Innovative recycling of Li-based electric vehicle batteries

Innovatives Recycling von Li-basierten Batterien für Elektrofahrzeuge

H. Wang, B. Friedrich

RWTH Aachen University

IME Process Metallurgy and Metals Recycling

Intzestraße 3

52056 Aachen, Germany

Abstract

A large demand of electric vehicle (EV) Li-ion batteries is seen in the near future. The reutilization and recycling of EV Li-ion batteries are decisive for their widely applications in the automobile industry.

This paper presents and compares three recycling concepts for EV Li-ion battery recycling: "IME-Accurec H&P", "Gas Control" and "Direct". They vary in the application of pre-treatment (including pyrolysis and mechanical treatment) as well as hydrometallurgical and pyrometallurgical modules. Validation experiments in lab-scale have been conducted and the industrial approval is foreseeable.

This paper has focused on the hydrometallurgical route which is combined in the above mentioned recycling concepts. The metal values from the batteries are leached, purified and recovered. The whole process is composed of leaching, Cu cementation, Fe&Al precipitation, Mn oxidation, Co(and Ni) precipitation and lithium carbonate crystallization. The reusing of recycled products has

been evaluated. The influences of operating parameters have been investigated to obtain the optimum working conditions.

Synopsis

In naher Zukunft wird der Bedarf für die Automobil-Lithium-Ionen-Batterien(LIBs) dramatisch zunehmen. Allerdings ist das Problem der Wiederverwertung von Altbatterien. Automobil-Lithium-Ionen-Batterien bestehen aus vielen wertvollen Metallen wie Lithium, Kobalt, Nickel, Mangan, Kupfer und Aluminium.

Drei Recycling-Konzepte wurde dargestellt und vergleicht: "IME-Accurec H & P", "Gas Control" und "Direct". Sie unterscheiden sich in der Vorbehandlung (z.B. Demontage, Pyrolyse und mechanische Behandlung) sowie hydrometallurgischen und pyrometallurgischen Module. Dieses Papier fokussiert auf der hydrometallurgischen Route. Der Prozess umfasst die Laugung, Laugenreinigung, Mn Oxydation, Kathode Metalle Rückgewinnung und Li_2CO_3 Kristallisierung. Die Wiederverwendung von Recycling-Produkten wurde ausgewertet. Die Einflüsse der Betriebsparameter wurden untersucht um die optimalen Arbeitsbedingungen zu erhalten.

1.   Introduction

In recent years, CO_2 emission reduction and utilization of clean energy are more and more obligatory because of the large vehicle exhaust. The electric engine can significantly increase the energy efficiency especially in urban areas and reduce the CO_2 exhaust. Automobile Li-ion batteries are very completive in the field of energy store to serve as the energy carrier. The demand for automotive lithium ion batteries will increase dramatically in the foreseeable future.

The automobile lithium ion batteries consist of many valuable metals, such as Li, Co, Ni, Mn, Cu and Al. They need an appropriate circulation to the LIBs production. The new German Battery Law "Batteriegesetz" (BattG) turned into action in December 2009. The BattG is the implementation of the EU directive 2006/66/EC and commits producers and traders of all kind of batteries to take used batteries back and assure a state of art treatment and recycling. The recycling processes for batteries have to reach at least a 50 wt-% recycling efficiency.

The IME, Institute for Metallurgy and Metal Recycling of the RWTH University of Aachen is continuously researching on Li-Ion battery recycling since 2004. The IME and its industrial partner ACCUREC Recycling GmbH are developing an integrated recycling process for Li-Ion batteries. Many attempts, including pyrometallurgical and hydrometallurgical methods, have been done to

recycle them. However, they need further improvement to winning the valuable metals more efficiently, economically and environmental friendly.

2. Characterization of automobile lithium-ion batteries

The function of lithium-ion batteries is realized by transportation of lithium ions between the cathode and anode. The performance of lithium-ion batteries is apparently superior to lead acid and nickel cadmium batteries. The voltage of lithium-ion battery is around 3.7 V, which is three times that of conventional nickel batteries, such as Ni-Cd, Ni-MH. Besides, Lithium-ion batteries have no memory effect and have high cycle times. The inorganic compounds, e.g. $LiCoO_2$, $LiNiO_2$, $LiFeO_4$, are used as cathode, carbonaceous material is used as an anode material.[1]

An automobile Li-Ion battery package is composed of many components: casings (mainly stainless steel), electronic devices (Cu cable and circuit board), cooling devices (Cu), plastic, battery cells. The mass content of these components after dismantling is shown in Figure 1. The cells take about 50 % weight of the whole battery. The dismantled cells contain conductor foils (Al and Cu), organic separator (membrane), electrolyte, cathode material (Li-Me-Oxide), anode material (graphite), organic binder. The majority of cell is graphite and organic compounds, which is about 45 % of the cell. Al and Cu foils are 24.5 % and 19 % respectively. Co, Ni and Mn are in the form of metal oxide with Li and serve as cathode materials. Each of them is about 3 % of the whole cell. Li takes a part of 2 %. [2]

The compositions of electrode powder differ a lot according to different types of batteries. Co, Ni, Co, Cu and Li are relatively expensive. The economic benefit of recycling is very sensitive to the price of them.

3. Potential recycling routes

To build up an appropriate recycling process of automobile batteries, many conditions have to be fulfilled:

- Highly flexibility to different battery systems
- Recovered product which can be sold with profit
- Environmental friendly
- Long term access to spent batteries
- Meet political demands (recycling efficiency)

Figure 2 has illustrated the IME-Accurec recycling processes which are combined with other possible recycling processes. In process "Direct", spent automobile lithium ion cells are directly charged in an electric arc furnace with smelting temperatures above 1500 °C. All organic components of the cells burn or reduce metal oxides. The metallic Al burns exothermally and enters into slag. Li is partly vaporized and partly slaged. The products are a multi-alloy, a slag, a flue dust and a halide containing off gas. The multi-alloy containing Co, Ni, Mn, Fe and Cu is because of its complexity not sellable and needs therefore further hydrometallurgical treatment. The alloy is leached and each metal is selectively precipitated or via solvent extraction separated. At the end high purity metal salts are gained.

