The possibilities of cobalt and lithium recovery from spent portable lithium accumulators in laboratory scale

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ABSTRACT: Recycling of spent lithium batteries and accumulators has primary aim to obtain cobalt, because the price of cobalt is much higher in the compare with price of others metals and lithium is necessary for a lot of industrial applications. Due to lithium battery and accumulators production, price of lithium has increased as well. Seeing that spent portable lithium accumulators are valuable source of Li and Co the optimal way of recovery these metals from this waste is still studied. Hydrometallurgical methods or combined methods are used to recover Co and Li in laboratory scale. Nowadays there are some companies which recycle spent portable LiA, but their technologies are robust with low material recovery rate. Effect of incineration on cobalt recovery was experimentally studied in this article. Incineration at 700°C was realized in order to remove organic compounds. Material after incineration was leached in 2M H_2SO_4 at 80°C with s/l (1:80). Cobalt extractions at leaching of samples without thermal treatment and after thermal treatment were compared. In general, positive effect of incineration on cobalt extraction was observed.

1. INTRODUCTION

The necessary part of our everyday life is using of spent portable batteries and accumulators. Portable lithium accumulators are found in our cell-phones, laptops, beepers, mp3-players, etc. and of course lithium accumulators are used in our cars as well. At present, the majority of accumulators are on the base of nickel-cadmium, nickel-metal-hydride or lithium-ion and lithium polymer accumulators. Nowadays nickel-cadmium and nickel-metal-hydride accumulators are often replaced by lithium accumulators (LiA) in some areas due to absence of heavy metals and their better technical properties.

Production rate of portable lithium accumulators still increases and it tends to be higher because of production of hybrid electric vehicles. World LiA production reached 500 million units in 2000 and was expected to reach 4.6 billion in 2010 [1].

Although portable LiA have a long life-cycle, it happens that electric equipments which use LiA are replaced by new one earlier then they are functionless and so LiA become a waste too.

On the other hand portable LiA represent valuable secondary raw material and source of metals as cobalt, lithium, copper, aluminium, etc. LiA contain approximately 15-27% Co and 1.7-3.2% Li [2]. Current price of cobalt is approximately 33€/kg (e.g. it is ten times more than price of copper) [3]. Production of lithium carbonate is around 120,000 tons per year and it still increases due to lithium accumulators' demand. The fourth part of this production is used for battery and accumulator production [4]. The price of lithium carbonate is around 5€/kg.

Seeing that spent portable lithium accmulators are valuable sourse of mentioned metals the efforts to find optimal way of treatment are necessery. There are three main ways of treatment of this waste in laboratory scale: mechanical, hydrometalurgical and combined way. Mechanical methods are ussualy used for pre-treatment or separation foils and active mass, which contains majority of cobalt and lithium. Hydrometallurgy includes leaching for metal extraction. Then the precipitation, solvent extraction and electrolysis are used for metal recovery. Combined methods ussualy use thermal pretreatment. Thermal treatment is mainly used for organic compounds and graphite removal. Organic compounds are used as binder and cause problems during leaching and solid-liquid separation. Graphite causes a lower lithium extraction, because it acts as adsorbent for lithium [5]. Research in this area is mainly focused on cobalt and lithium recovery.

Effect of incineration on cobalt exctraction was studied in this article. Thermal incineration was realized in order to remove organic compounds. Material after incineration was leached and cobalt extractions of samples without thermal treatment and after thermal treatment were compared. In general, positive effect of incineration on cobalt extraction was observed.

2. CHARACTERIZATION OF SPENT PORTABLE LIA

Since lithium metal (which is used in primary lithium batteries) is naturally unstable, especially during charging, the focus is shifted to non-metallic lithium accumulators using carbon as an anode material and $LiCoO_2$ as cathode material. The new lithium ion system using carbon as an anode has a lower energy density lower which is lower than the old lithium metal system, but it is safer provided that certain precaution are taken during charging and discharging. Sony was first company which commercialized the lithium ion accumulators in 1991 [6]. In the presence there are two main types of lithium accumulators:

1. lithium ion accumulators (liquid electrolyte)
2. lithium polymer accumulators (solid electrolyte)

Even thought lithium ion accumulators do not contain metallic lithium, but most lithium systems contain toxic and flammable electrolyte. Lithium-ion-polymer batteries are similar to Li-ion, but the system enables slim geometry and simple packing at the expense of higher cost per watt/hour [7].

