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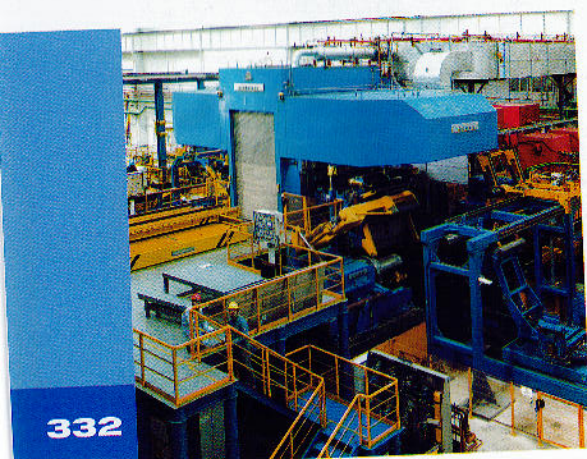
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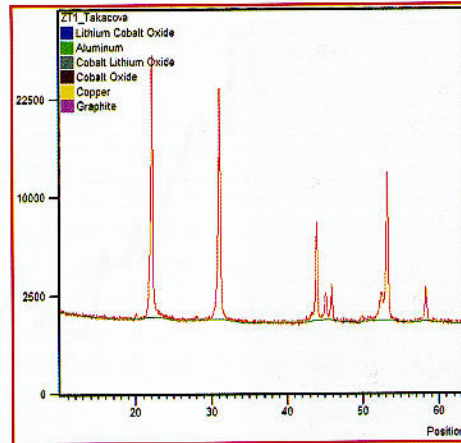
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Die Besucherplattform des Eiffelturms glänzt mit eloxiertem Aluminium (s. S. 326)
 (Foto: Klaus Sikora)

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Thermodynamic aspects of the extraction of Co and Li from active mass of LiBs

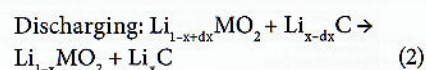
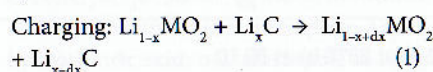
Takáčová, Z.; Havlík, T. (1)

This work deals with the thermodynamics of leaching of the active mass from spent Li-ion batteries (LiBs) in acidic media - in sulfuric acid and hydrochloric acid. The active mass contains oxide phases of cobalt, lithium, manganese and nickel in the form of LiCoO_2 , LiNiO_2 , LiMn_2O_4 , graphite and others. In the active mass, other phases of cobalt and lithium can be present as a result of decomposition of the constituents during the discharge or overcharging of LiBs in their life cycle. Thermodynamic study was carried out by software HSC Chemistry 6.1. Change of standard Gibbs free energy ΔG° was calculated for the predicted chemical reactions in the temperature range 20-80 °C and E-pH diagrams were constructed as well. It was found that ΔG° reached the negative values almost for all reactions in the monitored temperature range in both of leaching media. It means that the expected chemical reactions can proceed during the leaching in the direction of product formation. For the design of E-pH diagrams, the acidic pH range was considered. According to the E-pH diagrams, cobalt is present in ionic form in both leaching agents throughout the whole water stability area to the pH ~ 5-7, depending on the temperature. At higher pH, cobalt can precipitate from solution as $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (only in sulfate medium) or $\text{Co}(\text{OH})_2$. Lithium is present in ionic form throughout the whole water stability area in the whole acid pH range. Thermodynamic study confirmed the viability of cobalt and lithium leaching from spent LiBs in the sulfuric acid and hydrochloric acid as well.

Nowadays, the consumption of portable batteries and accumulators based on lithium is markedly growing because of the information technology expansion, increased application of new laptops and exchange of obsolete laptops, mobile phones etc., where a most commonly used source of electricity are lithium cells. From published data follows that the annual rate of increase in world consumption of primary lithium cells is 3.7%, in consumption of secondary lithium cells 5.6% [1]. Cobalt is one of the main metals, which is present in lithium accumulators and can be obtained by recycling. Another metal that can be obtained from spent lithium cells is lithium. About 25% of world lithium production is used for lithium cells production [2].