The process "Gas Control" starts with a mechanicals separation step. Automobile lithium ion batteries cells still contain a high amount of energy and with contact to atmosphere are highly reactive. They easily burn and even explode during the mechanical treatment. In order to assure safe processing during all process steps, the processes have to be implemented under protective atmosphere, so called "Gas Control". The cells are shredded and then separated into metallic fractions (casing, conductor foils), a light fraction (plastics, separator) and a fine fraction called as Li-Co-Ni-Mn-C concentrate. All fractions are contaminated with organic electrolyte, which is hazardous for the following treatment.

The recycling concepts "IME-Accurec H&P(Hydro und Pyro)" start with a permanent deactivation of the cells to assure save handling in the following process steps. During deactivation the cells are pyrolysed at temperatures around 500 °C under vacuum atmosphere. The pyrolysed cells are then shredded and sorted in conventional equipment. A metal fractions (casing, conductor foils) and a fine fraction (active mass of the anode and cathode) are gained.

In the IME-Accurec Pyro route, the fine fraction needs to be agglomerated firstly. At temperatures 1500°C, the carbon reduces the metal oxides like Co, Ni, and Mn, which form a metal alloy. The Li stays in the slag or evaporates. The evaporated Li is oxidized in the atmosphere and then collected as flue dust. The slag can be optimized to support the Li evaporation to achieve a valuable Li-oxide flue dust concentrate. The flue dust can be treated by existing hydrometallurgical Li wining processes.

IME-Accurec Hydro route starts with a leaching step of the electrode material with acid, followed by a filtration step of the residues. The valuable metals are selectively precipitated. At the end different metal salts are gained.

4.   Experimental

4.1   Pre-treatment of spent automobile lithium-ion batteries

The spent automobile Li-ion batteries can be obtained from different sources, such as batteries producer, automobile company, repair shop, and recycler. They should be identified and sorted before they are supplied to recycling step. The batteries may be broken in a car accident or during transportation. The whole battery must be sent to safety check in case catching fire in the following dismantling step. In the following dismantling step, the steel casing, electric cables and plastic label were separated from the battery module.

Deactivation (Vacuum-Thermal Treatment): In order to refine the valuable metal containing raw material further, the electrolyte should be got rid from the dismantled cells. They were treated under thermal and vacuum conditions to deactivate the cells and meantime extract the electrolyte. The cells were charged in an inductive heating vacuum furnace. The pressure of the furnace was decreased to 100 mbar. Meantime the temperature was increased to 500 °C. At this temperature the volatile components like organics, halides and cracking products evaporate and leave the cell through a pressure vent and are recovered in a condenser. After pyrolysis the cells are free of halides. The generated organic condensate with halide contents was also incinerated.

Mechanical Treatment: After vacuum-thermal treatment, the deactivated cells were granulated and sieved. The electrode powder was obtained and subsequently supplied to hydrometallurgical process. Even though most of steel casing is already removed in the dismantling step, the rest steel scrap is further removed by magnetic separator. In this single step, several marketable products can be obtained, such as electrode powder, copper, aluminum foil scrap, steel-scrap. The electrode powder has a particle size which is lower than 200 μm. The chemical composition in one trial is shown below (s. Table 1)

4.2   IME-Accurec Hydro process

The electrode powder from pretreatment was subsequently supplied to hydrometallurgical process which is illustrated in Figure 3. In the leaching process, the metal values in the raw materials (s. Table 1) are extracted from the raw material by the reaction with the sulfuric acid .The previous experimental results have shown that the temperature between 60 °C and 80 °C is optimum and the effect of hydrogen peroxide still require further investigation.[3] Four trails with different combination of temperatures (60 and 80 °C) and oxidation reagent (no H_2O_2 and 20 g/L H_2O_2) have been executed with a solid/liquid ratio 40 g/L. The sulfuric acid concentration is 1 mol/L. The retention

time is 2 hours and the solution samples were taken in 15, 30, 60, 90, 120 minutes. The filtrated leachate and residual were assayed by ICP-OES method.

In the solution refining steps, Cu has been firstly cemented by adding Fe powder at different temperature. The reduction and oxidation potential (ROP) of the solution have been monitored. In the following Al&Fe precipitation step, the Fe^{2+} is first oxidized to Fe^{3+} by adding hydrogen peroxide. The Fe and Al are subsequently precipitated by adjusting the pH value with sodium hydroxide.

After Cu cementation, the valuable cathode metals, Co, Ni and Mn, can be recovered together or separately. In this paper, Mn was firstly recovered from the solution by oxidative precipitation by adding potassium permanganate ($KMnO_4$). The effect of temperature and pH during the reaction has been investigated. The other cathode metal Co was precipitated by adding sodium carbonate solution. Subsequently, The Li after concentration by water vaporization was recovered from the solution in the Li_2CO_3 crystallization step.

5.   Results and discussion

5.1 Leaching

The extraction rate of each metal has been evaluated in the whole retention time. (s. Figure 4) Li is a quite ignoble metal even in the form of compound. The extraction rate of lithium has reached 90 % in the first 15 minutes. The extraction rate keeps almost 100 % in the following time. The influence of temperature and additive reagent hasn't shown much effect on it.

Cu which comes from the anode foil is the noblest metal among these metals. The potential of solution has critical effect on copper extraction. At the present of hydrogen peroxide, the solution becomes oxidative and the copper metal will be dissolved easily. (s. Figure 5) The final extraction rate of Cu in the trail has reached 91 % at 60°C and 98 % with a 20 g/L hydrogen peroxide. The high temperature is favored by the extraction. In the trials without hydrogen peroxide, the dissolution of Cu didn't occur until 90 minutes. The extraction rate of Cu at 80 °C is 15 % in 2 hours.

The leaching performance of Ni has been shown in Figure 6, the extraction rate of different trials differ a lot under different conditions. The fastest extraction has been obtained at 80 °C and at the present of hydrogen peroxide. The extraction rate has already reached 98.4 % since 30 minutes. The slowest extraction rate is under condition of 60 °C and without hydrogen peroxide. According to the result, the performances of 4 trails are in sequence: 80 °C + H_2O_2 >80 °C > 60 °C+ H_2O_2 > 60 °C. The high temperature and hydrogen peroxide (20 g/L) are favored by Ni leaching. The evaluation of Co has shown the similar results but the average speed of leaching is faster the Ni. (s. Figure 7)

The extraction of Fe is shown Figure 8. The trials at 80 °C proceed faster than that at 60 °C. Almost all the Fe has been dissolved in 15 minutes at 80 °C. The extraction rates of Fe at 60 °C are around

90 % at the end. The addition of hydrogen peroxide can increase several percentages of extraction rates at the same time point. In the aspect of Al leaching (s. Figure 9), high temperature is also favored. At the same temperature, the trials with adding hydrogen peroxide proceeds faster than ones without hydrogen peroxide.