The lithium ion accumulator is mainly composed of an external case, a printed circuit board and a core. The structure and materials usually used in LiA are listed in Table 1. The external case is always made of stainless steel, aluminum alloy or polymer. The printed circuit board provides protection to the accumulator. The core part consists of a positive electrode, a negative electrode and insulating separator, which are wrapped together and soaked in electrolyte. Materials like LiX_mO_n are always used in the positive electrode and graphite in the negative electrode. LiX_mO_n materials usually include $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$, among which $LiCoO_2$ is typical [8]. Metals like copper and aluminium are used as current collectors. In LiA, the anodes and cathodes are made from materials that allow the migration of Li-ions through an electrolyte solution. The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium salts (e.g. $LiClO_4$, $LiBF_4$ and $LiPF_6$) [9].

Tab.1: Structure and materials of LiA[8]

Structure	Compositions
External case	Stainless steel, aluminum alloy, or polymer
Positive electrode	Active materials as $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$
Negative electrode	Graphite conductor
Electrolyte	$LiClO_4$, $LiPF_6$ or $LiBF_4$
Electrolyte solvent	PC (propylene carbonate), EC (ethylene carbonate), DEC (diethyl carbonate), or MEC (methyl ethyl carbonate)
Insulating separators	PE (polyethylen)or PP (polypropylen) films
Adhesives	Polymer adhesive
Current collector	Aluminum, and copper foils
Printed circuit board (PCB)	Thermosetting plastics, components, solders, etc
Current joining	Gold-plated pad

The chemical composition of particular accumulators is different and depends on type of accumulator as well as on brand. Typical chemical composition of Li-ion ion accumulator is: Al (15–25%), carbon amorphous powder (0.1–1%), Cu foil (5–15%), diethyl carbonate (1–10%), ethylene carbonate (1–10%), methyl ethyl carbonate (1–10%), $LiPF_6$ (1– 5%), graphite powder (10–30%), $LiCoO_2$ (25–45%), polyvinylidene fluoride (PVDF) (0.5–2%), steel, Ni and inert polymer [10].

The chemical composition of lithium accumulators still varies and there is some development of particular accumulators´ components too. There is an expectation that alloys of lithium with titanium, silicon and tin will be used for new type of anode material. The compounds such as $LiMn_2O_4$, $LiNi_{0.8}Co_{0.2}O_2$, $LiFePO_4$, $LiNi_{1/3}Co_{1/3}O_2$ will be used for cathode material.

3. TREATMENT OF SPENT PORTABLE LIA IN LABORATORY SCALE

In general spent portable LiA are recycled either by hydrometallurgical or combined method in laboratory and in industrial scale. Hydrometallurgical way mostly includes mechanical pre-treatment, leaching and extraction of particular metals. Combined way usually includes mechanical and thermal pre-treatment, extraction of metals by leaching and recovery of metals. Thermal treatment is mainly used for organic compounds and graphite removal. Organic compounds are used as binder and cause problems during the leaching and solid-liquid separation. Graphite causes a lower lithium extraction, because it acts as adsorbent for lithium [5].

3.1. Hydrometallurgical methods

Different leaching reagents are used for extraction of particular metals from spent portable LiA in hydrometallurgical treatment in laboratory scale. The sulphuric acid, hydrochloric acid and nitric acid are usually used for leaching. The hydrogen peroxide is used as reductant. The addition of reductant is applied to ensure reduction of Co^{3+} to Co^{2+}, which is more leachable than Co^{3+}. There are some studied leaching conditions and obtained results from different authors shown in Table 2.

