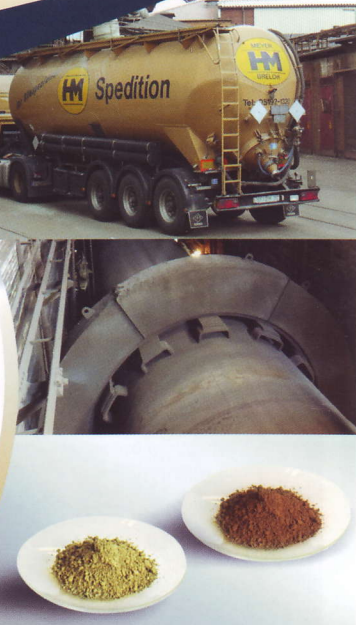Member of RECYLEX - GROUP

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Solvent extraction of cobalt from leach liquor after leaching of the active mass of spent lithium accumulators

Takáčová, Z.; Marcišová, S.; Havlík, T. (1)

The work focuses on cobalt solvent extraction from synthetic solution and leach liquor after the leaching of the Li-ion accumulators active mass in H_2SO_4. The aim was to study the effect of a pH on the extraction and stripping separately. Also the effect of the phase ratio A:O and O:A was verified. The synthetic sulfate solution containing 3.8 mg/ml Co was used for the experiments. The following conditions were investigated: pH = 4-8, A:O = 0.5, 1, 2, O:A = 0.5, 1, 2. The optimal pH for the Co recovery (100 %) from the synthetic solution was pH = 8 in the extraction and pH = 6 in the stripping. During the Co extraction from the leach liquor containing 5 mg/ml Co the effect of pH = 4-8 for recovery Co, Li, Mn and Ni was determined. The highest Co extraction was achieved at pH = 8, but other present metals (Ni, Mn, Li) were co-extracted, too. The pH = 7 value was chosen as optimal, because nickel remains in the solution. Mn and Li are co-extracted and co-stripped at this pH. This can be avoided by their removal from the solution before the extraction or by providing selective stripping.

Cobalt raw materials are among 14 critical raw materials listed by the European Commission on the basis of their high relative economic importance and high relative supply risk [1]. Cobalt can be considered a strategic metal of the future because of its increasing demand, which is closely linked with the development of information technology. The current price of cobalt is about 30 USD/kg [2].

Cobalt is widely used in many applications; the data from 2011 indicate that 30 % of the cobalt world production is used in the manufacture of electrochemical cells [3]. Its consumption is currently growing in this area, particularly in the production of lithium accumulators (LiA) for the charging of mobile phones, laptops and other electronic devices. For example, 4-10 % of the annual growth rate of the LiA market for mobile phones and laptops is assumed by 2015 [4]. Their importance for the application in the hybrid and electric vehicles is increasing as well. Whereas the cobalt content in the primary raw materials is 0.06-0.7 %, the spent LiA accumulators contain 5 – 20 % of Co [5-7].

From the above it results that cobalt recovery from waste is important. Spent LiA accumulators are an interesting secondary raw material for cobalt recovery. The LiA component with the Co content is a cathode active material, which forms active or "black" mass together with the anode active material. Chemically, it is mainly the $LiCoO_2$ compound. In addition to LiA, cobalt can be obtained from the Ni-Cd accumulators, where cobalt content is 1-5 % [8].

The possibilities of the cobalt recovery from LiA can be divided into pyrometallurgical and hydrometallurgical. The pyrometallurgical or combined treatment is currently more used in the plants. Current research in laboratory scale focuses mainly on the sophisticated hydrometallurgical processing. It involves the leaching of the spent LiA active mass and the subsequent extraction of cobalt from the leach liquor. The leaching is mostly carried out in an acidic medium such as HCl, H_2SO_4, HNO_3, usually with the addition of H_2O_2 as a reducing agent. In addition to cobalt, other present metals are co-leached as well, for example Mn, Ni, Cu, etc. The leach liquor containing cobalt can be processed by

precipitation with NaHS, H_2S, $Ca(OH)_2$, NaOH, Na_2CO_3 or MgO, by means of ion exchange, or solvent extraction. In the production of $CoSO_4$, evaporation and crystallization procedures are used [9].