5.2 Solution refining

Copper cementation

The time dependent Cu concentration in trials with different temperature has been shown in Figure 11. The process proceeds fast and more than 95% Cu has been cemented in 30 minutes. It is obvious that high temperature has been favored by Cu cementation. The ROP (Reduction oxidation potential)of the solution has been measured and shown in Figure 12. The higher the temperature, the more negative is the potential. The noble Cu^{2+} ions can be easily reduced by Fe which makes the potential of solution low. The potential diagram has agreed with the Cu concentration changing. Table 2 shows the chemical composition in a verification experiment. The composition of Cu has reached 90 °%, which is highly marketable for Cu industry.

Aluminium & Iron precipitation

Fe and Al hydroxide precipiation have been investigated by adjustment of pH. The optium pH are searched to make sure removal of Fe and Al and least lost of other valuable metals.

Figure 13 shows the Al concentration at different pH at different temperatures. The precipitation of Al are very sensitive to pH value. The concentration decreases very significantly since pH 2.5 and nearly to zero until 3.5. The similar results are found in the Fe precipitation. The efficiency of Fe and Al precipitation is larger than 97%. (s. Figure 14).

The loss of valuable metals is shown in Table 3. The loss of metals are evaluated at pH 4.4.. They require further refining steps to recover valuable metals. The effect of temperature was investigated. At room temperature the kinetic of chemical reaction is low. The co-precipitation and absorption also happens when the temperature are higher. The optimum temperature for Al/Fe precipitation is 40 °C.

Manganese oxidation precipitation

Potassium permanganate($KMnO_4$) is a highly reactive substance, which can oxidize a wide variety of inorganic and organic substances. In the redox reaction, potassium permanganate (Mn^{+7}) is re-

duced to manganese dioxide (MnO_2, Mn^{+4}) which precipitates out of solution. Under acidic condition the oxidation half-reactions are: [8]

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \qquad \text{(E°=1.68V)} \tag{1}$$

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \qquad \text{(E°=1.51V)} \tag{2}$$
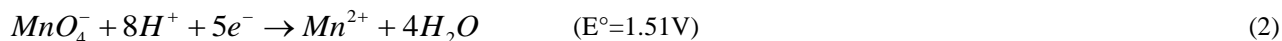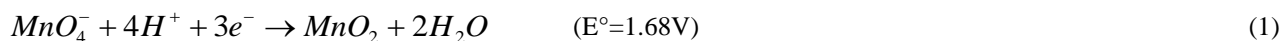
Permanganate will oxidize Mn from +2 to +4 state. The oxidized form will precipitate as an oxide form. The reaction for the oxidation of Mn is:

$$3Mn^{2+} + 2KMnO_4 + 2H_2O \rightarrow 5MnO_2(s) + 2K^+ + 4H^+ \tag{3}$$
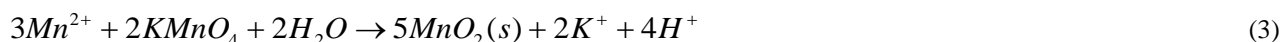
To investigate the influence of pH on the removal of manganese, the trails have been operated with different initial pH, they are 2.2, 2.9, 4.1, 5.1 respectively at 40 °C. The result has shown that the concentration of Mn has decreased continuously with adding the potassium permanganate. Almost all Mn was removed. The pH range from 2.2 to 5.1 hasn't difference on the oxidation performence. The ROP has also been recorded simultaneously, different from pH, the potential has played an important role in the process. The higher the potential, the lower is the metal concentration. (s. Figure 16) Mn^{+7} is the main element which dominate the potential of the solution.

The verification experiment has been done to obtain Mn oxide. The product has a high MnO_2 composition, however several percentage of Co also got lost. (s. Table 4) The reason is that a part of Co can was oxidized and co-precipitated. This powder needs a further refining process to recovery more cobalt.

Cathode metal precipitation and Li₂CO₃ crystallization

The precipitation starts with a refined solution which contains little Ni. After adding stoichiometric amount of soda solution, the $CoCO_3$ has been formed in the liquid. The evaluated efficiency is 99.5%. **Table 5** shows the chemical composition of the powders. The purity of cobalt oxide is quite high and marketable.

The solution after Co precipitation is ready for the lithium carbonate crystallization. The solution was boiled at 90 °C to concentrate the lithium. The 200g/L soda solution is filled and the temperature was kept at around 95 °C. At this temperature, the solubility of lithium carbonate is much lower than room temperature. The verification test has indicated that the crystallization of Li_2CO_3 after solution refining is successful. The chemical composition is shown in Table 6.

6. Conclusions

In IME-Accurec H&P recycling process, pre-treatment steps (including identification, dismantling, vacuum-thermal treatment and mechanical treatment) can maximize the separation of valuable frac-

tions. The obtained electrode concentrate is cleaner than "Gas Control". The initial investment is lower than "Direct" and meantime obtained alloy is simpler than "Direct" alloy. The electrode concentrate also contain less iron, copper which makes the process easier.

The following hydrometallurgical process has been demonstrated to be capable to recover the valuable metals. Leaching in the sulfuric acid media at 80 °C, 20 g/L hydrogen peroxide has the highest recovery rate. The filtered graphite has high purity and is qualified for reusing in new anode production of Li-ion batteries. The copper cementation has been demonstrated very simple and efficient. The high copper composition in the product makes it highly marketable. The following solution refining steps, Fe&Al hydroxide precipitation and Mn oxidation makes the solutions less impurities. The main metals Co and/or Ni are successfully precipitated and serve as the raw material for new electrode powder production. The lithium carbonates which as the main raw material for lithium industry is also recovered from the solutions.

