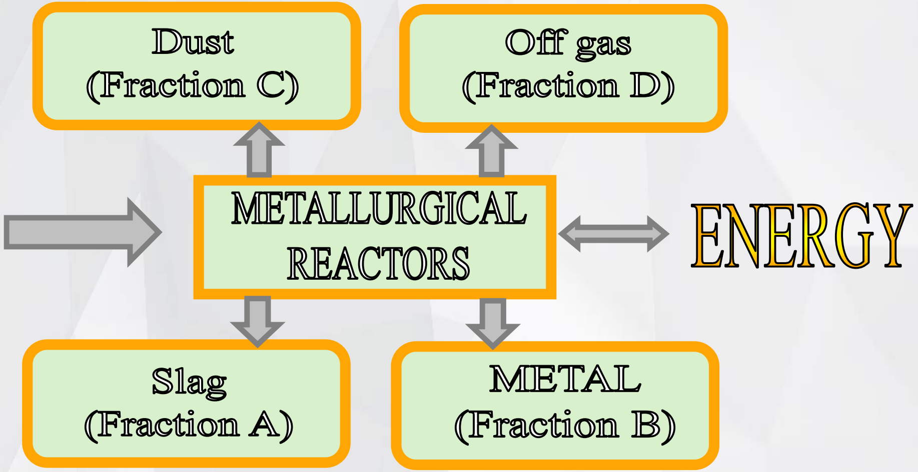
# Pyrometallurgy for Recycling of Spent Batterires

Guozhu Ye, Xianfeng Hu, Astrid Robles
Dept. of Process Metallurgy, Swerim

# Metallurgical principle for recycling


A: CaO, SiO2, **Al2O3**, MgO, **Li2O**

B: **Ni, FeO, MnO**, V2O3, Cr2O3, P2O5, **Cu, Co,** Mo

C: Zn, Pb, Na, K, Cl, **F,** Cd, Hg, **Li**

D: C-H-O, plastics/textile/fluff, **C**

# Pilot trials with DC furnace technology

**Dust/Sludge**
- Fe, Ni, Cr
- Zn, Pb, Cd
- Slag cement

**Steel slags**
- Fe, Mn, V, Ni, Cr
- Slag cement

**Catalyst**
- Fe, Ni, Cu, Co
- V-slag for FeV production

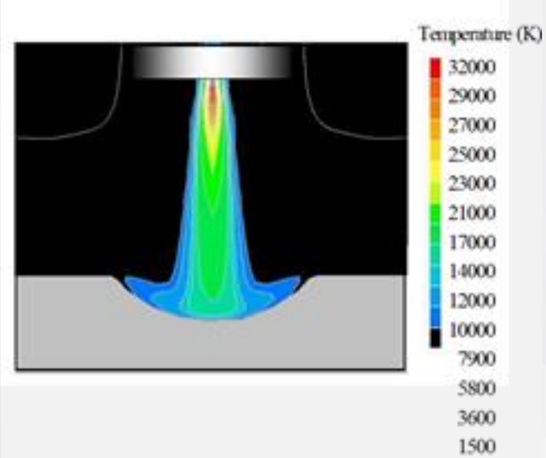
**Ashes**
- Na, K rich fume
- Slag product → Road construction

**Sludge**
- Syngas
- Slag product

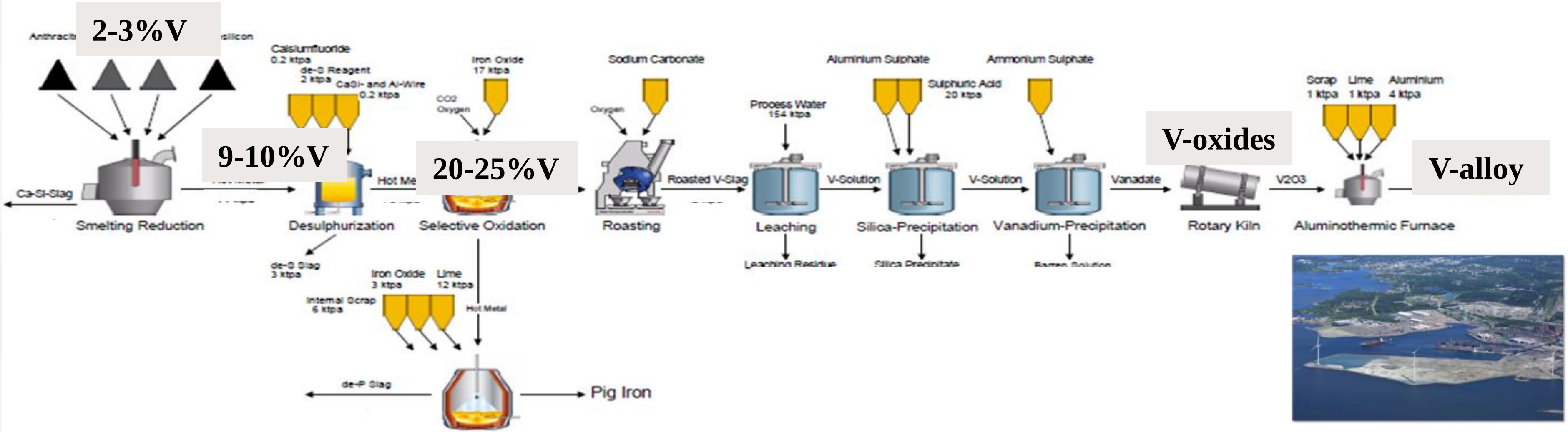
**Mn-Sludge**
- Zn, Na, K rich dust
- Mn-slag for FeMn/SiMn production