The solvent extraction (SX) is one of the most common and the most effective procedures for the cobalt recovery from the solutions. SX is a selective separation procedure for isolating and concentrating the valuables metals from the aqueous solutions with the aid of an organic solution. SX provides the selective cobalt recovery from the solution as well as the opportunity for an effective separation of Co from Ni, which is difficult to separate due to the similar properties. The advantages are: the application of the simple devices, high selectivity and process flexibility. SX is environmentally friendly because of the possibility to regenerate and recycle the organic agents. It is considered to be a low-waste technology. The disadvantages are the high price, the high consumption and the hazardous properties of the organic agents [10-12].

The current state in the area of cobalt solvent extraction

The solvent extraction consists of the following steps: extraction, scrubbing and stripping [10]. The efficiency and selectivity of the extraction depend on a type and concentration of organic and stripping agents, pH, temperature, extraction time and presence of other metals [11, 12]. The SX process can be described by the following parameters [13, 14]: distribution ratio, extraction efficiency and a separation factor.

The current research in this field focuses on the cobalt recovery from the leach liquor after the leaching of wastes containing cobalt, especially the LiA or Ni-Cd accumulators. These leach liquors contain cobalt and other minor metals, e.g. Li, Mn, Ni, Cu, etc. The SX process is the method for obtaining the purest and the most concentrated cobalt solution. Subsequently, the concentrated and refined solution with the high cobalt content can be processed by electrowinning.

An overview of the available results of laboratory research in the field of the Co solvent extraction from the synthetic solutions or the leach liquors is shown in Table 1.

The overview showed that the entrance solutions for the research of the cobalt sol-

Entrance solution	Investigated conditions		Optimal conditions	Co extraction [%]	Source
	Extraction	Stripping			
Sulfate leach liquor from leaching of LiA	0.03 – 0.54 M Cyanex 272, pH, 25-75 % saponification	2 M H_2SO_4, O:A=11.7/1	0,4 M Cyanex 272, pH= 5.5-6, 50 % saponification	95- 98	[5]
Sulfate leach liquor from leaching of LiCoO$_2$	2-stage extraction: 1,5 M Cyanex 272, pH=5, 0,5 M Cyanex 272, pH=5,35	0.1 – 0.75 M H_2SO_4, O:A=1	0.5 M Cyanex 272	>99	[15]
Synthetic sulfate solution of Co^{2+} and Li^+	c Na-Cyanex 272, pH, temperature, c Co^{2+}, Li^+	H_2SO_4, HCl, HNO$_3$	0.03 M Na-Cyanex 272, pH =5	> 99	[16]
Synthetic sulfate solution	Cyanex 272, D2EHPA, Cyanex 302, t= 25-60 °C, pH	H_2SO_4 200 g/l	D2EHPA< D2EHPA - Cyanex 272 < D2EHPA - Cyanex 302	non-specified	[17]
Sulfate leach liquor from leaching of Ni-Cd accumulators	0,1- 0,6 M Cyanex 272, pH	pH=1	3- stage extraction 0.03 M Cyanex 272, pH = 5.8	> 99	[18]
Chloride leach liquor from leaching of Ni-Cd accumulators	c TOPS 99, PC 88A, Cyanex 272, phase ratio, pH =1.57-6.03	1 M HCl, pH 1-2, O:A=1:1, 2:1	Cyanex 272, pH=5.78, A:O=1	99.9 Co	[19]
Sulfate leach liquor from leaching of Ni-Cd accumulators	c Cyanex 272, pH	0.5 M H_2SO_4, A:O=0.4, in 3-stages	0.5 M Cyanex 272	99.5 Co	[20]

