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PROMETIA SCIENTIFIC SEMINAR

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Recovering Critical Raw Materials from Batteries through Theory, Laboratory Research, and Pilot Trials

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Critical/Strategic Raw Materials and their roles in batteries

Bauxite	**Coking Coal**	**Lithium**	**Phosphorus**
Antimony	**Feldspar**	Light rare earth elements	Scandium
Arsenic	Fluorspar	Magnesium	Silicon metal
Baryte	Gallium	**Manganese**	Strontium
Beryllium	Germanium	Natural Graphite	Tantalum
Bismuth	Hafnium	Niobium	Titanium metal
Boron/Borate	**Helium**	Platinum group metals	Tungsten
Cobalt	Heavy rare earth elements	Phosphate Rock	Vanadium
		Copper	**Nickel**

- Seven essential elements for batteries
- Li-ion batteries:
  - Li/Ni/Mn/Co for NMC batteries
  - Li/P for LFP batteries;
  - Graphite for anode
  - Cu for current collectors and wiring
- Primary batteries
  - Mn for alkaline and Mn-Zn batteries
  - Li for Li-metal batteries

Mineral extraction and recycling are essential to secure and diversify access to raw materials in the EU

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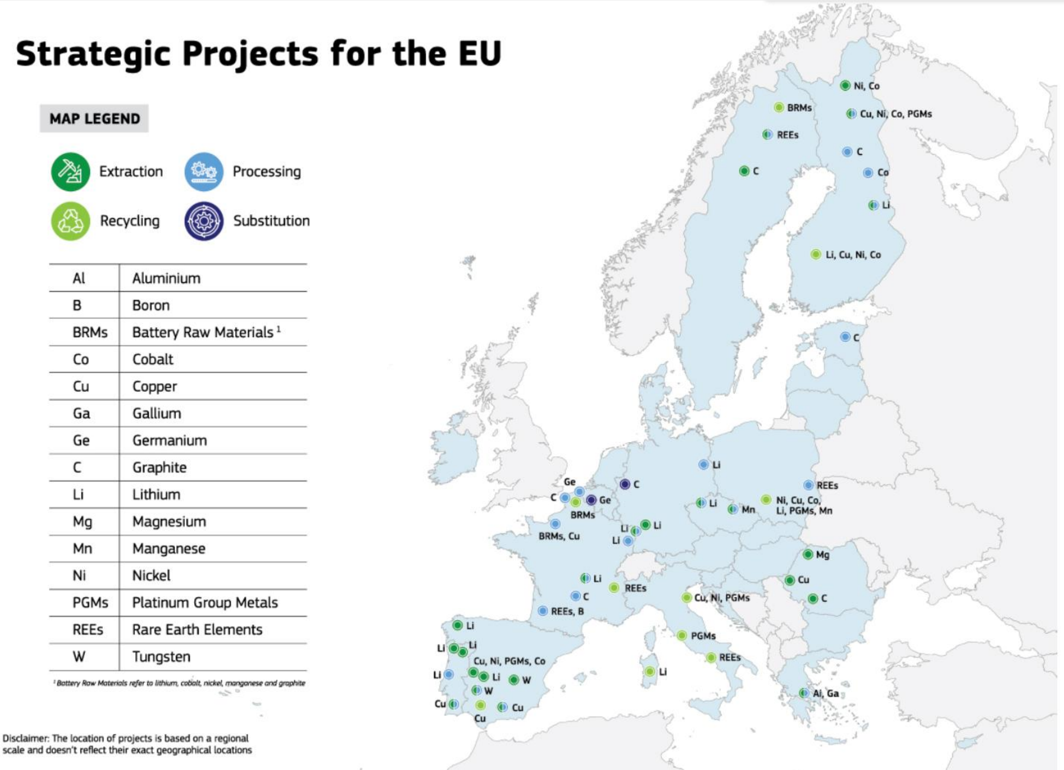
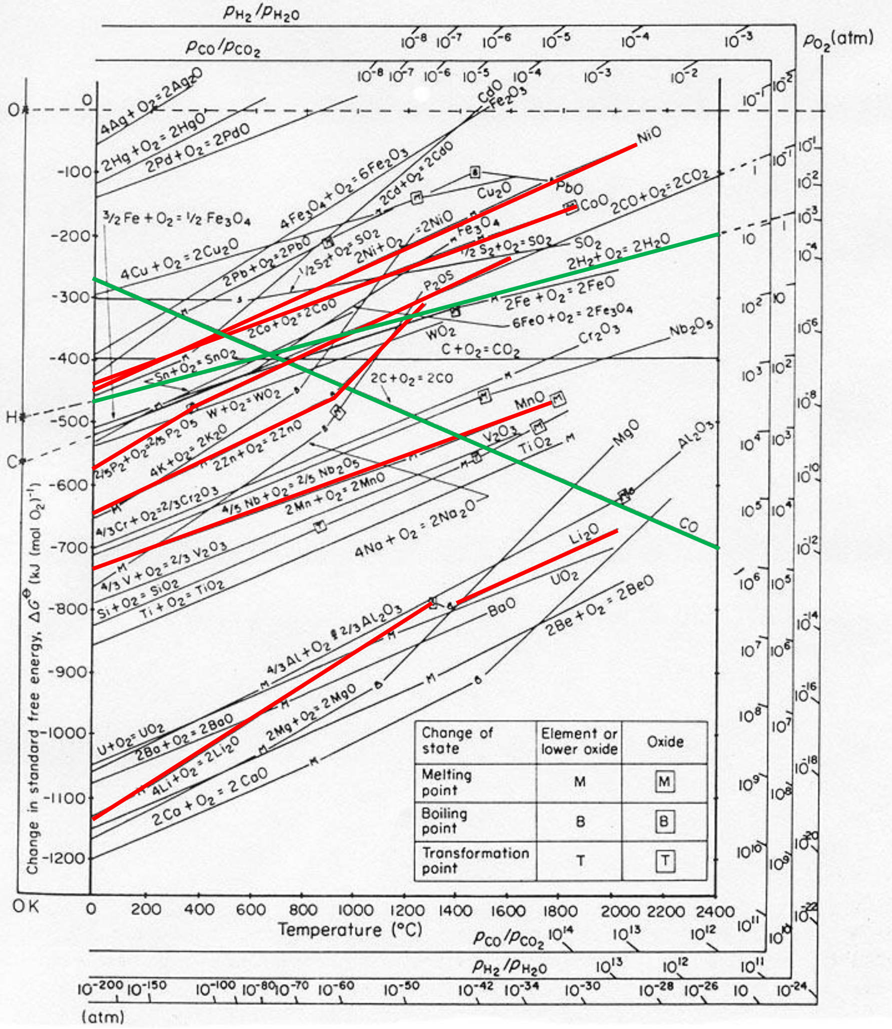