According to the composition of lithium accumulators they can be divided into Li-ion and Li-ion polymer accumulators. Generally, electrochemical cells consist of cover, electrode (anode and cathode), electrolyte and separator. Anode and

cathode powder material forms together active material called "active mass" or "black mass". While in primary lithium cells metallic lithium is present, in lithium accumulators is lithium only in the compounds, which form the active cathode material. Components containing lithium, which can be used for the construction of lithium batteries cathode, are LiCoO_2 , LiNiO_2 , LiMn_2O_4 and LiFePO_4 . As the anode material, graphite, fine and hard carbon is used. In both types of cell electrolytes, organic solvents containing lithium salts, for example LiI , LiPF_6 , LiBF_4 and LiClO_4 are present. As a separator for separating the cathode and anode, micro porous polypropylene film is used, a good alternative are fluorocarbons or glass fibres. During charging and discharging (chemical reaction 1, 2) can be expected a degradation of cathodic active material what can lead to formation of new phases as CoO_2 , CoO , Li_2O and so on [3, 4].



where M = Co, Mn, Ni and others.

Spent lithium cells can be processed by hydrometallurgical, pyrometallurgical or combined way. From point of view maximum recovery of interest metals as cobalt and lithium can be considered hydrometallurgical processing as more suitable. That includes metal leaching and recovery of metals from leach liquor. By hydrometallurgy can be processed one component from spent Li-ion batteries - active mass. Active mass is obtained by mechanical treatment. Active mass concentrates interest metals and it is the finest powder fraction after mechanical treatment.

Thermodynamic data in hydrometallurgy are used for prediction of behaviour of various metal components during leaching and recovery from solutions. Studying thermodynamics is very important step before hydrometallurgical treatment. It is important mainly for choice of leaching parameters as a type of leaching solution, pH and temperature for achieving maximum metal extraction. For thermodynamic study of leaching condition were chosen two common acid leaching agents - sulphuric acid and hydrochloric acid at 20 °C (ambient temperature) and 80 °C. The aim of study was describe thermodynamics of leaching process of active mass from spent Li-ion batteries by E-pH diagrams and change of standard Gibbs free energy ΔG° . Using these parameters can be predicted behaviour of component of active mass and their transfer to the leach liquor in ionic state.

Experimental

Material

It is necessary take into account for thermodynamic study the real composition of observed material. Active mass obtained by mechanical treatment was subjected to the analysis of chemical composition by AAS on Varian AA-240. The chemical composition of active mass was as follows: Co 24.43%, Li - 3.42%, Ni - 0.88%, Cu - 2.74, Al 1.06 % Mn 0.72 %, Fe 1.41%.

The sample of active mass was also submitted to the X-ray diffraction qualitative phase analysis. The resulting XRD pattern is shown in Fig. 1, from which the presence of phases such as CoLiO_2 and

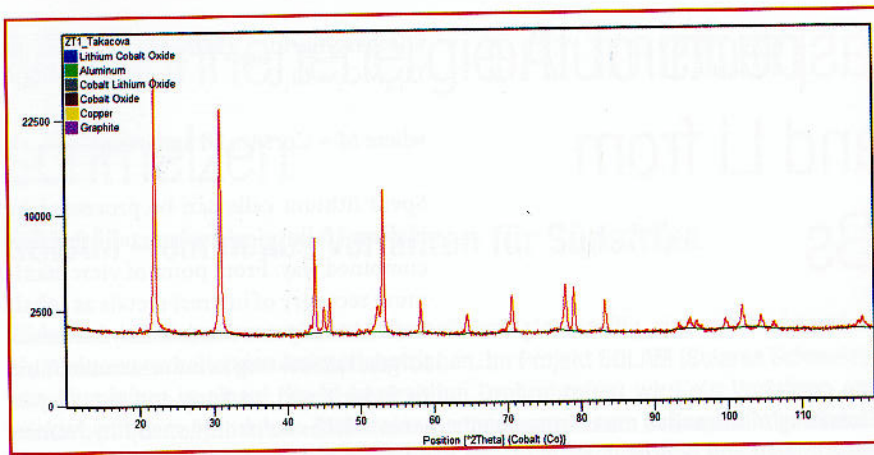


Fig. 1: XRD pattern of the active mass sample

carbon can be identified. Other potentially present phases containing cobalt and lithium such as cobalt oxides with formal formula Co_3O_4 and CoO and lithium carbides were identified in the sample.

E-pH diagrams

Thermodynamics studies systems in equilibrium state and predicts the probability of reactions in the system, depending on the external conditions. Thermodynamic

calculations were carried out using the software HSC Chemistry 6.1 [5].

E-pH diagrams indicate possible stable phases of an aqueous electrochemical system. Predominant ion boundaries are represented by lines. The E-pH diagrams were calculated for the acid pH range (0-7).