Tab. 1: The overview of the current research results of the Co solvent extraction

vent extraction are usually the sulfate or chloride leach liquors from the leaching of the spent LiA active mass and Ni-Cd accumulators. In some cases, the authors examine the possibility of the cobalt recovery by SX from the synthetic solutions containing Co, Li, Ni and other metals and thus imitate a composition of the real leach liquor. The authors usually examine the effect of the pH, concentration and type of the extraction and stripping agents, the temperature, or the phase ratio, while in many cases the cobalt extraction achieves almost 100 %. However, the publications, in which the efficiency of the extraction from the pure synthetic solution and the leach liquor is compared, are missing in the current research. Also there is only little information about the effect of pH on the cobalt extraction efficiency and the cobalt stripping efficiency separately. Then it would be possible to determine the appropriate pH for both steps individually. In this way, a high selectivity could be achieved, and a high cobalt extraction without any intensification such as using a higher temperature and concentration of the extraction agent etc. Relatively few publications focus on the study of co-extraction of other present metals, which are present in the active mass in addition to Ni - Li and Mn. Also it is necessary to determine the effect of the phase ratio A: O and O: A, which is important mainly due to the economy of the process.

According to the above mentioned information, the following aims of this work were determined:

■ To investigate the effect of the pH on the cobalt extraction efficiency from the synthetic solution using Cyanex 272 in the extraction step and in the stripping step separately,

■ To investigate the effect of the ratio of the inorganic (aqueous) phase to the organic phase during extraction (A:O) and the ratio of the aqueous to the organic phase during stripping (O:A).

■ To investigate the effect of the pH on the extraction and stripping efficiency of cobalt and the accompanying metals from the leach liquor obtained by the leaching of the spent LiA active mass and to compare the extraction efficiencies of the synthetic solution and the leach liquor.
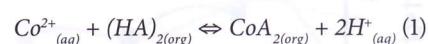
Experimental

Material and methods

In order to avoid the influence of the accompanying metals on the cobalt extraction, the cobalt sulfate synthetic solution and the leach liquor from the leaching of the spent LiA active mass were used for the experiments. Under these conditions it was possible to compare the cobalt behavior during the extraction and stripping from the pure cobalt solution and the solution

containing other metals. In both cases the medium was H_2SO_4.

The synthetic solution was obtained by leaching of a mixture of Co_2O_3 and Co_3O_4 in 2 M H_2SO_4, where the effort was to obtain a solution with a similar concentration as the available leach liquor (3.5 - 5 mg/ml). The cobalt content in the synthetic solution was 3.7 mg/ml and pH = 0.55. The leach liquor was originated by leaching of the fine fraction (-0.71 + 0 mm), called the active mass, from spent LiA in H_2SO_4. The metal content was: 5 mg/ml of Co, 0.9 mg/ml of Li, 0.6 mg/ml of Ni and 0.5 mg/ml of Mn.

Cyanex 272 (purity > 85 %) that was kindly supplied by Cytec Canada Inc. company was used as the organic agent. The solvent extraction of Co with Cyanex 272 can be expressed as follows [21]:

$$Co^{2+}_{(aq)} + (HA)_{2(org)} \Leftrightarrow CoA_{2(org)} + 2H^+_{(aq)} \quad (1)$$

