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Challenges and approaches on characterisation of LIB recycling slag by ETV-ICP-OES

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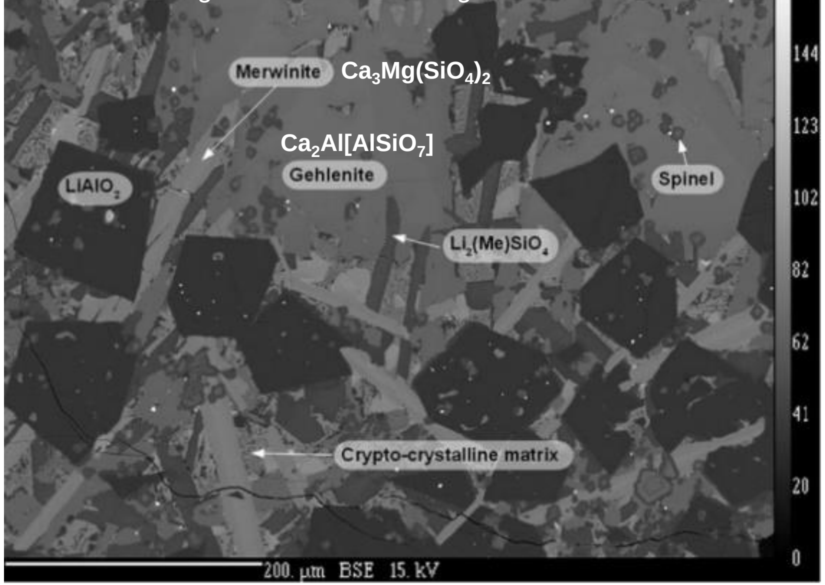
LIB recycling slags

Recycling of end-of-life lithium-ion batteries (LIB) commonly done in a combination of pyro- and hydro-metallurgy.

- Conventional pyrometallurgical processing with 74.26 % of the total Li in the slag
- 25.39 % Li in flue dust (volatile behavior, solubility limit of the slag)
- 0.35 % Li in obtained alloy (ignoble character, insignificant amount)
- Hydrometallurgical processes with 30 % Li loss

SEM / BSE image of "current" real slag



Bulk compositions [wt.-%]	Current	Hi_Mn	Hi_Al
Al_2O_3	33.57	44.52	47.37
SiO_2	21.25	17.52	12.81
CaO	23.46	16.08	23.42
Li_2O	11.04	8.29	8.96
MgO	5.11	1.44	2.65
MnO_2	0.31	9.52	0.36

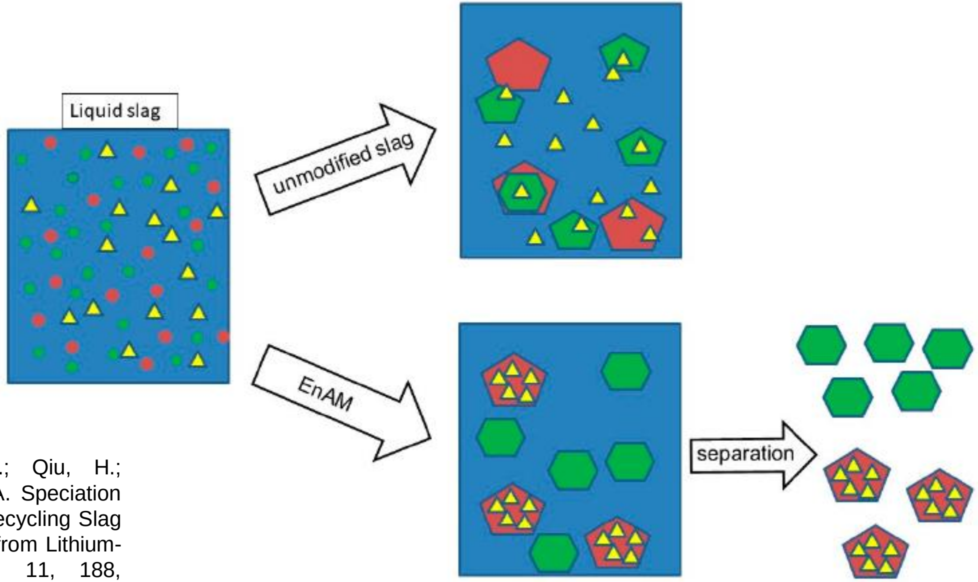
Image & Table from: Elwert, T.; Goldmann, D.; Schirmer, T.; Strauß, K. Phase composition of high lithium slags from the recycling of lithium ion batteries. *World of Metallurgy – Erzmetall* 2012, *65*, 163–171.