- 47 new Strategic Projects are located across 13 EU Member States
- 5 projects comprising extraction activities, 24 processing, **10 recycling** and 2 substitution of raw materials
- **Li (22 projects), Ni (12 projects), Co (10 projects), Mn (7 projects) and graphite (11 projects)** which will particularly benefit the EU battery raw material value chain.

https://ec.europa.eu/commission/presscorner/detail/en/ip_25_864

Pyro recycling & extraction of CRMs from batteries by reduction- Thermodynamics

- CRMs in batteries mostly exist in the form of oxides
- CRMs can be extracted by carbothermic reduction
- Carbothermic reduction potential
  Ni/Co > P > Zn >... > Mn >...> Li



Separation and possible recovery of high volatile elements/compounds in the flue dust

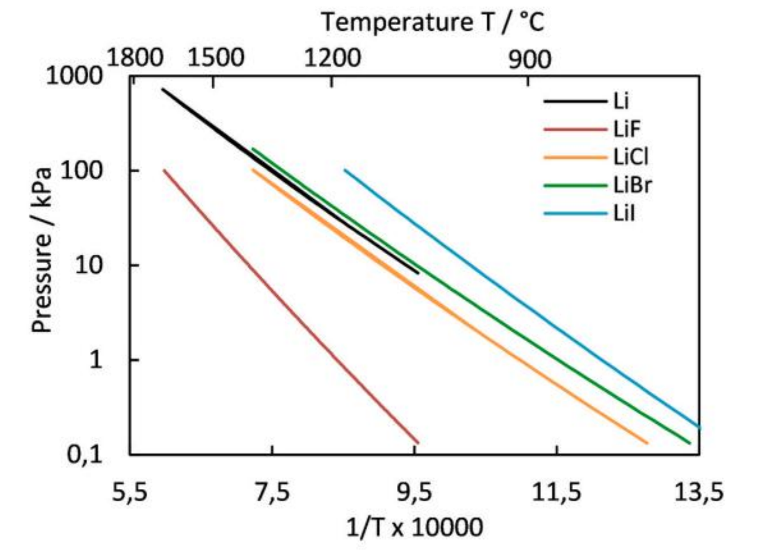
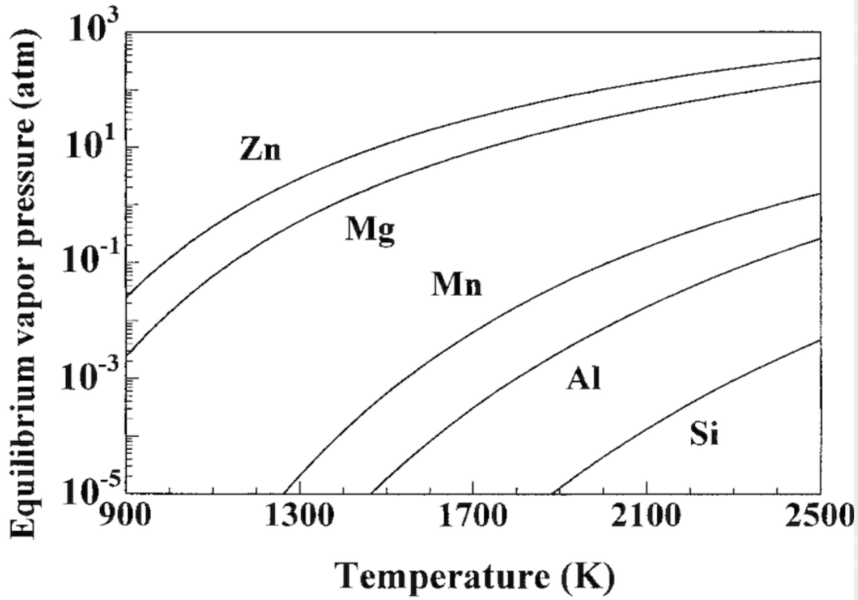