Acknowledgement

Reference

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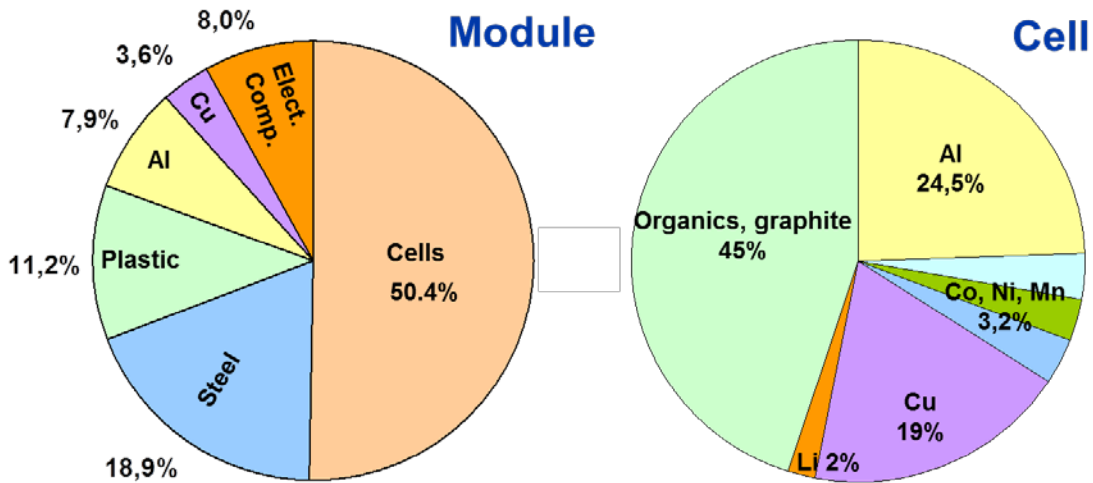
Figure 1 Composition (wt-%) of different components from automobile lithium-ion module (left) and cell (right)
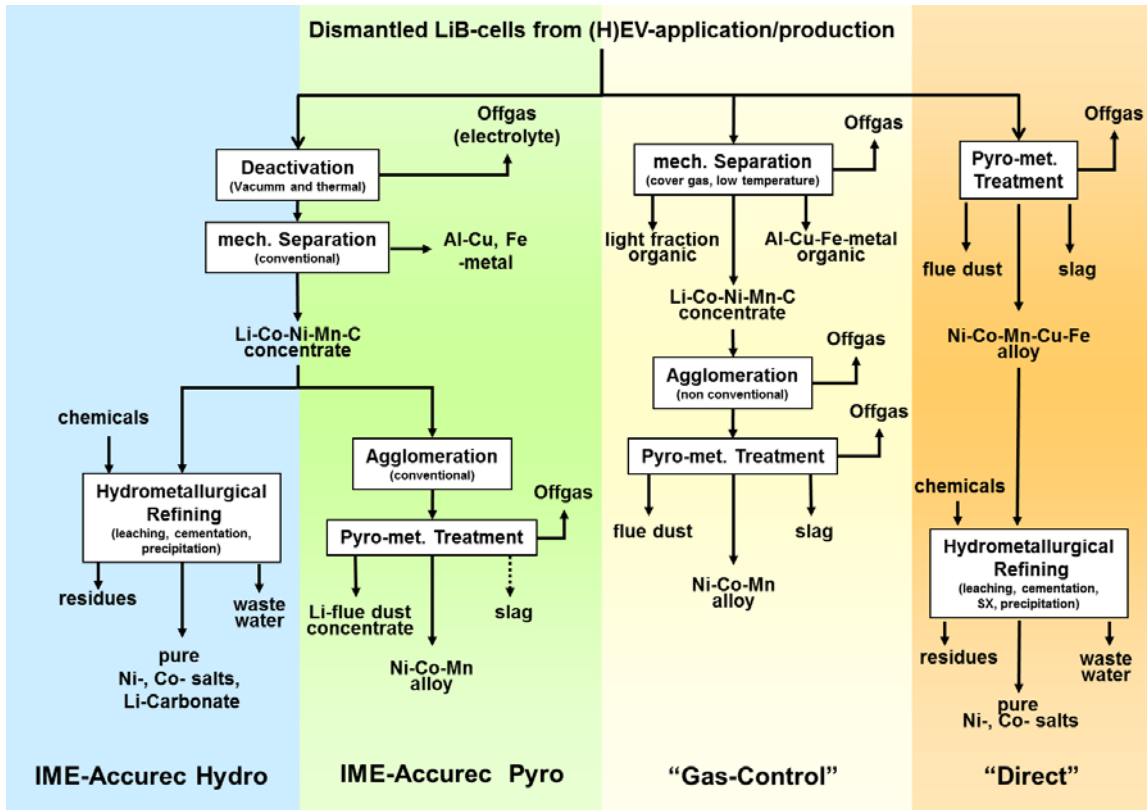
Figure 2 The possible metallurgical recycling process for automotive Li-ion batteries
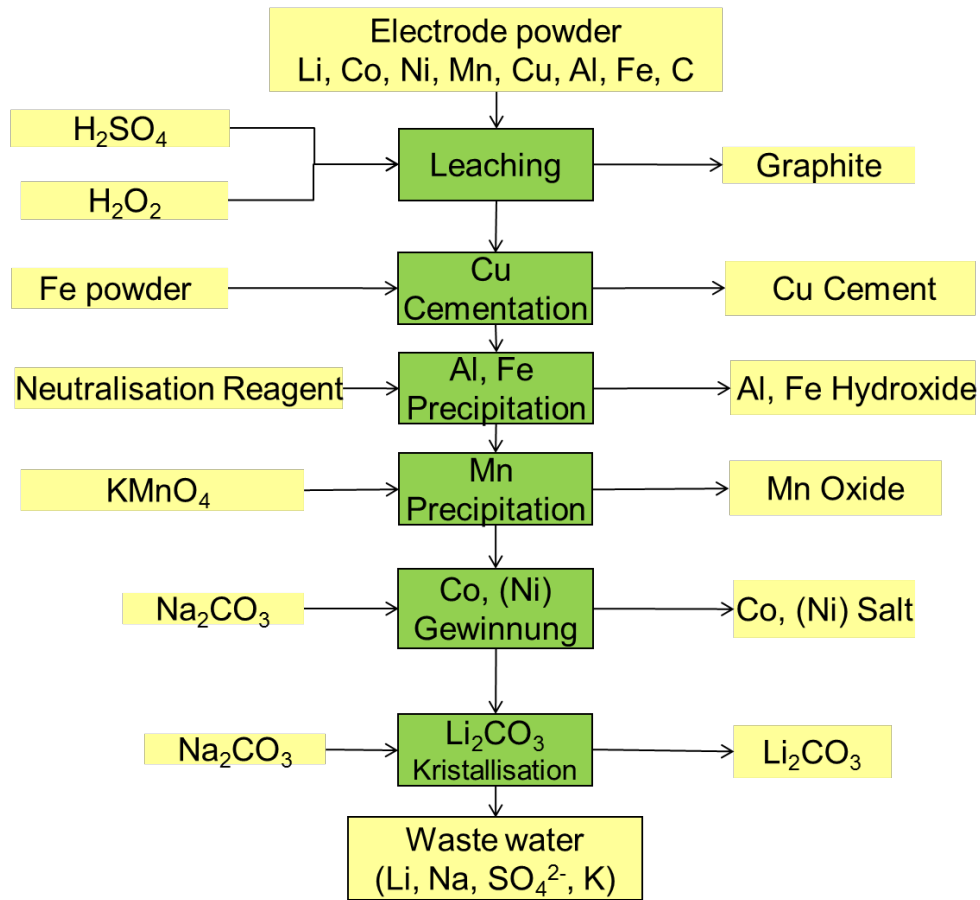
