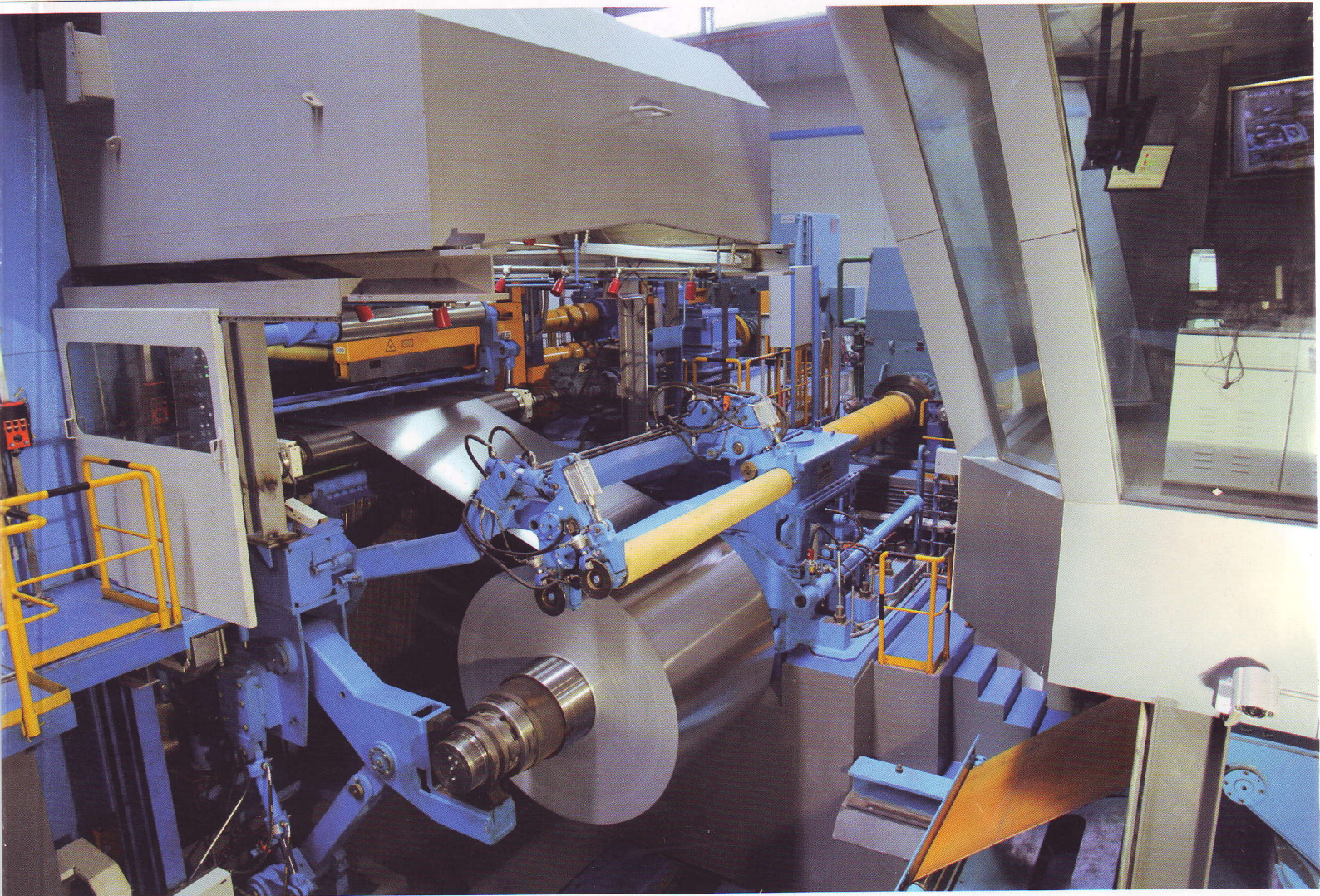


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Acidic leaching of active mass from spent lithium ion batteries with addition of saccharides