2 M H_2SO_4 and 250 g/l NaOH solution were used for the pH adjustment. The constant conditions for all experiments with the synthetic solution were as follows: the organic solvent 0.1 M Cyanex 272 in kerosene, the extraction time = 15 min, the stripping reagent 2 M H_2SO_4 with pH = 0.14, the stripping time = 10 min, the temperature 20 °C. The following aspects were investigated: the effect of pH = 4-8 on the cobalt extraction and stripping efficiency, the effect of the phase ratio A: O = 0.5, 1, 2
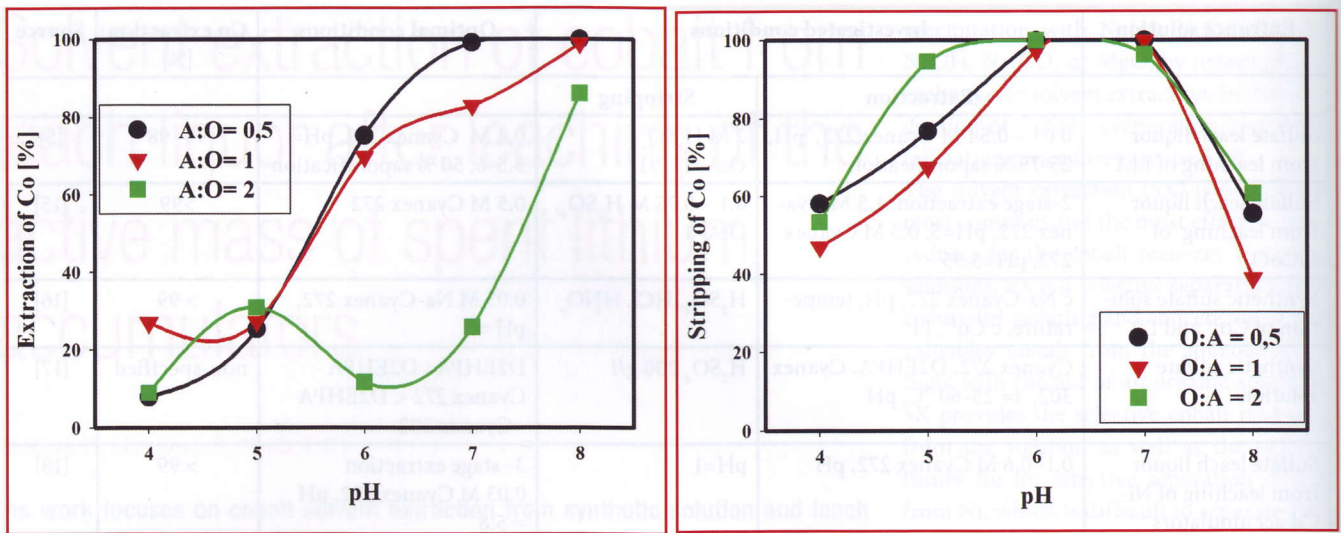
Fig. 1: The effect of pH on the efficiency of a) Co extraction b) Co stripping

in the extraction step and O: A = 0.5, 1, 2 in the stripping step.

For all experiments with the leach liquor the same constant conditions were used as in case of the synthetic solution; and, moreover, the phase ratio A: O = 0.5 and O: A = 2 was constant, too. These phase ratios have been established as the optimal results from the experiments with the synthetic solution, where cobalt extraction was almost 100 %. The effect of the pH = 4-8 on the extraction and stripping efficiency was investigated.

The experiments were carried out in a separating funnel. Shaking was performed by a laboratory shaker. The pH of the entrance solution was adjusted at the beginning of the experiment after the short shaking of both phases together to an equilibrium value by the NaOH solution. Then the separating funnel was placed to the shaker for 15 minutes. This

step was followed by the phase separation, and taking a sample for the analysis. The stripping was carried out using a similar procedure, but without any pH adjustment.

The cobalt content was analyzed only from the aqueous samples by AAS (atomic absorption spectrometry), after the extraction – a poor aqueous phase, after the stripping – a loaded aqueous phase. In the leach liquor experiments Li, Mn and Ni were analyzed as well.

The extraction efficiency (E) toward a specific metal was calculated as [22]:

$$E = [Me]_{org} / [Me]_{total} * 100 \ [\%] \qquad (2)$$

Where:

$[Me]_{total}$ is the total concentration of metal determined in the aqueous solution before the extraction,

$[Me]_{org}$ is the extracted metal determined as the difference between $[Me]_{total}$ and concentration on the aqueous phase after extraction.

Results

The synthetic solution

The effect of the pH on the cobalt extraction and stripping efficiency from the synthetic cobalt solution is shown in Fig. 1 a-b.

The effect of the phase ratio on the cobalt extraction and stripping efficiency from the synthetic cobalt solution is shown in Fig. 2 a-b.

