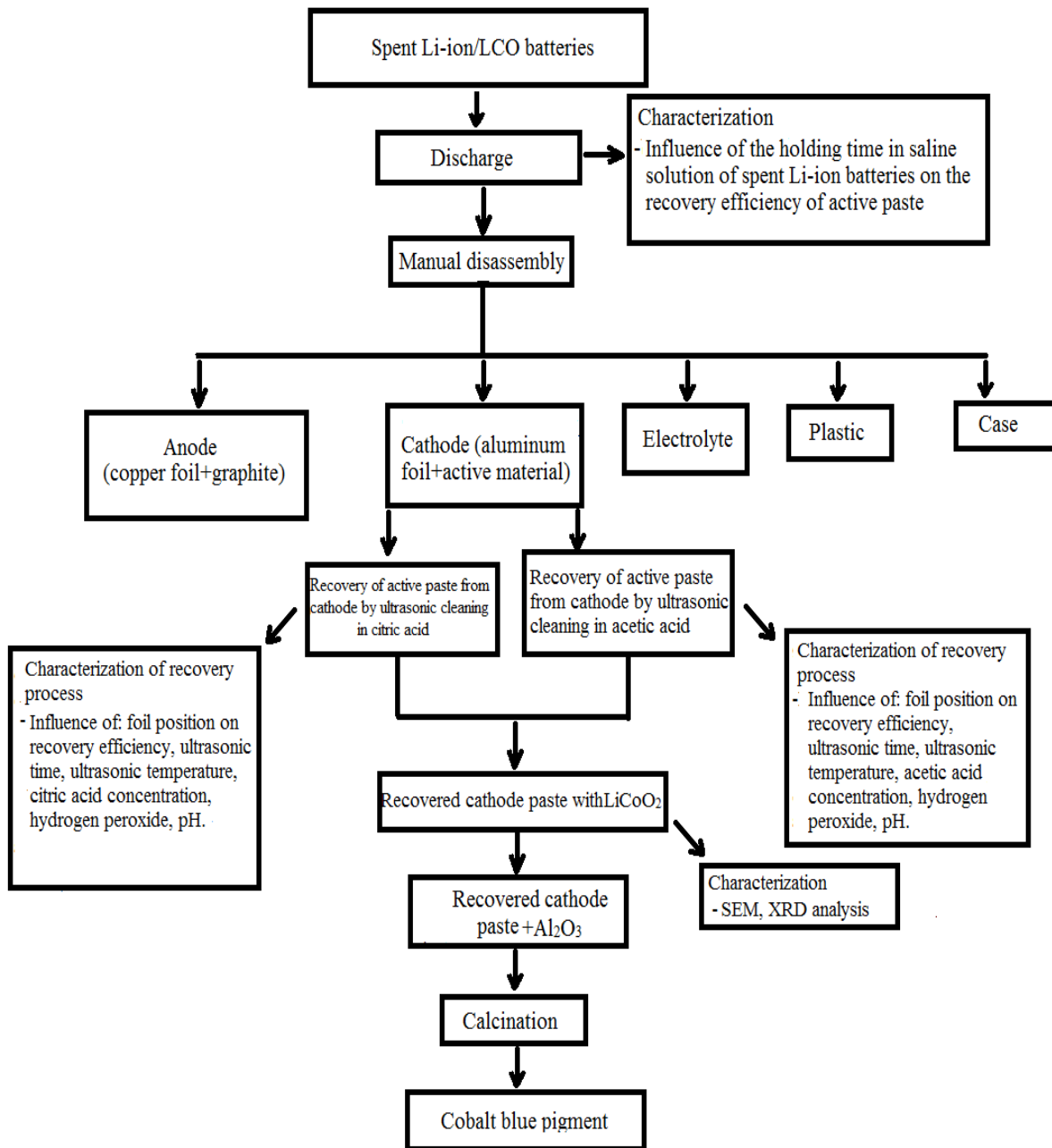
The United States Geological Survey estimates the world's cobalt reserves at 7,100,000 metric tons. Democratic Republic of Congo (DRC) produces 63% of the world's cobalt separately. This market share could reach 73% by 2025, if the planned expansion by mining producers such as Glencore Plc takes place as expected. And by 2030, global demand could be 47 times higher than in 2017 [2]. The demand for cobalt puts a lot of pressure on researchers to find solutions to recover and recycle cobalt-containing Li-ion batteries. The current solutions offered are at laboratory level, at most pilot. The main Li-ion battery recycling plants are in China and South Korea (which are also the main manufacturers of such batteries) and currently store more than they process these batteries in anticipation of more viable recycling solutions.

Concentration of the extractive metallurgy of this metal in a small, politically unstable perimeter, with harsh and inhumane conditions of labor use (moral issues raised by the use of children by Chinese mining companies gaining ground in the DRC and Africa in general), led researchers working in the field of Li-ion batteries to try to limit the proportion of this metal in the composition of cathode paste and replace it with other metals such as Ni, Ti.

An equally important reason for research in this area is environmental protection. It is known that spent, completely unloaded Li-ion batteries that end up in the landfill can cause devastating, hard-to-extinguish fires. This is due to the interaction of air with the flammable electrolytes in the batteries, when the battery is not completely discharged and the housing fails.

In 2018, the amount of batteries, which reached recycling, was estimated at 97,000 tons. Of these, more than 67,000 tons were processed in China and 18,000 tons in South Korea. In 2018, more than 14,000 tons of cobalt, the equivalent of more than 10 percent of the supply from mined sources, was available through recycling. In the future, the market value of the lithium-ion battery recycling industry is estimated to \$ 2.6 billion (2025) at metal prices in December 2018. Of this, cobalt will account for 58% and 17% lithium.

If we take into account only these reasons to justify the choice of this topic, we can consider that the recovery of useful metals from secondary sources (improperly called waste) is an economic necessity and an ecological obligation.



#### 4. Research project scheme

## PART I Current state of knowledge regarding capitalization of spent Li-ion batteries

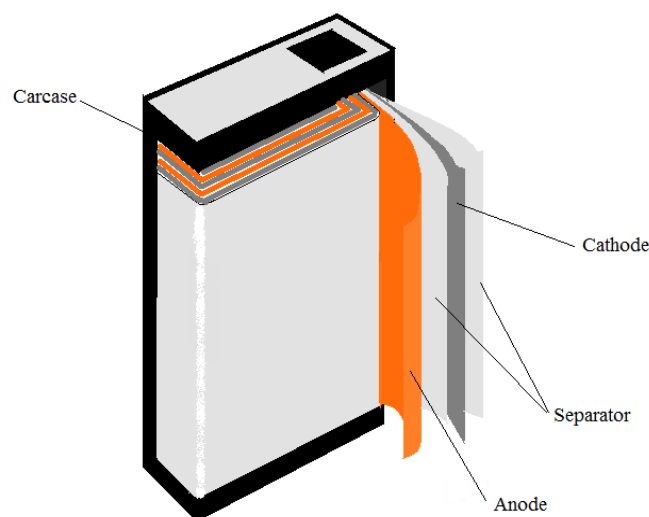
### Chapter 1.3. Components of a Lithium-ion battery

A battery is by definition any source of electricity generated by the direct conversion of chemical energy and is composed of one or more primary cells (non-rechargeable) or consists of one or more secondary cells (rechargeable). The portable battery or accumulator is defined as any type of battery, round battery or accumulator that is sealed, and can be transported; and it is neither an industrial battery or accumulator, nor a car battery or accumulator.[5]

Li-ion batteries are composed more precisely of the following components: cathode, anode, separator, electrolyte, housing, closing elements (Fig.1.6).[34]

Among the metals contained in Li-ion batteries are Co and Li, the main elements of interest due to the price and depletion of resources of these ores. Co and Li in spent Li-ion batteries are 5-15% in the case of Co and 2-7% in the case of lithium, respectively, these percentages are particularly high compared to the percentages of Co and Li in natural ores.