Stallmeister, C.; Schwich, L.; Friedrich, B. Early-Stage Li-Removal – Vermeidung von Lithiumverlusten im Zuge der Thermischen und Chemischen Recyclingrouten von Batterien. In *Recycling und Rohstoffe*; Holm, O., Thomé-Kozmiensky, E., Goldmann, D., Friedrich, B., Eds.; TK-Verl.: Neuruppin, 2020; pp 545–557, ISBN 9783944310510.

LIB recycling slags

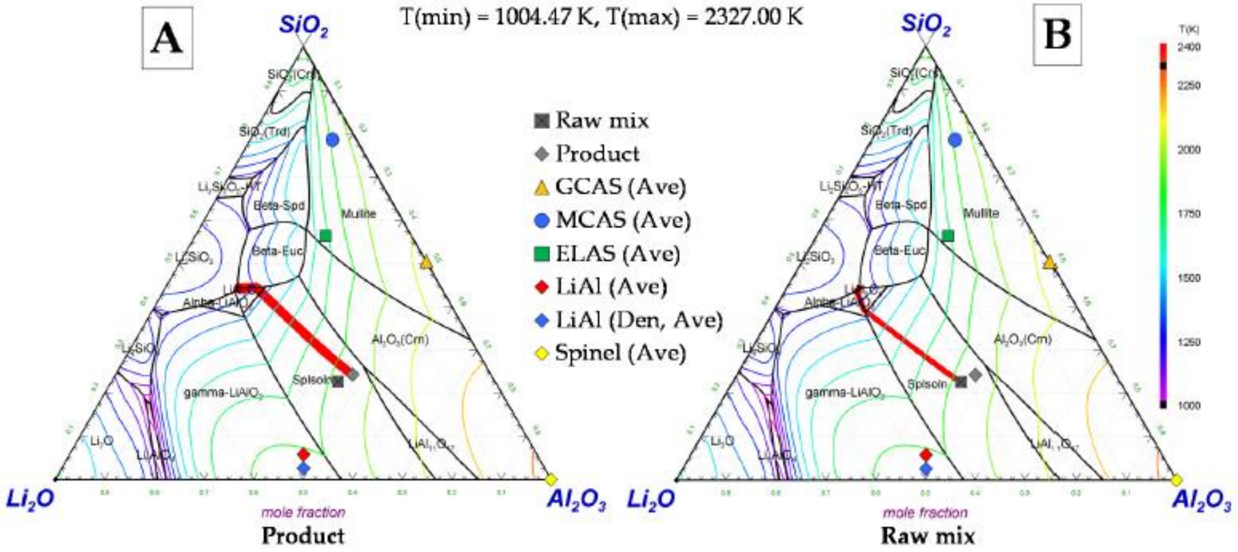
Strategy for higher recovery rates:

- Modification of slag phases forming Engineered Artificial Minerals (EnAM)



Wittkowski, A.; Schirmer, T.; Qiu, H.; Goldmann, D.; Fittschen, U.E.A. Speciation of Manganese in a Synthetic Recycling Slag Relevant for Lithium Recycling from Lithium-Ion Batteries. Metals 2021, 11, 188, doi:10.3390/met11020188.

LIB recycling slags



Calculated Li_2O-Al_2O_3-SiO_2 liquidus projection.

Red line: equilibrium solidification paths starting at the initial point of the "product" (A) and „raw mix" (B).

Schirmer, T.; Qiu, H.; Li, H.; Goldmann, D.; Fischlschweiger, M. Li-Distribution in Compounds of the Li2O-MgO-Al2O3-SiO2-CaO System - A First Survey. Metals 2020, 10, 1633, doi:10.3390/met10121633.