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The work deals with the acidic leaching of the active mass from the spent lithium ion batteries. The active mass was obtained by mechanical pretreatment and contained 22.43 wt.% of cobalt and 3.65 wt.% of lithium. The active mass was further subjected to acidic leaching in 2M sulfuric acid with the addition of reducing agents from the group of saccharides – glucose, fructose and saccharose. In this work, the influence of the reducing agent for recovery of interest metals – cobalt and lithium – at 60°C was investigated in order to compare the efficiency of these agents and select the most appropriate reducing agent. It was found that by leaching in 2M H_2SO_4 without saccharides addition, the maximum cobalt extraction reached 50 %. Addition of reducing agents increased the extraction of cobalt by 10-14 % in such conditions. The fructose was chosen as the most suitable reagent because of the highest extraction of cobalt (about 60 %) under used conditions (60°C, 2M H_2SO_4 , 90 minutes). During the leaching at higher temperatures with the addition of fructose cobalt extraction nearly 98 % can be reached, simultaneously it is possible to achieve almost 100 % extraction of lithium.

Currently, the lithium ion batteries (LiBs) are an integral part of modern electrotechnics. They represent a mobile source of electricity in many electronic devices. Because of the expansion of information technologies as well as hybrid and electric vehicles (HEV and EV), consumption of LiBs is constantly increasing. The annual growth rate of LiBs world consumption is 5.6 % (Fuel cell and battery technology, 2011). It can be concluded from the above that increasing consumption of lithium cells will result in long-term increasing amount of LiBs in waste. From that reason, their successful recycling is highly actual issue.

A cathode material of LiBs is mainly composed of metal oxides based on $LiMO_2$, where $M = Co, Mn, Ni$ etc., which are deposited on an aluminum foil. The most common cathode material is $LiCoO_2$. An anode material is carbon or graphite deposited on a copper foil. Anode and cathode materials are electrically insulated by a porous polyethylene or polypropylene separation

film. An electrolyte is an organic solvent with a low viscosity. In the solvent conductive lithium salts are dissolved, for example LiI , LiF , $LiPF_6$, $LiBF_4$, $LiClO_4$ (Wakihara, 2011).

Polymer LiBs are a special kind of LiBs, which differ from conventional LiBs by used separator and electrolyte. In the case of polymer LiBs, conductive gel polymers (for example polyvinylidene fluoride) containing lithium salts are simultaneously used as a separator and an electrolyte. These polymer compounds are used also as binders (Linden and Reddy, 2011, Wakihara, 2011).

In terms of recycling, the most interesting component in LiBs is the cathode material due to the presence of valuable metals such as cobalt and lithium. Other materials that can be obtained by LiBs recycling are steel and/or aluminum from the package and copper and aluminum from electrode foils. Approximately 25 % of global production of lithium (Gaines and Nelson, 2009) and 30 % of cobalt (Crundwell et al.,

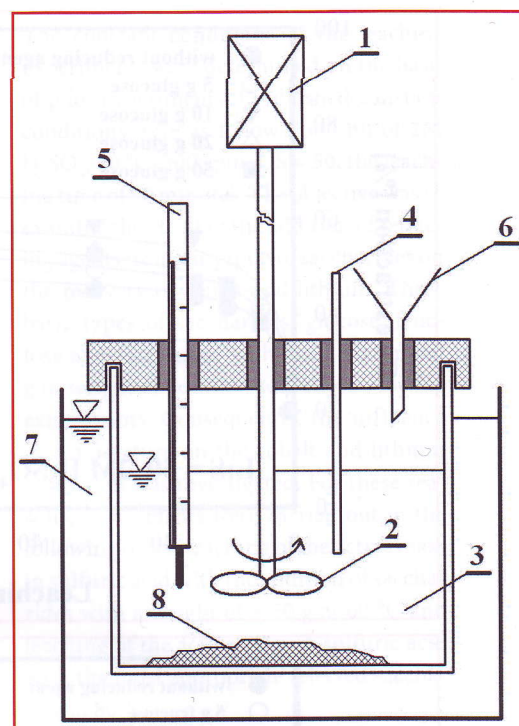


Fig. 1: The scheme of the leaching apparatus

2011) are used for the lithium cells production. Lithium content in ores is in range of 2-5 %, alike in lithium cells. Cobalt content in ores is very low - 0.06-0.7 %, but its content in LiBs is significantly higher – up to 20 % (Miskufova et al., 2009). For these reasons, spent LiBs can be considered as a valuable secondary raw material for cobalt and lithium recovery.