Figure 3 The developed hydrometallurgical recovery process (IME-Accurec Hydro)
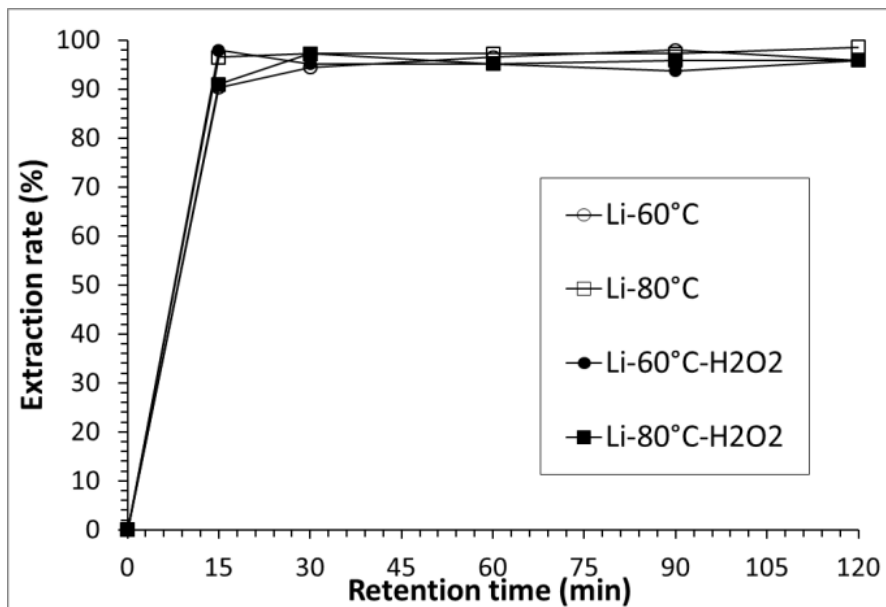
Figure 4 The extraction rate of lithium
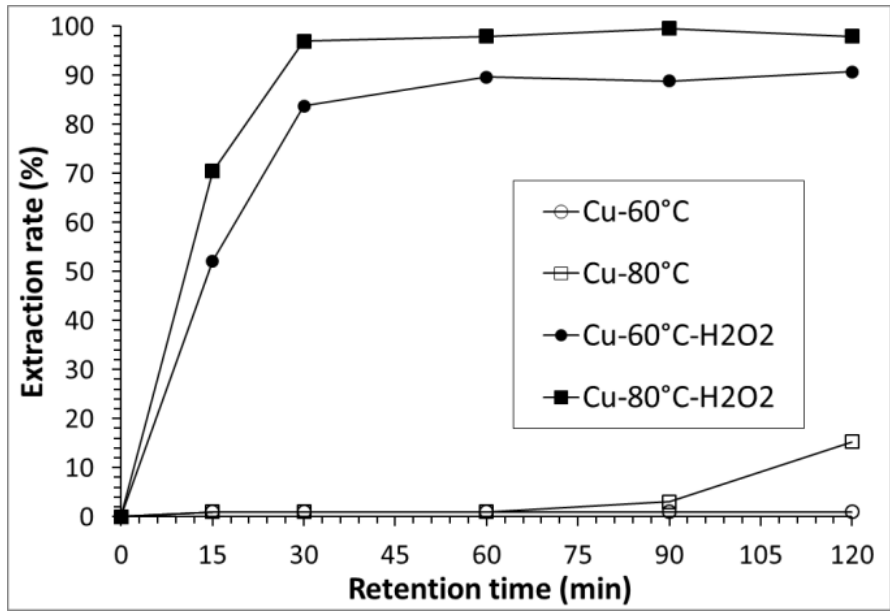
Figure 5 The extraction rate of copper
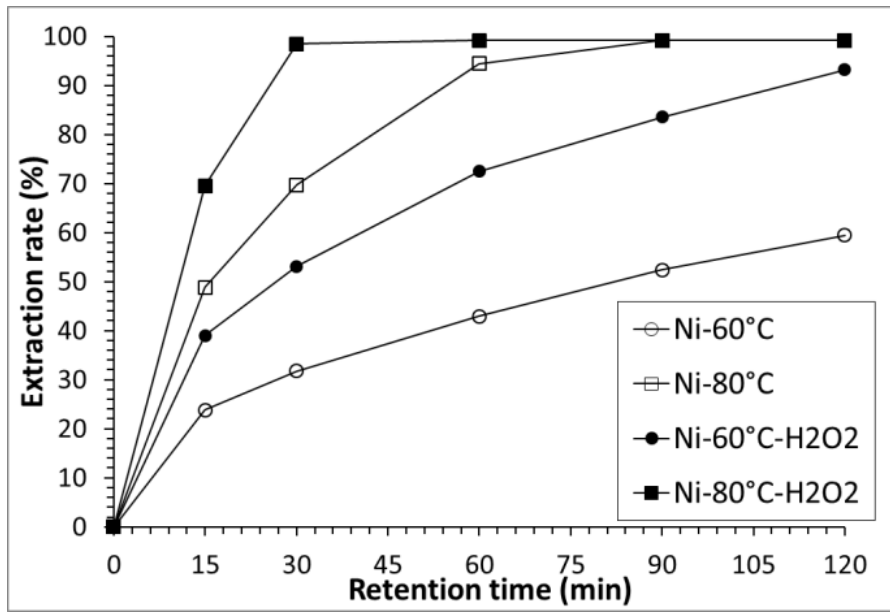
Figure 6 The extraction rate of nickel
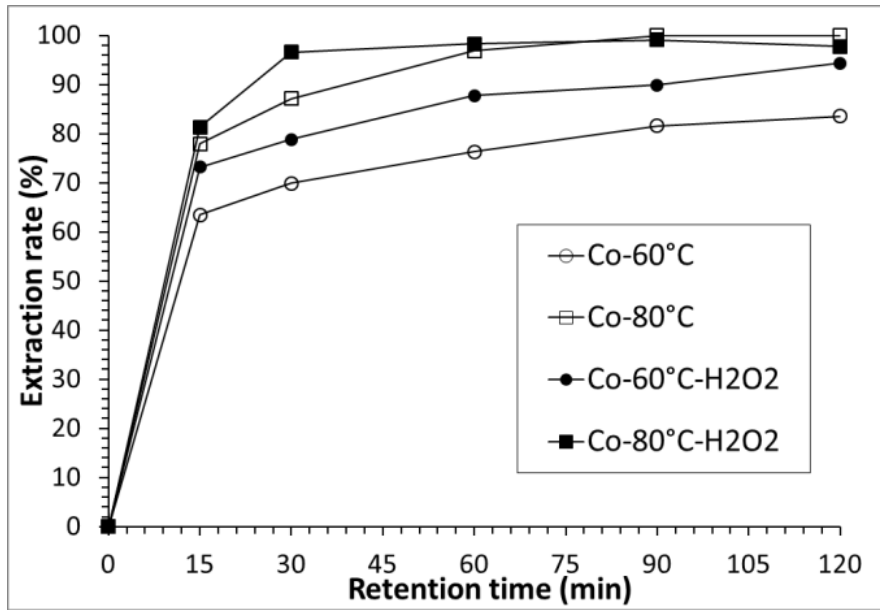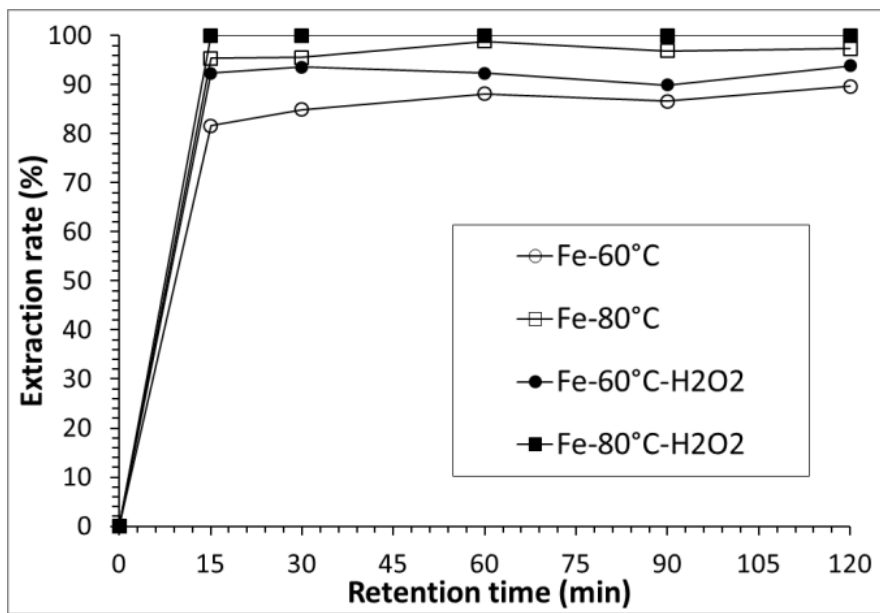
Figure 7 The extraction rate of cobalt