LIB recycling slags

- Artificial slags for research in slag analytics and processing
- Slags in Al_2O_3-CaO-Li_2O-MgO-SiO_2-(MnO) systems
  - formed from the oxides
- Li-behaviour depending the slag composition
  - in Al-rich slags mostly as lithium aluminates
  - less Al and more Si: additional lithium silicates
  - in Mn-rich slags Li-containing spinels / spinel solutions

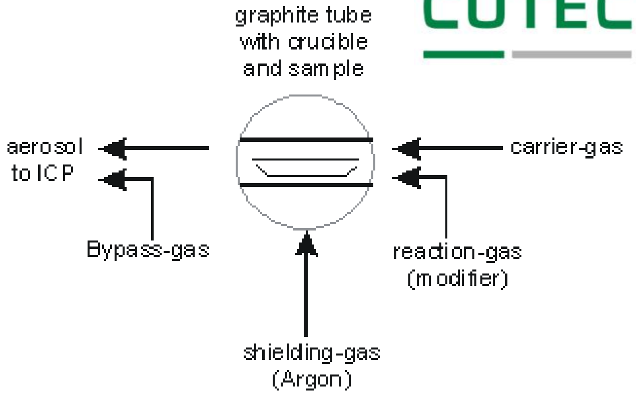
Hi Al

- Al_2O_3 49.76 %
- SiO_2 13.46 %
- CaO 24.58 %
- Li_2O 9.42 %
- MgO 2.79 %

Hi Mn

- Al_2O_3 46.59 %
- SiO_2 18.30 %
- CaO 16.74 %
- Li_2O 8.70 %
- MgO 1.49 %
- MnO 8.10 %

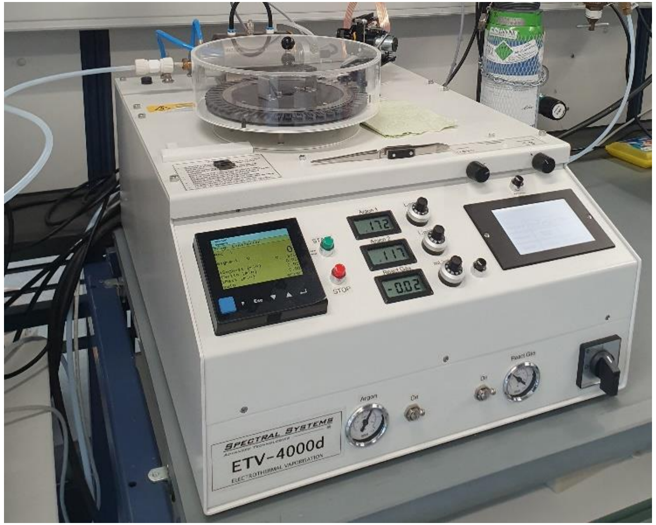
Instrumentation



http://www.spectral-systems.de/prod01-Dateien/Schema%20ETV.gif

ETV: Electrothermal Vaporisation

- ETV 4000d
  with AD-50-III autosampler
  - Spectral Systems



Reaction gas

- Tetrafluoromethane CF_4 (Freon R 14)

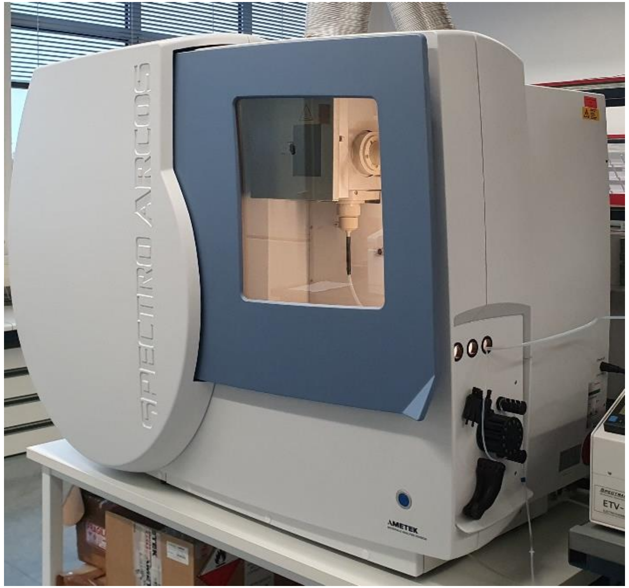
Typical flowrates

- Transport gas Argon 1.8 L/min
- Bypass gas Argon 0.5 L/min
- Reaction gas CF_4 2.5 mL/min

