Slag Design for Lithium Recovery from Spent Batteries

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Abstract

Based on EU directive 2006/66/EC, the German "Batteriegesetz" (battery law) came into force in December 2009, and commits producers and traders of all kind of batteries to take back used batteries after end of life (EOL). Treatment and recycling is mandatory and forbids any landfilling or incineration. The qualification of a battery recycling process is measured by a Recycling Efficiency (RE), which has to reach at least 50 wt.%.

The IME Institute for Process Metallurgy and Metal Recycling of RWTH University Aachen, and its industrial partner ACCUREC Recycling GmbH are developing an integrated recycling process for Li-ion automotive batteries, allowing to fulfil RE requirements of 50 wt.%. After dissembling, vacuum-thermal treatment of discharged battery modules, mechanical treatment and separation, a fine fraction is gained, which contains most of the Li and all of the Co, Ni and Mn content of a Li-ion battery. This fine fraction is agglomerated and treated in a pyrometallurgical SAF process. Co, Ni and Mn are reduced and collected in a metal alloy with high yields. So far the lithium input is split up more or less equally to the flue dust and the slag phase. The project's goal is to design a slag in order to shift the Li distribution towards maximum concentrations in the flue dust.

The paper will light up the general recycling concept for Li-ion Batteries with special focus on future electric driven vehicles, discuss in detail the slag criteria which were selected to design and evolve an optimized slag for the Li Recycling process and finally present the actual status of experiments.

Keywords: lithium, Li-ion batteries, recycling, slag design, solubility, EV, HEV, EOL.

1 Introduction

A new German Battery Law turned into action in December 2009. This so called "Batterriegesetz" is the implementation of the EU directive 2006/66/EC and commits producers and traders of all kind of batteries in the European Union to take back used batteries from the market and assure state-of-art treatment and recycling. The EU directive forbids any kind of landfilling and commits battery recyclers to reach at least 50 wt.% recycling efficiency. A recycling process for Li-ion batteries achieving these requirements does not exist yet.

IME and its industrial partner ACCUREC Recycling GmbH are developing an integrated recycling concept for Li-ion automotive batteries allowing for recycling efficiencies even above 50 wt.%. This R&D project is funded for a period of 3 years by the German Federal Ministry of Education and Research (BMBF).

Li-ion batteries for electric vehicles have unit weights of over 100 kg and consist of steel casings, electric conductors and controlling devices, cooling systems and cells for energy storage. The cells themselves consist of aluminium casings, copper and aluminium conductor foils, organic separators, organic electrolytes, and different ma-

terials for anode and cathode. Graphite is usually used as anode material while at the moment a huge variety of different cathode materials exist. The R&D activity presented here focuses on the better developed cobalt based cathode materials like $LiCoO_2$, Li-Co-Ni-Al-oxide (NCA), and Li-Ni-Mn-Co-oxide (NMC), to limit the number of potential input materials and elements. The IME-ACCUREC Recycling Concept is illustrated in Figure 1.

Li-ion batteries are disassembled and sorted into casings, waste of electronic and electrical equipment (WEEE), plastics and the battery cells. Casings, plastics and WEEE will be integrated into existing recycling infrastructure. Firstly battery cells are deactivated at 500 °C to evaporate organics, to assure a save handling and to remove halogenides (fluorides and chlorides) safely. Afterwards the battery cells are shredded and separated into a Cu/Al-foil and a fine fraction. The foil fraction will be integrated into existing recycling infrastructure while the fine fraction contains the valuable electrode materials Co, Ni, Mn, and Li and will be referred to in the following as electrode material (EM). EM is treated in a pyrometallurgical process to gain the valuable metals as a molten alloy and to concentrate Lithium in the generated flue dust. Afterwards this flue dust can be treated hydrometallurgically to generate a high quality Li-compound e.g. Li_2CO_3.
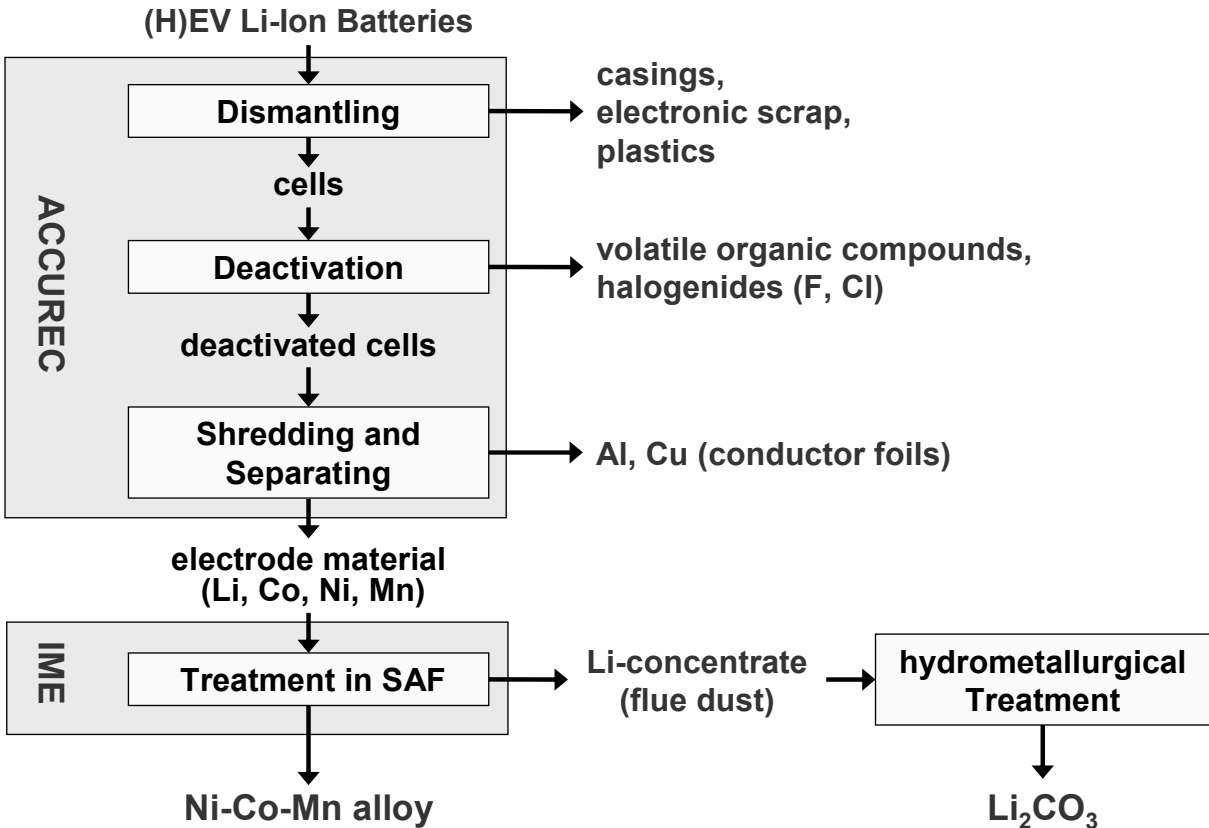