Figure 8 The extraction rate of iron

Figure 9 The extraction rate of aluminium
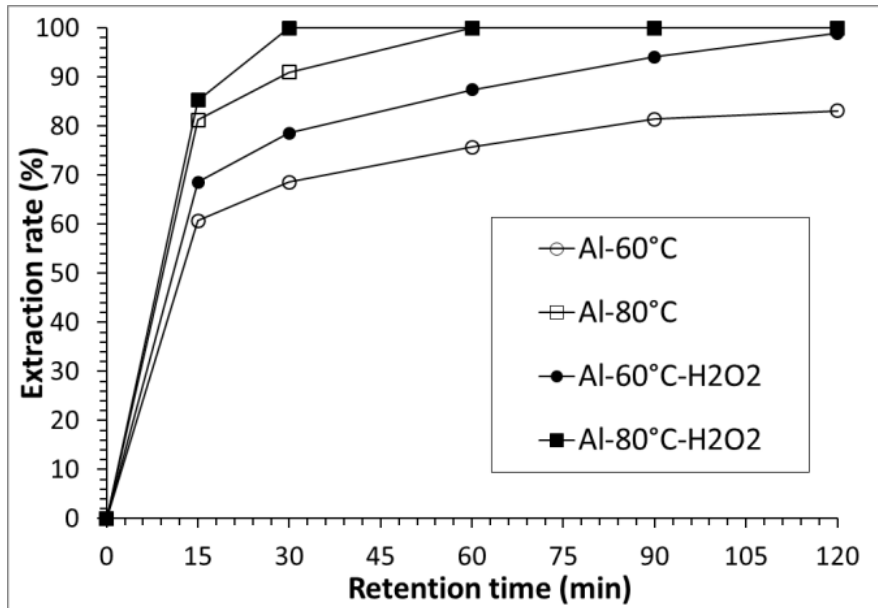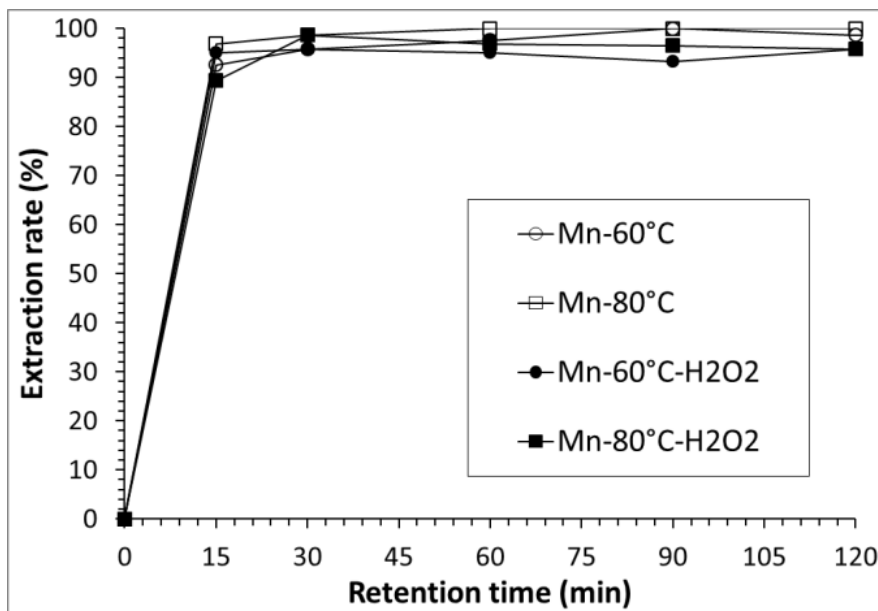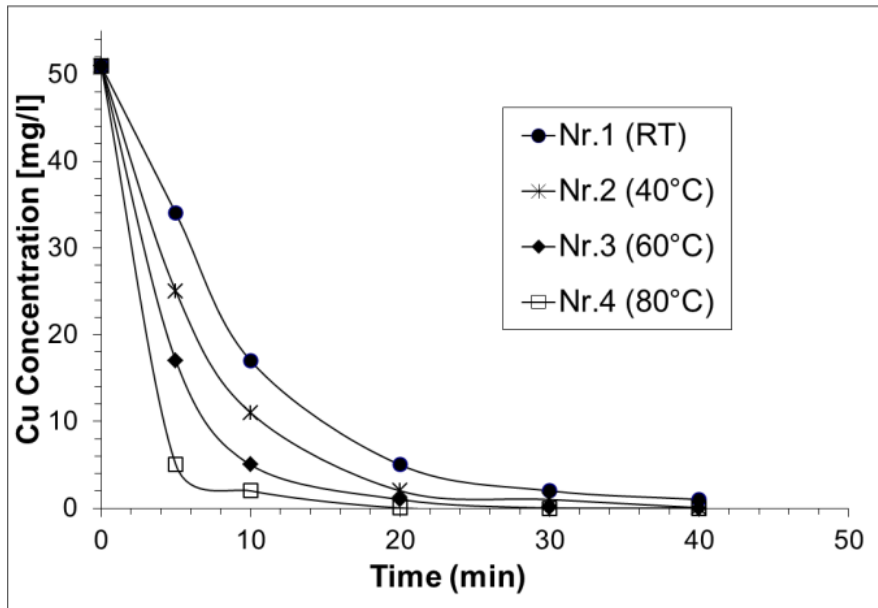