Instrumentation

ICP-OES: inductively coupled plasma optical emission spectroscopy

- Spectro Arcos II MV 130 (FHM 22)
  - Spectro Analytical Instruments

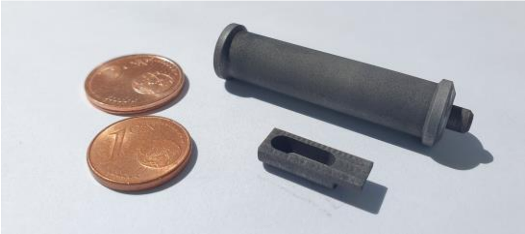


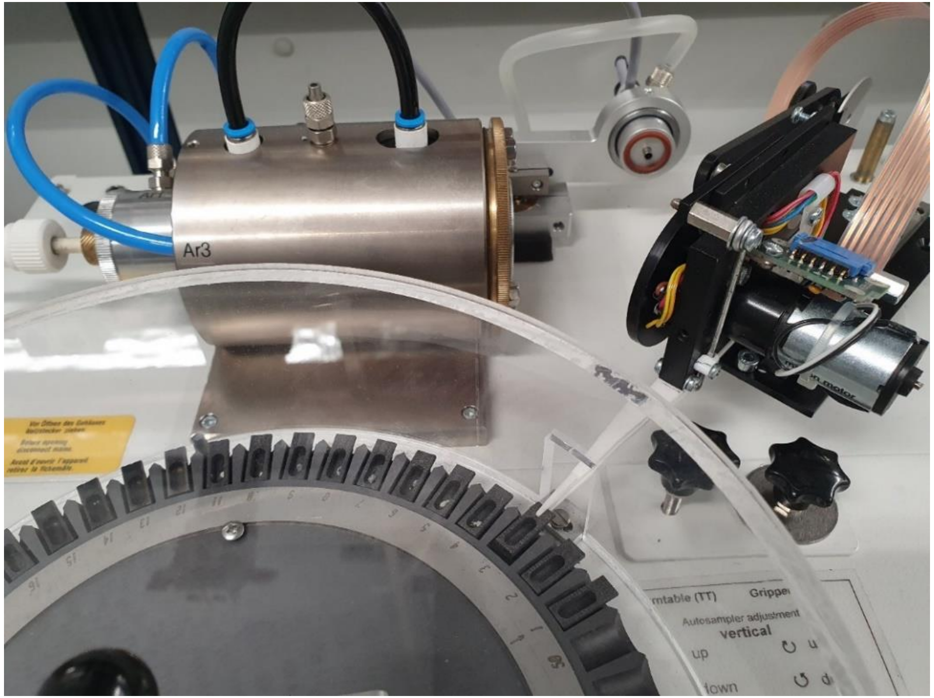
- MultiView: interchangeable radial/axial plasma observation
- detectors in Rowland circle alignment
- wavelength range 130 – 770 nm
- simultaneous spectrum capture