Figure 1:　　　Flow sheet of the IME-ACCUREC Recycling Concept

Pyrometallurgical treatment of EM is facilitated in a submerged (electric) arc furnace (SAF). SAF processes are predestined for battery recycling because of their high flexibility concerning input materials and process parameters, their high productivity by relatively small plant sizes and low offgas emissions. The process can be simply adapted to different input materials by choosing an adequate slag composition. Basically this slag phase controls the chemistry of the process. Depending on the slag's

composition different metals accumulate in the alloy, in the slag phase or in the flue dust (s. Figure 2).

Slag characteristics as basicity, solubility of metals, density, melting point and viscosity at process temperature have to be controlled in order to operate such a process as desired.
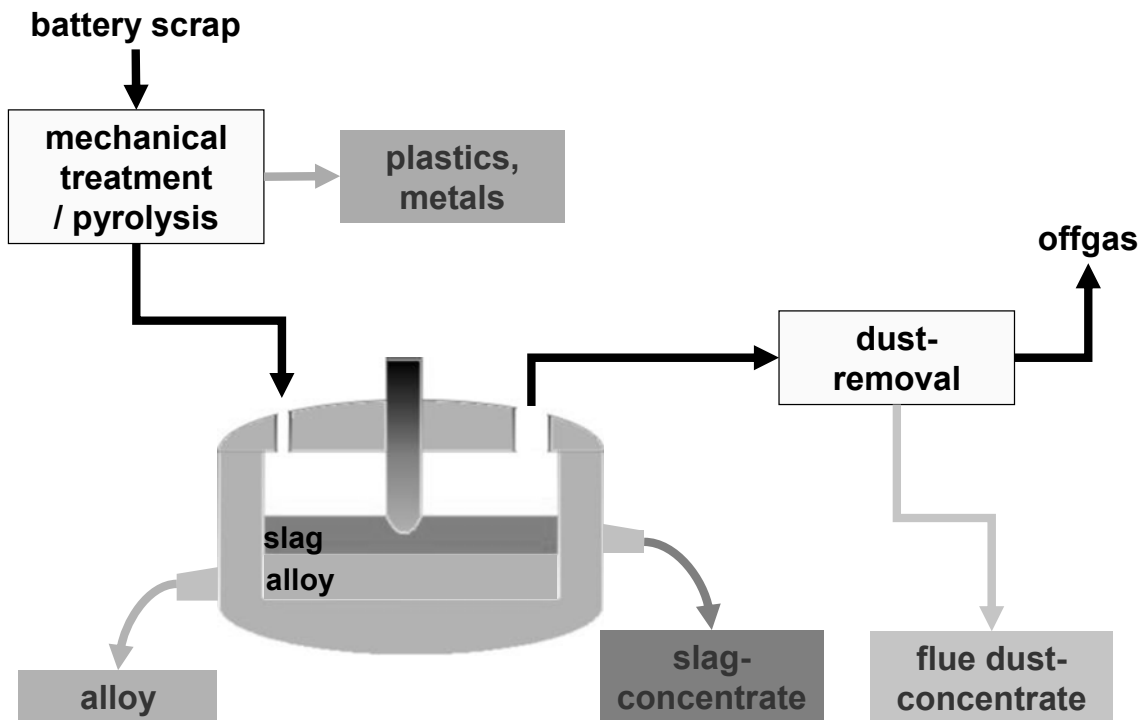

Figure 2: Schematic drawing of the possible output materials for the IME-ACCUREC-Process

2 Slag design

The slag is supposed to chemically separate the metals Co, Ni, Mn from Li contained in EM. Since Li is not stable in the alloy at a process temperature of approx. 1450 °C (Li boiling point at 1342 °C [1]) a separation from the alloy can be easily achieved. At the present state of development Li accumulates equally in the slag and the flue dust. However Li in the flue dust is much easier to extract than Li in the slag. Therefore the target is to design a process in order to concentrate most of the Li in the flue dust. To reach this goal the slag has to follow the characteristics:

- low capacity/solubility for Li-oxide
- low permeability for oxygen to protect the Co-Ni-Mn-alloy from oxidation
- low capacity/solubility for Co, Ni and Mn to reduce metal losses
- liquid at process temperature of approx. 1450 °C
- low viscosity at process temperature for good phase separation
- sufficient difference in density between alloy and slag for good phase separation
- high capacity for impurities e.g. Al, Cu, etc.

2.1 Evaluation of existing slag data

Lithium is mainly processed hydrometallurgically and therefore no literature was found concerning interaction of Li metal and different slag systems. However the two most available oxidic Li ores are petalite ($Li_2O \cdot Al_2O_3 \cdot 8SiO_2$), and spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$), which has a high natural affinity of lithium, alumina and silica [1].

There are several slag systems which are used in Co and Ni metallurgy. Three of them have already shown good performance for Ni-Co-alloys in the past and were thus selected for further investigation in the present case:

