# 8TH INTERNATIONAL SLAG VALORISATION SYMPOSIUM

## TACKLING FUTURE CRITICAL CHALLENGES

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# PROCEEDINGS

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# EVALUATION OF Li AND Mn INFLUENCE ON Al-Ca-Si-O SLAG SYSTEM REGARDING PYROMETALLURGICAL LIB TREATMENT

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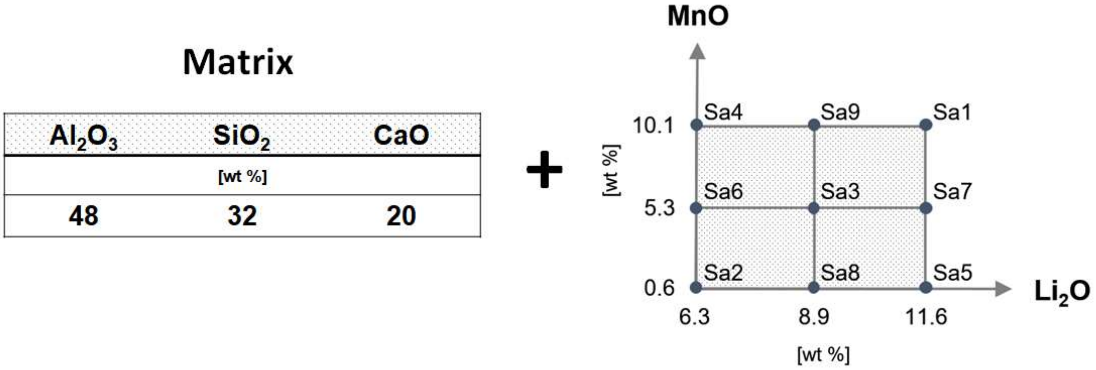
## Introduction

Lithium-ion-battery (LIB) recycling through a combined pyro- and hydrometallurgical route is an appropriate method to process batteries with a wide range of cell chemistries and sizes. Copper, Co and Ni are already recovered on an industrial scale by this process route, whereas Li is not. Lithium, Al and Mn are transferred into Ca- and Si-rich slags during the pyrometallurgical process step[1]. Currently these slags are disposed or sold as construction material[2]. Studies on Mn-free LCO battery slags[3] have already shown that by optimising the chemical composition, Li can be selectively enriched in γ-$LiAlO_2$ crystals and effectively recovered by flotation. However, if the slag contains more than 3 wt% $MnO_2$, Li is distributed among several oxides and silicates that are not suitable for flotation. Building on these findings, the PyroLith project will develop a methodological approach for the recovery of Li from NMC-type LIB via a combined pyro- and hydrometallurgical process route. The results presented here, summarise investigations on the influence of increasing Li and Mn contents on the phase evolution of $Al_2O_3$-$SiO_2$-CaO slags. The knowledge of this relationship allows to deduce suitable process parameters to specifically control the crystallisation of preferred slag phases.

## Materials & Methods

Slag samples of 50 g each were produced with pure (≥ 98 wt%) $Li_2CO_3$, MnO, CaO (Sigma Aldrich), $Al_2O_3$ (Nabalox) and $SiO_2$ (Sibelco IOTA) as starting materials. The samples were sintered using a Nabertherm high-temperature resistance furnace and isostatic graphite crucibles. The slag compositions were varied within the five-component system using design of experiments (DOE). The experimental plan consists of nine samples (Sa1-Sa9), heated up to 1450°C (500°C/h) with a holding time of 45 min under Ar atmosphere and then cooled down at 50°C/h under air atmosphere. The sample matrix of $Al_2O_3$-$SiO_2$-CaO remains at a fixed ratio, while $Li_2O$ and MnO contents are added at three different levels (Figure 1). The mineralogical composition was analysed using a PANalytical X'Pert Pro