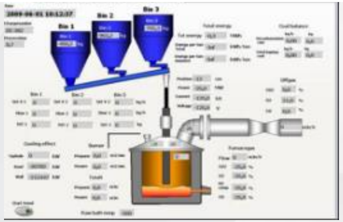
**Alkaline batteries**
- Zn for zinc production
- Mn for FeMn production

**Nickel slags/dusts**
- Ni recovery
- Slag cement



# Recovery of V from Steel Slag



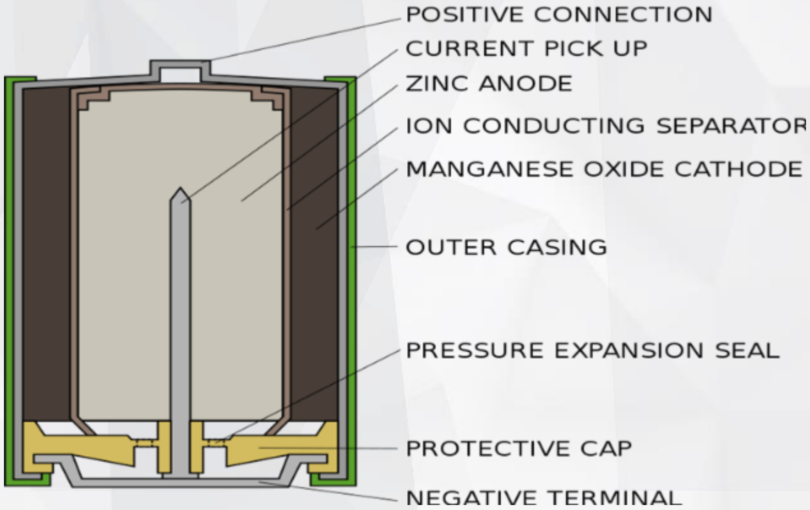




# Spent Alkaline batteries

SWERIM

- DC furnace processing (Battery Foundation)

- EBaR (MISTRA)