Fig. 1. Vapor pressures of lithium and its associated halides as a function of temperature (in °C). Plots were made by using the data from Ref. [30].



Equilibrium vapor pressure of metals at different temperatures.

Li and its compounds

Zn and Mn

https://doi.org/10.1016/j.jpowsour.2020.228936
https://doi.org/10.1007/s11663-001-0018-6

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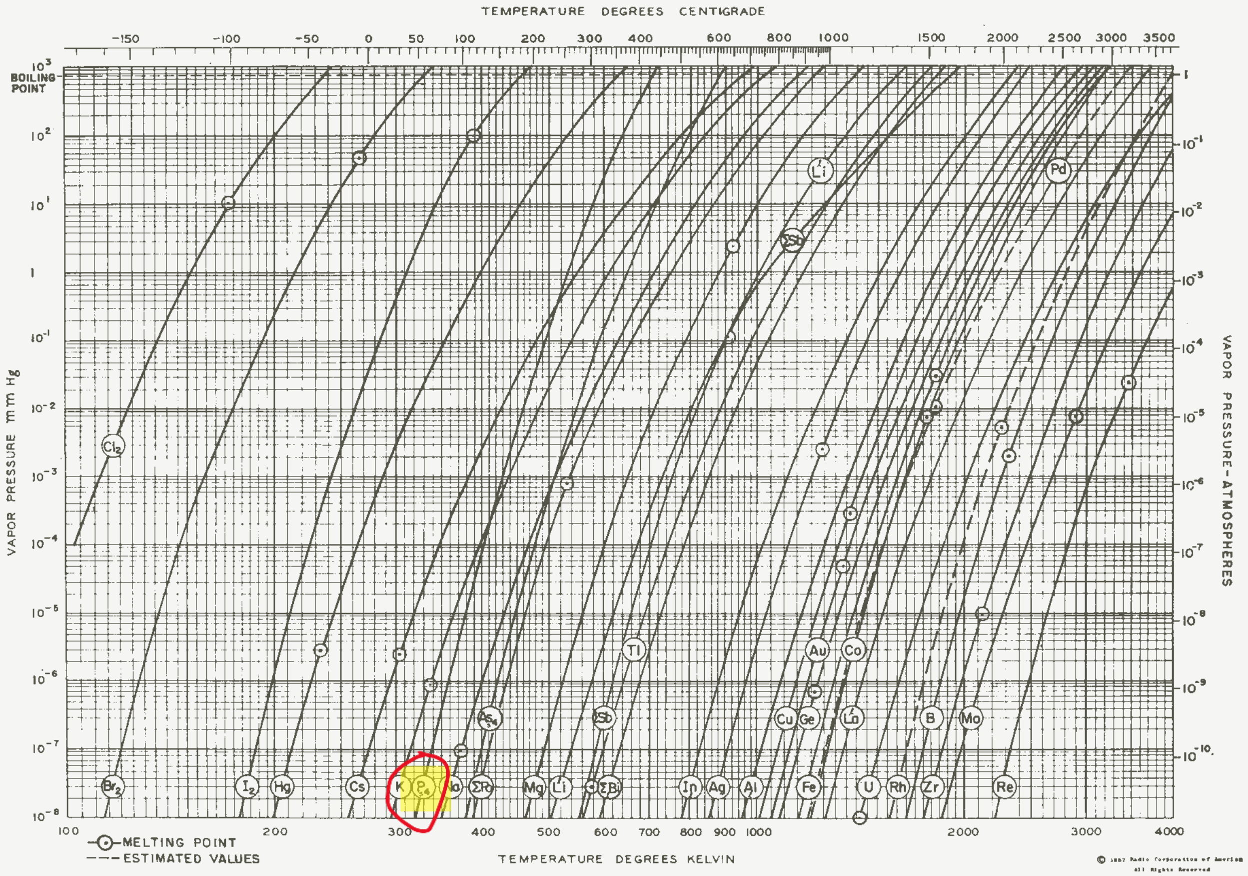
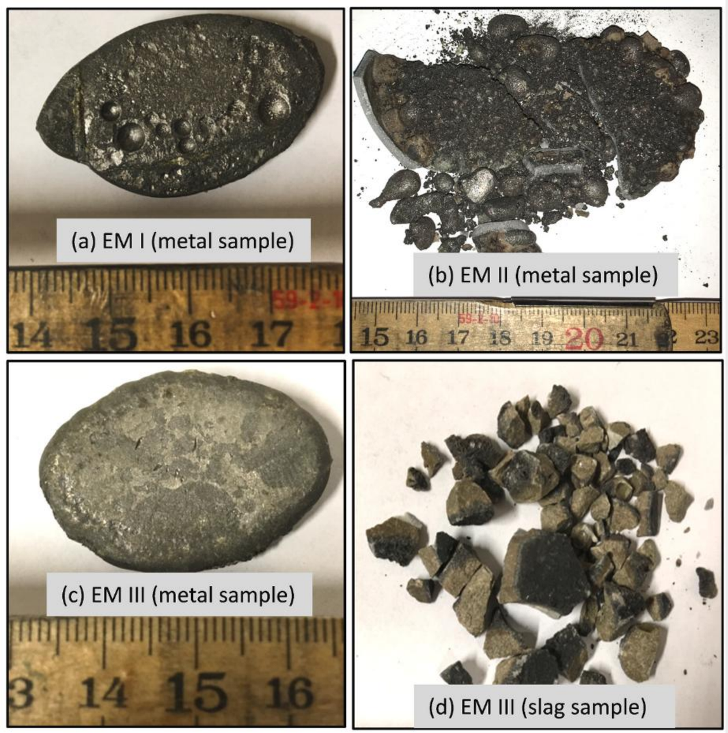