The **CaO-SiO$_2$-Al$_2$O$_3$** system is well known and investigated because of its wide use in the iron and steel metallurgy. Ni and Co belong to the iron group and they have similar chemical and physical characteristics to Fe, which is why this slag system is also often used for Co and Ni. In Figure 3 the phase diagram of the system is shown with the high lighted areas marking slag compositions with a melting point below the process temperature of approx.1450 °C.
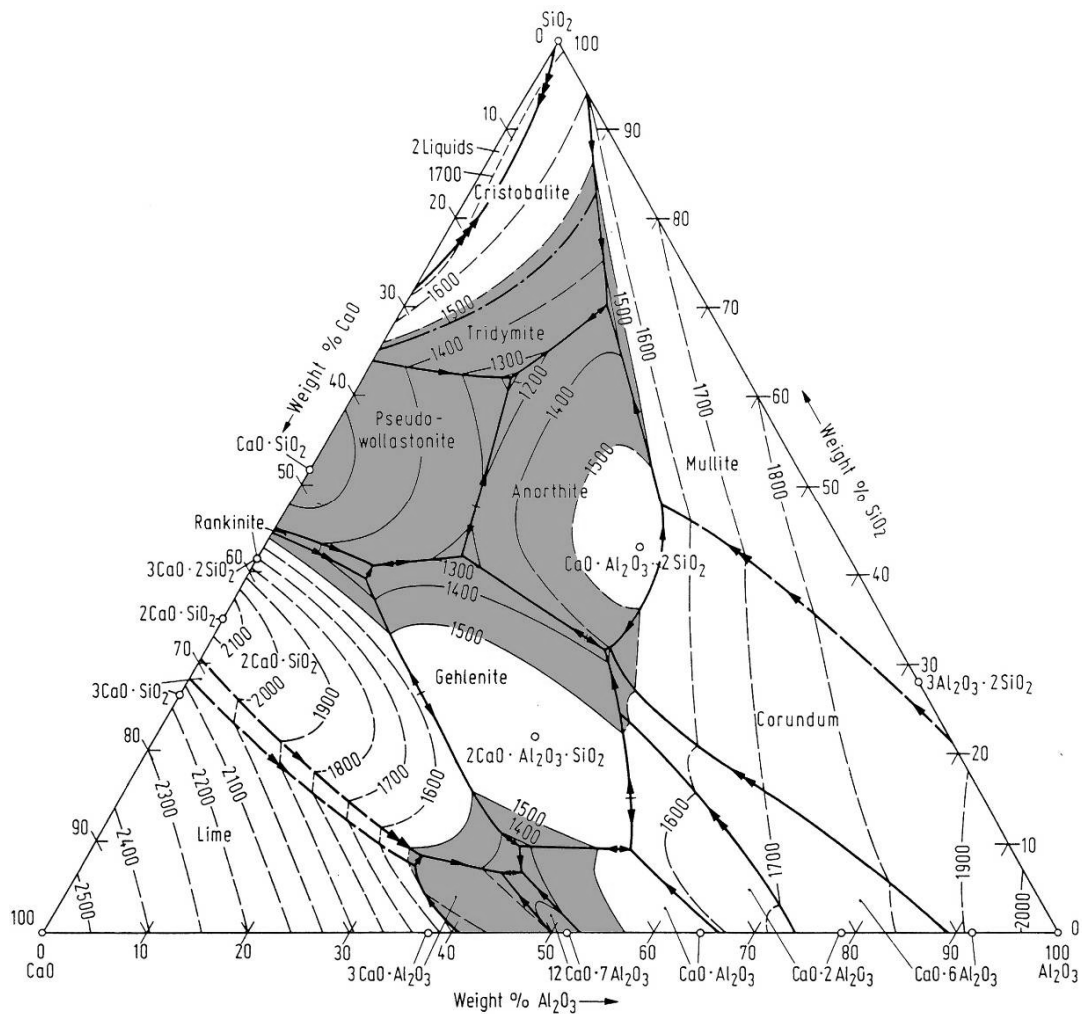

Figure 3: CaO-SiO$_2$-Al$_2$O$_3$ phase diagram with the high lighted areas of slag compositions with a melting point below 1450 °C [3]

The **CaO-CaF₂** system and the **CaO-SiO₂-MgO** system have been successfully test-ed in a comparable recycling process for NiMH batteries with the goal to archive a Ni-Co-alloy [2]. In Figure 3 the phase diagram for the CaO-CaF₂ system is shown. With CaO concentrations rising beyond the eutectic point the melting point of the slag in-creases. According the investigation of Zhamaidin and Chatterjii a melting tempera-ture of 1450 °C is reached by a CaO concentration of 18 %, while according to Mül-ler, there had been also good results in NiMH recycling trials with a CaO content of 35 % at process temperatures of 1600 °C [2], which is backuped by the findings of other authors represented in Figure 4.
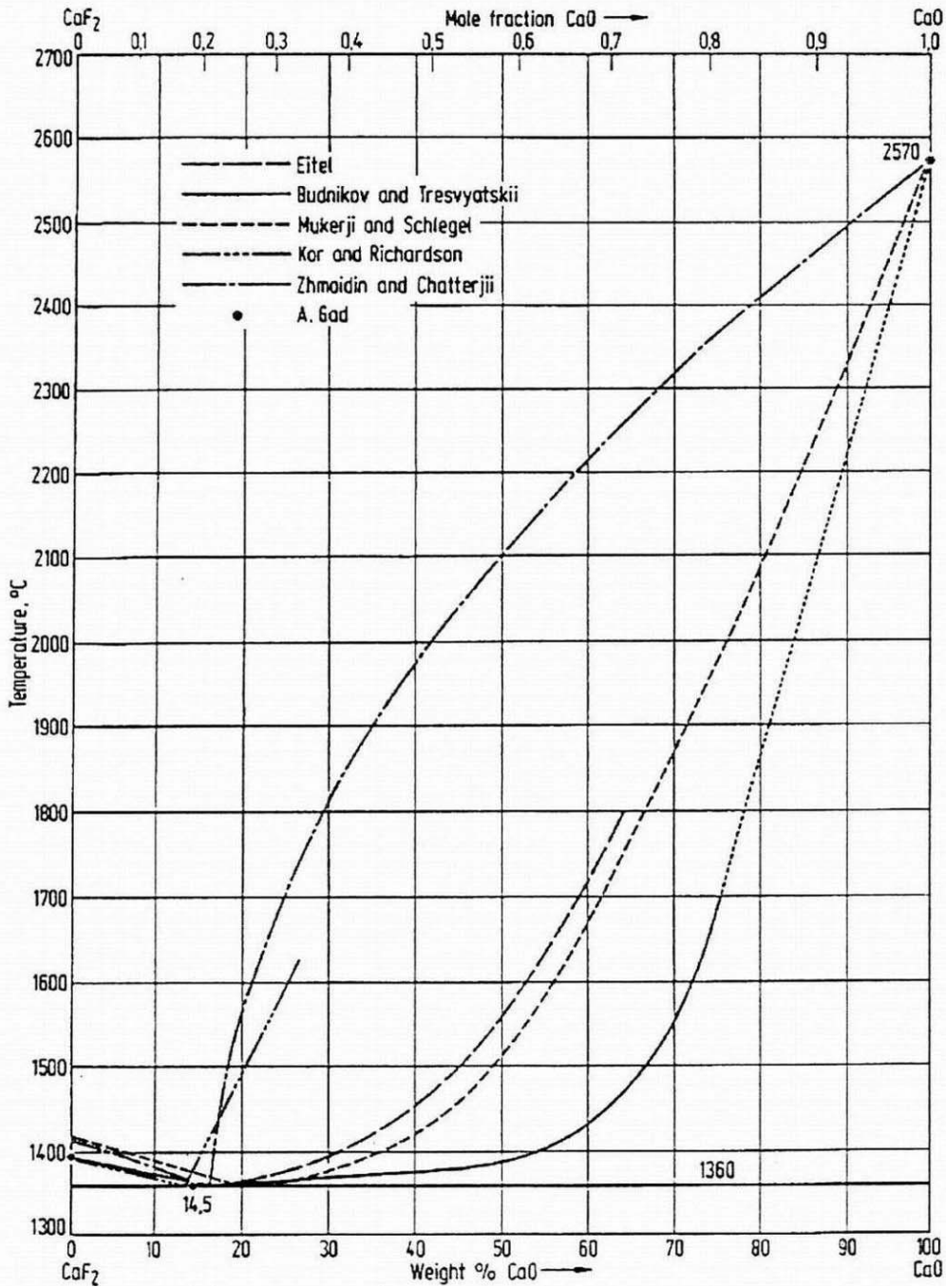