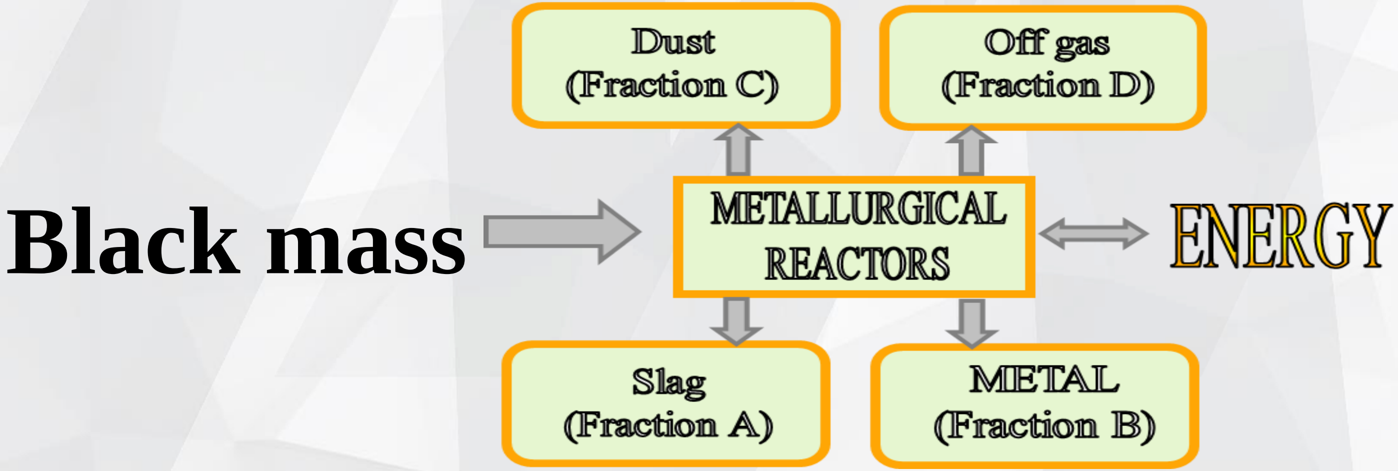


# Black mass, chemical analysis

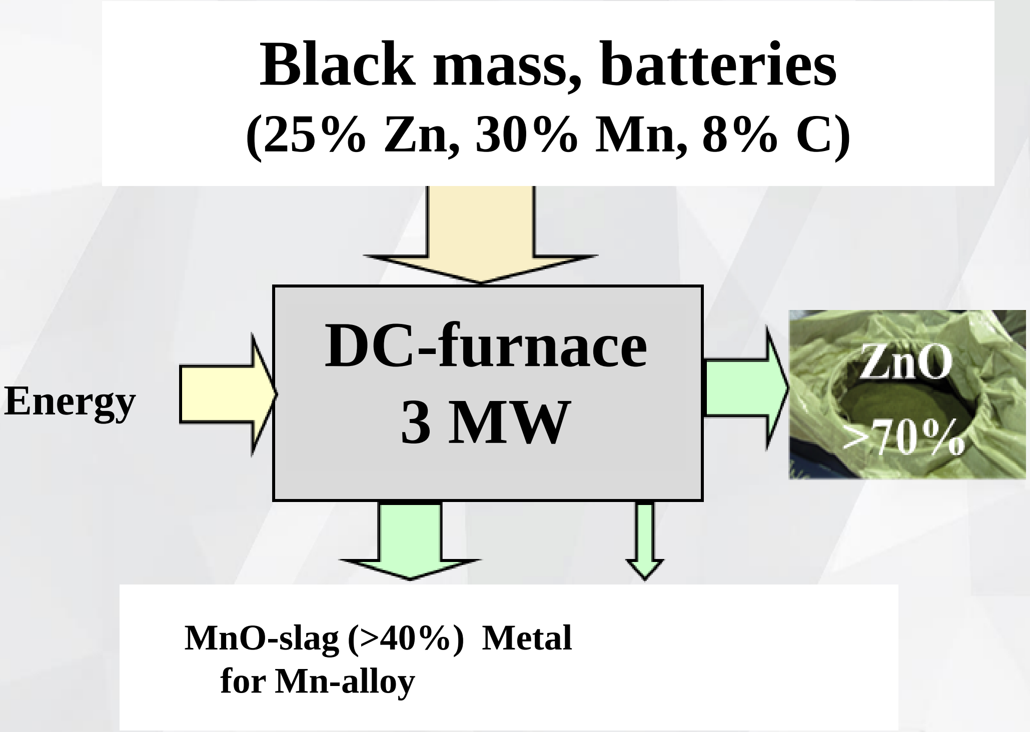
SWERIM

| Mn | Fe | Zn | Cl | KOH | Cd | Hg | C |
|---|---|---|---|---|---|---|---|
| 30 | 1.5 | 25 | 4 | 5 | 0.6 | 0.1 | 8 |