The leach liquor

The effect of the pH on the metals extraction and stripping efficiency from the leach liquor is shown in Fig. 3 a-b.
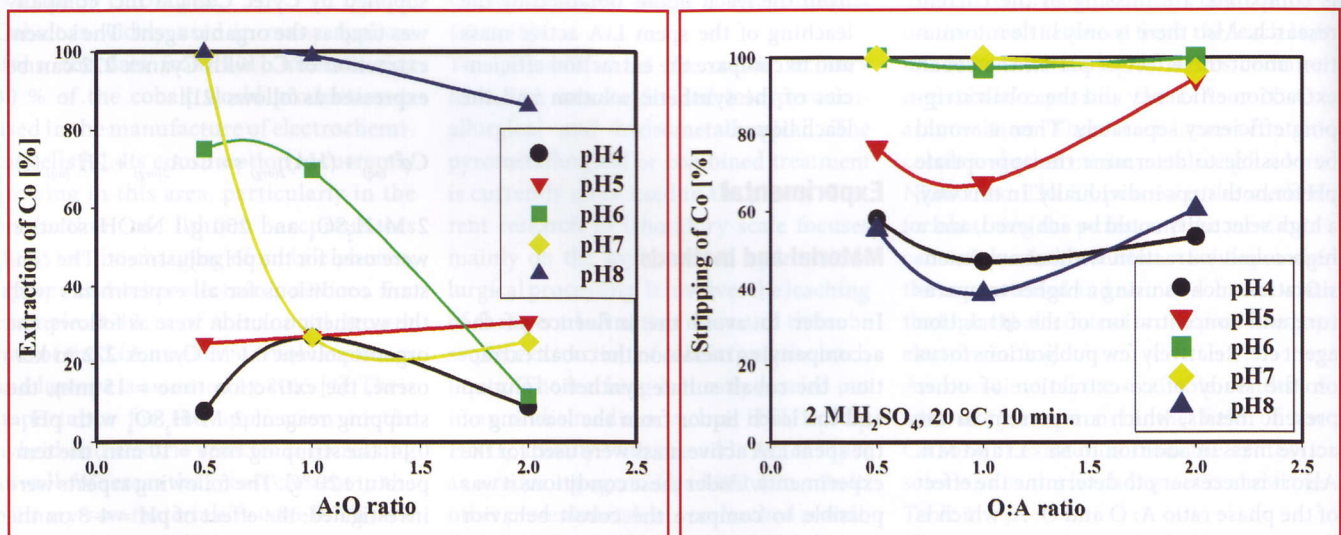

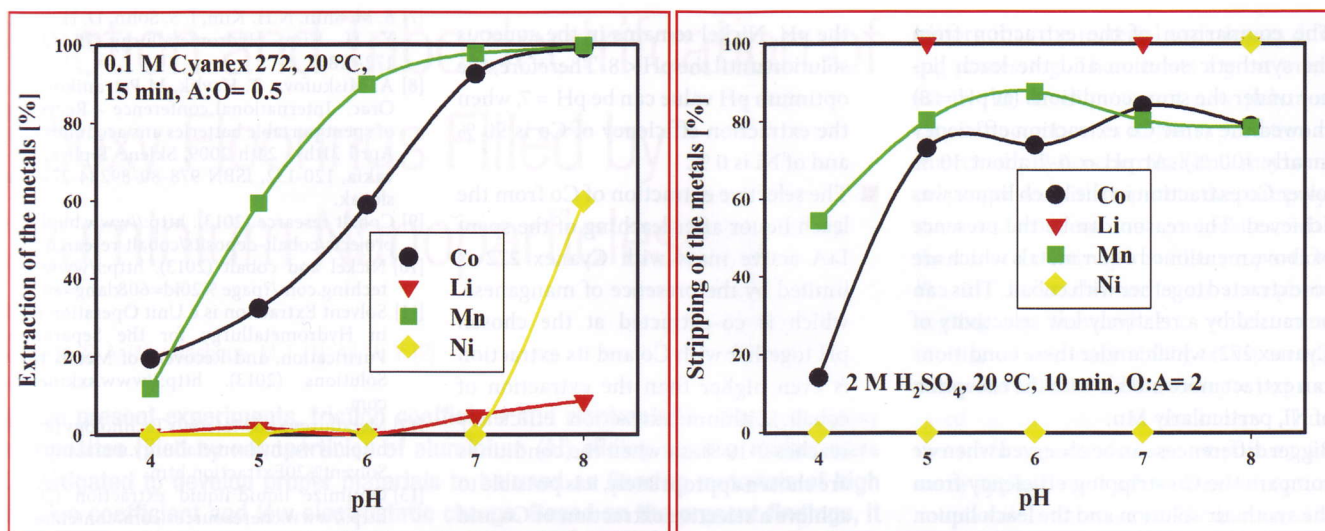**Fig. 2: The effect of phase ratio on the efficiency of a) Co extraction b) Co stripping**