Tab.2: Summary of leaching conditions and obtained results from different authors

authors	used regents	optimal conditions			Co extraction [%]	Li extraction [%]
		reagents	temperature [°C] / time [min.]	s/l [g/ml]		
Tsai et al.[11]	H_2SO_4, HNO_3, HCl,	4N HCl	70/120	1/33	96.4	99.7
Ferreira et al.[12]	aqua regia, H_2O_2, H_2SO_4, NaOH,	4%(v/v) H_2SO_4, 1%(v/v) H_2O_2	40/-	1/30	97	100
Mantuano et al.[13]	H_2SO_4	5 vol.% H_2SO_4	80/ -	1/30	30	2.5
Castillo et al.[14]	HNO_3	2 M HNO_3	80/120	-	-	100
Nan et al.[15]	H_2SO_4	3M H_2SO_4	70/240	1/5	98	98
Zhang et al.[16]	HCl, H_2SO_3 $NH_2OH.HCl$,	4M HCl	80/60	1/100	99	99
Dorella et al.[17]	H_2SO_4, H_2O_2	6%(v/v) H_2SO_4, 1%(v/v) H_2O_2	65/60	1/30	75	100
Kang et al.[18]	H_2SO_4, H_2O_2	2M H_2SO_4, 6%(v/v) H_2O_2	60/60	1/100	99	99
Swain et al.[19]	H_2SO_4, H_2O_2	2M H_2SO_4, 5%(v/v) H_2O_2	70/30	1/100	93	94
Li et al.[20]	H_2SO_4, H_2O_2	3M H_2SO_4, 1.5M H_2O_2	70/60	-	99.4	99
Xia et al.[8]	H_2SO_4, H_2O_2	3M H_2SO_4, H_2O_2	-	-	99	99
Sakultung et al.[21]	H_2SO_4, HNO_3, HCl	5M HCl	80/60	1.5/100	84	-

As follows relatively high extraction rates were reached using concentrated hydrochloric acid or sulphuric acid with addition of hydrogen peroxide at higher temperatures.

Recovery of particular metals from solution after leaching can be carried out by:
a, precipitation,
b, solvent extraction,
c, electrolysis.

3.1.1. Precipitation

Chemical precipitation method for recycling spent portable LiA is to use precipitation agents to precipitate precious metals such as cobalt from spent portable LiA.

Contestabile et al.[22] studied a laboratory process aiming to the treatment and recycling of spent LiA and being composed of sorting, crushing and riddling, selective separation of the active materials, lithium cobalt dissolution and cobalt hydroxide precipitation. The cobalt dissolved in the hydrochloric solution was recovered as cobalt hydroxide $Co(OH)_2$ by addition of one equivalent volume of a 4M NaOH solution.

Xia et al.[8] used $(NH_4)_2C_2O_4$ for recover Co after leaching with sulphuric acid with addition of hydrogen peroxide. The process was carried out at room temperature. Co was recovered in form CoC_2O_4.

Li et al.[20] used 1M $Na_2C_2O_4$ after previous leaching with sulphuric acid with addition of hydrogen peroxide to precipitate Co. The 99.5% of cobalt was recovered at 50°C. Lithium in the surplus filtrate after the removal of cobalt was recovered with a saturated Na_2CO_3 solution. The recovery of Li was 94.5%.

Nan et al.[15] leached spent portable LiA with sulphuric acid and after this ammonium oxalate was used for precipitation of Co. About 90% cobalt was recovered as oxalate with less than 0.5% impurities. The solution was then treated with sodium carbonate to recover Li. About 80% lithium was recovered as a precipitate and the content of cobalt in the precipitate was less than 0.96%.

Zhang et al.[16] used precipitation to recover Li after leaching with hydrochloric acid and after the recovery of cobalt by solvent extraction. The solution was concentrated and treated with a saturated sodium carbonate solution to precipitate lithium carbonate. The content of cobalt in the precipitate was less than 0.07% and about 80% of the lithium was recovered as a precipitate.