A-fraction B-fraction C-fraction D-fraction



# DC furnace processing (1550-1600C, reducing, molten slag)



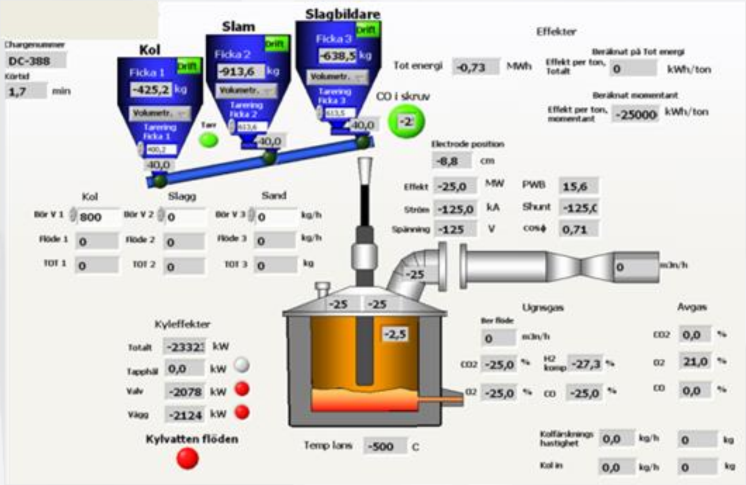

3 MWDC-furnace

# Test results from pilot test campaign, 2015

SWERIM

| | Energy | Feed rate | Temp tap | B2* | $K_2O$-slag | ZnO-slag | Mn-slag | $K_2O$-dust | ZnO-dust |
|---|---|---|---|---|---|---|---|---|---|
| Heat no | kWh/ton BM | ton/h | °C | | wt-% | wt-% | wt-% | wt.-% | wt-% |
| **DC627** | 1118 | 1.0 | 1703 | 1.09 | 1.19 | 0.03 | 19.70 | 9.87 | 71.40 |
| **DC628** | 1053 | 1.0 | 1636 | 1.08 | 1.46 | 0.08 | 25.72 | 8.31 | 79.60 |
| **DC629** | 1022 | 0.9 | 1662 | 1.09 | 1.22 | 0.04 | 30.36 | 8.98 | 74.20 |
| **DC630** | 913 | 1.0 | 1673 | 1.25 | 1.27 | 0.03 | 32.74 | 15.80 | 64.40 |
| **DC631** | 893 | 1.0 | 1600 | 0.51 | 1.37 | 0.07 | 36.43 | 6.69 | 67.80 |
| **DC632** | 1219 | 0.9 | 1621 | 0.45 | 1.71 | 0.04 | 39.94 | 8.27 | 77.90 |
| **DC633** | 1191 | 0.8 | 1651 | 0.40 | 1.71 | 0.03 | 42.29 | 8.82 | 76.20 |
| **Avg** | **1058** | **0.9** | **1649** | **0.84** | **1.42** | **0.05** | **32.46** | **9.53** | **73.07** |

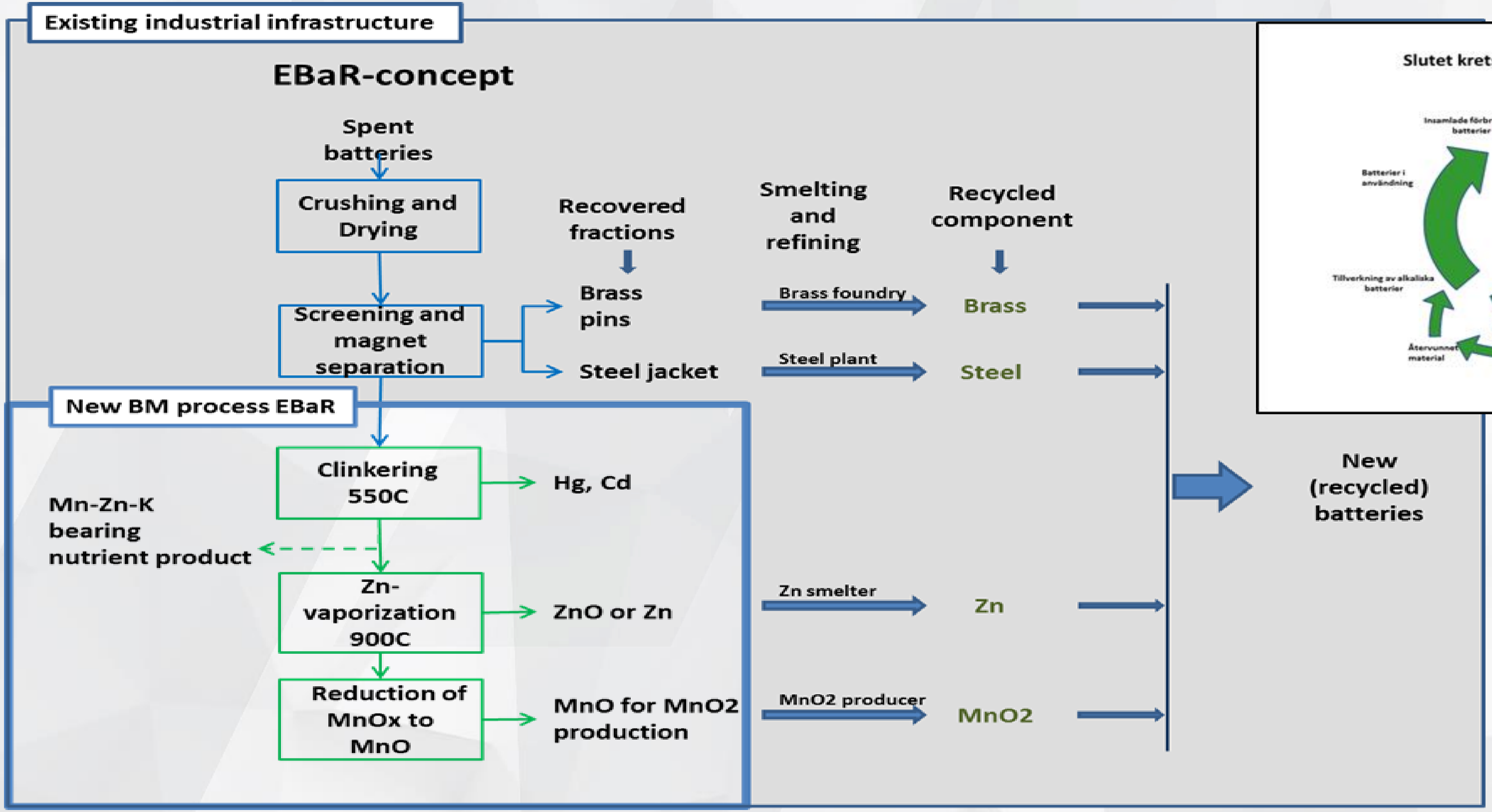
# DC furnace for processing spent alkaline batteries