MP diffractometer with Co-Kα radiation. For the Rietveld refinement, Profex/BGMN[4] with crystal structure data from the CCDC, COD and AMCSD databases was utilised. To determine the amorphous content an internal standard (20 wt% corundum) was added to each powder sample. Microstructure and spatially resolved chemical analysis were conducted on polished, carbon coated samples embedded in epoxy resin using a FEI MLA 650 F Quanta FEG scanning electron microscope (SEM-MLA) and a JEOL JXA-8530F Hyperprobe electron beam microprobe (EPMA). The mass fractions of $Al_2O_3$, $SiO_2$, CaO and MnO were measured with a wavelength dispersive PANanlytical Axios XRF spectrometer on glass beads. The Li concentration was determined from dilute, acidified, aqueous solutions using a Thermo Fischer iCAP triple quadrupole ICP mass spectrometer. FactSage 8.2 with the FT-Oxide database was used to calculate the equilibrium solidification process through the Calphad method[5].



**Matrix**

| $Al_2O_3$ | $SiO_2$ | CaO |
|---|---|---|
| | [wt %] | |
| 48 | 32 | 20 |

**Figure 1:** Central composite design with Li2O and MnO as experimental factors

## Results & Discussion

Calphad is a suitable methodology for modelling slag solidification of LIB slags[6,7], and is applied herein for solidification simulation of Mn-containing LIB slag systems. The model is initialised with a slag composition corresponding to sample Sa7. The predicted equilibrium solidification process of a slag of this composition shows, that Li-Al spinel ($LiAl_5O_8$-rich spinel solid solution) precipitates first and is followed by γ-$LiAlO_2$ during linear cooling of the liquid slag. Afterwards, the stoichiometric compound $LiAl_5O_8$ and subsequently gehlenite crystallise. Finally, the remaining liquid generates Mn-Al spinel ($MnAl_2O_4$-rich spinel solid solution), eucryptite and glaucochroite during further cooling. A comparison of the initial composition with the measured chemical composition of the solidified slags shows that the measured $Li_2O$ content in all samples is significantly lower than the weighed-in $Li_2O$ content. The recovery rate ranges from 83 wt% to 98 wt%. In accordance with other studies[8], this indicates that parts of the $Li_2O$ are lost at the high production temperatures.

Figure 2 presents the Rietveld quantitative phase analysis of the samples. In addition to variable contents of amorphous components, a total of six Li-containing, three Mn-containing and one Li- and Mn-free crystalline phases from the mineral groups of oxides and silicates were identified and quantified in the examined slags. Gehlenite ($Ca_2Al_2SiO_7$), eucryptite ($\beta$-$LiAlSiO_4$) and $\gamma$-$LiAlO_2$ are present in all samples. $LiAl_5O_8$ or $Li_5AlSi_2O_8$ occur in samples with 0.6 wt% MnO. $(Li,Mn)Al_5O_8$, $Li_2MnSiO_4$, glaucochroite ($CaMnSiO_4$) as well as amorphous components are only found in samples with ≥ 5.3 wt% MnO. The bar chart (Figure 2) illustrates that the amount of $\gamma$-$LiAlO_2$ depends on the added $Li_2O$ content, but not on the MnO content. Most of the main phases in sample Sa7 could be correctly predicted by the thermodynamic model, except for amorphous phases and $Li_2MnSiO_4$. The causes are that amorphous constituents cannot be considered under equilibrium conditions and the thermodynamic properties of $Li_2MnSiO_4$ are missing in the FT-Oxide database.