Figure 4:   CaO-CaF₂ phase diagram [3]

In Figure 5 the CaO-SiO₂-MgO phase diagram is shown. The area of slag composi-tions with a melting point below 1450 °C is slightly smaler than the area of the Al₂O₃-

CaO-SiO$_2$ system, but leaves still more room for modifying the slag composition than the CaO-CaF$_2$ system.
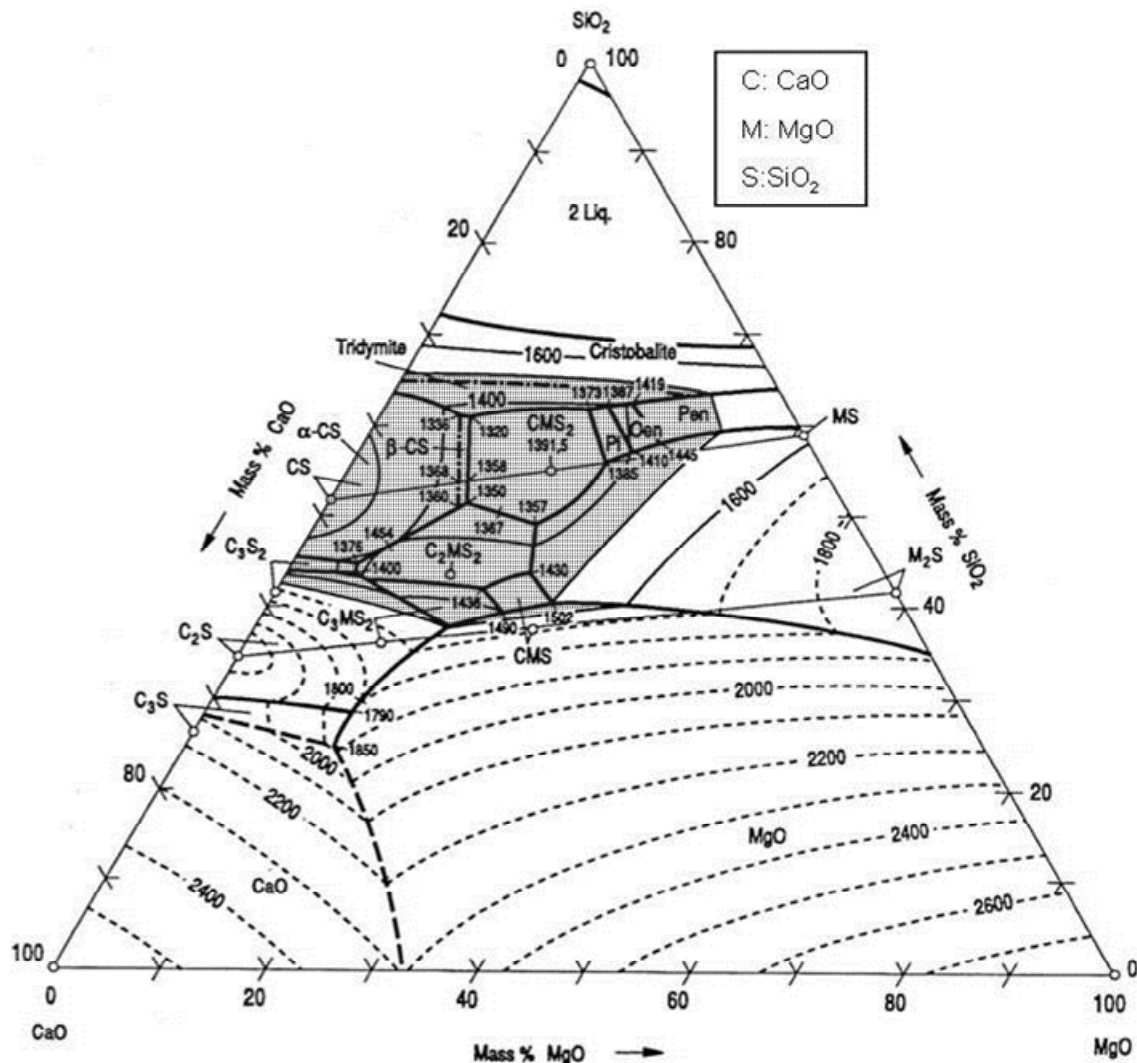

Figure 5: CaO-SiO2-MgO phase diagram with the high lighted areas of slag compositions with a melting point below 1450 °C [3]

2.2 Thermo-chemical modelling

Modelling of a process is the first step into identifying the relevance of the various parameters and is an important tool to reduce the amount of experiments. The goal was to find slag systems, which have a low solubility for Li-oxide and still have a good performance with a Ni-Co-Mn-alloy.

The fact that there is presently a lack of reliable data for the solution of Li and Li-oxides was a big challenge for the calculations. Especially data for solution phases of slags and metals which is needed to calculate e.g. the slags' solubility for Li-oxides does not exist yet. Therefore the determination of the solubility had to be done experimentally.

The calculation step met a huge drawback. This represent by lack of Li and Li-oxides data, particularly the data for mixed phases needed for Li-oxide slag solubility calculation. Therefore the determination of the solubility had to be obtained experimentally.

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Nevertheless thermochemical modelling with the software FactSage^{TM} using the databases FACT53, FToxid and SGSL still has been used to define slag compositions with good performance for Ni-Co-Mn-alloys. Since the above described slag systems Al_2O_3-CaO-SiO_2, CaO-CaF_2 and CaO-SiO_2-MgO are already used for Ni-Co-alloys, they have been chosen as starting point for further investigations with the goal was to find a composition in those systems, with low slagging of Mn and a melting point below 1450 °C. For calculations of the alloy-slag-gas system an idealized composition of 40 wt.% Ni, 40 wt.% Co and 20 wt.% Mn was for the metal phase, along with CO-atmosphere as the gas phase, a slag-alloy-ratio of 1:4 and a temperature of 1450 °C.