Precipitation provides simple operation and relatively high recovery rates of metals from spent LiA. It can get the product of high purity meeting with the general requirements of chemical products and its recycling cost will be low if it is chosen to remove impurity or purify recovered products in the process of recycling spent LiA [23].

3.1.2. Solvent extraction

Such extractants as di-(2-ethylhexyl) phosphoric acid (D2EHPA), bis-(2,4,4-tri-methyl-pentyl) phosphinic acid (Cyanex 272), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC-88A) were usually used as extractants to separate the metals in some hydrometallurgical processes, in which Co, Li and Cu are usually recovered from spent LiA.

Solvent extractant Cyanex 272 was used to recover cobalt after leaching with sulphuric acid without addition of hydrogen peroxide [15] and with addition of hydrogen peroxide [13,17,18,19,24].

Swain et al.[19] recovered around 85.42% of the cobalt using 1.5M Cyanex 272 as an extractant at an O/A ratio (organics/aqueous ratio) of 1.6 from the leach liquor at pH 5.00. The rest of the cobalt was totally recovered from the raffinate using 0.5M of Cyanex 272 and an O/A ratio of 1, and a feed pH of 5.35. Then the co-extracted lithium was scrubbed from the cobalt-loaded organic using 0.1M Na_2CO_3. Finally, the cobalt sulfate solution with a purity 99.99% was obtained from the cobalt-loaded organic by stripping with H_2SO_4.

Nan et al.[15] firstly precipitated a cobalt as oxalate after leaching with sulphuric acid. Then Acorga M5640 was used to recover Cu by solvent extraction. 1M Cyanex 272 (10% saponification ratio) at 1:1 (O/A) phase ratio, room temperature and 1 min of contact time, and stripping with a 2M H_2SO_4 solution at 1:1 (O/A) phase ratio, room temperature and 1 min of contact time for two times were used to recover Co. Over 98% of the copper and 97% of the cobalt was recovered in the given process.

Dorella et al.[17] used Cyanex 272 (0.72M) to recover Co after leaching in sulphuric acid with addition of hydrogen peroxide and after precipitation of Al with NH_4OH. Around 85% of cobalt was recovered.

Lupi et al.[24] used solvent extraction with modified Cyanex 272 (0.5M) in kerosene to separate Co from Ni. The saponification agent was a 5 M KOH solution added to the organic phase in a quantity equal to 4% by volume. By using an O/A ratio equal to 3 with three stages it was possible to leave few ppm of Co in the aqueous raffinate.

Kang et al.[18] used sulphuric acid with addition of hydrogen peroxide to leach spent portable LiA. Metal ion impurities such as copper, iron, and aluminium were precipitated as hydroxides from solution by adjusting pH to 6.5. Cobalt was then selectively extracted from solution with 50% saponified 0.4M Cyanex 272 at pH 6 with A/O ratio of 1/2. Around 92% cobalt was recovered from the spent lithium ion batteries.

Zhang et al.[16] used two different solvent extractants after leaching with hydrochloric acid. It was found that PC-88A is capable of recovery of cobalt more completely and has a better selectivity for cobalt than D2EHPA does. Quantitative recovery of cobalt was achieved by extraction with 0.90 M PC-88A in kerosene at an O/A ratio of 0.85:1 and pH = 6.7 in a single stage. The purity of the cobalt recovered could reach 99.99%.

Solvent extraction has the advantages of easy operational conditions, low energy consumption and good separation effect. High recoveries of recycled metals such as cobalt, nickel, copper and lithium could be achieved and the recovered products have high purities. At the same time, it still has the disadvantage. Some solvent extractants are very expensive and consequently it might result in too high treatment cost when it is scaled-up in industry [23]. Presence of copper in solution during process of solvent extraction of cobalt is the next disadvantage of this process. So copper has to be removed.

3.1.3 Electrolysis

Electrolysis is used mainly for recovery of nickel and cobalt from spent portable LiA, whereby cobalt has to be removed from solution before electrowinning of nickel.