The E-pH diagrams for the systems $\text{Co-S-H}_2\text{O}$ and $\text{Co-Cl-H}_2\text{O}$ at 20 and 80 °C are shown at Fig. 2-3, where can be seen the stability of ions in an aqueous medium of sulfuric acid and hydrochloric acid.

The E-pH diagrams for the systems $\text{Li-S-H}_2\text{O}$ and $\text{Li-Cl-H}_2\text{O}$ at 20 and 80 °C are shown at Fig. 4-5, where can be seen the stability of ions in an aqueous medium of sulfuric and hydrochloric acid.

Similarly, at Fig. 6-9 are diagrams for the systems with Mn and Ni as main metals in sulfuric and hydrochloric acid as well. Mn and Ni are present in active mass as minor

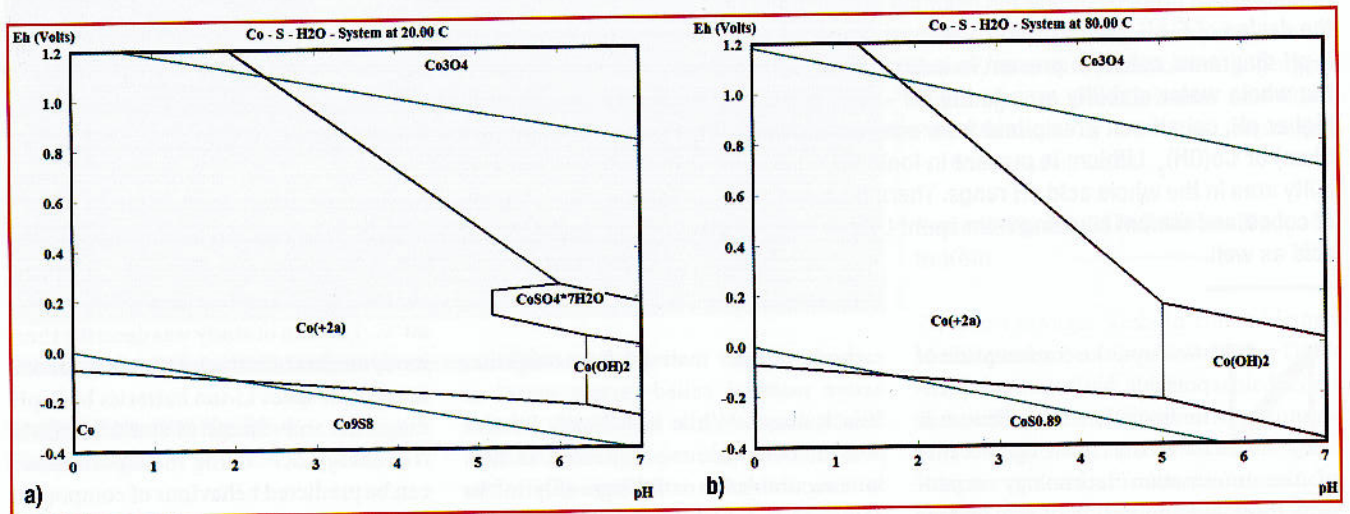


Fig. 2: E-pH diagrams for the system $\text{Co-S-H}_2\text{O}$ a) at 20 °C b) at 80 °C