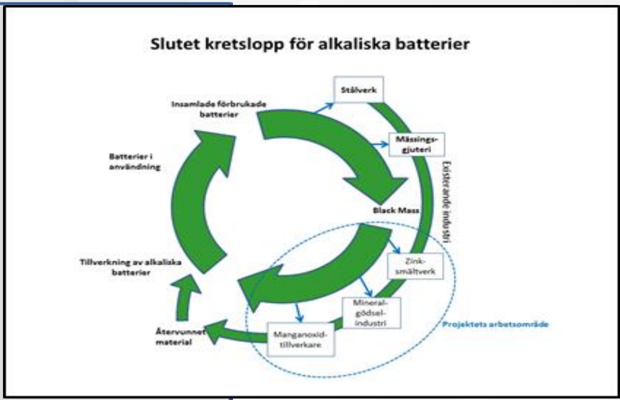



- +Full recovery of batteries
- +2-3 products (ZnO, MnO and metal)
- +Zero waste
- +Aiming for a low-cost and flexible furnace
- +Possible for co-processing of Mn-sludge
- +Possible to feed ”whole batteries” directly
- - Higher CAPEX

SWERIM

# MISTRA project – EBaR (7.95 MSEK)



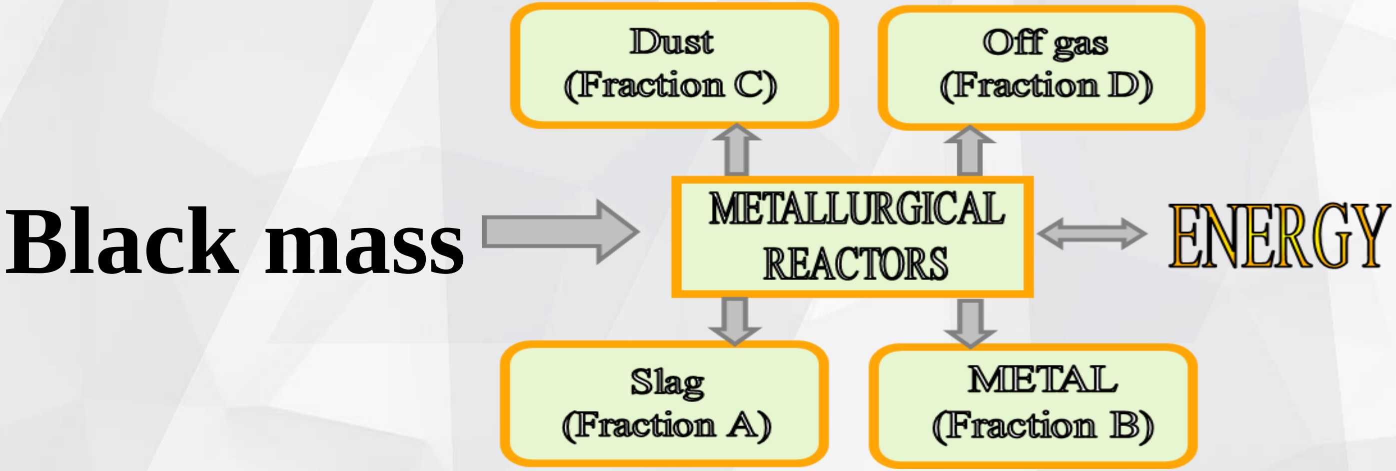



# Black mass, chemical analysis

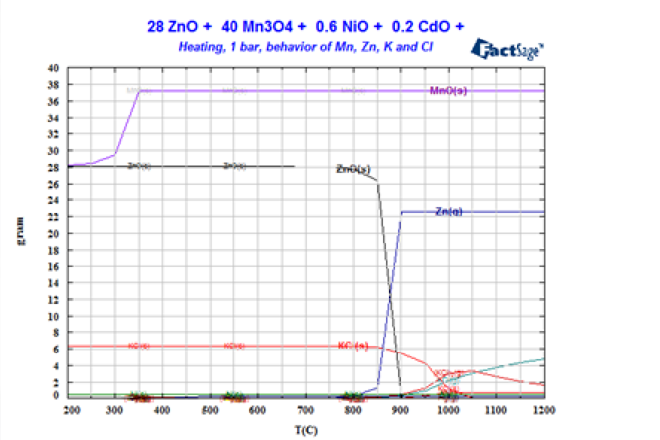
| Mn | Zn | C | Cl | KOH | Cd | Hg |
|---|---|---|---|---|---|---|
| 30 | 25 | 8 | 4 | 5 | 0.6 | 0.1 |