European Union
European Regional Development Fund

Europa für Niedersachsen

Measurements



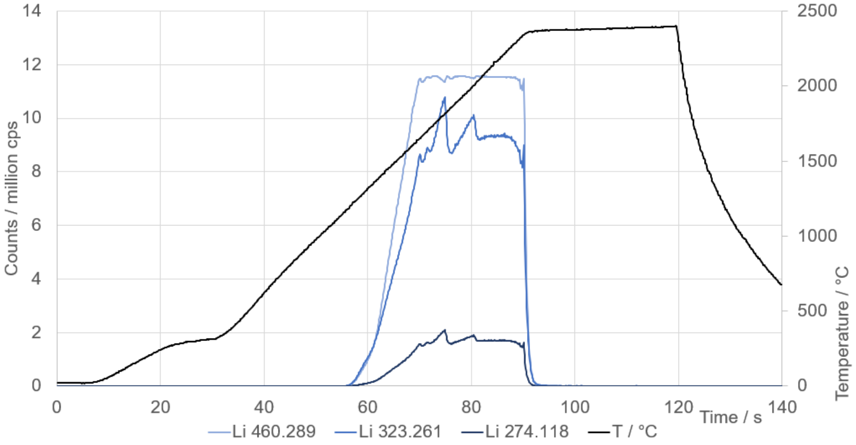


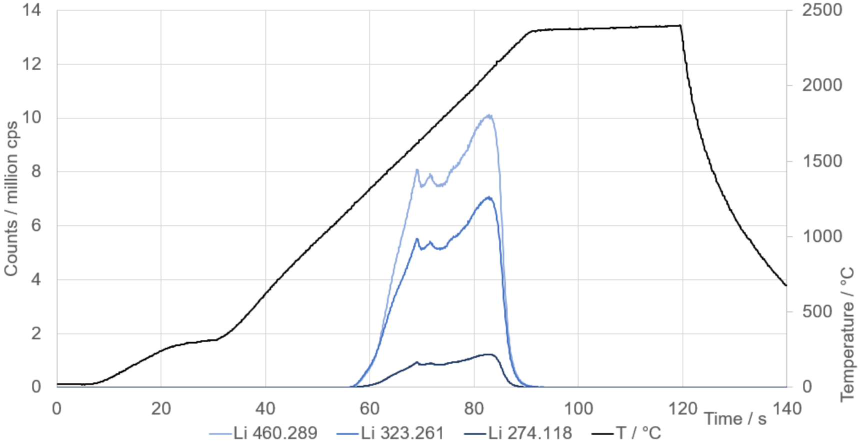
- ETV commonly used for trace element determination
- Challenge in measuring main and matrix elements
  - operating parameters
  - selection of suitable element emission wavelengths
- Interest in elemental release behaviour, foremost of Li and Mn

Measurements

Spill overs and wavelength selection

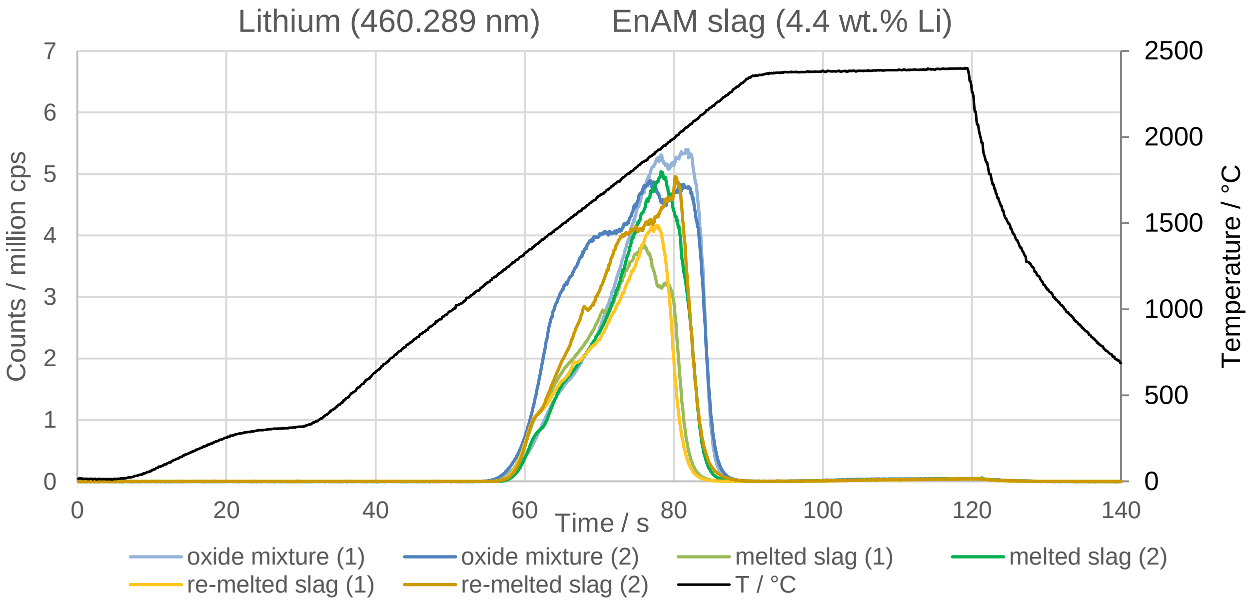
- axial ICP-OES measurement, spill over at 12 million cps
  - 1.0 vs 0.5 mg slag with 6.5 wt.% Li