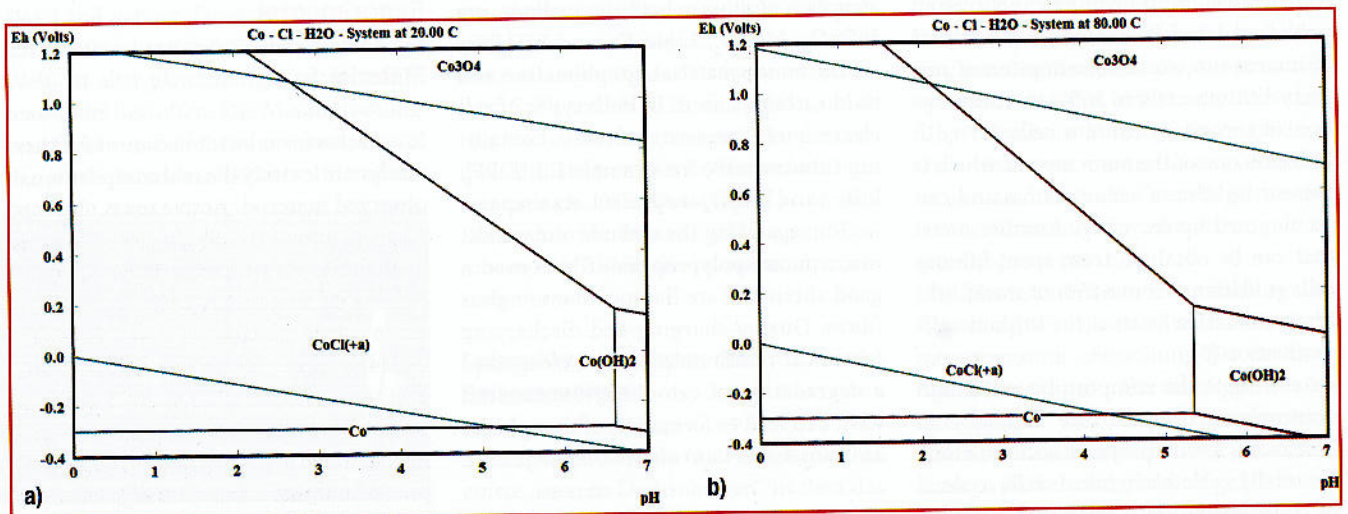


Fig. 3: E-pH diagrams for the system $\text{Co-Cl-H}_2\text{O}$ a) at 20 °C b) at 80 °C