Current research in laboratory scale focuses mainly on the sophisticated hydrometallurgical processing. It involves the leaching of the spent LiBs active mass and the subsequent extraction of metals from the leach liquor. Research on the leaching of the active mass of spent LiBs focuses on selecting a suitable leaching agent, temperature, L:S ratio and other parameters, by means of which it is possible to obtain a high extraction of cobalt and lithium, or other present metals such as nickel and manganese. The leaching is mostly carried out in an acidic medium such as HCl , H_2SO_4 , HNO_3 (Chen et al., 2011, Kang et al., 2010a, Lee and Rhee, 2003, Paulino et al., 2008, Shin et al., 2005). The most common leaching agent from point of view availability and price is H_2SO_4 at various concentrations with addition of H_2O_2 as a reducing agent (Dorella and Mansur, 2007, Ferrerira et al., 2009, Chen et al., 2011, Kang et al., 2010a, 2010b, Paulino et al., 2008, Shin et al., 2005).

Granata et al., 2012, used glucose as an alternative reducing agent. In this case, cobalt and lithium extraction was in

Metal amount [wt.%]						
Co	Li	Ni	Cu	Al	Mn	Fe
22.43	3.65	1.54	1.33	0.72	1.49	1.27

Tab. 1: Chemical composition of the active mass from spent LiBs

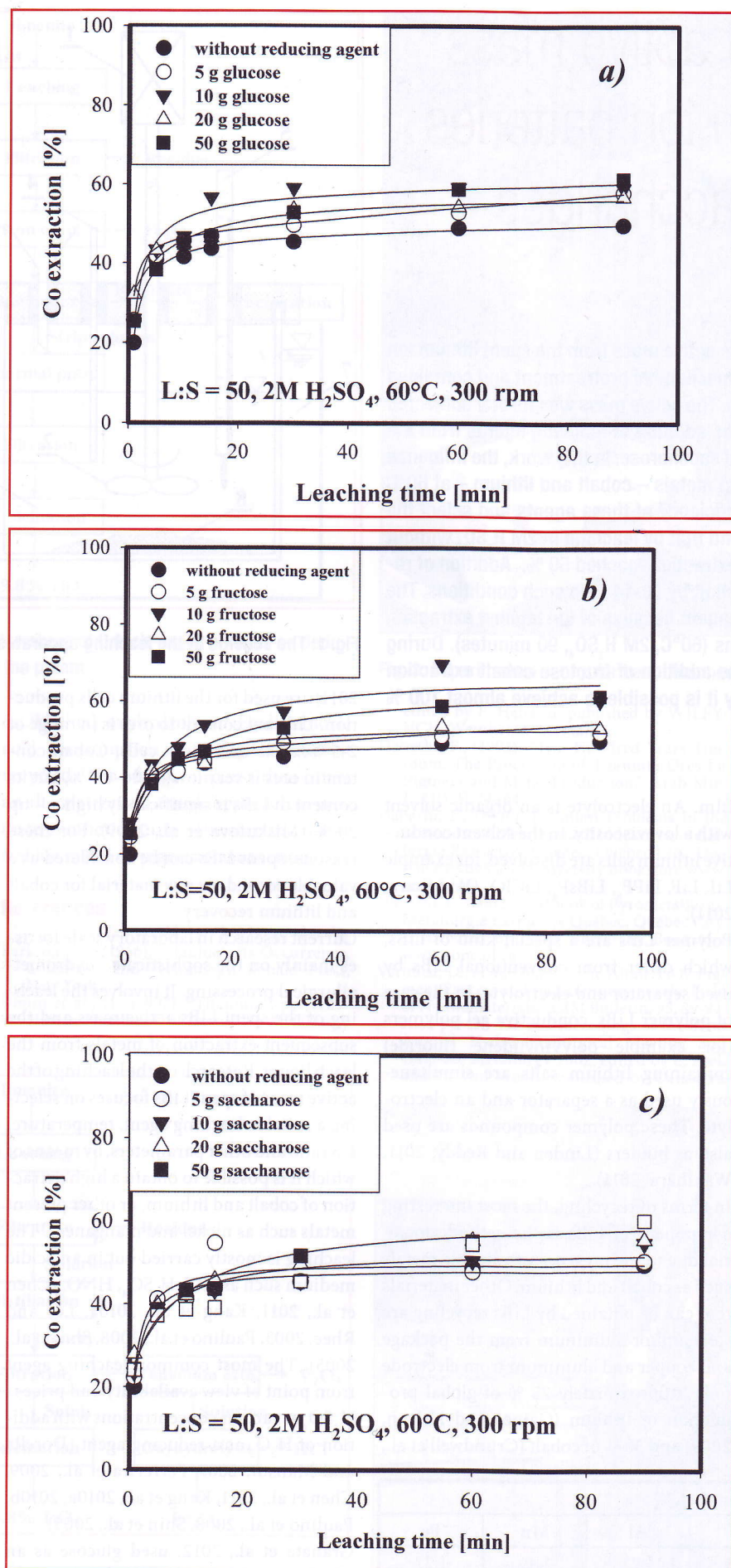


Fig. 2 a-c: Kinetic curves of cobalt extraction – effect of reducing agent addition

range 33-98 % and 67-98 %, respectively. The final cobalt and lithium extraction depended on added amount of reducing agent, temperature, etc.

The objective of this work is a comparison of using three kinds of saccharides – glucose, fructose and saccharose, as reducing agents for cobalt and lithium extraction from active mass of LiBs during acidic leaching.