Figure 10 The extraction rate of manganese

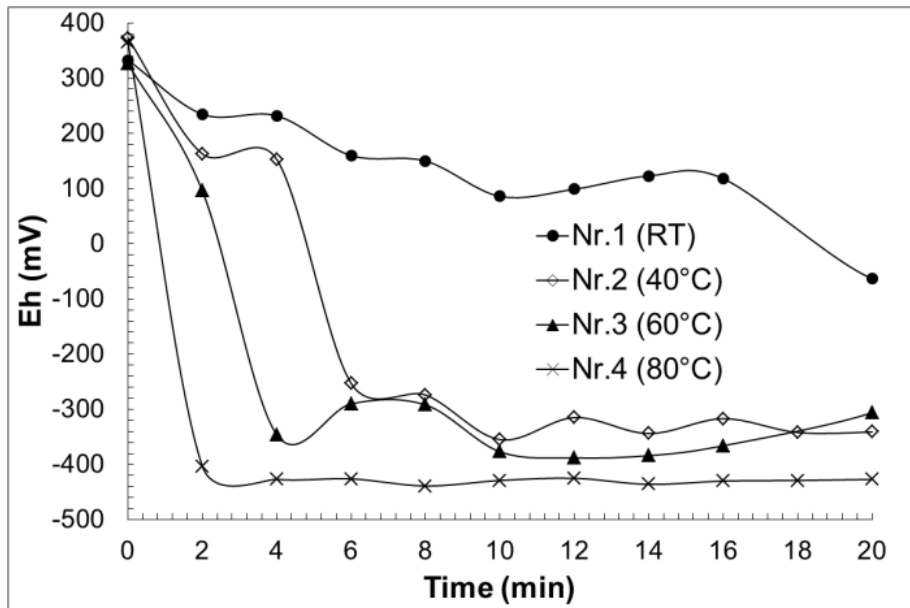Figure 11 Copper cementation at different temperatures

Figure 12 The ROP (reduction oxidation potential) changing at different temperature
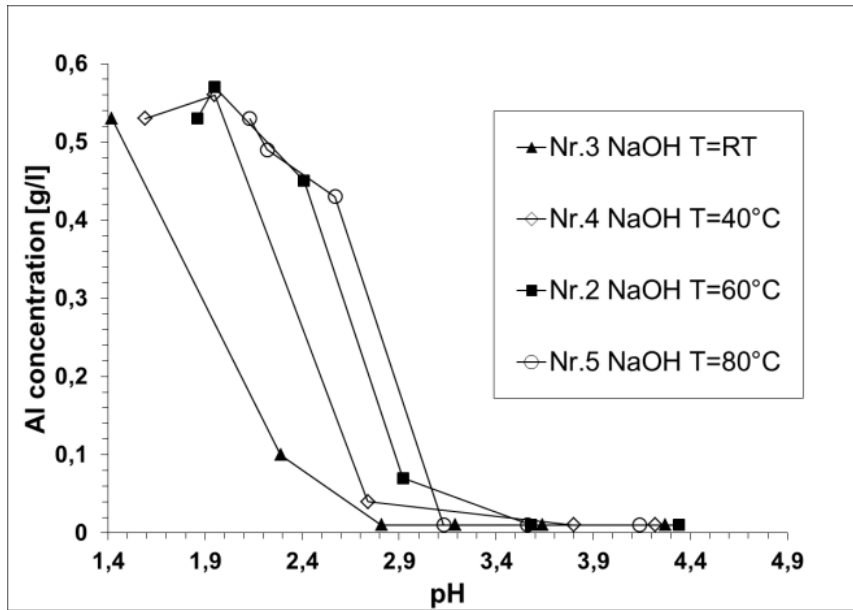
Figure 13 The aluminium concentration at different initial pH solution.
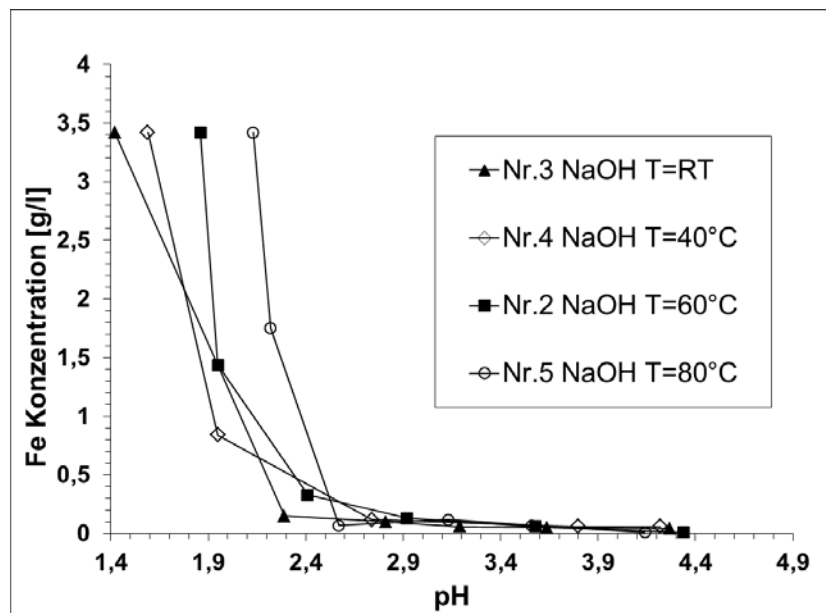