Fig. 3: The effect of pH on the efficiency of a) extraction b) stripping of Co, Li, Mn, Ni

The comparison between the results from the leach liquor and the synthetic solution

The comparison between the Co extraction and stripping efficiency from the synthetic solution and the leach liquor is shown in Fig. 4 a-b.

Discussion

The work was divided into two parts - the study of the Co solvent extraction from the synthetic solution and the study of the Co solvent extraction from the real leach liquor after the leaching of the spent LiA active mass.

From the results of experiments with the synthetic solution it can be seen that the highest efficiency of the Co extraction (almost 100 %) were achieved at pH = 8. It was confirmed that the phase ratio affects the Co extraction efficiency. The

phase ratio of A:O = 0.5 was determined to be optimal despite the increased consumption of the organic agent which can be regenerated and reused. The optimal phase ratio for stripping was O: A = 2 with nearly 100 % efficiency of the Co extraction, where the obtaining of an aqueous solution with the identical or lower volume than the volume of the entrance synthetic solution was taken into account. The highest Co stripping efficiency (nearly 100 %) was achieved at pH = 6.

In the experiments with the real leach liquor the constant phase ratios of A: O = 0.5 and O: A = 2 were used, which have been chosen as optimal in the previous experiments. In case of the synthetic solution as well as in case of the leach liquor, the Co extraction achieved nearly 100 % at pH = 8. One of the main disadvantages is the co-extraction of accompanying metals, almost 100 % of Mn, 60 % of Ni and less than 10 % of Li. At the pH = 7, the

extraction efficiency is 90 % of Co, 100 % Mn and 5 % Li, but under these conditions Ni remains in the entrance aqueous solution. Therefore, pH = 7 can be considered the optimum pH for the Co extraction from the leach liquor, when it is possible to achieve the effective separation of Co from Ni.

The highest Co stripping efficiency (80 %) was achieved from the entrance Co-loaded solutions with pH = 6-7. A disadvantage in this case is co-stripping of Mn (almost 80 %) and Li (100 %). For the removal of these metals from solution it is possible to use a number of options, namely:

1. A preferred removal of the accompanying metals from the leach liquor before the liquid extraction, for example by a selective precipitation,
2. A selective extraction of a required metal using a suitable extraction agent,
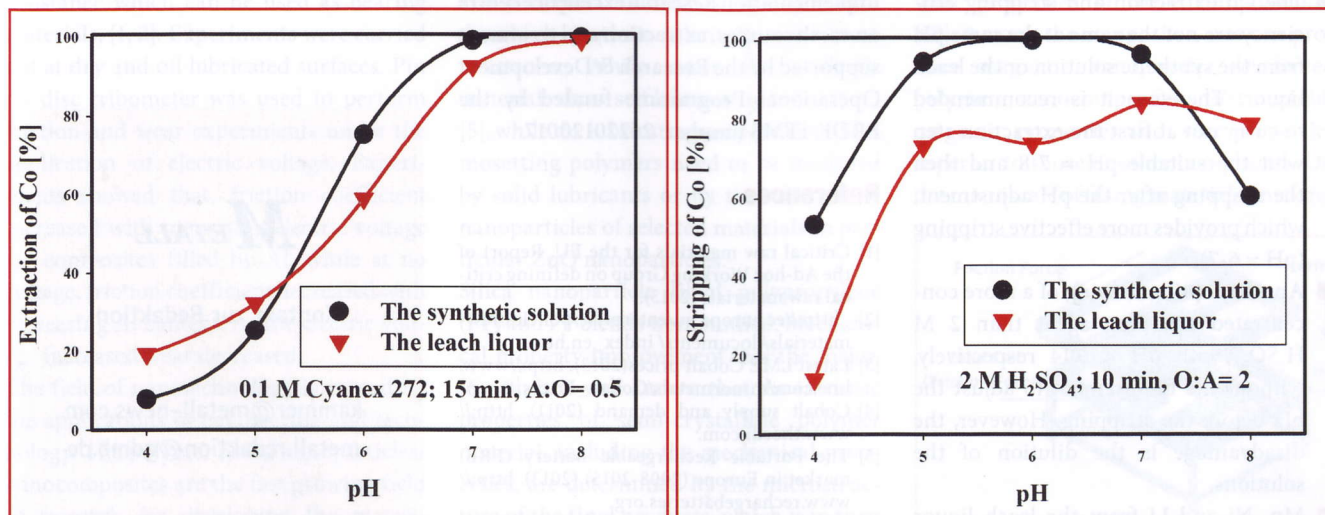3. A selective stripping of the present metals using a suitable stripping agent.