Experimental

Material

A sample of spent portable LiBs from mobile phones and laptops coming from real collection and weighing 20 kg, was used for the experiments. The sample contained 80 wt.% of LiBs and 20 wt.% of polymer LiBs. The sample was subjected to the mechanical pretreatment, consisting of multiple crushing and sieving followed by drying to constant weight. Loss by drying was 3.26 wt.%.

Sieving was performed with a sieve with mesh size 0.71 mm, which allowed the effective separation of the active mass, which accounted for 37.88 wt.% of the total weight. The active mass is a mixture of cathode and anode active material with residue of separators and electrode films and also it contains organic electrolyte. Active mass as a bearer of cobalt and lithium was subjected to qualitative and quantitative analysis and represents the input for all leaching experiments.

The results of the chemical analysis of the active mass by AAS are shown in Tab. 1. Content of cobalt and lithium in the sample was 22.43 wt.% and 3.65 wt.%, respectively. Except metal components, active mass contains a certain proportion of oxygen from oxides, carbon and other elements.

The sample of active mass was also submitted to the X-ray diffraction qualitative phase analysis, where the presence of phases such as LiCoO₂ and carbon was identified. Other potentially present phases containing cobalt and lithium such as cobalt oxides with formal formula Co₃O₄ and CoO and lithium carbides were identified in the sample. These phases confirm the chemical composition of the active mass, which is shown in the Tab. 1.

Leaching experiments

Methods

Leaching tests are performed in the apparatus, of which a scheme is given in Fig. 1.