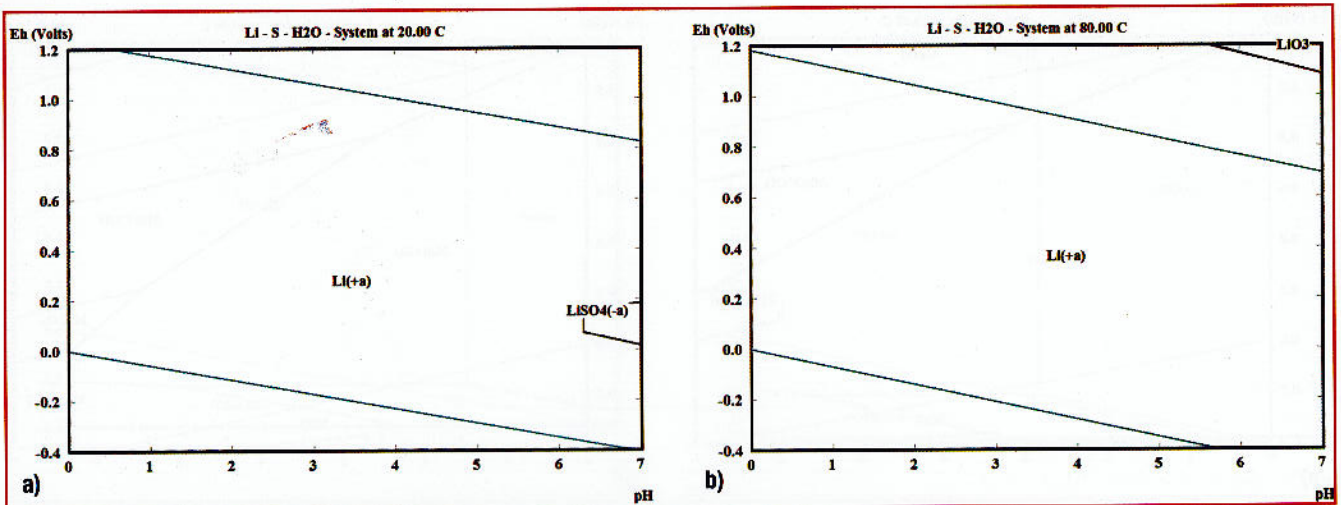


Fig. 4: E-pH diagrams for the system Li-S-H₂O a) at 20°C b) at 80 °C

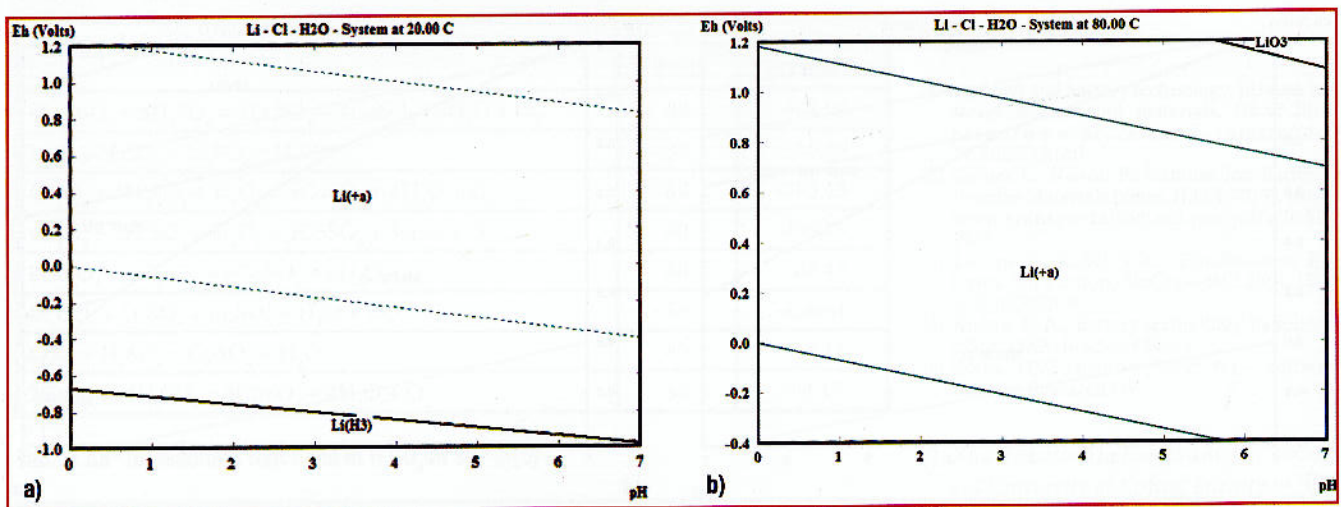


Fig. 5: E-pH diagrams for the system Li-Cl-H₂O a) at 20°C b) at 80 °C

metals but they can leach into leach liquor and can impact on Co and Li leaching.

Thermodynamic probability of chemical reaction course

In thermodynamics, change of standard Gibbs free energy ΔG^0 indicates spontaneity of the chemical reaction:

- $\Delta G^0 < 0$ for spontaneous reaction,
- $\Delta G^0 > 0$ for nonspontaneous reaction.

Values of change of standard Gibbs free energy ΔG^0 for the estimated chemical reactions during the leaching of the active mass in H₂SO₄ at 80 °C are shown in Tab. 1. Tab. 2 shows the values of ΔG^0 for leaching reactions in HCl at 80 °C.

Results and Discussion

E-pH diagrams for the systems of Co-S-H₂O at 20 °C (Fig. 2a) show that Co (II) is stable in the water stability area to pH ~ 6. This zone is decreasing to the pH ~ 5 at

80 °C (Fig. 2b). Than cobalt can precipitate from solution as Co(OH)₂.

E-pH diagrams for the systems of Co-Cl-H₂O at 20 °C (Fig. 3a) show that Co (II) is present in aqueous solution of hydrochloric acid as CoCl⁺ to pH ~ 6.7. At 80 °C CoCl⁺ is stable to pH ~ 5.3 (Fig. 3b).

Lithium (Fig. 4, 5) is stable as Li⁺ in whole water stability area throughout whole acid pH range.