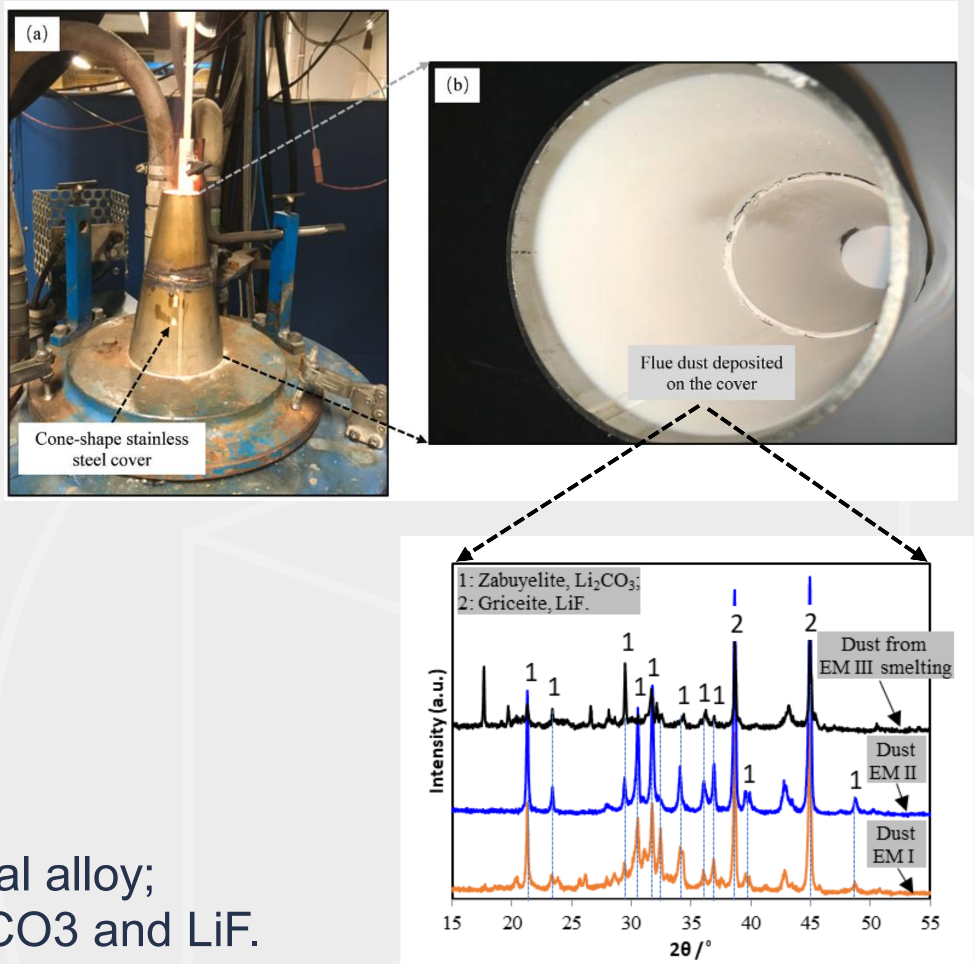
Figure A1(a). Vapor pressure curves for the more common elements. After Honig (Ref. 5:14). (*Courtesy RCA Laboratories.*)