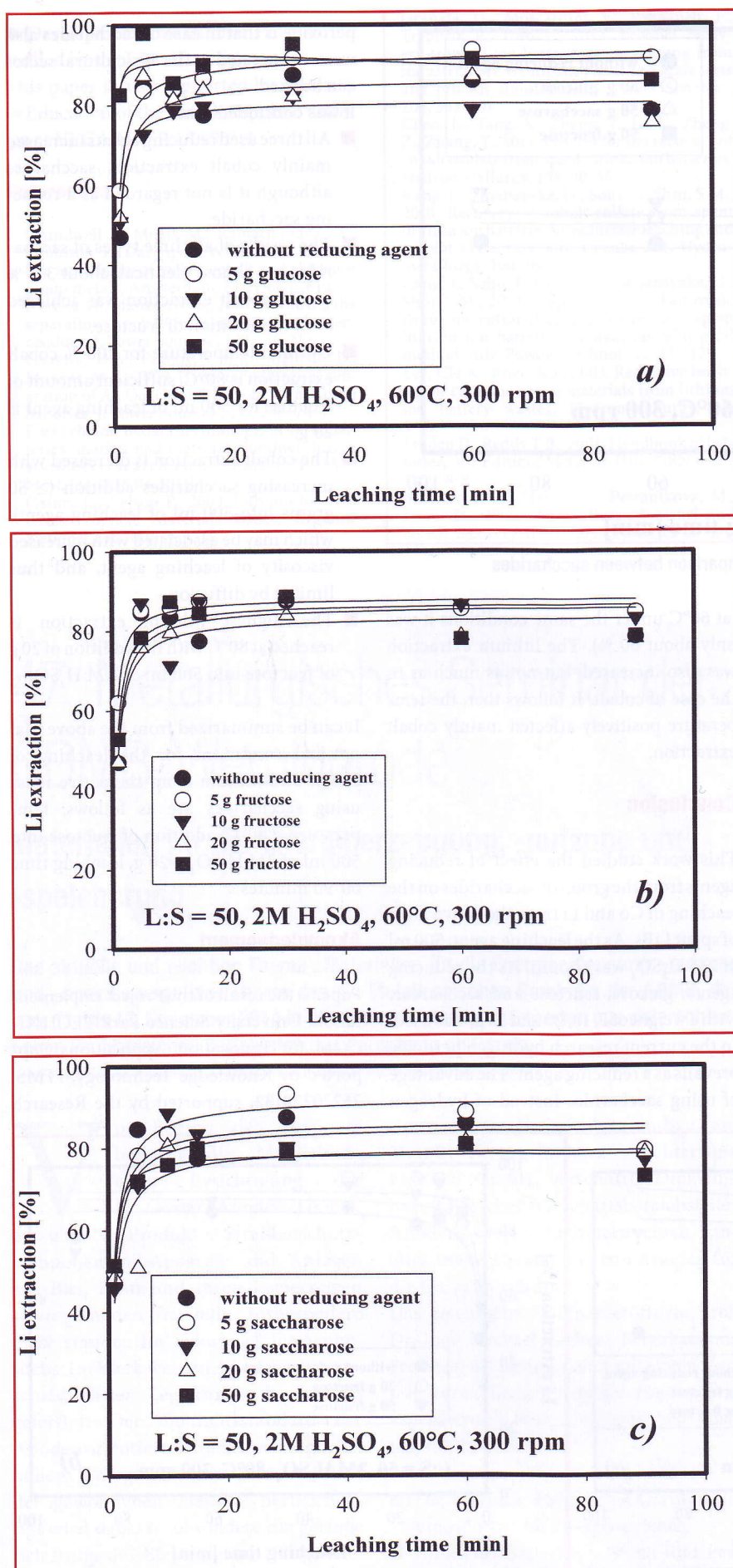


Fig. 3 a-c: Kinetic curves of lithium extraction – effect of reducing agent addition

The constant conditions of the leaching experiments were determined on the basis of pilot experiments. Established constant conditions were as follows: 500 ml of 2M H₂SO₄, 60 °C, 300 rpm, L:S = 50, the leaching time of 90 minutes. The objective was to examine the effect of the addition of reducing agents from the group of saccharides on the recovery of cobalt and lithium. Three basic types of saccharides: glucose, fructose and saccharose with 5, 10, 20 and 50 g of weight of addition was chosen for the experiments. Consequently, the influence of temperature on the cobalt and lithium extraction was investigated. For these reasons, experiments were carried out in the following order: leaching of the active mass in sulfuric acid with the addition of saccharides with a weight of 5-50 g at 60 °C and leaching of the active mass in sulfuric acid with the most appropriate selected saccharide at 80 °C.

Results and discussion

Behavior of cobalt

Kinetic curves of cobalt extraction during the leaching of the active mass from LiBs in 500 ml of 2M H₂SO₄ at $t = 60^{\circ}\text{C}$, L:S = 50 without and with the addition of glucose, fructose and saccharose as the reducing agents are shown in Fig. 2.

Behavior of lithium

Kinetic curves of lithium extraction during the leaching of the active mass in 500 ml of 2M H₂SO₄ at $t = 60^{\circ}\text{C}$, L:S = 50 without and with the addition of glucose, fructose and saccharose as the reducing agents are shown in Fig. 3.

As the kinetic curves of cobalt extraction show, the transfer of cobalt into the leachate increases with the addition of a reducing agent. Without addition of reducing agent, the maximum cobalt extraction was less than 50 %. Addition of reducing agent increases the cobalt extraction to 60 % with each kind of saccharides according to their quantity. Comparison of the effect of reducing agents (weighing 50 g) to cobalt extraction is shown in Fig. 4.