In Figure 6 the calculated metal losses for the CaO-CaF_2 system are shown. With higher CaF_2 contents the metal losses are rising. For Co and Ni, the losses with a maximum of 3.93 % for Co and 0.44 % for Ni are in an acceptable range while the slagging of Mn with losses of 47–93 % is unacceptably high.
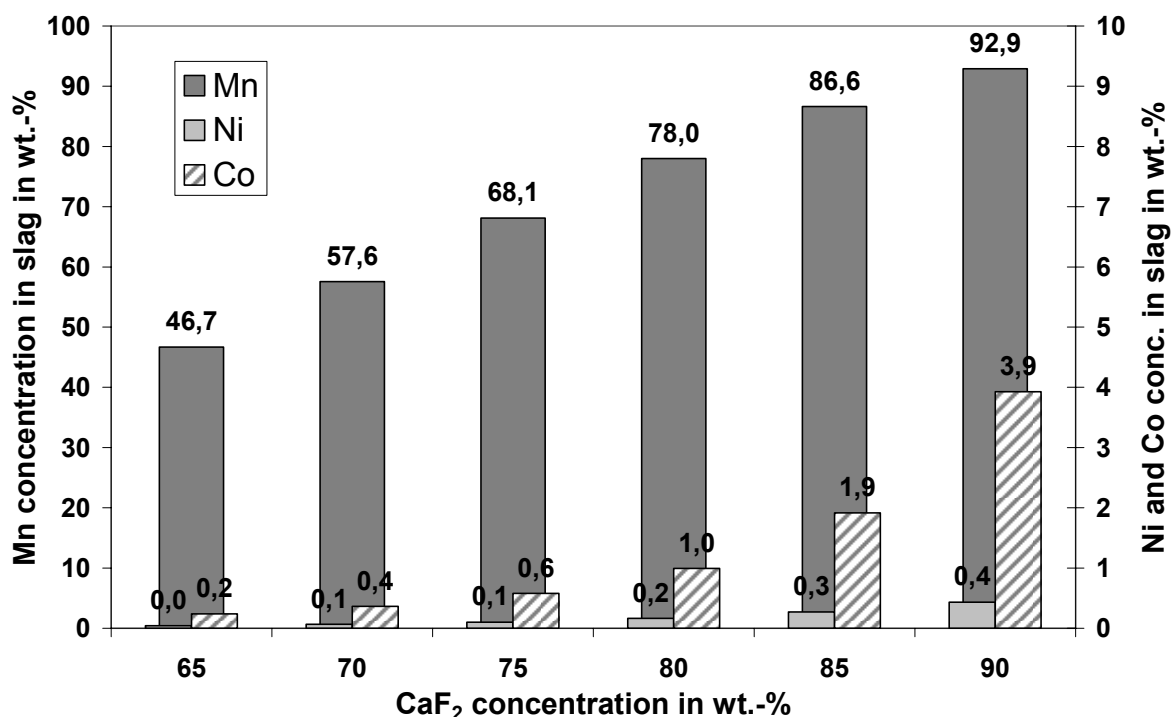

Figure 6: Calculated metal losses for rising CaF_2 concentrations

The considered slag compositions of the CaO-SiO_2-MgO system are listed in Table 1. In Figure 7 the calculated metal losses for each slag composition are shown. According to the equilibrium calculations there are no metal losses for Ni and Co. The slagging of Mn varies between 9 % and 16 % depending on the slag composition.

Table 1:   Slag compositions in wt.% and basicity of the CaO-SiO2-MgO system

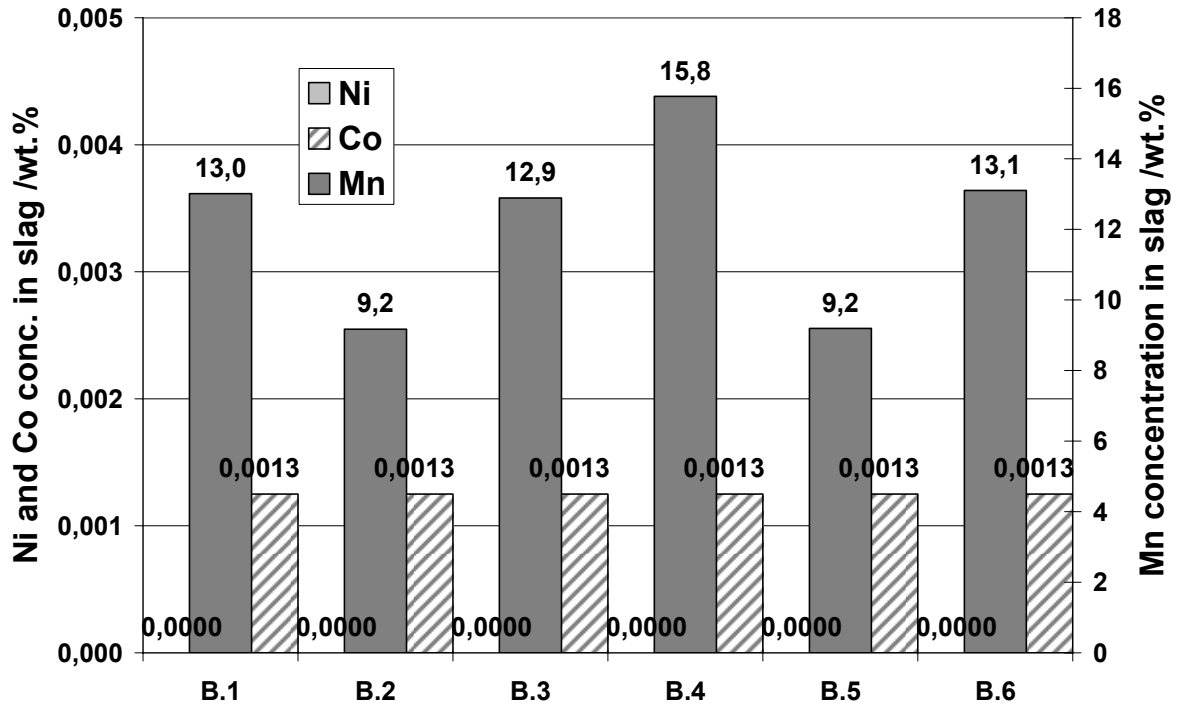| Slag:	B.1	B.2	B.3	B.4	B.5	B.6
CaO	40	45	45	40	40	35
SiO$_2$	45	40	45	50	40	45
MgO	15	15	10	10	20	20

Figure 7:   Calculated metal losses for various slag compositions in the CaO-SiO$_2$-MgO system

In Table 2 and Figure 8 the considered slag compositions in the CaO-SiO$_2$-MgO system with their calculated metal losses are listed. Also with this slag system the Ni and Co losses are almost zero, but Mn losses are expected between 17 % and 29 % and therefore higher than in the CaO-SiO$_2$-MgO system.