Manganese (Fig. 6-7) is present in the sulfuric acid in stable form as Mn²⁺ at 20 °C almost in the whole acid pH range. In HCl, manganese is present as MnCl⁺ and at 20 °C is stable in the whole acid pH range. At 80 °C, Mn can precipitate from solution as Mn(OH)₂ in sulfuric acid (pH > 6.3) as well as hydrochloric acid (pH > 6.8). Present of nickel in ionic state in sulfuric acid is limited in whole acid pH range at 20 °C and it can crystallize from solution as NiSO₄·4H₂O. At 80 °C, nickel in sulfuric acid is stable in ionic state to pH ~ 3.5. In hydrochloric acid, nickel is stable in ionic

state at 20 °C to pH ~ 5, at 80 °C to pH ~ 3.5.

The ΔG^0 values for the reactions changed minimally and become negative in full range which means that the reactions is very likely to happen in the direction of product formation. Except of the reaction (14), all calculated values of ΔG^0 were negative at all range of temperatures (20-80 °C). It follows that the reactions occur in the direction of product formation with a high probability. The numeric value of ΔG^0 indicates the statistics order in which these reactions will occur. The reaction (14) with a positive value of ΔG^0 probably happens in the direction of formation of the reactants.

Thermodynamic study showed that cobalt and lithium can be leached out into sulfuric and hydrochloric acid solutions. The values of ΔG^0 for individual reaction indicate greater probability of reaction with increasing temperature (20 → 40 → 60 → 80 °C) during the leaching in both of the leaching agents.