The addition of a reducing agent has a positive impact on the lithium recovery as well, although lithium theoretically does not need a reducing agent for its leaching. The increase in lithium extraction is related to simultaneous cobalt leaching. The lithium extraction of 90 % was achieved, Fig. 3, even at the lowest addition of a reducing agent. The highest extraction was achieved by

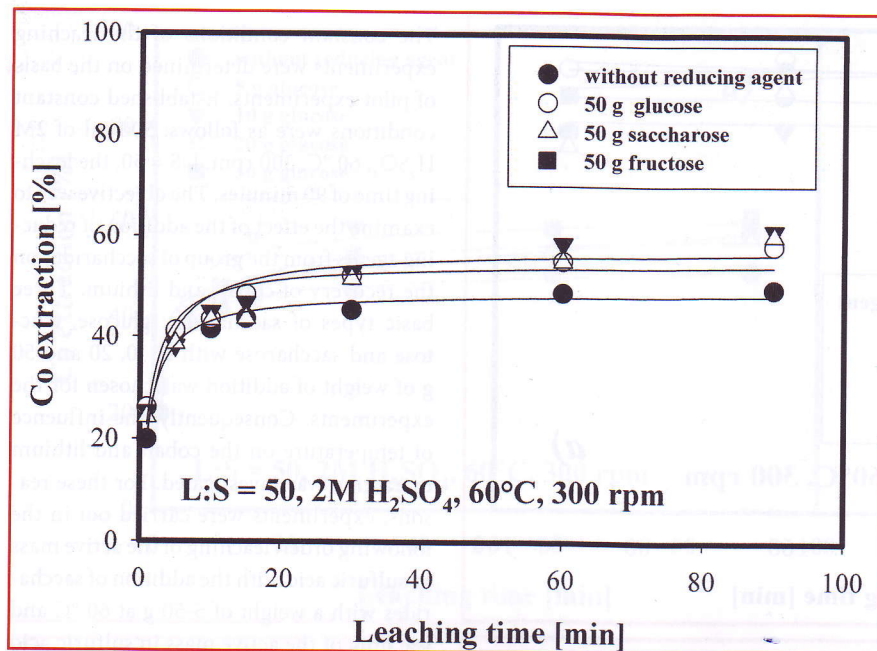


Fig. 4: Kinetic curves of cobalt extraction – comparison between saccharides

using glucose or fructose. For these reasons, preferable reducing agent was selected on the basis of the results of cobalt extraction. Fructose was determined as the most suitable reducing agent for the leaching of cobalt, but the maximum extraction of 60 % cannot be considered as a satisfactory result. For this reason the experiments at higher temperature were proceed, as temperature has a positive impact on the recovery of metals. Additional experiments were performed with fructose at 80 °C, other conditions were the same as in the previous experiments.

Fig. 5 shows the kinetic curves of the cobalt and lithium extraction, with the addition of fructose to 500 ml of 2M H_2SO_4 at 80°C. By addition of fructose (20 g into 500 ml of 2M H_2SO_4), cobalt extraction reached 98 %

(at 60°C under the same conditions it was only about 60 %). The lithium extraction was also increased, but not as much as in the case of cobalt. It follows that, the temperature positively affected mainly cobalt extraction.

Conclusion

This work studied the effect of reducing agents from the group of saccharides on the leaching of Co and Li from the active mass of spent LiBs. As the leaching agent, 500 ml of 2M H_2SO_4 was chosen. As the reducing agents, glucose, fructose and saccharose, with a weight of 5, 10, 20 and 50 g, was used. In the current research hydrogen peroxide prevails as a reducing agent. The advantage of using saccharides instead of hydrogen

peroxide is that in case of saccharides also wastes generated in the agricultural sector can be used.