Fig. 4: The comparison between a) Co extraction b) Co stripping efficiency from the synthetic solution and the leach liquor

The comparison of the extraction from the synthetic solution and the leach liquor under the same conditions (at pH = 8) showed the same Co extraction efficiency (nearly 100 %). At pH = 6-7 about 10 % lower Co extraction in the leach liquor was achieved. The reason can be the presence of above mentioned other metals which are co-extracted together with cobalt. This can be caused by a relatively low selectivity of Cyanex 272, which under these conditions can extract more metals with the exception of Ni, particularly Mn.

Bigger differences can be observed when we compare the Co stripping efficiency from the synthetic solution and the leach liquor. The Co stripping efficiency is reduced by 20 % from the leach liquor, which can be due to the consumption of an acid for the stripping of the accompanying metals, an unacceptable pH change, etc. It follows that the stripping step offers several possibilities to influence the results of the solvent extraction, in particular a type, concentration and pH of the stripping agent. In this case, a selective stripping seems as ideal for stripping of one or two specific metals. Based on these findings, our further research will focus on the selective stripping of cobalt and the accompanying metals, which are found in the leach liquor from the leaching of the spent LiA active mass.

Conclusions

From this work the following conclusions and recommendations can be made:

- The optimal phase ratios, with the respect to the consumption of the agents and the process economy, are A:O = 0.5, O:A = 2.
- The Co extraction and stripping efficiency are not the same at the same pH from the synthetic solution or the leach liquor. Therefore it is recommended to carry out at first the extraction step whit the suitable pH = 7-8 and then the stripping after the pH adjustment, which provides more effective stripping (pH = 6-7).
- Another option is using of a more concentrated stripping agent than 2 M H_2SO_4, with pH < 0.14 respectively, without the requirement to adjust the pH before the stripping. However, the disadvantage is the dilution of the solutions.
- Mn, Ni and Li from the leach liquor are co-extracted with Co according to

the pH. Nickel remains in the aqueous solution until the pH < 8. Therefore, the optimum pH value can be pH = 7, when the extraction efficiency of Co is 90 % and of Ni is 0 %.

- The selective extraction of Co from the leach liquor after leaching of the spent LiA active mass with Cyanex 272 is limited by the presence of manganese, which is co-extracted at the chosen pH together with Co and its extraction is even higher than the extraction of cobalt. Lithium extraction efficiency reaches 0-10 %, so when the conditions are chosen appropriately, it is possible to achieve a selective extraction of Co and Li (pH = 4-6).
- The Co stripping efficiency in the leach liquor is about 20 % lower than in the synthetic solution. This is probably due to the consumption of the acid for the stripping of co-extracted metals. Therefore, it is recommended to recover the accompanying metals (Mn and Li) from the leach liquor before the solvent extraction, for example by the selective precipitation, or to carry out the selective stripping of metals.
- It is not necessary to remove nickel from the leach liquor before the solvent extraction and the Ni selective stripping is not necessary either, because its extraction is almost zero up to pH = 8. At the pH <8, the separation of Co from Ni is successful.

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