Measurements

Lithium release behaviour of pre-treated slag



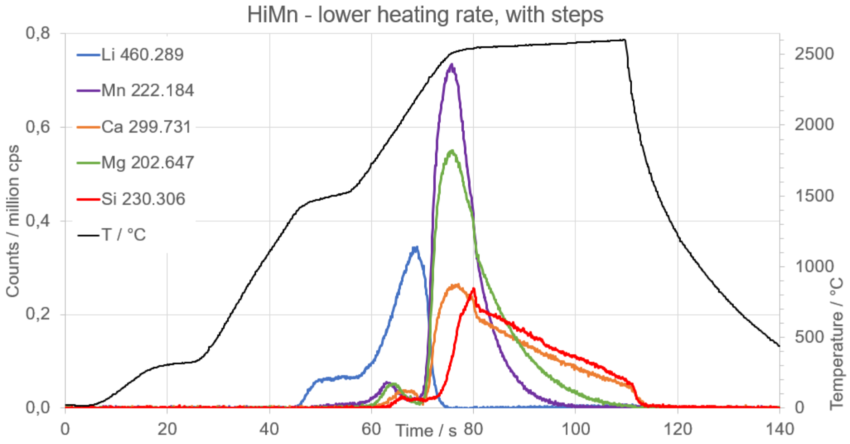
- blue: oxide mixture, untreated
- green: melted slag, via heating microscope, $T_{melt} < 1600$ °C
- gold: re-melted slag, via heating microscope, $T_{melt} < 1600$ °C

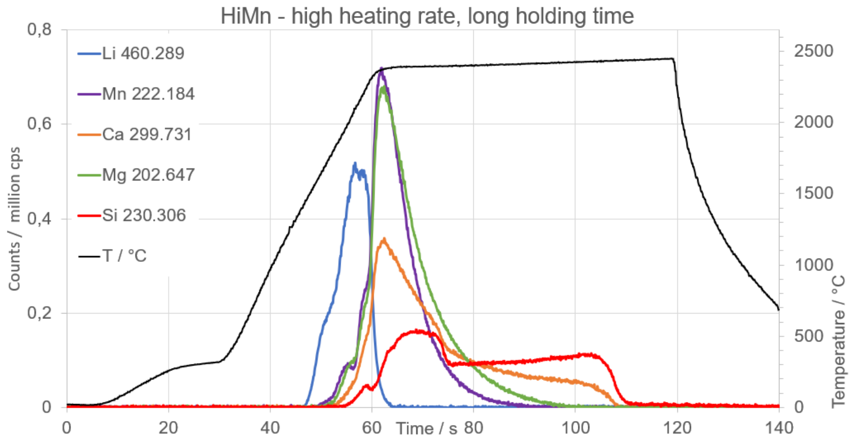
With work from student research internship by Frithjof Mähler.

Measurements

Possible adjustments of ETV temperature profiles:

- Heating rate
  - Lower heating rates show defined and even masked release peaks.
- Holding time
  - Complete elemental release and a possible separation.