Table 2:   Slag compositions in wt.% and basicity of the CaO-SiO$_2$-Al$_2$O$_3$ system

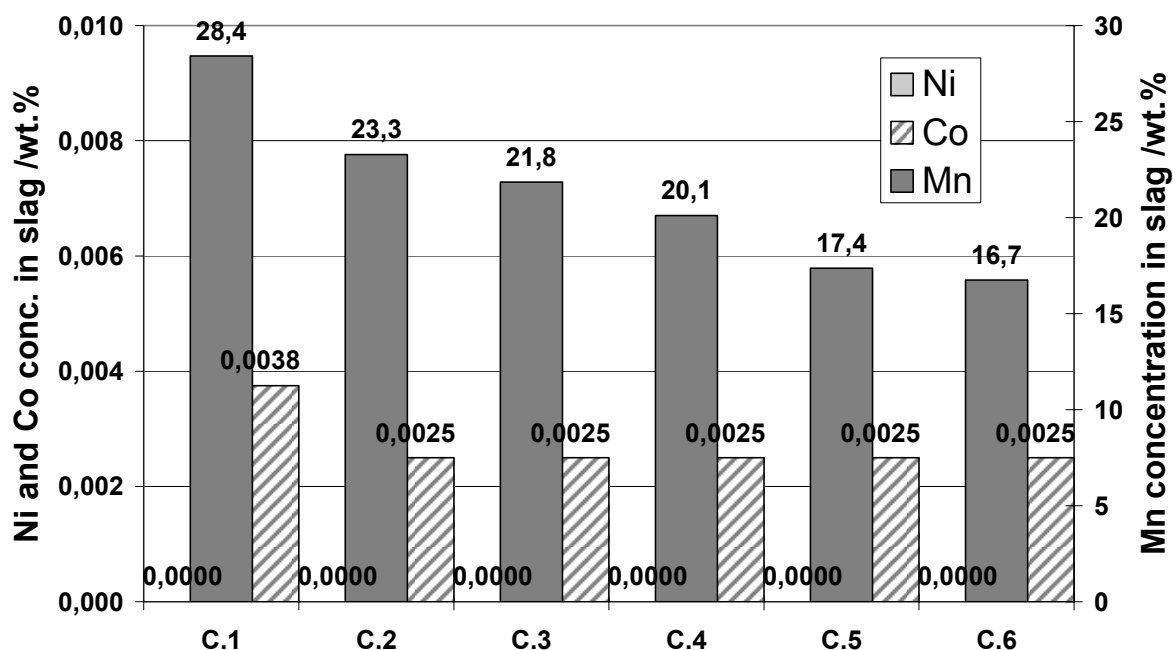| Slag:	C.1	C.2	C.3	C.4	C.5	C.6
CaO	15	25	30	30	40	35
SiO$_2$	70	55	55	45	45	35
Al$_2$O$_3$	15	20	15	25	15	30

Figure 8: Calculated metal losses for various slag compositions in the CaO-SiO$_2$-Al$_2$O$_3$ system

2.3 Li-solubility test

A test method for the determination of the Li-oxide solubility in the observed slags had to be created due to the lack of data a mentioned above. The concept of this solubility test is to heat 80 g of slag composition mixed with varying amounts of Li-oxide in a resistance furnace up to 1450 °C and to homogenize the mixture for 3 hours. Afterwards the slag-Li-oxide mixture is cooled down rapidly in a water quench, in order to freeze the equilibrium state at process temperature. The solidified slag-Li-oxide mixture is then analysed by X-Ray-Diffraction (XRD). The dissolved Li-oxide should not be detectable in the amorphous structure of the slag while crystal-line Li-phase can be detected by XRD and indicates if Li-Oxide was not completely soluble in the slag during melting. The Li-oxide capacity of the slag can be quantified as the difference between the amount of Li-oxide originally added to the mix and the amount of the detected crystalline phase.

Since the results of the previous calculations make high Mn losses with the CaO-CaF$_2$ system probable and since the CaO-CaF$_2$ system is very aggressive to cruci-bles and refractories, it was decided to test only the slag compositions of the CaO-SiO$_2$-MgO and the CaO-SiO$_2$-Al$_2$O$_3$ system for Li solubility. In a first trial all slags have been tested with an addition of 10 wt.% of Li-oxide. Instead of adding the more expensive Li-oxide (Li$_2$O) an equivalent amount of Li-carbonate (Li$_2$CO$_3$) was used, which decomposes at temperatures higher than 600 °C into Li$_2$O and CO$_2$. Since the slag mixture is still solid at that temperature, the produced CO$_2$ is easily discharged and does not further affect the investigation [4].

All slag compositions of the CaO-SiO$_2$-Al$_2$O$_3$ system completely dissolve 10 wt.% of Li$_2$O. This supports the assumption stated in chapter (2.1) that Lithium has a high af-finity to alumina and silica. Therefore no further trials were conducted with the CaO-SiO$_2$-Al$_2$O$_3$ system.

The slag compositions B.1 and B.2 of $CaO-SiO_2-MgO$ system (s. Table 1) were tested positive for Li-compounds. In Figure 9 the 2-theta-diagramm for B.1 with 10 wt.% Li_2O is shown, which has Bragg reflexes for Li_2O as well as for Li-silicate (Li_4SiO_4). In Figure 10 the equivalent 2-theta-diagramm for B.2 with Bragg reflexes for a Li-oxide-silicate-spinel ($Li_2O \cdot 2SiO_2$) is presented. The compositions B.3 - B.6 have all been tested negatively for Li-compounds and have therefore a capacity for Li-oxide higher than 10 wt.%.