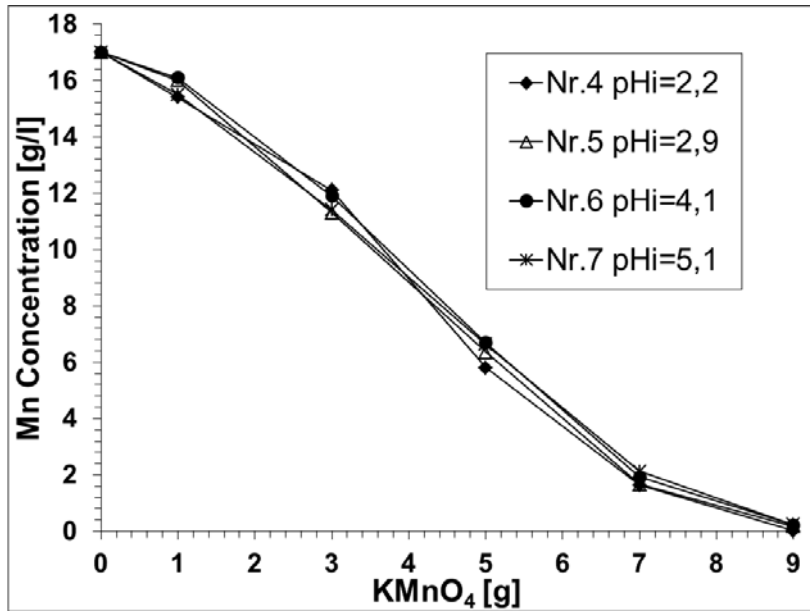Figure 14 The iron concentration at different initial pH solution.

Figure 15 The manganese concentration with adding oxidation reagent
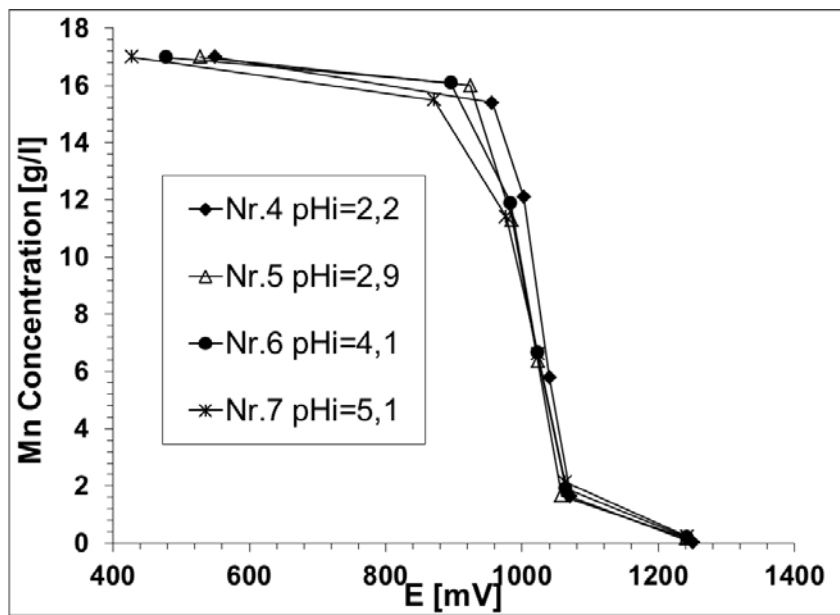

Figure 16 The manganese concentration with oxidation potential

Table 1 The chemical composition of electrode powder for leaching trials

Element	Li	Co	Cu	Fe	Ni	Mn	C	Al
Composition (%)	4.00	8.98	1.10	1.57	18.80	5.83	37.9	0.94

Table 2 The chemical composition of cemented copper powder

Element	Al	Co	Cu	Fe	Li	Mn	Ni
Composition (%)	0.017	0.05	90	0.013	0.17	0.1	0.03

Table 3 The metal lost in the residual at different temperatures

	Cobalt	Lithium	Manganese
F-3 (T=RT)	6%	5%	4,5%
F-4 (T=40°C)	2,2%	2,6%	1,4%
F-2 (T=60°C)	2,7%	2,8%	1,9%
F-5 (T=80°C)	5,3%	5,8%	4,4%

Table 4: The chemical composition of precipitated MnO_2 powder

Element	MnO_2	Al	Co	Cu	Li	Ni	Fe	Na
Composition (%)	82.1	<0.01	5.73	<0.01	0.13	<0.01	0.07	0.11

Table 5: The chemical composition of precipitated $CoCO_3$ powder

Element	$CoCO_3$	Al	Cu	Li	Ni	Mn	Fe	Na
Composition (%)	99.0	<0.01	<0.01	0.39	0.11	0.02	0.06	2.29

Table 6: The chemical composition of precipitated Li_2CO_3 powder

Element	Li_2CO_3	Al	Co	Cu	Ni	Mn	Fe	Na
Composition (%)	95.1	0.02	1.36	<0.01	0.04	<0.01	<0.01	3.39