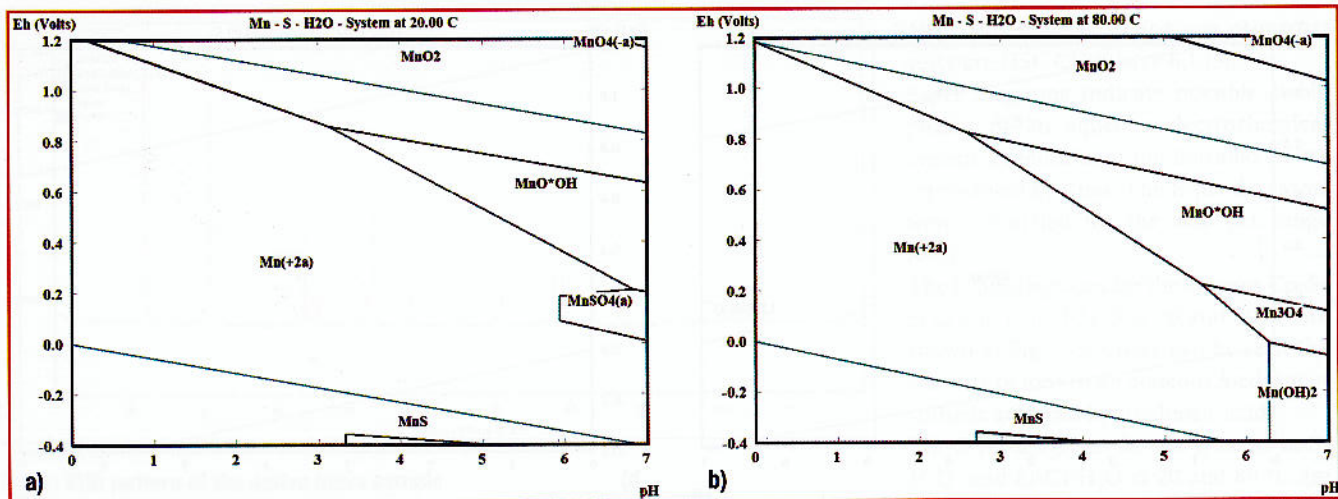


Fig. 6: E-pH diagrams for the system Mn-S-H₂O a) at 20°C b) at 80 °C

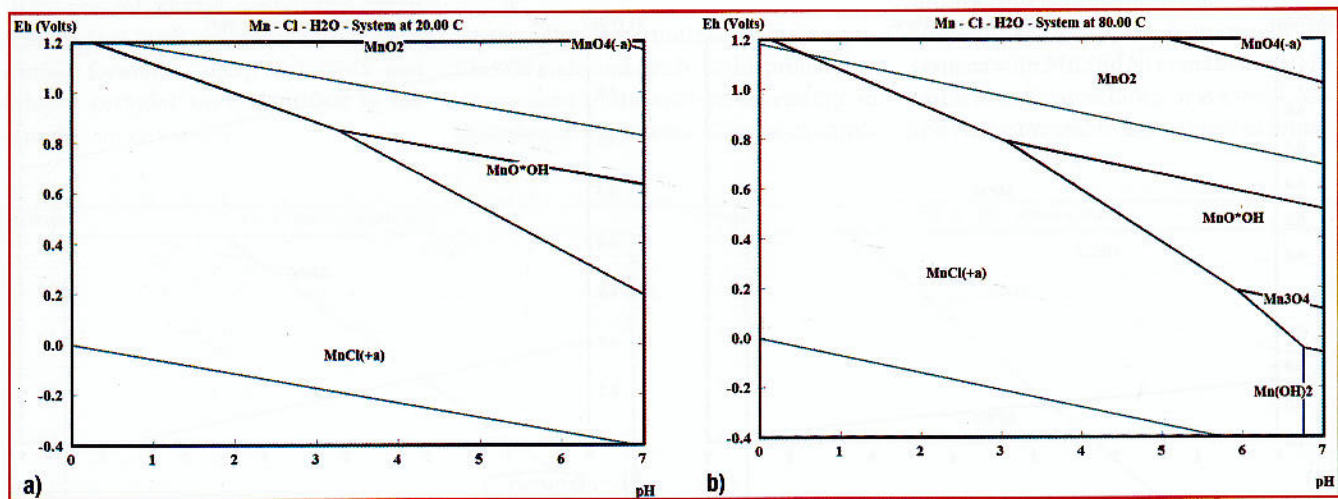


Fig. 7: E-pH diagrams for the system Mn-Cl-H₂O a) at 20°C b) at 80 °C

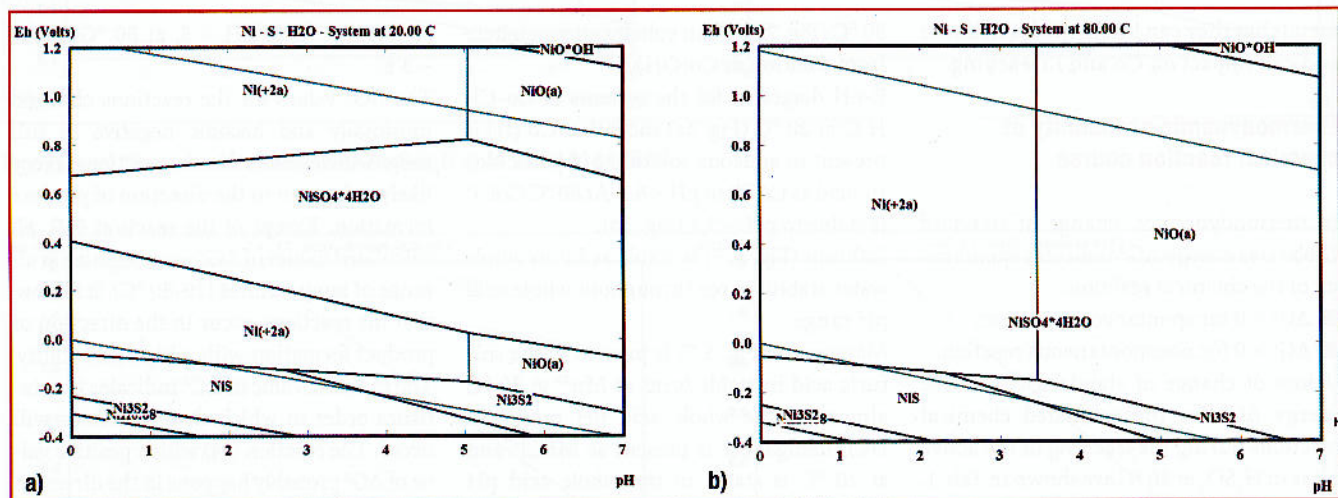


Fig. 8: E-pH diagrams for the system Ni-S-H₂O a) at 20°C b) at 80 °C

Conclusion

Thermodynamic study in hydrometallurgy is important step for prediction of leaching condition. Active mass, obtained from spent Li-ion batteries, contains more

than 20 % of cobalt and 3 % of lithium and is very interesting secondary material for cobalt recovery.

There are some problems with thermodynamic study of hydrometallurgical treatment of spent Li-ion batteries active mass:

- Processes are out of equilibrium,
- Processes occur in the ionic state,
- There is a lack of thermodynamic data.

From E-pH diagrams it is possible to evaluate that acidic leaching of cobalt, lithium