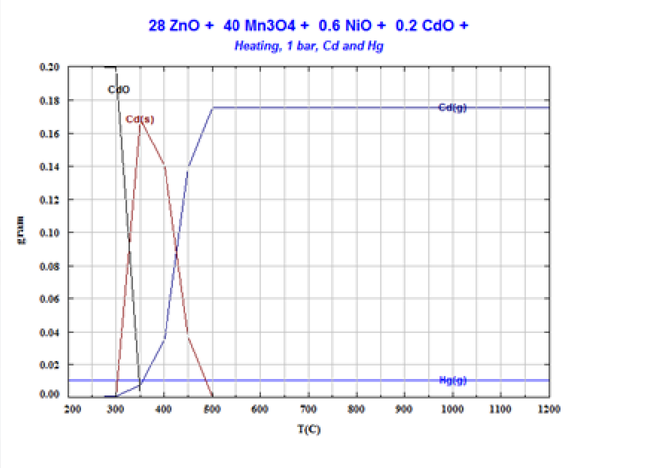
A-fraction

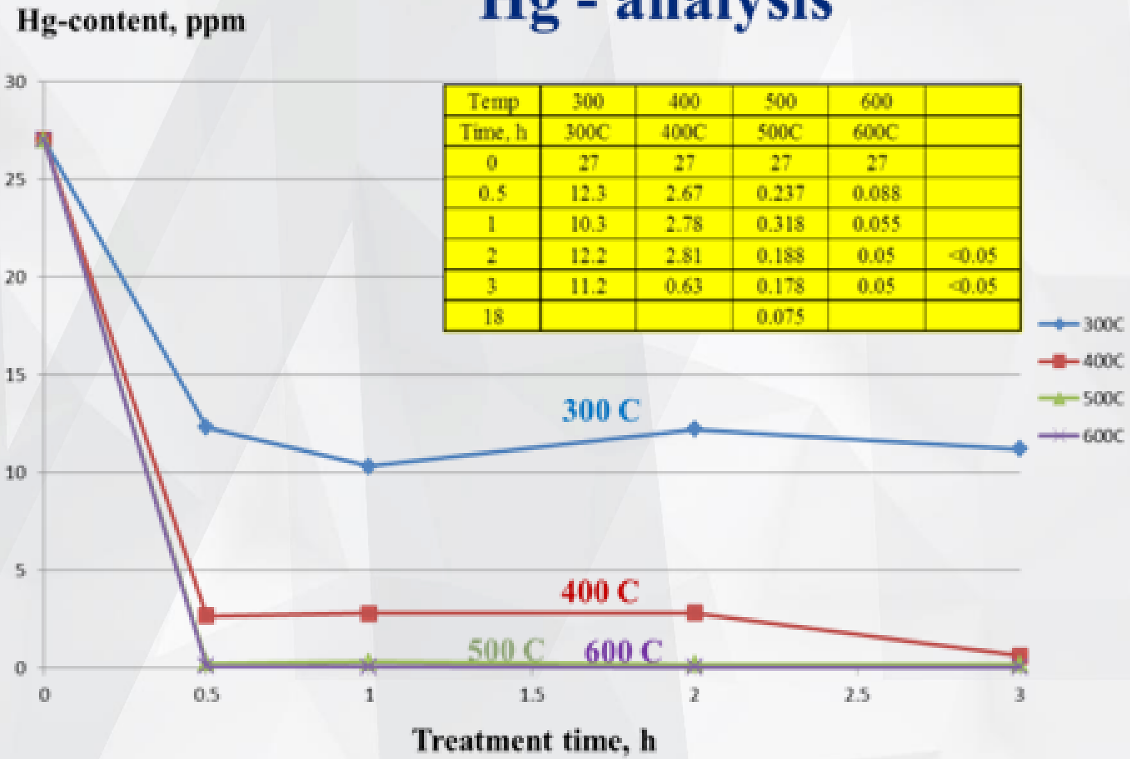
D-fraction



# Hg - analysis

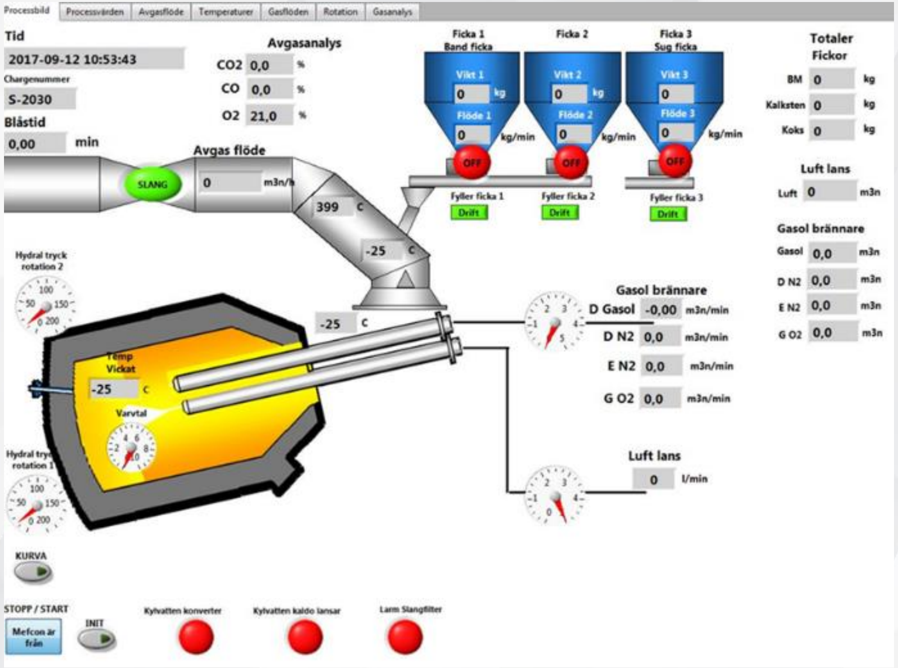


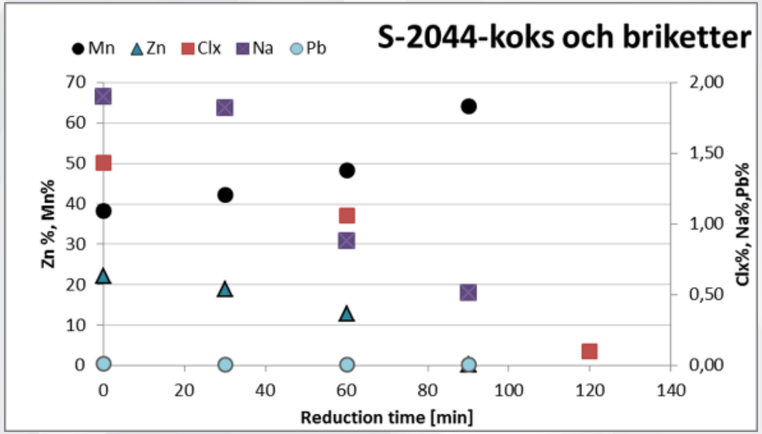



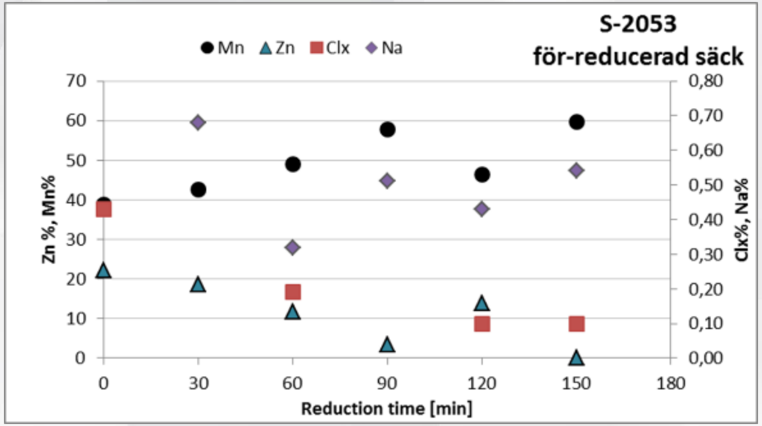




| Temp | 300 | 400 | 500 | 600 | |
|---|---|---|---|---|---|
| Time, h | 300C | 400C | 500C | 600C | |
| 0 | 27 | 27 | 27 | 27 | |
| 0.5 | 12.3 | 2.67 | 0.237 | 0.088 | |
| 1 | 10.3 | 2.78 | 0.318 | 0.055 | |
| 2 | 12.2 | 2.81 | 0.188 | 0.05 | <0.05 |
| 3 | 11.2 | 0.63 | 0.178 | 0.05 | <0.05 |
| 18 | | | 0.075 | | |