The battery works on the basis of the permanent movement of lithium ions between the two electrodes. The cathode is an aluminum foil covered with an active material, which in most cases is  $\text{LiCoO}_2$ , adhesives - PVDF and electrical conductors. The anode is a copper foil covered with a mixture of graphite, electrical conductors and PVDF adhesives. The electrolyte consists of a lithium salt in a mixture of organic solvents. The separator is a microporous film made of polymers, which separates the two electrodes from each other preventing their short circuit to a direct contact, and the housing is made of a mixture of aluminum and plastic. [34, 35, 36]



**Fig.1.6.** Li-ion battery components

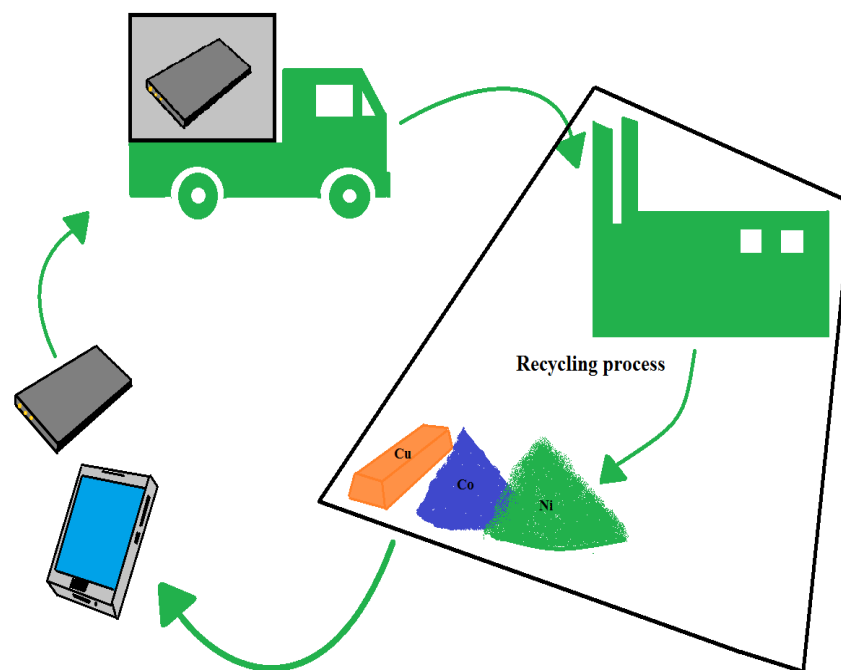
Lithium batteries are widely used as sources of electrochemical energy in modern everyday devices. They are often preferred over conventional aqueous electrolyte systems, such as Ni-Cd rechargeable batteries. [37] Most Li-ion systems use a  $\text{LiXMA}_2$  type material at the positive electrode and graphite at the negative electrode. The materials used at the cathode include  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$ . Li-ion batteries contain toxic and flammable electrolytes and an organic liquid of soluble substances such as  $\text{LiClO}_4$ ,  $\text{LiBF}_4$  and  $\text{LiPF}_6$ . [38]

Lithium-ion batteries contain mainly metals (5-20% Co, 5-10% Ni, 5-7% Li), plastics (7%), organic chemicals (15%); the composition may vary slightly depending on the different manufacturers. [39]

## Chapter 2. Recycling technologies of spent Li-ion batteries

The recycling process can be defined as the process, which starts after the collection and possible sorting and / or preparation for recycling of waste batteries and accumulators obtained from a recycling facility and which ends when the output fractions are produced for use in their original purpose or for other purposes, without being subjected to further treatment and which have ceased to be waste.

Recycling processes for spent Li-ion batteries must aim to recycle 50% of the average weight of spent Li-ion batteries. [52] The process of recycling spent Li-ion batteries involves 2 steps: separation of the fractions belonging to the battery and recovery of metals, metal compounds, plastics, all useful products. The recycling process begins after the preparation operation for recycling spent batteries and ends after obtaining some recovery compounds. [52].



**Fig.2.1.** Stages of the recycling process

The main processes underlying these technologies are either physical or chemical processes, but most often it is necessary to combine several methods to achieve the desired result. Classic technologies for recycling used Li-ion batteries require first the complete discharge of the battery, its disassembly and finally the application of advantageous physical and chemical methods of processing. [53] [54]



## PART II

### EXPERIMENTAL RESEARCHES REGARDING THE RECOVERY AND CAPITALIZATION OF COBALT FROM ACTIVE PASTE OF SPENT LI-ION/LCO BATTERIES

#### Chapter 3.1. Materials used in experimental researches

In Table 3.1. are presented some types of batteries used in experiments performed in the Hydrometallurgy Laboratory within the Department of Engineering and Management of Obtaining Metallic Materials, Materials Science and Engineering Faculty, Politehnica University of Bucharest.

Before being disassembled, the batteries were completely discharged to avoid ignition of the electrolyte in contact with air.

The batteries were weighed before and after disassembly, by components (Table 3.2.) And the determined values are in accordance with those published by other researchers [82].

**Table 3.1.** Characteristics of the batteries used in experimental stage

Component	Material	Weight	Weight
		g/battery	%
Housing		5,290	29,21
Plastic elements	plastic	0,919	5,07
Negative electrode	Graphite	5,020	27,72
Positive electrode	LiCoO <sub>2</sub>	6,881	37,99
TOTAL	-	18,11	100
Full battery	-	19,29	
Material loss	-	1,18	

**Table 3.2.** Average mass of Li-ion battery components

Component	% weight
LiCoO <sub>2</sub>	27,5
Steel/Ni	24,5
Cu/Al	14,5
Carbon	16
Electrolyte	3,5
Polymers	14

In all experimental studies, spent Li-ion batteries from mobile phones were used (Fig.3.1).

For safety reasons, spent LCO batteries used in research, were first completely discharged by holding in a saline solution of NaCl (200g / l) for 1 hour, otherwise there is a danger of ignition of the electrolyte on contact with air.

In Fig.3.2., the cathode - aluminum foil coated with active paste (a) and the anode - copper foil coated with graphite are shown, after dismantling an LCO battery.

In Fig.3.3., the rest of the elements resulting from the dismantling of an LCO battery (housing, separators) are presented.



**Fig.3.1.** Battery types utilized in cobalt recovery

Li-ion batteries components are shown in figures 3.2, 3.3.



**Figure 3.2.** Li-ion/LCO battery electrodes - a) positive electrode (cathode) b) negative electrode (anode)



**Figure 3.3.** Housing, plastic elements (supports, separators) from dismantling of a LCO battery.

### Chapter 3.2. Used investigation equipment. Procedure. Calculating the recovery efficiency

The following devices were used to perform experimental research work at laboratory level for the active paste recovery from the cathode of spent Li-ion batteries, as follows:

- **Electronic balance type EMB 200-3, Kern** (Fig.3.4), on which can be weighed max. 200 g.  
 Reproducibility = 0.001 g;  
 Linearity = +/- 0.005 g;  
 Housing dimensions = 170 x 240 x 54 mm  
 Large LCD screen with a digit size of 15 mm



**Fig.3.4.** Electronic balance type EMB 200-3, Kern

- **Ultrasonic bath type Emmi-12HC** (Fig.3.5) with the following characteristics:  
 Housing material - stainless steel; cleaning frequency = 45 kHz; cleaning time = 1-60 min; volume = 1.2 l; heating temperature = 20 - 80 ° C; bath size 200x100x65 mm; maximum ultrasonic power = 80 W; ultrasonic power regulator = 50/75/100%; dimensions L x W x L 260 x 160 x 180 mm; heating temperature 20-80 °C.