In a second trial with 10 wt.% Li_2O the results for B.1 and B.2 could not be reproduced, but in a third and fourth trial with 20 wt.% Li_2O Li-compounds were detected. Therefore the capacity for Li_2O for both slag compositions has to be very close to 10 wt.%, so that minor changes in the procedure effect the formation of Li-compounds. However the capacity is definitely below 20 wt.% Li_2O.
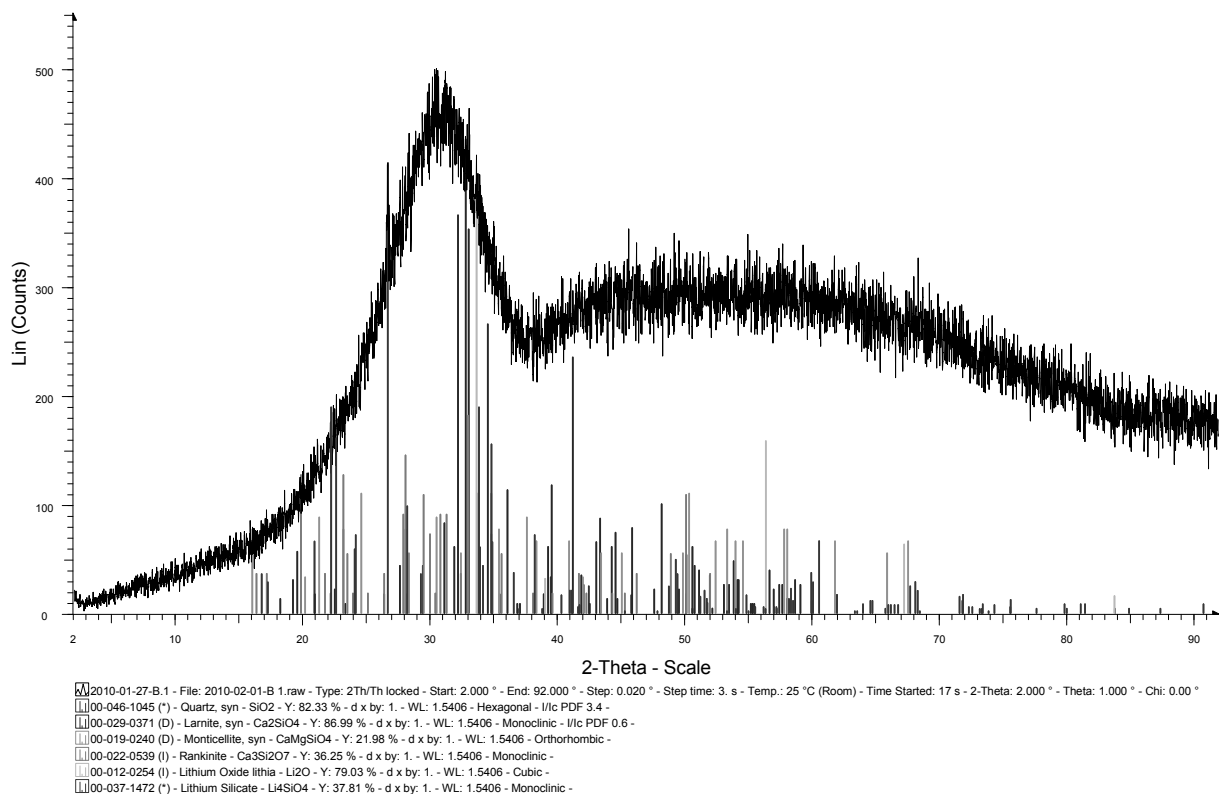

2010-01-27-B.1 - File: 2010-02-01-B 1.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 92.000 ° - Step: 0.020 ° - Step time: 3. s - Temp.: 25 °C (Room) - Time Started: 17 s - 2-Theta: 2.000 ° - Theta: 1.000 ° - Chi: 0.00 °
00-046-1045 (*) - Quartz, syn - SiO2 - Y: 82.33 % - d x by: 1. - WL: 1.5406 - Hexagonal - I/Ic PDF 3.4 -
00-029-0371 (D) - Larnite, syn - Ca2SiO4 - Y: 86.99 % - d x by: 1. - WL: 1.5406 - Monoclinic - I/Ic PDF 0.6 -
00-019-0240 (D) - Monticellite, syn - CaMgSiO4 - Y: 21.98 % - d x by: 1. - WL: 1.5406 - Orthorhombic -
00-022-0539 (I) - Rankinite - Ca3Si2O7 - Y: 36.25 % - d x by: 1. - WL: 1.5406 - Monoclinic -
00-012-0254 (I) - Lithium Oxide lithia - Li2O - Y: 79.03 % - d x by: 1. - WL: 1.5406 - Cubic -
00-037-1472 (*) - Lithium Silicate - Li4SiO4 - Y: 37.81 % - d x by: 1. - WL: 1.5406 - Monoclinic -

Figure 9:   XRD 2-theta-diagramm for the slag composition B.1 with 10 % Li_2O
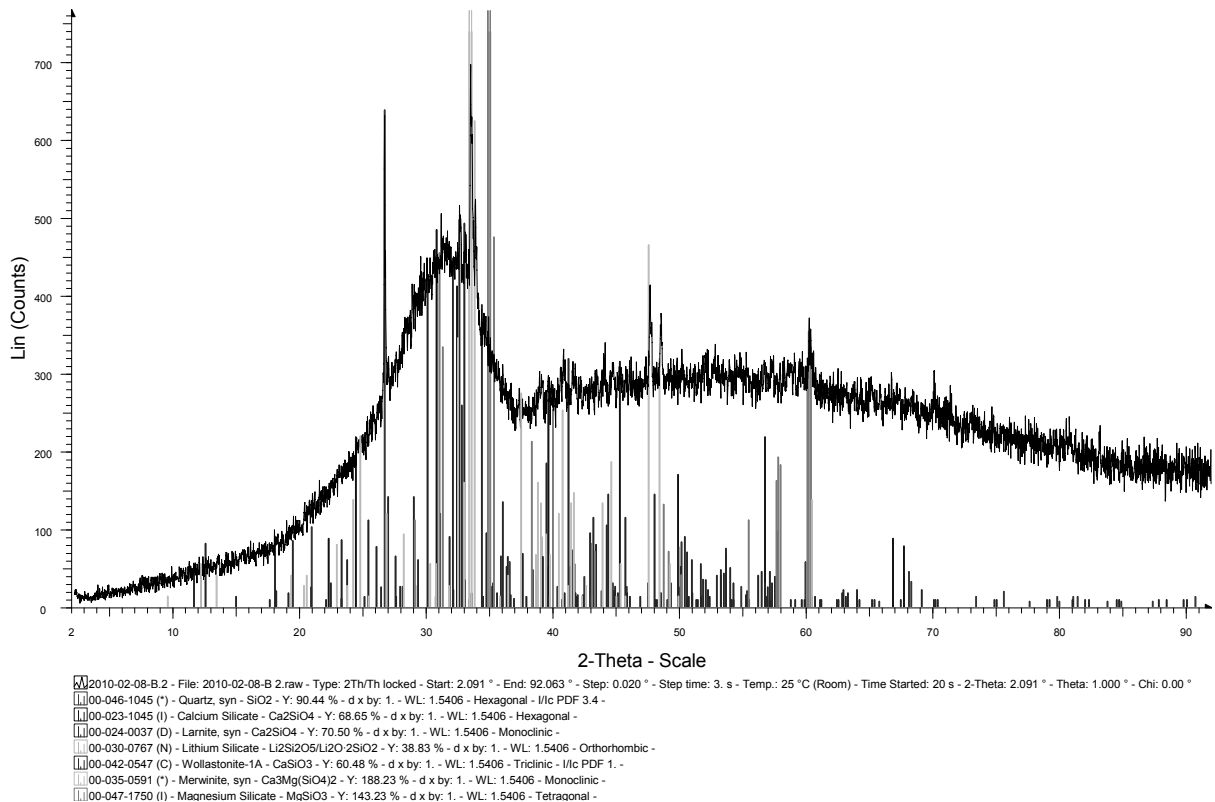
Figure 10: XRD 2-theta-diagramm for the slag composition B.2 with 10 % Li_2O