Lupi et al.[24] used electrolysis for Ni recovery from solution after leaching in sulphuric acid with addition of hydrogen peroxide and after solvent extraction of cobalt with Cyanex 272. Nickel electrowinning performed at 250 A/m^2 current density at 50°C, pH 3–3.2, with an electrolyte having about 50 g/l Ni and 20 g/l H_3BO_3, produces a good aspect Ni deposit with a current efficiency and a specific energy consumption of about 87% and 2.96 kWh/kg respectively. The electrolysis at constant potential of solution containing 1.7–1.8 g/l of Ni produces very pure powder in 80 min, leaving less than 100 ppm of nickel in solution.

The cobalt recovery process from spent LiA by sulfuric acid leaching and electrowinning was published at work[23]. The cathode cobalt is produced by electrowinning in current density 235A/m^2. The recovery of cobalt was more than 93%.

Compared with other hydrometallurgical processes for recycling metals from spent LiA, the electrolysis process can achieve the cobalt compound of very high purity from spent LiA since it does not introduce other substances and therefore avoid introduction of impurities. However, this process has a disadvantage of consuming too much electricity.

Hydrometallurgy seems to be very convenient way of recycling spent lithium accumulators. Sulphuric acid with addition of hydrogen peroxide as reducing agent is mostly used for leaching this material and high extraction rate can be reached. Precipitation with oxalates (ammonium oxalate or sodium oxalate) is usually used for recovery of cobalt. It is considered that most of the cobalt can be recovered by precipitation as oxalate, reducing the treatment cost effectively compared with solvent extraction or electrolysis methods. Lithium is possible to recover by precipitation using Na_2CO_3. Cyanex 272 as extractant is usually used for solvent extraction of cobalt from solution after previous leaching with sulphuric acid. Relatively high recovery rates can be achieved. High operating costs are the main disadvantages of this process. Electrolysis is usually used for nickel recovery from solution after previous treatment.

3.2. Combined methods

Even thought hydrometallurgical methods are widely used in laboratory research of treatment this waste, it was published that presence of organic compounds and carbon causes inconviences during the treatment. Shin et al.[25] published that particles from crushing and mechanical separation include carbon and organic binder cause a problem in the filtration process of leachate after acid leaching. In the same work it was published that leaching efficiency of cobalt after incineration is significantly lower compared with that obtained without thermal treatment, but leaching efficiency of lithium is higher. Following incineration caused that the surface of lithium cobalt oxide particles was covered with molten aluminum foil, which obstructs cobalt leaching. Kim et al.[26] published that the surface of black mass ($LiCoO_2$ and graphite) is covered with PVDF what is kind of Teflon binder and has hydrophobic property. Paulino et al.[5] published that recovery of lithium from lithium salts by extraction with water gave very low yields (less than 20 wt%) because of the presence of a strong absorbent medium (graphite). Some of works, which used thermal treatment, are mentioned, but just few of them studied effects of thermal treatment on leaching extraction of particular metals.

Lee a Ree[27] leached LiA after incineration at temperature 700 - 900°C. After thermal treatment cathode material was grinded in ball mill, dried and leached with nitric acid with and without addition of hydrogen peroxide. Extraction of cobalt was 40% and extraction of lithium was 75% in case without addition of hydrogen peroxide. By addition of hydrogen peroxide (1.7 vol.%) cobalt extraction increased to 85% and extraction of lithium was 85% at temperature 75°C.

Paulino et al.[5] calcined active material from LiA and active material from LiA mixed with $KHSO_4$ at 500°C. After thermal treatment material was leached with distilled water. It was found out, that calcination increased lithium recovery, because of carbon (adsorbent) removal. Cobalt was recovered either in form of $Co(OH)_2$ using NaOH or $CoSO_4.7H_2O$ using H_2SO_4 with addition of hydrogen peroxide.