**Fig.3.5.** Ultrasonic bath type Emmi-12HC

### **Phmetru HI 83141**

Phmetru HI 83141 (Fig.3.6) able to measure pH and temperature with a high degree of accuracy and a fast response time. Use the HI 1230B pH electrode and the HI 7669AW temperature probe, with the following characteristics:

measuring range 0.00 to 14.00 pH, +/- 1999 mV, 0.0 to 100.0 ° C

resolution 0.01 pH / 1 mV / 0.1 ° C

accuracy +/- 0.01 pH, +/- 1 mV, +/- 0.4 ° C

dimensions 145x 80x 36 mm

weight 230 g



**Fig.3.6.** Phmetru HI 83141

### **Structural and microstructural analysis**

#### **X-ray diffraction system (Fig.3.7)**

Manufacturer: PANalytical

Model: X'Pert PRO MPD

Year of production: 2008



**Fig.3.7.** X-ray diffraction system

Description [83]

X-ray source: X-ray tube with Cu anode, linear and point focus;

Goniometer: vertical theta-theta;

Detector: proportional to a channel;

Sample stages: for work in reflection and transmission;

Microprocessor system for controlling measurements and electrical components;

High voltage generator;

Ceramic tube containing the X-ray tube (alpha);

PREFIX modules.

### **Scanning Electron Microscope (SEM) (Fig.3.8)**

Manufacturer: FEI

Model: QUANTA 450 FEG

Year of production: 2015



**Fig.3.8.** Scanning Electron Microscope (SEM)

Description[84]

Minimum resolution in 30kV secondary electron imaging:

- 1 nm or better in high vacuum operation mode;

- 5 nm or better in low vacuum mode.

Precise temperature control over a temperature range between -20°C and 60°C

Color mixing of directly acquired images from 2 or 3 independent detectors to obtain a pseudocolored image to highlight the angular or energetic scatter signal.

Simultaneous acquisition, at a single scan, of 4 images with different sources (detectors or segments of the same detector) to decrease the scanning time.

1) Conventional Everhart-Thornley Detector (SED) for secondary electron signal (SE) detection, can operate in two modes-SE and BSE-polarization function.

2) Large Field Detector-Gaseous Secondary Electron Detector (LF-GSED) for low vacuum imaging at both high and low voltages.

3) Gaseous Secondary Electrons Detector (GSED) optimized for ultra-low vacuum (ESEM) and gas medium secondary electron imaging.

4) Solid State-Directional Back-Scattered Detector (DBS) optimized for working in High Vacuum and Low Vacuum for compositional imaging and surface topography studied by detecting sample scattered electrons from different angles, from 0° to 90°.

5) In-Column Detector (ICD) is a scintillation detector that has the possibility to detect the SE signal with a resolution of 1.0 nm in the high vacuum beam deceleration mode.

6) STEM detector with semiconductors for high-resolution imaging in light and dark field for low-density samples prepared for TEM and measurement of critical dimensions.

7) WetSTEM detector and Peltier / Heating Stage Control Kit temperature controller that offers the possibility of analyzing thin or thick samples (bulk) completely hydrated, offering the possibility to control both temperature and pressure during viewing and analysis of studied samples.

8) EDS detector with Silicon Drift (SDD) technology - EDAX Octane Plus

9) IR-CCD camera for safe viewing and positioning of the sample.

10) Color CCD optical camera, called Nav-Cam 450, for global viewing of the sample in order to achieve an easy and intuitive navigation.

### **NABERTHERM oven (Fig.3.9)**

Specification [85]

Control type C440

Interior dimensions (length x depth x height) 250 x 500 x 140 mm

Exterior dimensions (length x depth x height) 800 x 900 x 600 mm

Table model

Temperature control: Minutes to Tmax: 120

Capacity: 17 L

Temperature (maximum) 1280 ° C





**Fig.3.9.** Furnace for Preheating Metallic Materials and for Heat Treatments type

## Procedure

In all experimental studies, spent Li-ion batteries from mobile phones were used. The first step was to insert the Li-ion batteries in a saline solution of NaCl (200 g / l) for 1 hour, in order to completely discharge them.

The Li-ion batteries were then dismantled manually, and the contents were separated into components (anode - copper foil coated with graphite, respectively cathode - aluminum foil coated with active paste with cobalt content).

The method used to recover the active paste from Li-ion batteries cathode is that of ultrasound in acid medium. As can be seen in Fig.3.10., ultrasound plays an important role in the process of cleaning the active paste from cathode foil, because it send impulses to the foil, which helps to detach the active paste into pieces of different sizes. [86]

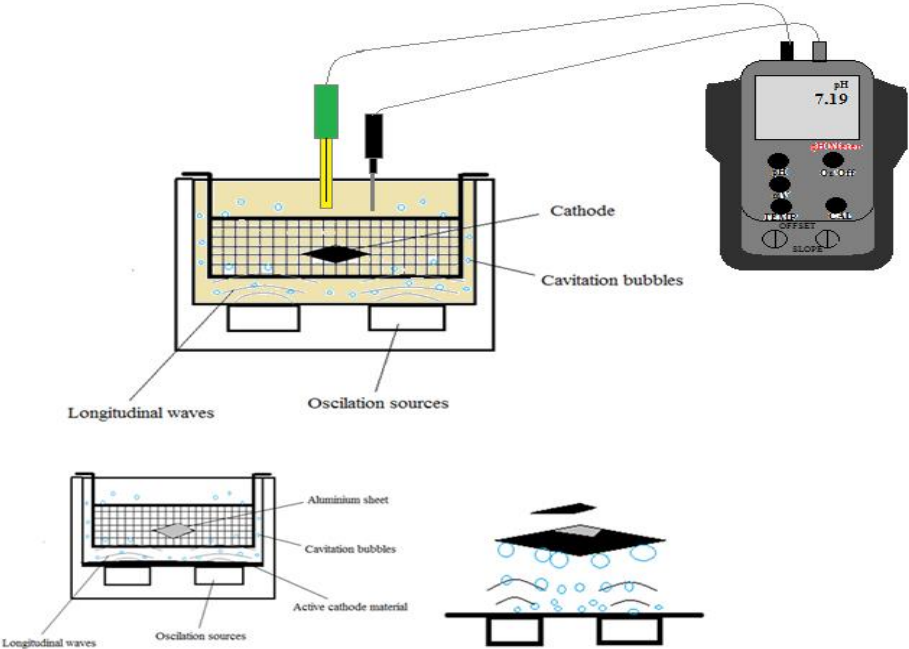
Recycling of  $\text{LiCoO}_2$  cathodic material by ultrasonic technology was first used in 2009 by Jinhui Li et al.[87], who developed a combined process (ultrasonic washing and stirring the solution). Jinhui Li et al. established that by using both agitation and ultrasonic washing, a high percentage of the cathodic material was separated from the Al foils. They also studied the influence of temperature on recovery efficiency. The result was that with increasing temperature, the efficiency of active paste recovery decreases (at room temperature, the removal ratio was greater than 90%).

In 2014, L. Li et al. [39] also used an ultrasound-assisted extraction process to remove the active paste from the cathode of spent LCO batteries. They investigated the effect of ultrasound power, ultrasound duration and temperature on the process of recovering active materials in order to optimize the process. To get the best result, they used different acid reagents and came to the conclusion that citric acid was more efficient and environmentally friendly at the same time.

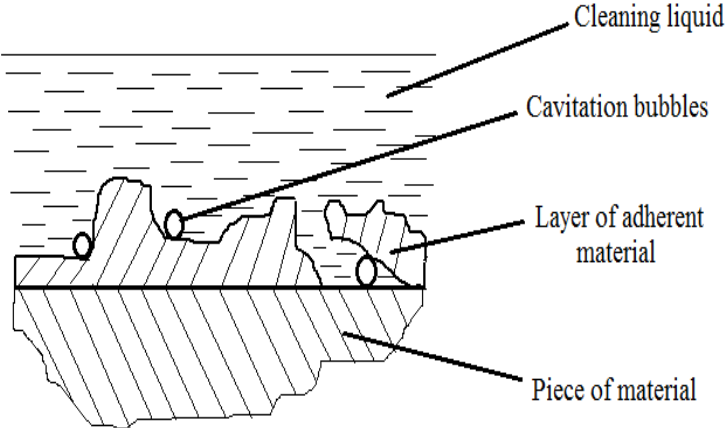
Ultrasonic cleaning was investigated and presented in the literature in 2015 by Li-Po He et al. [88], which also proposed an environmentally friendly process for recycling cathodic

materials from spent Li-ion batteries. They used the ultrasonic cleaning mechanism using different solvents in order to obtain a high release efficiency, which depends on the dissolution of PVDF caused by ultrasound. The process proposed by Li-Po He et al. it is not very environmentally friendly, because in the experiments performed, it uses ultrasonic treatment for the detachment of the active paste from the aluminum foil in the presence of NMP (N-methyl-2-pyrrolidone), a toxic, polluting and controlled use substance.