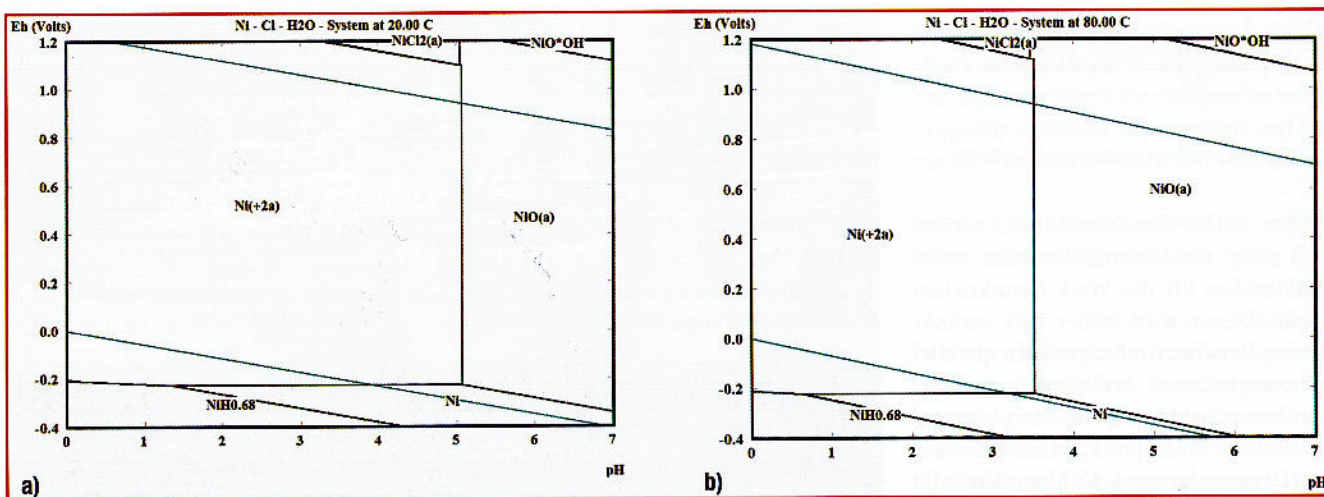


Fig. 9: E-pH diagrams for the system Ni-S-H₂O a) at 20°C b) at 80 °C

Chemical reaction	T [°C]	ΔG° [kJ·mol ⁻¹]
4LiCoO ₂ + 6H ₂ SO ₄ = 2Li ₂ SO ₄ + 4CoSO ₄ + 6H ₂ O + O ₂	80	-608.96
Li ₂ O + H ₂ SO ₄ = Li ₂ SO ₄ + H ₂ O	80	-306.69
Co ₃ O ₄ + 3H ₂ SO ₄ + H ₂ O ₂ = 3CoSO ₄ + 4H ₂ O + O ₂	80	-283.43
Co ₂ O ₃ + 2H ₂ SO ₄ + H ₂ O ₂ = 2CoSO ₄ + 3H ₂ O + O ₂	80	-199.15
2Co ₃ O ₄ + 6H ₂ SO ₄ = 6CoSO ₄ + 6H ₂ O + O ₂	80	-188.42
Li ₂ CO ₃ + H ₂ SO ₄ = Li ₂ SO ₄ + H ₂ O + CO ₂	80	-126.61
CoO + H ₂ SO ₄ = CoSO ₄ + H ₂ O	80	-114.12
2Co ₂ O ₃ + 4H ₂ SO ₄ = 4CoSO ₄ + 4H ₂ O + O ₂	80	-94.17

Tab. 1: ΔG° for leaching reactions in H₂SO₄ at 80 °C [5]

Chemical reaction	T [°C]	ΔG° [kJ·mol ⁻¹]
2LiCoO ₂ + 8HCl = 2LiCl + 2CoCl ₂ + 2H ₂ O + Cl ₂	80	-358.60
Li ₂ O + 2HCl = 2LiCl + H ₂ O	80	-713.59
CoO + 2HCl = CoCl ₂ + H ₂ O	80	-42.95
Co ₂ O ₃ + 6HCl = 2CoCl ₂ + 3H ₂ O + Cl ₂	80	-34.02
Li ₂ CO ₃ + 2HCl = 2LiCl + H ₂ O + CO ₂	80	-28.12
Co ₃ O ₄ + 8HCl = 3CoCl ₂ + 4H ₂ O + Cl ₂	80	24.05

Tab. 2 The values of ΔG° for leaching reaction in HCl at 80 °C [5]

and minor metals as Mn and Ni is possible. E-pH diagrams for aqueous solutions at 20 °C and 80 °C point on stable ionic phase of cobalt and other metals almost for whole acid pH. At higher pH it is possible a precipitation or crystallization of cobalt, manganese and nickel from solution. Lithium is stable as Li⁺ in the whole water stability area on the whole acid pH. ΔG° of predicted chemical reaction has negative values and therefore can be expected that these reactions take place in the direction of product formation. By thermodynamic study was revealed the viability of cobalt and lithium

leaching from spent LiBs in the sulfuric acid and hydrochloric acid as well.

Acknowledgements

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Energietechnik

Dieses Lehrbuch vermittelt ein grundlegendes Verständnis für die Zusammenhänge der Energieumwandlungsprozesse. Die Kapitel behandeln die Techniken der konventionellen und erneuerbaren Energieumwandlung. Grafiken und Tabellen veranschaulichen die technischen Zusammenhänge. Die Schwerpunkte reichen von der kompletten Beschreibung der nachhaltigen, erneuerbaren Energietechniken, über Gas- und Dampfturbinen-Kraftwerke sowie Kraft-Wärme-Kälte-Kopplungsanlagen bis hin zur Energieverteilung und zum Kyoto-Protokoll. Zu allen Kapiteln gibt es Aufgaben mit vollständigen Lösungen im Anhang.

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