Nan et al.[15] recovered metals from mixture of spent lithium-ion batteries and nickel metal hydride batteries. After incineration at temperature 580-630°C the mixture was leached with sulphuric acid with addition of hydrogen peroxide. About 90% of cobalt and nickel extraction was achieved using 3M H_2SO_4 with 3wt.% H_2O_2 at temperature 70°C after 5 hours.

Shin et al.[25] leached LiA with sulphuric acid and hydrogen peroxide. Incineration of LiA at temperature 900°C was applied in order to remove organic binders and graphite. It was found out, that incineration decreased cobalt extraction from 100% to 40%, because of presence aluminium foils, which covered lithium cobalt oxide particles when became molten at high temperature.

Li et al.[28] leached cathodic active material with citric acid and hydrogen peroxide after thermal treatment at temperature 700°C. About 100% of lithium and 90% of cobalt were extracted using 1.25 M citric acid with 1vol.% H_2O_2 at temperature 90°C.

Manually dismantled accumulators were usually used for experiments in the published works, but such separation of particular parts of spent portable accumulators is practically impossible in the plant scale. But separation of particular materials – plastic, aluminium foils, copper foils and active – black mass is possible and applicable in the plant scale. The separation of metals foils, plastic parts and black mass is the main aim of the separation. Then cobalt, lithium, nickel and other substances. can be recovered from black mass, but this mass contains organic compounds and graphite.

When mixture of spent portable LiA (e.g. after crushing or after milling) was used, previous recovery of metals such as Cu, Al, etc. was necessary before of cobalt and lithium recovery. Aluminium is ineligible, when process of precipitation of cobalt is about to be used. Copper causes inconveniences during the process of solvent extraction of cobalt. Then removal of these metal foils from mixture is necessary and can be carried out by different separation processes (e.g. sieving, fluid separation, etc.).

Seeing that majority of mentioned works used manually dismantled material, it is necessary to study possibility of metals recovery after separation, which is more applicable in the plant scale.

Organic compounds and graphite are ineligible during the process of treatment, because of their hydrophobic properties and graphite acts as absorbent of lithium.

Based on reported published works it is obvious that by thermal pretreatment carbon and organic binders are in general removed and extraction of Li and Co is consequently improved. On the other hand it was shown that presence of aluminium foils at thermal treatment caused barrier for Co leaching into the solution.

Hydrometallurgy seems to be convinient way how to recycle spent portable LiA and thermal treatment can be used to remove organic compounds and graphite, then investigation of effects of thermal treatment on metal recovery is necessary.

At this work the effects of incineration on cobalt exctraction was studied. The main aim was to compare extraction of cobalt from samples without previous thermal treatment and after incineration. Based on analysis of published results the leaching experiments were carried out in sulphuric acid with addition of of hydrogen peroxide. Majority of aluminium and copper foils were removed by sieving in order to avoid mentioned difficulties.

4. EXPERIMENTAL

4.1. Material characterization and methodics

For experiments the lithium accumulators obtained from collection of spent portable batteries and accumulators at the Technical University of Košice were used.

LiA without dismantling were crushed using a hammer SK 600. Samples for purpose of chemical analysis were obtained by quartation and following milling in vibration mill VM4. Chemical composition of sample after crushing is given in Tab.3. Chemical composition of sample with particle size less than 1mm after sieving is given in Tab.4. Chemical composition of samples before and after thermal treatment was carried out with Varian AA-20+ and X-ray diffractometer (Philips PW 3830, Cu-Kα).

Tab.3: Chemical composition of sample after crushing

Element	Co [%]	Cu [%]	Al [%]	Li [%]	Ni [%]	Fe [%]
Content [%]	10.81	9.15	10.68	1.815	2.34	0.385

Tab.4: Chemical composition of sample after sieving (-1 + 0 mm)

Element	Co [%]	Cu [%]	Al [%]	Li [%]	Ni [%]	Fe [%]
Content [%]	18.2	3.65	1.77	3.2	2.78	0.34

Samples of crushed LiA were introduced to grain size analysis by dry sieving method. For this purpose sieves with openings 9, 4, 1, 0.63, 0.4 and 0.09mm were used. Histogram of sample granularity is shown in Fig.1.