In figure 3.10. is presented schematically the development of separating process of active paste with cobalt content from the aluminum foil; in figure 3.11. the cavitation effect produced by ultrasound is presented in detail.



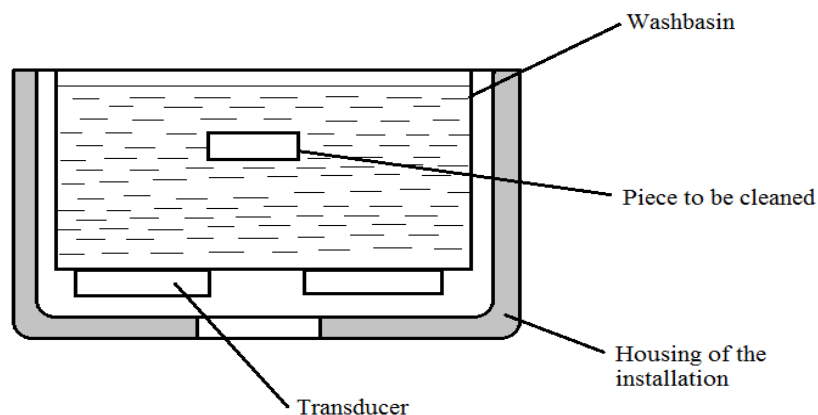
**Fig. 3.10.** Scheme of the separating process of active paste with cobalt content from aluminum foil



**Fig.3.11.** Visualization of cavitation effect on the cathodic foil [89]



An ultrasonic cleaning system consists of the following elements: housing, ultrasonic bath, transducer, as can be seen in Figure 3.12. [90]



**Fig. 3.12.** Components of an ultrasonic bath [91]

In experiments we used an ultrasonic bath type Emmi-12HV, and as a leaching medium, organic acid solutions (citric acid and acetic acid).

### **Calculation of recovery efficiency of the active paste**

Leaching efficiency can be calculated according to the following formula:

$$\eta = \frac{m_0 - m_f}{m_0} \times 100 \quad (3.1)$$

in which:

$m_0$  = initial weight of cathode foil (Al foil + paste),

$m_f$  = final weight (Al foil), after ultrasound in acid medium (citric acid)

### **Chapter 3.3. Recovery of active paste with cobalt content from aluminum cathode by using an ultrasonic bath and citric acid as a leaching solution**

The batteries were completely discharged by keeping in a brine NaCl solution (200g / l) for 1h, dry and dismantled; the cathode made of aluminum foil on which the cobalt-containing paste is fixed was cut into 10-12 sections, with which the first tests were performed.

- The Emmi-12HC type ultrasonic bath with a capacity of 1.2 l and a maximum ultrasonic power of 80W was used; worked with power sequences of 50/75/100%;

- The experiments were performed at room temperature, without the need for additional heat sources;

- The basket of the ultrasonic bath with the cathodic section was positioned and maintained at a height of 1.5 cm from the ultrasonic generator found on the bottom of the tub;

- The aim was to ensure that the cathode paste is completely detached from the aluminum foil in the shortest possible time and with the lowest possible energy consumption;
- Several concentrations of citric acid ( $C_6H_8O_7$ , known as lemon salt) were used, with the aim of recovering the paste as quickly as possible, in the shortest possible time and at a low power; three concentrations were recorded - 1.2 M, 1.23 M, 1.25 M. It was found that the optimal value of citric acid concentration is 1.25 M. At this concentration we obtain low recovery time and high recovery efficiency compared to the other concentrations tested;
- The maximum yield of more than 90% was achieved using a 1,25 M citric acid solution after ultrasound exposure under the following conditions:
  - o volume = 1.2 l;
  - o cleaning frequency = 45 kHz;
  - o heating temperature = 20° C;
  - o ultrasonic power = 50 W.
  - o cleaning time = 8 min;

### **Chapter 3.3.3. Mathematical modelling of the recovery process by ultrasonic cleaning in citric acid of spent Li-ion batteries**

Recovering useful metals from spent Li-ion batteries is an economical strategy and a commitment to protect the environment. This chapter presents the mathematical model of the separating process of active paste from the cathode foil using a solution of citric acid in an ultrasonic bath. Using a second order orthogonal program, the optimal working conditions were confirmed, which we obtained following the experimental results. To make the calculations easier and to obtain the answer surface, we used the trial version of the MathCAD 14 program.

Experimental studies have shown that the separating efficiency of active paste with cobalt content from cathodic foil, expressed by  $\eta$  [%], is influenced by 3 main parameters:

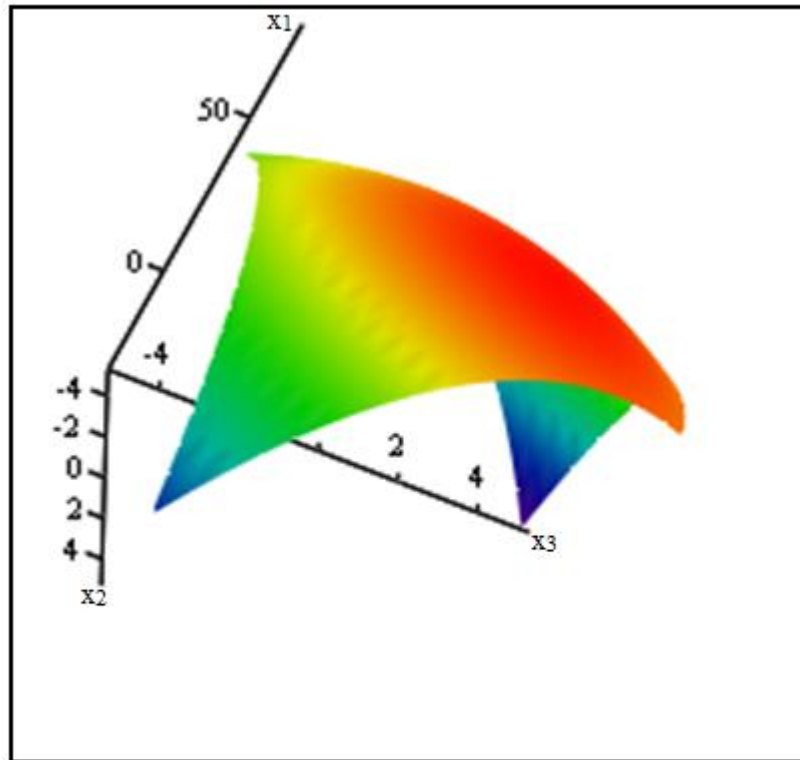
- ultrasonic power of the bath ( $z_1$ ) [W];
- citric acid concentration ( $z_2$ ) [mol / l];
- time ( $z_3$ ) [min].

Other parameters, such as working temperature, basket position in the ultrasonic bath relative to the ultrasonic generator ( $h = 3$  cm), addition of hydrogen peroxide (1 g / l), were maintained at a constant value.

An active experimental program, called the secondary orthogonal program (PO2), was used to determine the optimal conditions for the separating process of active paste from Li-ion batteries cathode in citric acid solution.

The prediction for maximum efficiency was  $\eta(x_{1op}, x_{2op}, x_{3op}) = 93.283$  ;  
 $\eta(x_{1op}, x_{2op}, x_{3op}) - \delta y = 83.492$  .