It was concluded that:

- All three used reducing agents increased mainly cobalt extraction, saccharose although it is not regarded as a reducing saccharide.
- The results of all three types of saccharides are almost identical, about 3-4 % higher cobalt extraction was achieved with the addition of fructose.
- Optimal temperature for 100 % cobalt extraction is 80°C, sufficient amount of fructose for 500 ml of leaching agent is 20 g.
- The cobalt extraction is decreased with increasing saccharides addition (≥ 50 grams into 500 ml of leaching agent), which may be associated with increased viscosity of leaching agent, and thus limited by diffusion.
- The highest lithium extraction is reached at 80°C with the addition of 20 g of fructose into 500 ml of 2 M H_2SO_4 .

It can be summarized from the above that optimal conditions for the leaching of cobalt and lithium from the active mass using saccharides are as follows: temperature $\geq 80^\circ C$, addition of fructose into 500 ml of 2M H_2SO_4 = 20 g, leaching time 60-90 minutes.

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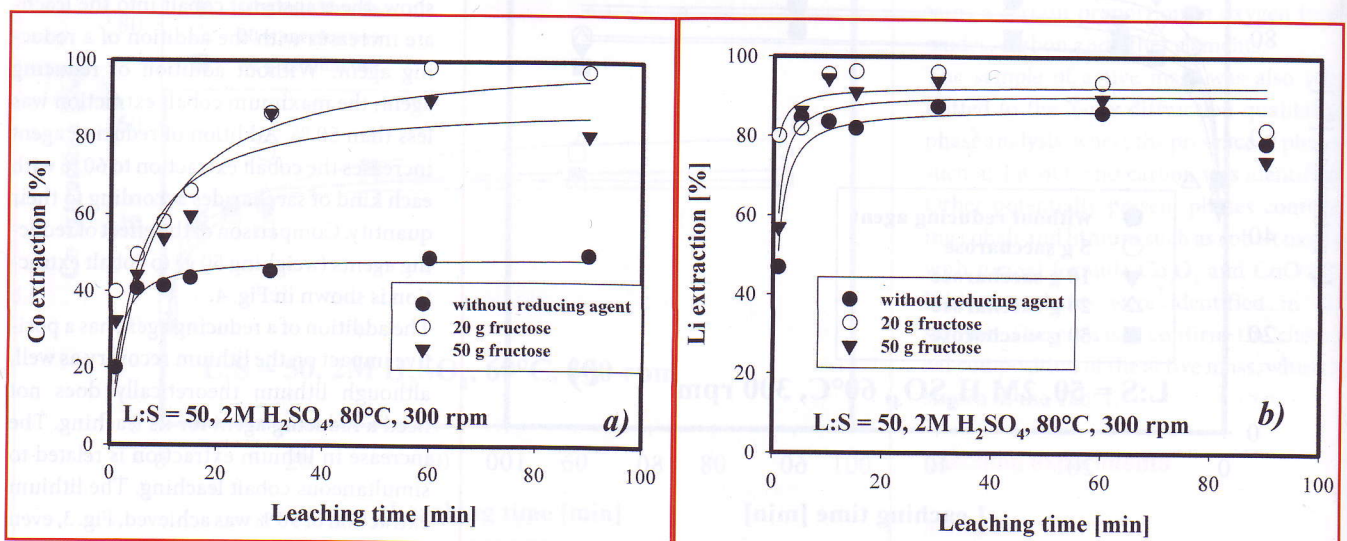


Fig. 5: Kinetic curves of cobalt and lithium extraction with fructose addition at 80 °C