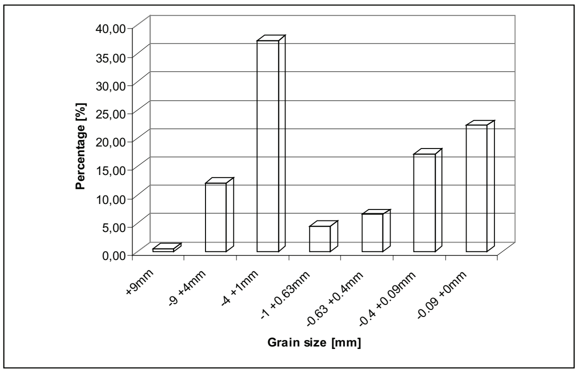


Fig.1: Histogram of crushed sample of LiA granularity.

Fraction over 1mm was sieved out in order to remove majority of aluminium and copper foils. Aluminium foils were removed to avoid negative effect on black mass during the incineration. Copper foils were removed to decrease the consumption of leaching reagents and to ensure lower content of copper in the solution. For experiments the size fraction under 1mm was used.

4.2. Thermal treatment - incineration

Thermal treatment was carried out in furnace SCANDIA OVEN TC 8000 (Fig.2). Samples were charged into the sample holder and inserted into the furnace, which was heated up at required temperature. The air supply to the sample holder was provided by compressor Masterflex GWB. Off-gas was taken away trough copper tube and cleaned by washing system consisted of five washing bottles. First of them was empty (safety reasons), the second one contained solution of 0.5M NaOH and the fourth one contained 0.5M H_2SO_4. Distilled water was placed into the third and the fifth bottle. Experiments were carried out at the 700°C for 60 minutes. Amount of sample was 25g. Loss on weight of sample was measured after incineration.

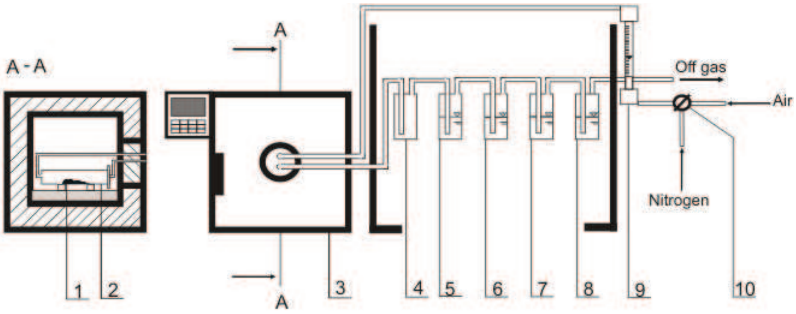


Fig.2: Apparatus for incineration.
1-sample, 2-sample holder, 3-furnace, 4-empty vessel, 5-NaOH solution, 6,8- distilled water, 7-H_2SO_4 solution, 9-flowmeter, 10-tap

4.3. *Leaching experiments*

Leaching was carried out in glass vessel inserted in water bath. Required temperature was adjusted using thermostat Lauda A100. For stirring the plastic propeller was used. As leaching agent the 2M sulphuric acid was used and as reducing agent 30% hydrogen peroxide. Amount of hydrogen peroxide was 0vol.% or 15vol.%. Solid to liquid ratio was always 1:80. Experiments were carried out at temperature 80°C for 60 minutes. For leaching experiments the samples without thermal treatment and after incineration were used. Amount of sample was 5g. Liquid samples were analyzed by AAS (Perkin Elmer 272).

5. RESULTS AND DISCUSSION

5.1. *Thermal treatment*

The loss on weiht of sample after incineration was around 25%. Xray diffraction analysis comfirmed that entire carbon wasn't removed and $LiCoO_2$ partialy decomposed on CoO and Co_3O_4.