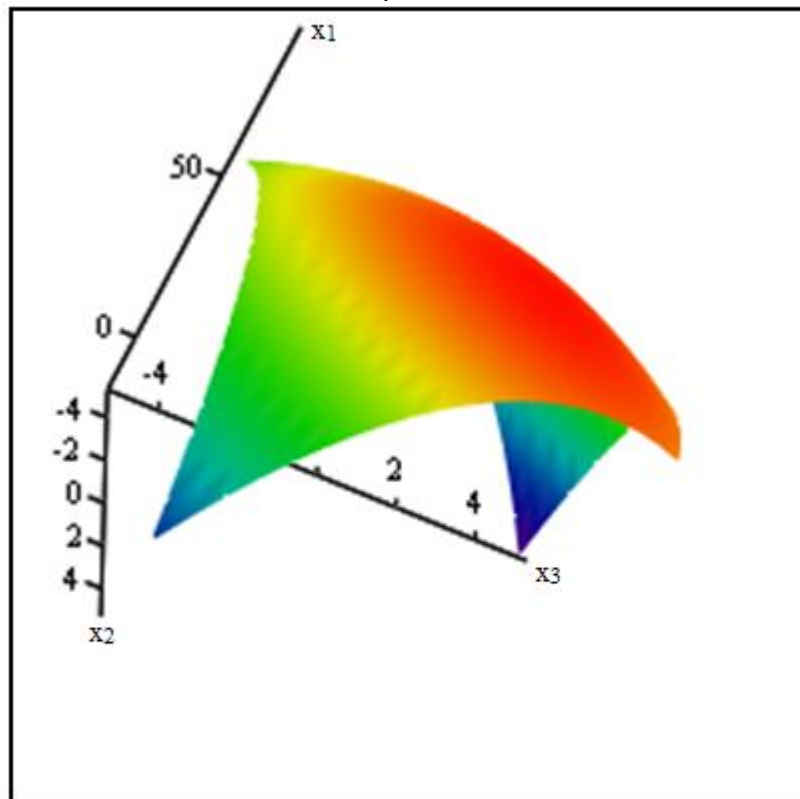
Recovery efficiency:



$\eta$

$$\eta(x_1, x_3); x_2 = -1$$

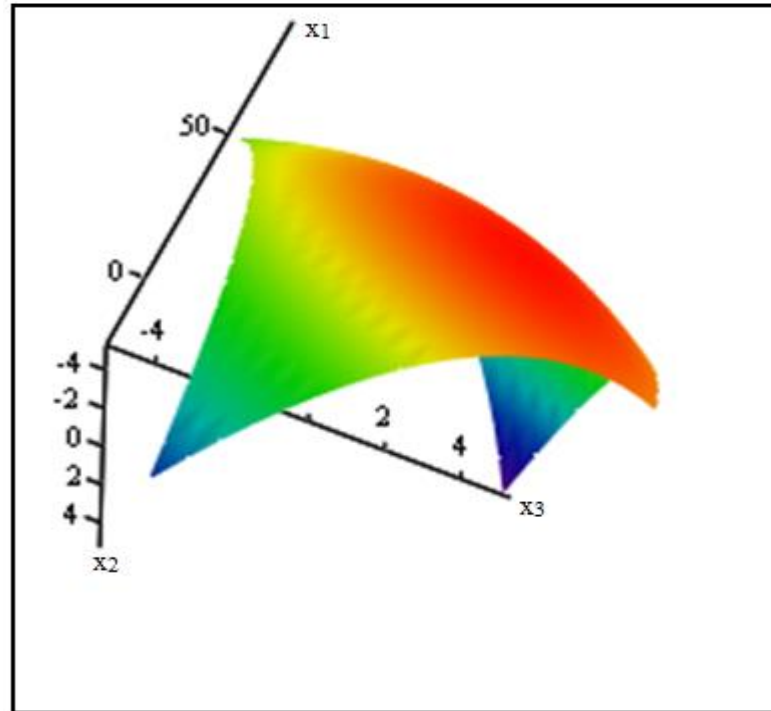
$$\eta = 75.9$$



$\eta$

$$\eta(x_1, x_3); x_2 = 0$$

$$\eta = 91.745$$



$\eta$

$$\eta(x_1, x_3); x_2 = 1$$

$$\eta = 84.689$$

**Fig.3.27.** Response surfaces  $\eta(x_1, x_3)$  for found concentration ( $z_2$ ): a)  $x_2 = -1$ ; b)  $x_2 = 0$ ; c)  $x_3 = 1$

### Chapter 3.4. Recovery of active paste with cobalt content from aluminum cathode by using an ultrasonic bath and acetic acid as a leaching solution

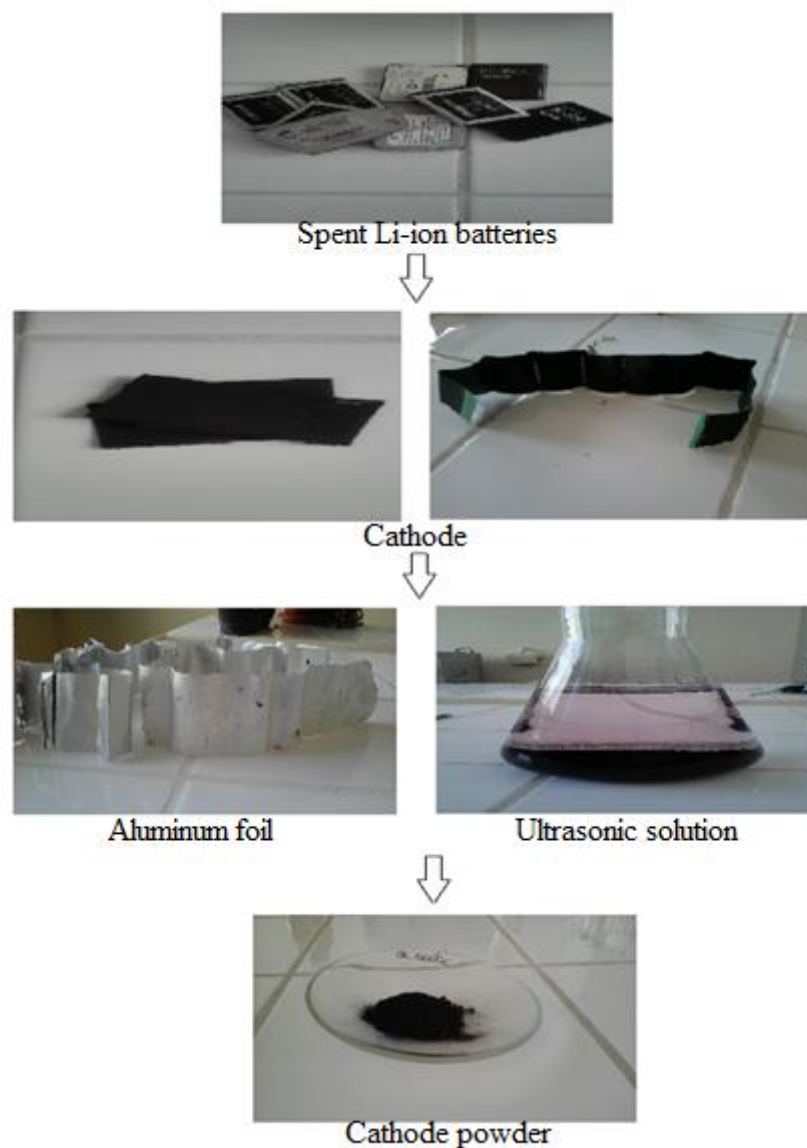
The batteries were completely discharged by keeping in a brine NaCl solution (200g / l) for 1h, dry and dismantled; the cathode made of aluminum foil on which the cobalt-containing paste is fixed was cut into 10-12 sections, with which the first tests were performed, and in the end the entire cathode was used. (Fig.3.28).