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References

- Crundwell F., Moats M., Ramachandran V., Robinson T., Davenport W. G., 2011. Extractive metallurgy of nickel, cobalt and platinum group metals, Amsterdam: Elsevier, p. 610.
- Dorella, G., Mansur, M.B., 2007. A study of the separation of cobalt from spent Li-ion battery residues, J. Power Sources, 170, 210-215.
- Ferreira, D.A., Prados, L.M.Z., Majuste, D., Mansur, M.B., 2009. Hydrometallurgical separation of Al, Co, Cu and Li from spent Li-ion batteries, J. Power Sources, 187, 238-246.
- Fuel cell and battery technology, lithium batteries: market nad materials [online]. <http://www.bccresearch.com/report/FCB028D.html>, [cited 18.04.2011].
- Gaines L., Nelson P., 2009. Lithium-ion batteries: Possible Materials Issues, Argonne National Laboratory, p. 16.
- Granata, G., Moscardini, E., Pagnanelli, F., Trabuco, F., Toro L., 2012. Product recovery from Li-ion battery wastes coming from industrial pre-treatment plant: Lab scale tests and process simulations, J. Power Sources, 206, 393-401.
- Chen, L., Tang, X., Zhang, Y., Li, L., Zheng, Z., Zhang, Y., 2011. Process for the recovery of cobalt oxalate from spent lithium-ion batteries, Hydrometallurgy, 108, 80-86.
- Kang, J., Sananayake, G., Sohn, J., Shin, S.M., 2010. Recovery of cobalt sulfate from spent lithium ion batteries by reductive leaching and solvent extraction with Cyanex 272, Hydrometallurgy, 100, 168-171.
- Kang, J., Sohn, J., Chang, H., Senanayake, G., Shin, S.M., 2010. Preparation of cobalt oxide from concentrated cathode material of spent lithium ion batteries by hydrometallurgical method, Adv. Powder Technol., 21, 175-179.
- Lee, C.H.K., Rhee, K.I., 2003. Reductive leaching of cathodic active materials from lithium ion battery wastes, Hydrometallurgy, 68, 5-10.
- Linden D., Reddy T.B., 2001. Handbook of batteries, 3th Edition, McGraw-Hill, ISBN 0-07-135978-8.
- Miskufova, A., Havlik, T., Petranikova, M., Orac, D., 2009. Perspectives of nickel and cobalt recovery from spent batteries in Slovakia, International conference - Recycling of spent portable batteries and accumulators, April 21-24 2009, Sklene Teplice, Slovakia, 120-132.
- Paulino, J.F., Busnardo, N.G., Afonso, J.C., 2008. Recovery of valuable elements from spent Li-batteries, J. Hazard. Mater., 150, 843-849.
- Shin, S.M., Kim, N.H., Sohn, J.S., Yang, D.H., Kim, Y.H., 2005. Development of metal recovery process from Li-ion battery wastes, Hydrometallurgy, 79, 172-181.
- Wakiyama M., 2011. Recent development in lithium ion batteries, Material Science and Engineering, 33, 109-134.

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47. Metallurgisches Seminar der GDMB, Wernigerode

Materialien für die Energieerzeugung, -nutzung und -speicherung

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Vor Beginn des Seminars bestand die Möglichkeit einer Besichtigung der JL Goslar Anoden GmbH, die u.a. NE-Produkte, Strahlenschutzkomponenten, Apparate und Anlagen aus Blei, Zinn und ihren Legierungen sowie Anoden herstellt. Insbesondere diese standen im Fokus des Firmenbesuchs: Im Werk werden Anoden in unterschiedlichsten Legierungen nach Maß gefertigt. Der Qualitätsstandard der Anoden orientiert sich an einer möglichst hohen Energieeffizienz und Reinheit der gewonnenen Metalle. Berücksichtigt wird dabei insbesondere die geringe Belastung des Elektrolyten. Eingeleitet durch einen geschichtlichen Firmenrückblick, Informationen zu Projekten,

einzelnen Tätigkeitsfeldern und zur am 01.01.2011 gegründeten Tochterfirma ELSOLD GmbH, verschaffte Dipl.-Ing. Bernd Böttcher (Geschäftsbereichsleiter Anoden) den Teilnehmern einen Einblick in die Herstellung von Anoden für die Galvanotechnik.

Das eigentliche Seminar eröffnete Prof. Dr.-Ing. Michael Stelter, Bergakademie Freiberg, als Seminarleiter mit einem Vortrag zum Thema Energieerzeugung und -speicherung. Weitere Referate behandelten die Themen:

- Die Virtuelle Batterie – Die Aluminiumindustrie als Energiespeicher
- Zink-Luft Batterien – Stand und Perspektiven der wiederaufladbaren Batterien

- Wasserstoffspeicherung in Metallhydriden
- Carbonfaserverstärkte Polymere als Energiespeicher
- Materialien und Verarbeitungstechniken für innovative elektrische Energiespeicher
- Anforderungen an und Verarbeitung von Energiespeichermaterialien zu Elektroden
- Hochtemperatur-Energiewandler und -speicher auf der Basis von Festelektrolyten
- Potentiale der Vakuummetallurgie zur Erzeugung von Materialien für die Energietechnik

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