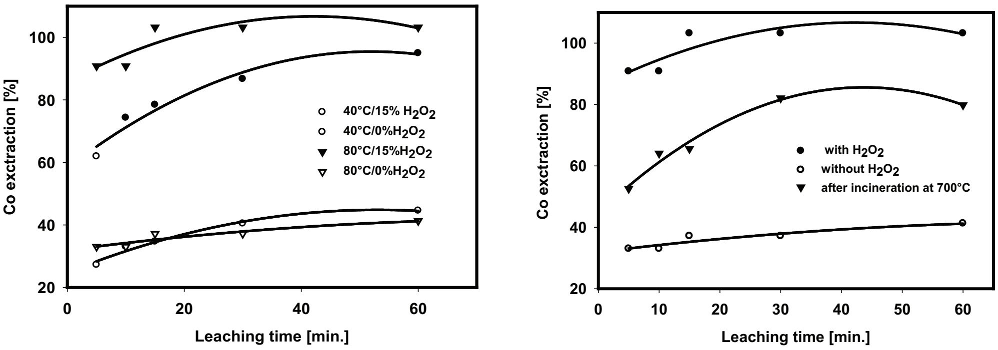
5.2. *Leaching*

Kinetic curves of cobalt extraction in 2M sulphuric acid at 40°C and 80°C with and without addition of hydrogen peroxide are shown in Fig.3a. Kinetic curves of cobalt extraction of samples without thermal treatment and after incineration at 700°C in 2M sulphuric acid at 80°C with and without addition of hydrogen peroxide are shown in Fig.3b. Temperature 80°C was chosen for next experiments according the results (Fig.3a).

As follows from results (Fig.3a), the addition of hydrogen peroxide significantly increases cobalt extraction, because of reduction Co^{3+} to Co^{2+}, which is more leachable than Co^{3+}. Cobalt extraction increases with temperature, but difference is not so significant.

As follows from results (Fig.3b) incineration increased the cobalt extraction. Extraction of cobalt increased from value 40% to value 80%. This is probably the consequence of fact that after incineration cobalt was partially present in the form of its oxides

Cobalt extraction of incinerated samples is lower than cobalt extraction of sample when addition of hydrogen peroxide was used. As X-ray diffraction analysis confirmed, during the incineration only partial decomposition of lithium cobalt occurred. So cobalt was partially present in the form of $LiCoO_2$, which is not as leachable as its oxides. It is obvious that addition of hydrogen peroxide was sufficient for reduction of Co^{3+} to Co^{2+}, while incineration didn't ensure total decomposition of $LiCoO_2$ and so extraction of cobalt was lower.



a) b)

Fig.3:
a) Kinetic curves of cobalt extraction in 2M sulphuric acid with and without addition of hydrogen peroxide at 40°C and 80°C (untreated sample), b) Kinetic curves of cobalt extraction in 2M sulphuric acid at 80°C with and without addition of hydrogen peroxide (untreated sample) and sample after incineration.

6. CONCLUSION

Possibilities of cobalt and lithium recovery from spent lithium accumulators were discussed in this work. It is obvious, that hydrometallurgical methods are widely studied for determination of optimal way of treatment of this waste. The hydrometallurgy is sometimes combined with thermal treatment in order to remove organic compounds and graphite. The graphite is part of electrode material, but it effects as adsorbent for lithium in leaching process. Organic compounds are used as binders and solvents. They are hydrophobic and cause difficulties in leaching and solid-liquid separation processes.

For experimental part an incineration was chosen for thermal pre-treatment of black mass from spent portable lithium accumulators. Samples of black mass were incinerated at 700°C for 60 minutes. Untreated samples and samples after incineration were leached in 2M H_2SO_4 at 80°C with and without addition of hydrogen peroxide.

In general from results follows that thermal treatment has positive effect on cobalt extraction. Seeing that total decomposition of $LiCoO_2$ didn't occur during the incineration, it is necessary to study the time of treatment as well as temperature of treatment.

To confirm total influence of incineration on leaching process of black mass it is necessary to study its effects on the others metals present in this material, mainly lithium, which is becoming a valuable part of this secondary raw material too.

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