- The Emmi-12HC type ultrasonic bath with a capacity of 1.2 l and a maximum ultrasonic power of 80W was used; worked with power sequences of 50/75/100%;
- The experiments were performed at room temperature, without the need for additional heat sources;
- The basket of the ultrasonic bath with the cathode section was positioned and maintained at a height of 1.5 cm by the ultrasonic generator found at the bottom of the tub;
- The aim was to ensure that the cathode paste is completely detached from the aluminum foil in the shortest possible time and with the lowest possible energy consumption;
- If at the beginning a section of the cathode foil (1/10 or 1/12) was inserted in the ultrasonic bath, in the end it was worked with whole cathodes;

- Several concentrations of acetic acid ( $C_2H_4O_2$  - a weak acid) were used, aiming at a recovery efficiency of the paste as high as possible, in a short time interval and with as little power as possible; acetic acid concentrations between 1.2 M and 1.6 M were used. It was found that the optimal value of acetic acid concentration is 1.5 M. At this concentration we obtain low recovery time and high recovery efficiency compared to the other concentrations tested;

- The maximum yield of more than 90% has been achieved using a 1,5 M acetic acid solution after exposure to ultrasound under the following conditions:

- volume = 1.2 l;
- cleaning frequency = 45 kHz;
- heating temperature = 20° C;
- ultrasonic power = 50 W.
- cleaning time = 6 min;



**Fig.3.28.** Images captured during the recovery process of cathode paste in ultrasonic bath in acetic acid solution. [97]

### **Chapter 3.5. Cobalt capitalization resulting from the separation of active paste from Li-ion batteries cathode to obtain cobalt blue pigment (CoAl<sub>2</sub>O<sub>4</sub>)**

Pigments are by definition insoluble powders used in the coloring process. They are divided into organic and inorganic. Inorganic pigments have a low color content, a fairly low coloring power, a high correction power, good chemical resistance and low costs.

Blue pigments are defined as cobalt oxides combined with aluminum or silicon.

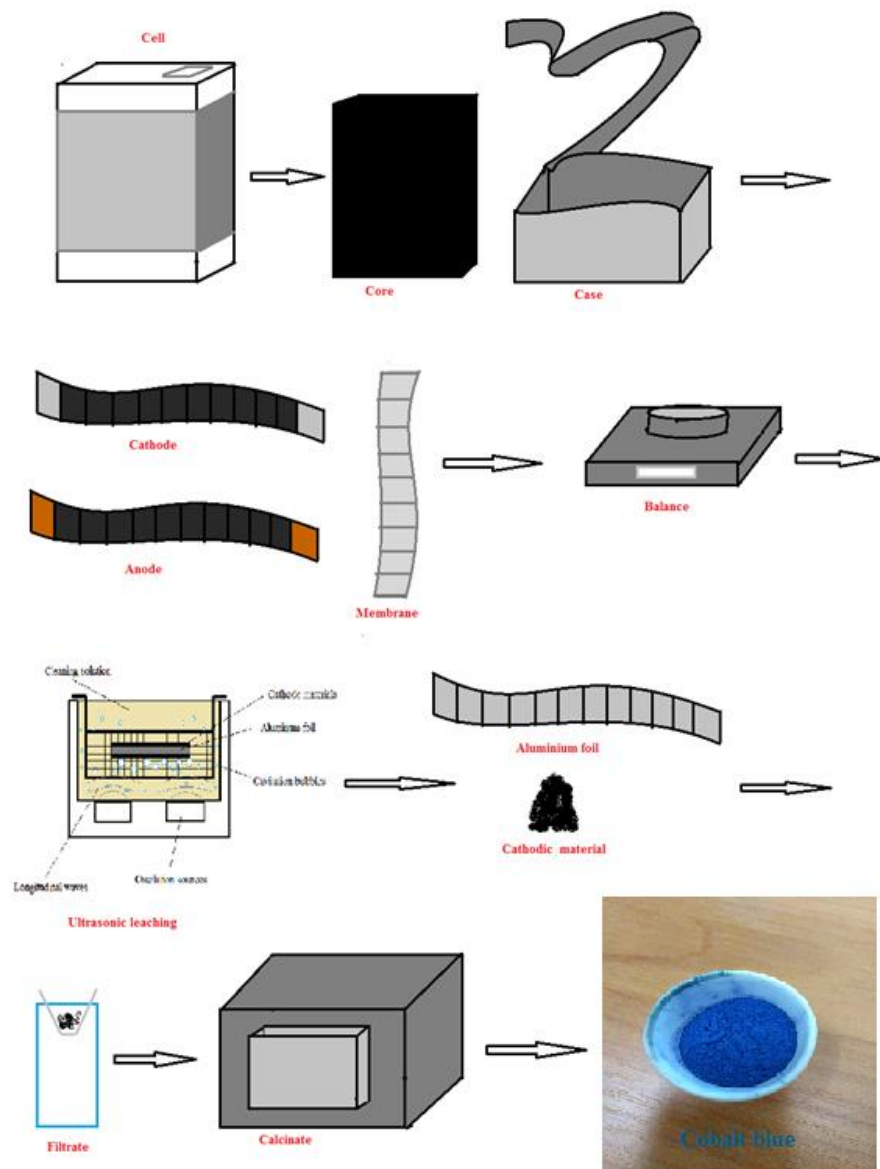
Cobalt blue is an inorganic pigment with an intense blue color, being composed of a cobalt aluminate spinel. Cobalt blue is characterized by thermal and chemical stability and is widely used for coloring ceramics, plastics and fibers.

Cobalt blue can be synthesized using the following methods: sol-gel, hydrothermal and low temperature combustion. Solid state reactions are the most widely used methods used in industrial practice for the purpose of synthesizing cobalt blue. They have the following advantages: simple production process and high performance cost. Aluminum hydroxide and alumina are used as sources of aluminum in obtaining cobalt blue.

The recipe for obtaining cobalt blue involves mixing aluminum and cobalt in a percentage of 1: 2, followed by calcination for 2 hours at a temperature of 1200°C at a heating rate of 1°C / min. [98].

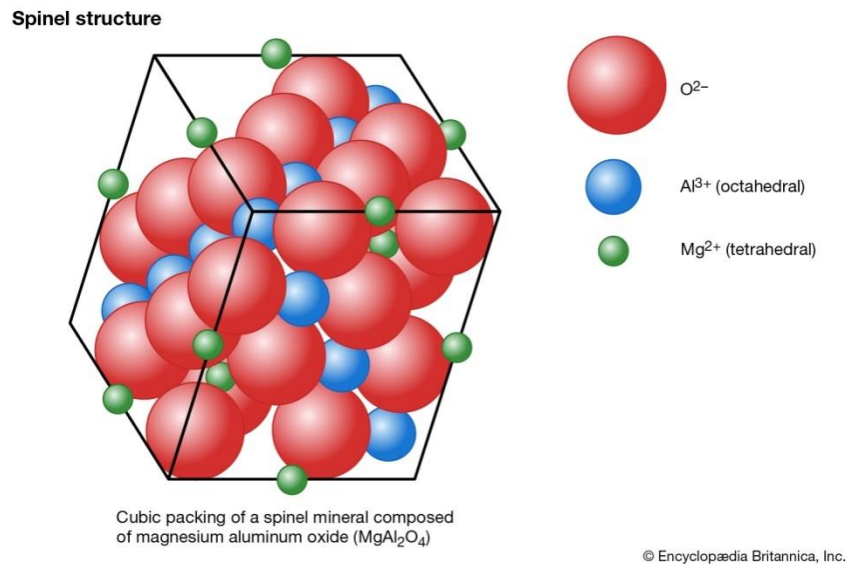
CoAl<sub>2</sub>O<sub>4</sub> belongs to the category of complex spinel-type oxides (MgAl<sub>2</sub>O<sub>4</sub>, TiFe<sub>22</sub> + O<sub>4</sub>); spinel - variously colored crystallized mineral, used as a precious stone (according to one of the DEX definitions). Mainly, these oxides are used as pigments, but with other applications (magnetic materials, gas-sensitive materials, catalysts).