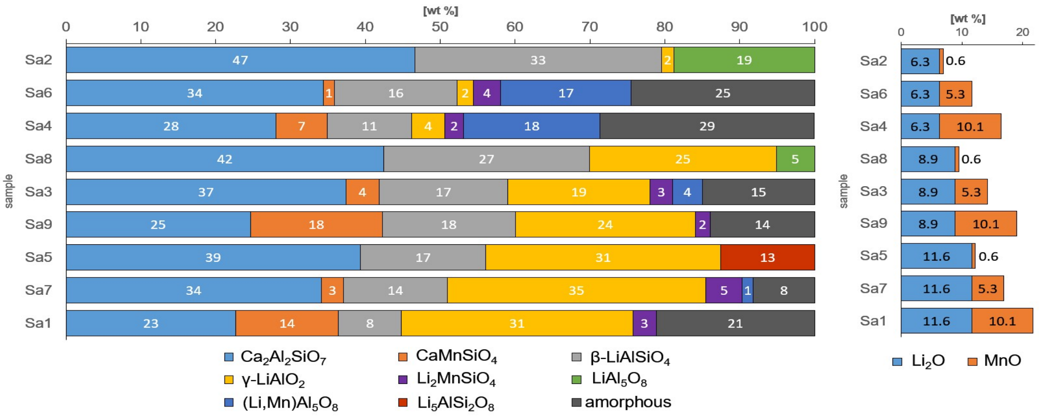


**Figure 2:** Rietveld quantitative phase analysis of the studied samples. The added Li2O and MnO amounts to the samples are given at the right side of the figure

The EPMA results show that the crystalline slag phases are complex solid solutions, partly with defect structures. With rising MnO content in the samples, Mn is incorporated as a foreign element into the crystal structure of Mn-free compounds to an increasing but minor extent. However, most of the Mn is bound to Mn phases and in particular to the amorphous components. Based on their chemical composition, two amorphous phases are distinguished, a nearly CaO-free, probably $Li_2O$-bearing phase and one containing CaO.

SEM-MLA studies reveal that the slags are solidified in a vesicular to compact, fine-grained, holo- to hypo-crystalline, microstructure with a silicate matrix. Euhedral to dendritic crystals up to 900 µm in size are embedded in the matrix[9]. Investigations on the microstructure suggest that the main Mn-bearing phases $Li_2MnSiO_4$ and $CaMnSiO_4$ crystallise after gehlenite and all other Li phases when the melt solidifies. This observation agrees well with the predictions of the thermodynamic model.

The statistical evaluation of the experimental plan confirms the results from the mineralogical investigations. The regression models show that the amount of γ-$LiAlO_2$ depends on the $Li_2O$ content. Increasing Mn contents have only a negligible effect on γ-$LiAlO_2$ crystallisation (Figure 3a), but a strong influence on the amount of the amorphous constituents (Figure 3b).

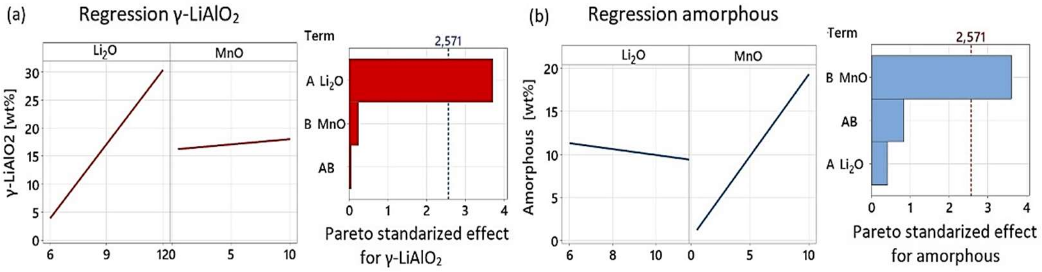


**Figure 3:** Response surface regression of $Li_2O$ & MnO vs. **a)** γ-$LiAlO_2$ **b)** amorphous phases

## Conclusion

In the presented study, the influence of increasing Li and Mn contents on the mineralogy of $Al_2O_3$-$SiO_2$-CaO slags was investigated. The results show that the amount of formed γ-$LiAlO_2$ depends on the specific $Li_2O$ content of the samples. Compared to $Al_2O_3$-$SiO_2$-CaO-MgO-$Li_2O$-$MnO_2$ slags, investigated by Wittkowski et al.[10], the results further show, that increasing MnO contents up to 10 wt% have no effect on γ-$LiAlO_2$ crystallisation. Elevated Mn contents lead to the formation of Mn phases like glaucochroite, partly high contents of Mn-rich and probably Li-containing amorphous phases and, as Elwert et al.[3] already found, to the distribution of Li to additional minor phases like $Li_2MnSiO_4$. Since the $Al_2O_3$ content of the slags is already relatively high, studies on the impact of variable $SiO_2$ and CaO contents on the formation of γ-$LiAlO_2$ are required to further maximise the γ-$LiAlO_2$ content and to suppress the crystallisation of Li-bearing minor phases.

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