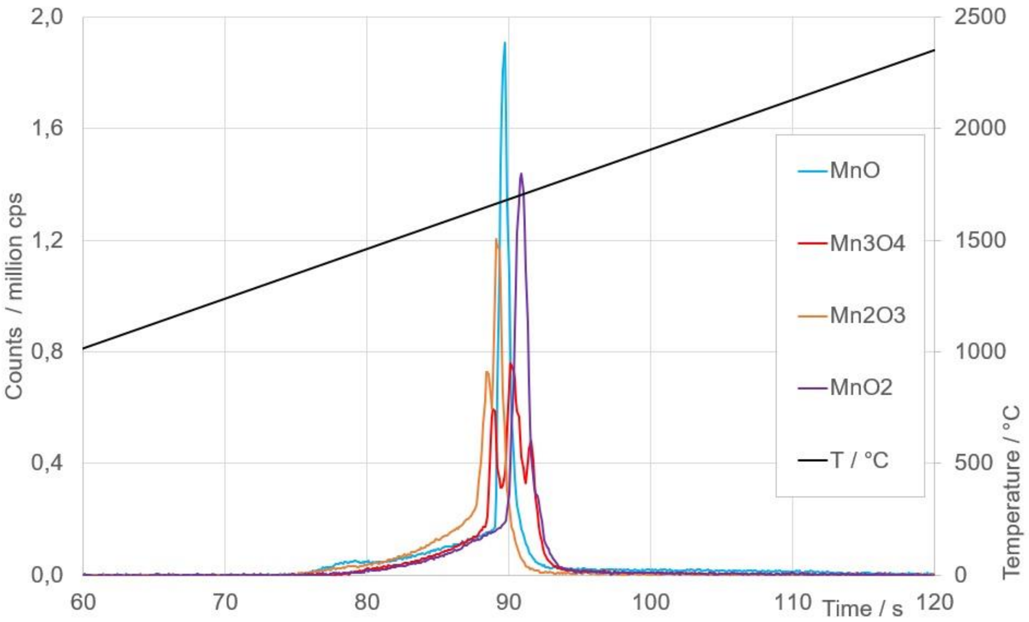




Measurements

Manganese oxides

- with different oxidation states of Mn
- Manganese(II) oxide MnO
- Manganese(II,III) oxide Mn_3O_4
- Manganese(III) oxide Mn_2O_3
- Manganese(IV) oxide MnO_2

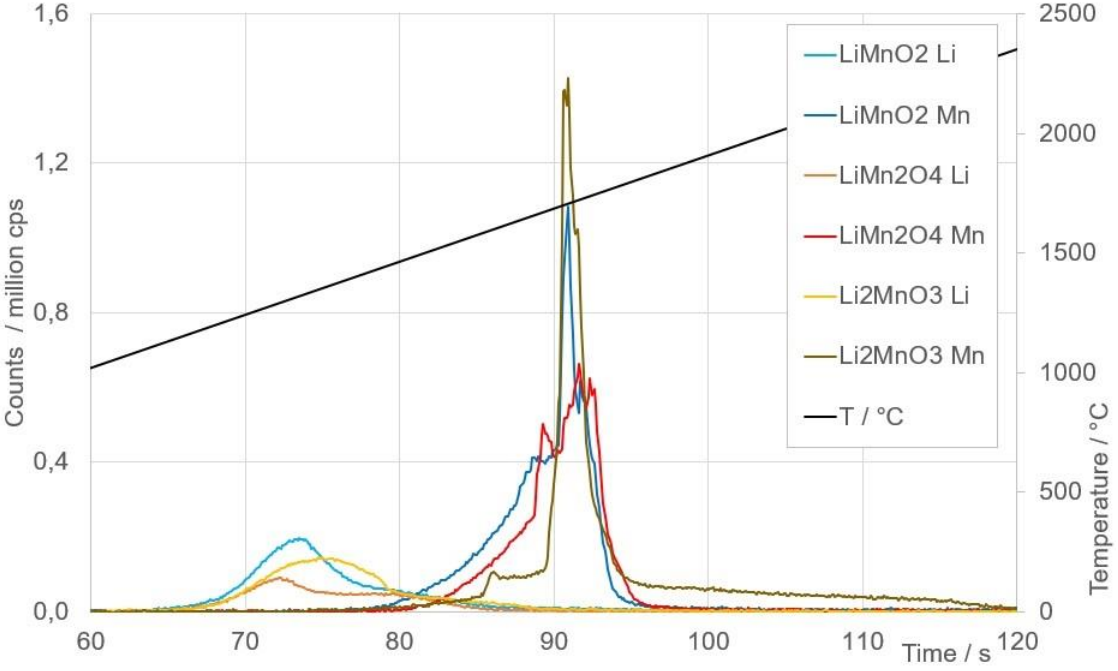


With work from student research internship by Mohsen Bahramiveleshkolaei and Anke Stark.