The technology scheme for obtaining CoAl<sub>2</sub>O<sub>4</sub> (cobalt blue) from the active paste recovered from spent Li-ion batteries is presented in Fig. 3.36.



**Fig.3.36.** Technology scheme for obtaining cobalt blue from spent Li-ion batteries cathode

Natural magnesium aluminate is part of magnesium oxides category that crystallize in the cubic system with the chemical formula  $MgAl_2O_4$ ; is a mineral that gave the name of the type of structure with the general formula  $AB_2O_4$  (Aluminum-spinel, Iron (III) spinel; Chromium-spinel; Titanium-spinel; Cobalt-spinel).



**Fig.3.37.** Spinel structure [99]

$\text{CoAl}_2\text{O}_4$ , ie cobalt aluminate is the best known spinel, has applications in the field of ceramics, glass, painting, as an intense blue pigment, stable, but also very expensive.

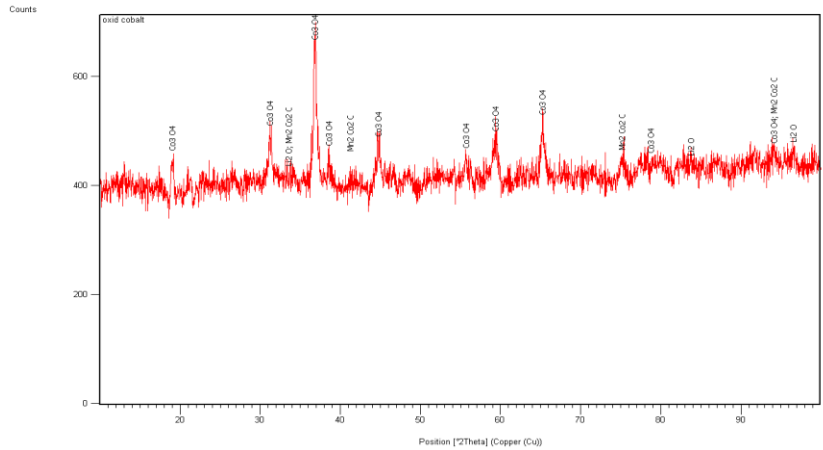
The classic method of obtaining the cobalt blue pigment is the calcination of  $\text{CoO}$  and  $\text{Al}_2\text{O}_3$  at a temperature of 1200-1300 °C.

The cathodic paste recovered from the cathode of spent LCO batteries was initially calcined at 400 °C and  $\text{Co}_3\text{O}_4$  was obtained (Fig.3.38) and analyzed by X-ray diffraction (Fig. 3.39.).



**Fig. 3.38.** Cathode paste calcined at 400 °C.





**Fig.3.39.** X-ray diffraction analysis performed to identify the composition of the cathodic paste calcined at 400 °C with the identification of  $\text{Co}_3\text{O}_4$  compound.

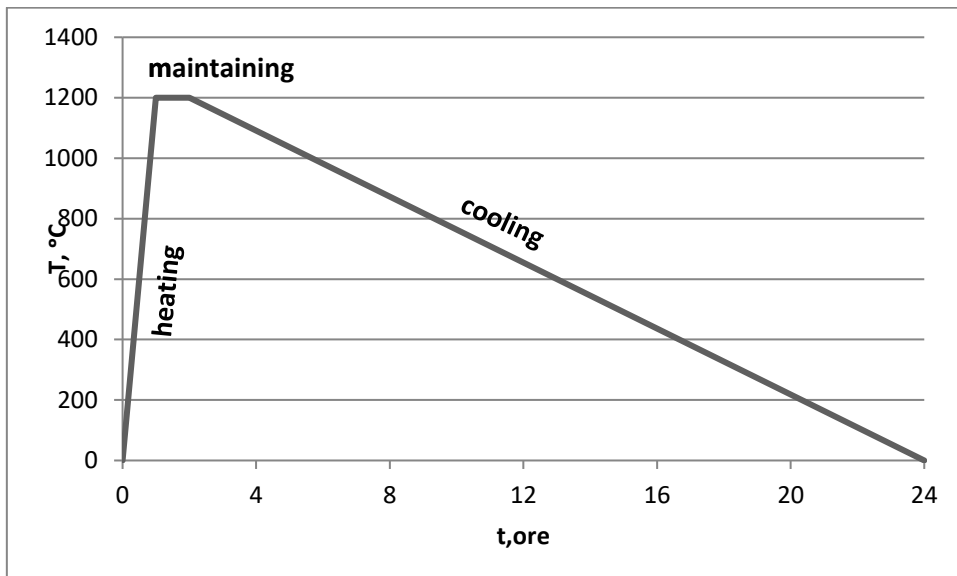
At over 900 °C, reaction (3.1) takes place and the  $\text{CoO}$  becomes stable:



At over 1200 °C the cobalt aluminate formation reaction takes place [100]:



The recovered paste was placed in ceramic crucibles, and the heat treatment was performed in a NABERTHERM N17 / HR type furnace. The heat treatment diagram (temperature / time) is shown in Fig. 3.40.



**Fig.3.40.** Time / temperature diagram for the calcination process at 1200 °C.

$\text{CoAl}_2\text{O}_4$ , being of type  $\text{AB}_2\text{O}_4$  crystallizes in spinel type.  $\text{O}_2^-$  ions make up a network in the cubic system,  $\text{Co}^{2+}$  partially fills (1/8) the meshes of the octahedral network, and  $\text{Al}^{3+}$  ions occupy the rest of the tetrahedral network.

Depending on the  $\text{Al}_2\text{O}_3$  content used, various shades of cobalt blue were obtained (Fig. 3.42. A, b, c, d).



Pastă catodică spălată cu alcool, filtrată și uscată, amestecată cu 40% alumina și calcinată la 1200 °C timp de 1 h

a)



Pastă catodică spălată cu alcool, filtrată și uscată, amestecată cu 50% alumina și calcinată la 1200 °C timp de 1 h

b)



Pastă catodică spălată cu alcool, filtrată și uscată, amestecată cu 60% alumina și calcinată la 1200 °C timp de 1 h

c)



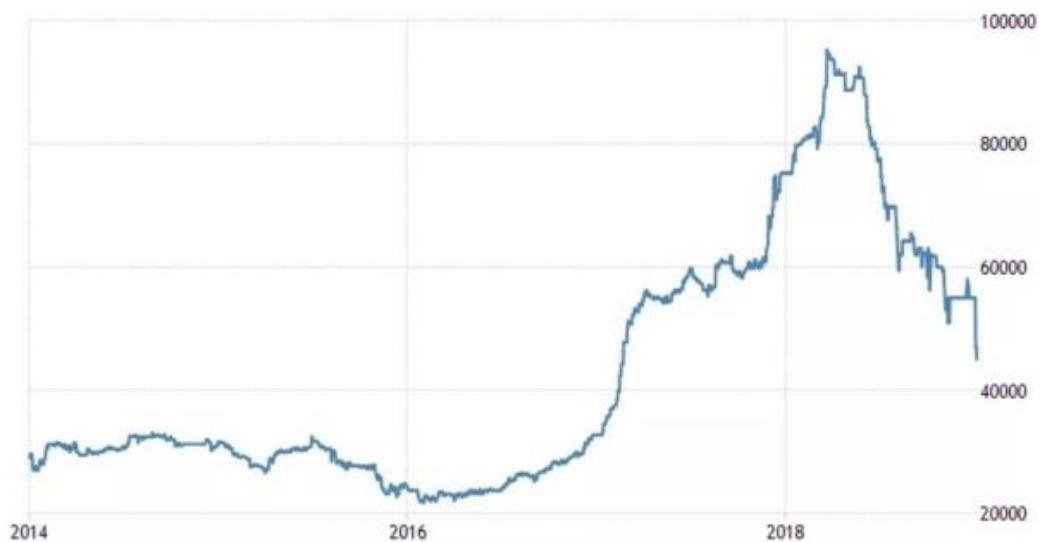
Pastă catodică spălată cu alcool, filtrată și uscată, amestecată cu 80% alumina și calcinată la 1200 °C timp de 1 h

d)

**Fig. 3.42.** Cobalt blue ( $\text{CoAl}_2\text{O}_4$ ) obtained from cathodic paste recovered from spent LCO batteries mixed with different percentages of alumina (a, b, c, d)

### Conclusions

The cobalt price is very high (Fig. 3.43.), And in addition, production is concentrated in one country: DPR Congo (formerly Zaire) supplies over 50% of cobalt mining production with a tendency to increase up to 68% in the coming years. Under these conditions, secondary sources of cobalt are even more valuable than primary sources. Today, most of the obsolete BLIs are LCOs with high cobalt content. Because there is no established cobalt recovery technology in spent LCO batteries today, a large number of these batteries are preserved / hoarded. Many laboratories are working to recover useful metals from spent LCO batteries and primarily cobalt.