Phosphorus

https://www.powerstream.com/vapor-pressure.htm

Laboratory study

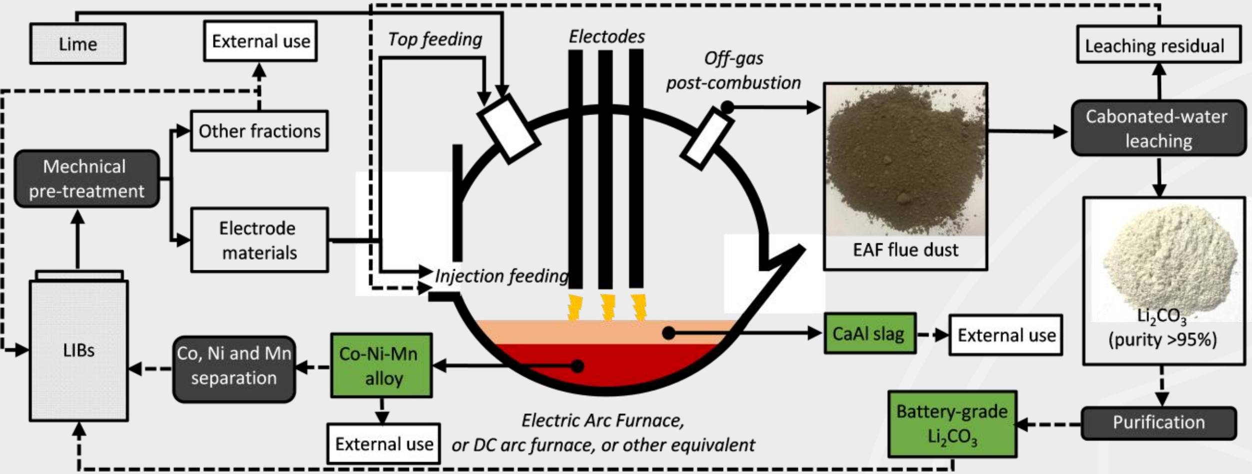




- Recovery of Co, Ni, and Mn as a metal alloy;
- Recovery of Li in the flue dust as Li2CO3 and LiF.

Re-Lion project supported by Energimyndigheten

Pilot testing



- Swerim's Re-Lion process was developed and demonstrated in a 10-ton scale in an electric arc furnace;
- Co, Ni, and Mn (>97%) were recovered as alloys; Li (~70%) was recovered as Li_2CO_3 in the flue dust.