2.4 Equilibrium trials

The objective of the equilibrium trials is to verify experimentally the calculated results for the slagging of Ni, Co and Mn regarding the slags B.1 and B.2. The trials were conducted in graphite crucibles in a resistance heated furnace at process temperatures of 1450 °C. The crucibles were filled with approx. 350 g of Ni-Co-Mn-alloy and with slag in a ratio of 4:1. The alloy had a composition of 39.65 wt.% Ni, 39.68 wt.% Co and 20.67 wt.% Mn. The crucible was heated up and held at a constant temperature for 3 hours. During that time equilibrium between molten slag and alloy was achieved. Afterwards melt and slag were cooled down in the crucible. The solidified slag and metal were separated, weighed and analysed by X-Ray fluorescence (XRF) and ion-coupled plasma (ICP) spectrometry. For each of the slags B.1 and B.2 three trials were conducted. In Table 3 the analysed Co, Ni and Mn concentrations in slag and alloy are listed. Except for the trial B.1.1 Co and Ni concentration in the slags were measured below 0.1 % and therefore very close to the calculated results. Mn losses for the slag B.1 are approx. 7 % and thus around 1.5 % higher than for slag B.2.

Figure 11 shows a direct comparison of the thermochemical modelling results and the equilibrium trial results for both slags B.1 and B.2 with regard to the calculated and experimentally achieved metal yields. Since the results of the trials were very similar, the standard deviation is very small.

Table 3: Metal concentrations in the alloy and in the slag after the equilibrium trials

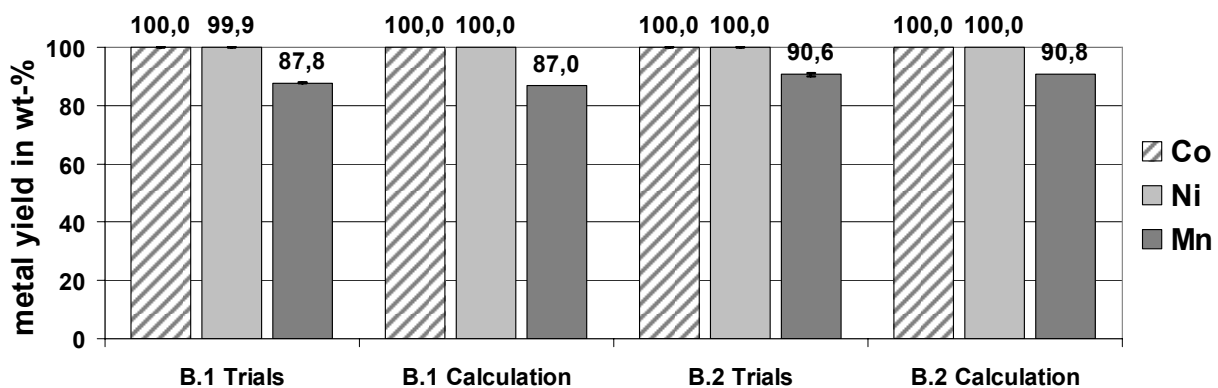| slag | metal concentration in wt.% | | | | | |
| | in alloy | | | in slag | | |
	Co	Ni	Mn	Co	Ni	Mn
B.1.1	37.7	39.3	16.4	0.18	0.21	7.37
B.1.2	37.4	39.1	16.3	0.00	0.06	7.16
B.1.3	37.6	39.0	16.3	0.00	0.00	7.02
B.2.1	36.7	38.5	16.5	0.00	0.00	5.42
B.2.2	37.0	38.6	16.6	0.00	0.06	5.78
B.2.3	36.7	38.4	16.7	0.00	0.06	5.47

Figure 11: Comparison of the calculated and the experimental metal yields for the slags B.1 and B.2.

2.5 Proof of principle in a lab scale EAF

As a proof of principle, the slags B.1 and B.2 have been tested in lab scale trials with the described electrode materials (EM) from Li-ion batteries to show that the slags also have a good performance under process conditions. In a lab scale electric arc furnace (EAF) 3 kg of EM were treated with 1,5 kg of slag under reducing melting conditions. So far metal yields in the first trials with these slags a in the range of approx. 60 wt.% and an accumulation of around 8 wt.% Li_2O in the flue dust was achieved.

3 Summary and Outlook

The IME-ACCUREC Recycling concept drafts a closed loop recycling process for automotive based Li-Ion batteries. Specifically for the pyrometallurgical treatment through and EAF furnace, a slag is needed which protects the Ni-Co-Mn alloy from oxidation and improves the accumulation of the Li in the flue dust at the same time. By literature research the slag systems $CaO-CaF_2$, $CaO-SiO_2-Al_2O_3$ and $CaO-SiO_2$-MgO were selected because of their good general performance for the melting of Ni-Co alloys. By thermochemical modelling several slag compositions for Ni-Co-Mn-alloys were selected. Additionally the Li-oxide solubility was successfully analysed by an innovative experimental method. Thus two slag compositions of the $CaO-SiO_2$-

MgO system were selected for further trials. They have already been tested with electrode materials from Li-ion battery recycling and so far showed promising results. Further trials in a lab scale EAF will be carried out in the following project period. On a long term perspective there will be trials in demonstrator scale with a throughput of several tonnes per day.

4 References

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