**Fig. 3.43.** Evolution of cobalt price in the last six years [US \$ / ton].  
[102]

According to [103], the price of Cobalt Blue Dark pigment (Fig.3.44) is 86 / 100g.



**Fig.3.44.** Cobalt Blue Dark

If a battery contains about 0.7g of  $\text{LiCoO}_2$  which turns to 1.4g of cobalt blue ( $\text{CoAl}_2\text{O}_4$ ), it would take 100 used batteries to get 100 g of pigment.

But things change if we talk about car batteries with cobalt content (in an electric car, Tesla 3 for example, the batteries weigh 600 kg).

## Chapter 4. Conclusions and original contributions

The technical-scientific objectives of the proposed doctoral thesis:

- recovery of the active cathode paste containing cobalt from the used BLIs, by dismantling the batteries (safely, ie completely discharged), separating the components and separating the active paste from the aluminum foil by ultrasounds in an acid medium (citric acid, acid acetic);

- the use of active cathode paste with cobalt content recovered from used BLIs, to obtain the pigment - cobalt blue, an expensive product, used in the chemical industry.

They were fulfilled.

1. The recovery of useful metals from spent batteries is an economic necessity and an ecological obligation. For many metals, primary resources are nearing depletion or becoming difficult to access.

2. Large amounts of spent Li-ion batteries will have a negative impact on the environment and will lead to a waste of scarce resources in the absence of adequate recycling measures.

3. The automotive industry of electric cars is maturing; the electric battery is the resistance piece, the solution of which is left to wait. Batteries will be just as important to the 21st century automotive industry as they were to the 20th century combustion engine. If in the case of Pb-acid batteries, we have a recovered metal and Pb recycling is well realized, there are appropriate technologies and regulated legislation, in the case of Li-ion batteries the problems are much more complex variety). The content of high value metals (Li, Co, Ni, Cu, Al) is in used batteries between 5-15% of the weight of batteries, while in ores, the content is 2-7%. In this context, in October 2017, the European Commission launched the European Battery Alliance (EBA) cooperation platform, together with key industry stakeholders, Member States and the European Investment Bank.

4. Li-ion batteries represent the present; Li and Co are strategic metals (Li deposits are concentrated in Latin America (lithium triangle) and probably Afghanistan; Co deposits are concentrated in the DRP Congo (Zaire) - politically unstable area, which is why we are trying to replace Co with other metals ( Ni, Ti).

5. The mechanical processes of separation, sorting, concentration are used in the preparatory stage of recycling of used BLIs, for the processing of external carcasses and the concentration of the metal fraction.

6. Grinding  $\text{LiCoO}_2$  with PVC in a humid environment to form Li and Co chlorides, and subsequently extracting Co and Li is a primary recovery alternative worth testing.

7. Treatment with N-methylpyrrolidone (NMP) at 100 ° C for 1 h allows  $\text{LiCoO}_2$  to be effectively separated from the support substrate and recovered. The disadvantage of this process is that N-methylpyrrolidone used to dissolve PVDF is an adhesive, expensive and polluting agent.

8. Current bio-hydrometallurgical technologies are not widely used for recycling spent Li-ion batteries because they are currently being researched - for example by the chemical precipitation method, Co dissolved in the hydrochloric solution can be recovered as cobalt hydroxide by adding a 4 M NaOH solution;

9. Leaching treatment with various reactants is improved by using ultrasound; the procedure is viable, but requires a thorough study.

10. The method of recovering cobalt-containing cathode paste from spent LCO batteries by ultrasound in citric acid is a viable method; it is true that manual disassembly and separation on components is difficult (and this is still being worked on), but it must be borne in mind that with the passage of BLI / LCO on electric cars that have other dimensions, batteries will standardize and disassembly methods will simplify;

11. The process of cleaning the active paste on the LCO cathode by ultrasonic uses as a medium - citric acid, organic acid, biodegradable, environmentally friendly; the process takes place at room temperature, no heat source is required, and the power of the ultrasonic bath is used at a minimum, so electricity consumption is low;

12. At a cleaning time of 8 minutes and a concentration of 1.25 M citric acid a cleaning efficiency of over 90% was obtained;

13. An orthogonal grade 2 (PO2) program was used to determine the optimal recovery conditions for cobalt-containing cathode paste from spent LCO batteries by ultrasonic citric acid. The mathematical model obtained using this program presented in the form of a polynomial equation of degree 2 was statistically analyzed and verified with the Fischer criterion. MathCAD (Free Trial) was used to determine calculation errors. The response areas were determined based on the canonical coefficients and the MathCAD program.

14. The experimental results obtained in the recovery of cobalt-containing cathode paste from spent LCO batteries by ultrasound in citric acid led to the conclusion that a significant influence on the efficiency of separation of active paste from cathode foil has: ultrasonic bath power ( $z_1$ ) [W]; citric acid concentration ( $z_2$ ) [mol / l]; time ( $z_3$ ) [min]. The other parameters, such as the working temperature, the position of the foil in the tank, the addition of hydrogen peroxide, do not have a significant influence on the process.

15. The concentration of citric acid plays the main role in the recovery process of the active paste with cobalt content; the time and power of the ultrasonic bath have a limited influence on the recovery efficiency.

16. The method of recovering cobalt-containing cathode paste from spent LCO batteries by ultrasound in acetic acid is a viable and faster method than using citric acid;

17. The process of cleaning the active paste on the LCO cathode by ultrasound uses as medium acetic acid, organic acid, biodegradable, environmentally friendly; the process takes place at room temperature, no heat source is required;

18. The power of the ultrasonic bath is used at a minimum level of 40W, so the electricity consumption is low;

19. At a cleaning time of 6 minutes and a concentration of 1,5 M acetic acid, a cleaning efficiency of over 90% was obtained;

20. Cobalt blue can be synthesized using solid state reactions (the most widely used methods used in industrial practice); they have the following advantages: simple production process and high cost of performance. Aluminum hydroxide and alumina are used as sources of aluminum in obtaining cobalt blue.

21. The recipe for obtaining cobalt blue used for the use of active paste with cobalt content involves mixing the paste with alumina in a percentage of 1: 2, followed by calcination for 2 hours at a temperature of 1200 °C at a heating rate of 1°C / min .

22. Cobalt blue pigment can be used either in corrosion protection or as a blue pigment in painting workshops, glassware; cobalt blue pigment price is \$ 86 / 100g.

### **Original contributions**

1. Structural analysis of high cobalt spent LCO batteries.
2. Structural characterization of spent LCO batteries with high cobalt content.
3. Separation of the active paste with cobalt content (in the form of  $\text{LiCoO}_2$ ) from the cathodic aluminum foil by ultrasound in citric acid and acetic acid medium.
4. Optimizing the process of separating the active paste with cobalt content from aluminum foil by ultrasonication in citric acid medium.
5. Recovery of cobalt from spent LCO batteries by transforming the recovered paste into cobalt blue ( $\text{CoAl}_2\text{O}_4$ ); the process is carried out by calcination at 1200 °C of the paste mixture recovered with alumina.

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