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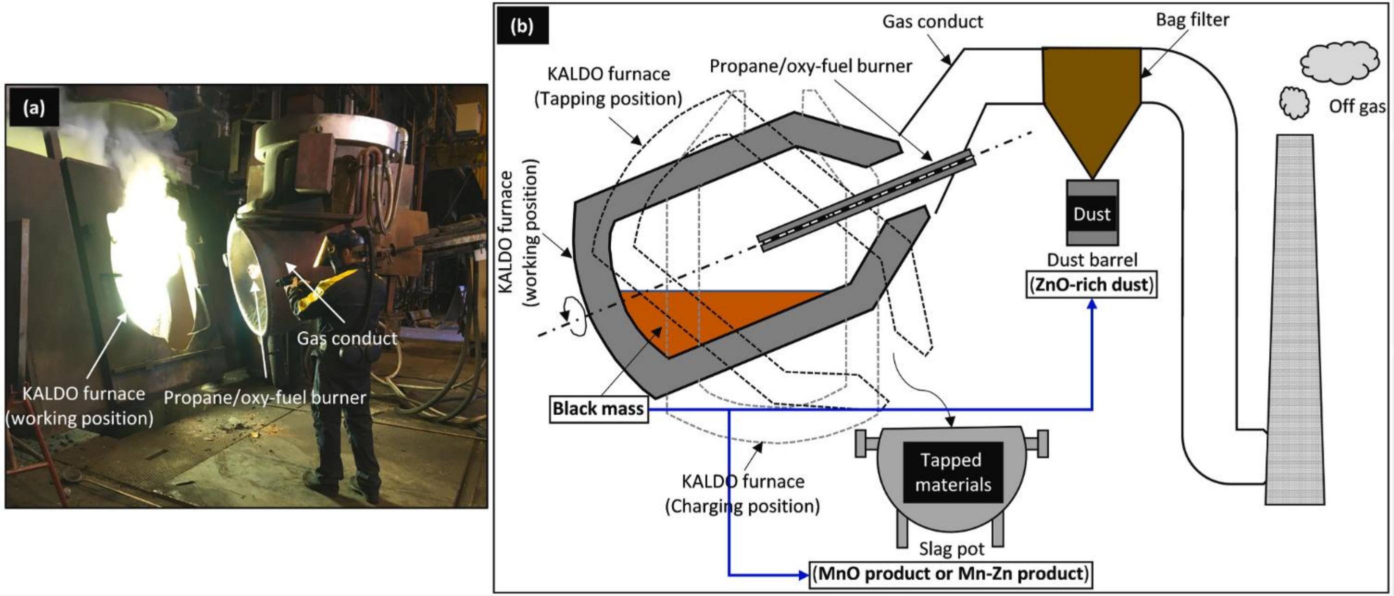
Pyrometallurgical processing of black mass from alkaline and Zn-C batteries in a pilot Kaldo furnace



Kaldo furnace:

- Outer diameter 2 m;
- Effective volume 1 m3;
- Rotation speed 0.1-0.5 r/s.
- Propane/oxy-fuel burner

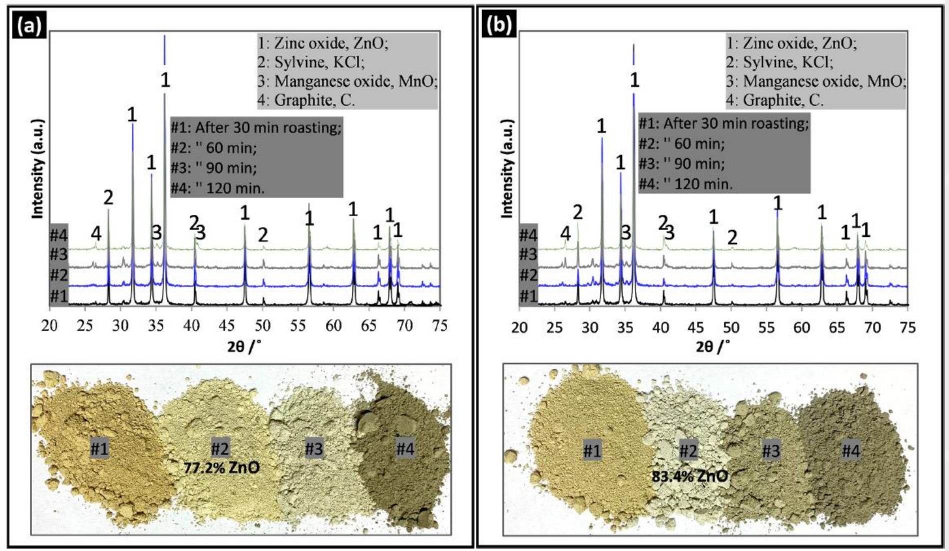
Testing material:

22 tonnes of black mass were tested in a two-week testing campaign.

Ebar project supported by MISTRA
Stiftelsen för miljöstrategisk forskning

Product for Zn metal production

- ZnO up to 85%.
- Cl and F in the ZnO product were removed by soda water leaching.
- The product can be used for Zn metal production.