Measurements

Lithium manganates
/ lithium manganese oxides

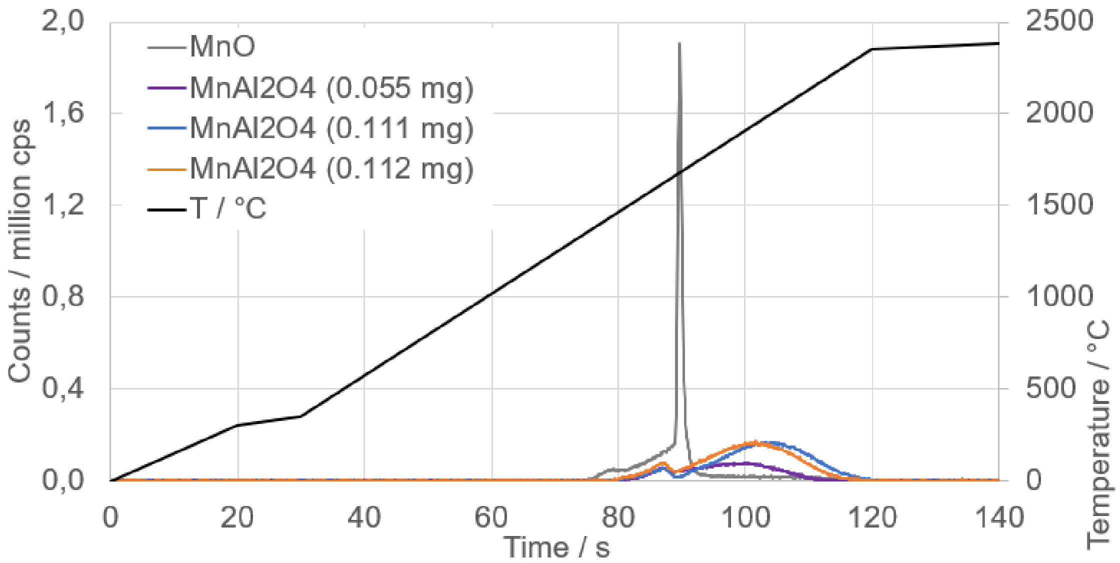
- with different oxidation states of Mn
- Lithium manganese(III) oxide $LiMnO_2$
- Lithium manganese(III,IV) oxide $LiMn_2O_4$
- Lithium manganese(IV) oxide Li_2MnO_3



With work from student research internship
by Mohsen Bahramiveleshkolaei and Anke Stark.

Measurements

- Manganese aluminate $MnAl_2O_4$
- Galaxite / Mn(II) spinel
- Reproducible
  release behaviour of Mn
- Different to Mn(II) oxide



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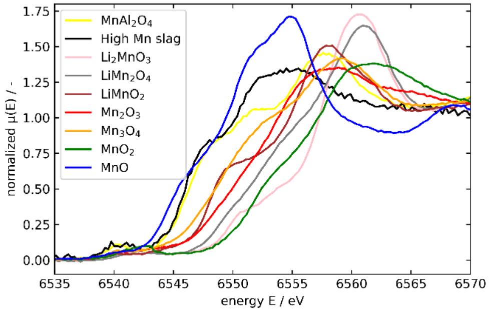
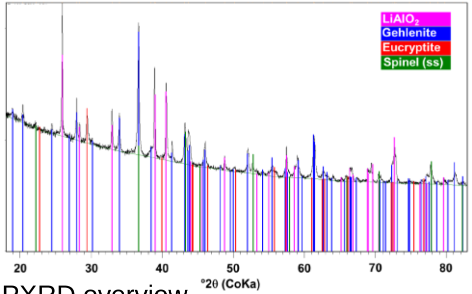
Collaborations on slag materials

Further slag phase analysis assisted by

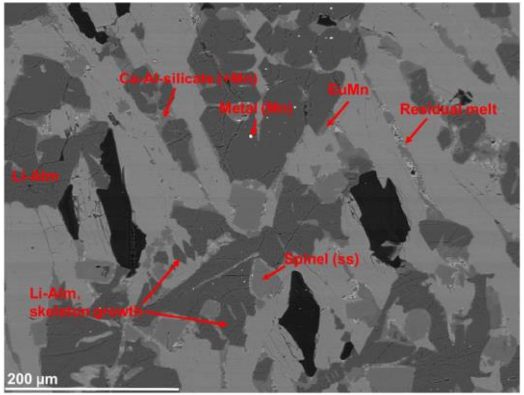
- X-ray absorption near edge spectroscopy (XANES)
  - Sven Hampel,
    Institute of Inorganic and Analytical Chemistry,
    Material Analysis and Functional Solid Matter,
    Clausthal University of Technology
- powder X-ray diffraction (PXRD)
- electron probe microanalysis (EPMA)
  - both: Thomas Schirmer,
    Institute of Disposal Research,
    Department of Mineralogy,
    Geochemistry, Salt Deposits,
    Clausthal University of Technology



XANES spectra of HiMn slag



PXRD overview



electron micrograph (BSE(Z))

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Open for questions

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