Chemical composition of the ZnO product (Hg is given in mg/kg)

Trial ID	Zn	Mn	Cl	F	Cd	[a]Hg	Pb	K	Na	[b]Others	[c]ZnO
B1	60	2.1	5.86	0.060	0.078	1.3	0.033	6.50	0.21	Balance	74.7
B2	62	1.3	4.95	0.060	0.052	0.6	0.042	5.70	0.17		77.2
C1	68	2.5	3.40	0.037	0.055	0.8	0.035	3.39	0.34		84.6
C2	67	3.0	2.18	0.042	0.048	0.5	0.026	4.19	0.35		83.4

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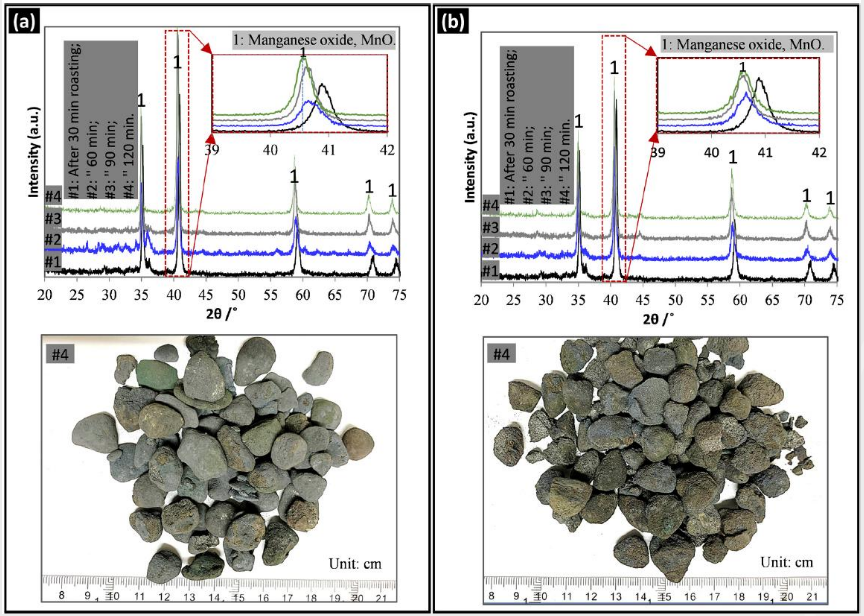
MnO product for ferroalloy production



- MnO up to 92%.
- No phosphorus, no silica, and low iron.
- Low alkali and zinc
- A good candidate material for SiMn production.

Chemical composition of the MnO product

Trial ID	Mn	C	Fe	F	K	Na	Zn	[a]Others	[b]MnO
B1	59	5.20	3.39	0.002	0.44	0.15	0.02	Balance	76.2
B2	71	1.83	3.89	0.002	0.14	0.14	0.03		91.7
C1	60	5.43	5.30	<0.002	0.95	0.22	1.95		77.5
C2	63	3.94	5.10	<0.002	0.92	0.17	0.30		81.3

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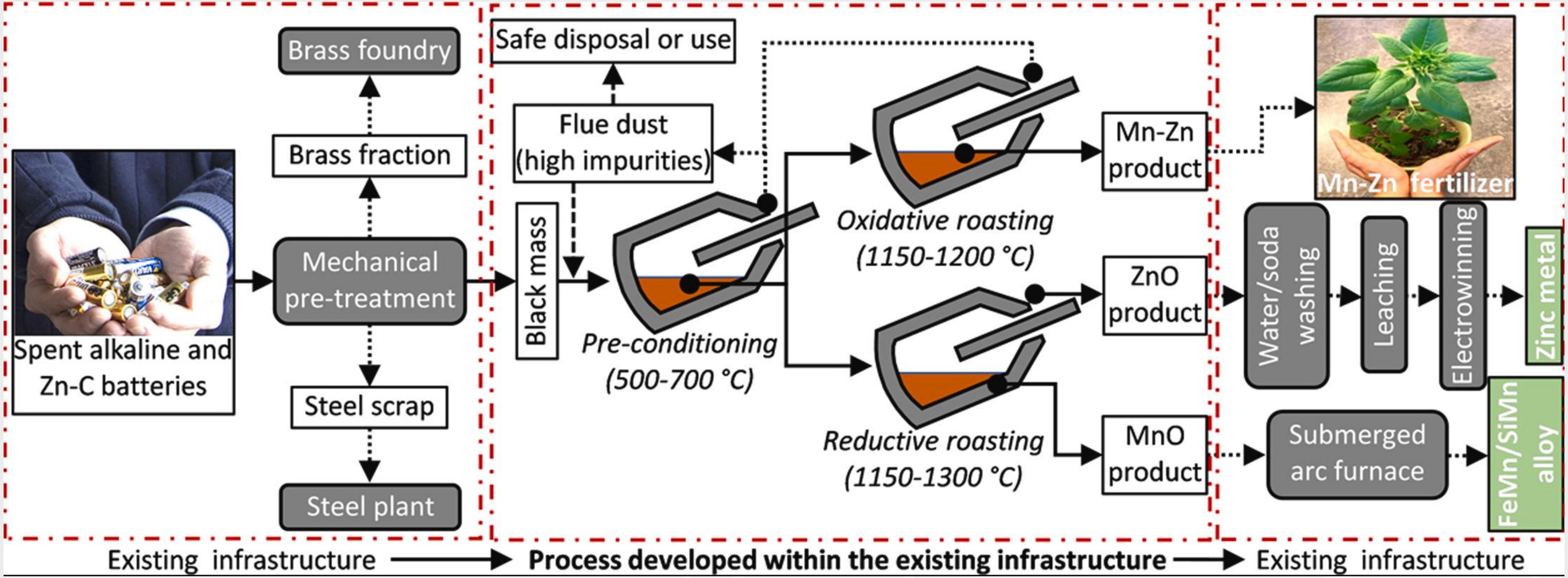
The developed process



Some of the results are published...

- Xianfeng Hu, Elsayed Mousa, Yang Tian, and Guozhu Ye. "Recovery of Co, Ni, Mn, and Li from Li-ion batteries by smelting reduction-Part I: A laboratory-scale study." Journal of Power Sources 483 (2021): 228936. **125 citations**

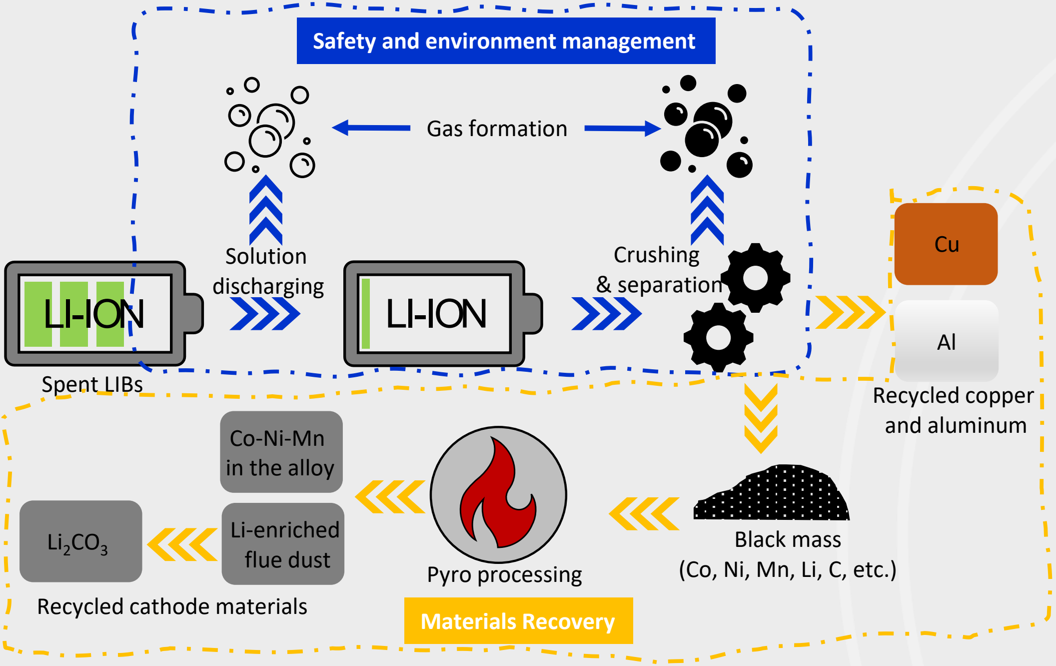
- Xianfeng Hu, Elsayed Mousa, and Guozhu Ye. "Recovery of Co, Ni, Mn, and Li from Li-ion batteries by smelting reduction-Part II: A pilot-scale demonstration." *Journal of Power Sources* 483 (2021): 229089. **98 citations**

- Xianfeng Hu, Astrid Robles, Tommy Vikström, Pekka Väänänen, Mats Zackrisson, and Guozhu Ye. "A novel process on the recovery of zinc and manganese from spent alkaline and zinc-carbon batteries." Journal of Hazardous Materials 411 (2021): 124928. **68 citations**

Conclusions

- Critical raw materials (CRMs) are vital for battery production, particularly for lithium-ion batteries.
- Pyrometallurgical recycling is an effective method for recovering CRMs from spent batteries.
- The expertise and experience gained through Swerim's laboratory and pilot-scale research strengthen the development of efficient CRM recycling processes.

Recycling of Spent Li-ion Batteries at Swerim



Focused research areas:

<u>Pyrometallurgy-based recycling process</u>

- 1.1 Recovery of Co, Ni, Mn, P and Li by smelting reduction
- 1.2 Thermal treatment of battery materials
- 1.3 Separation and purification of graphite

<u>Safety and environment management</u>

- 1.3 Toxic and flammable gas formation during mechanical and thermal treatment of LIBs cells
- 1.4 PFAS formation during the recycling process

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