# EBaR Pilot testing

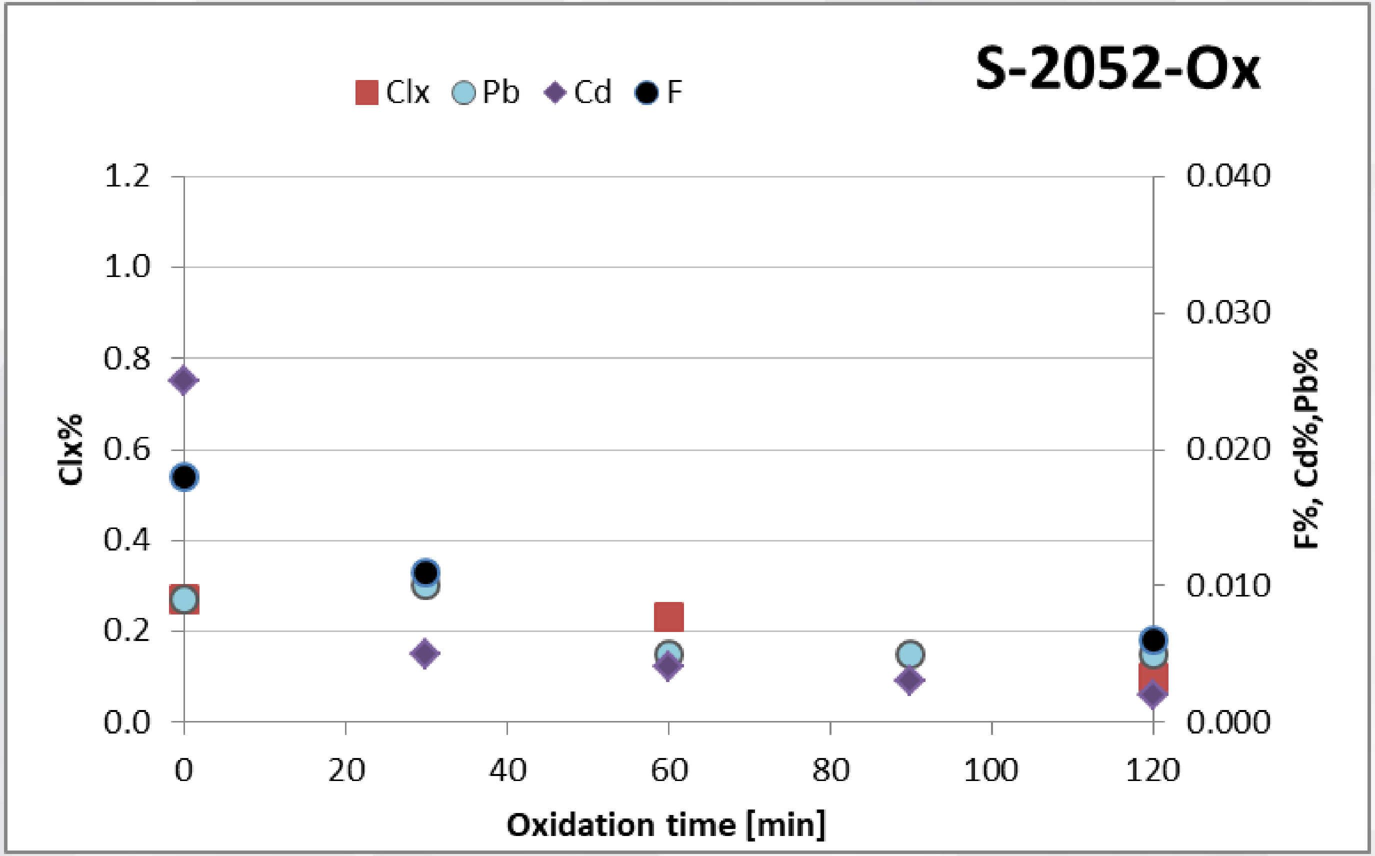


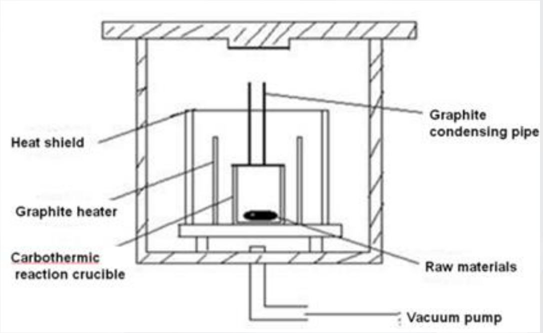

SWERIM

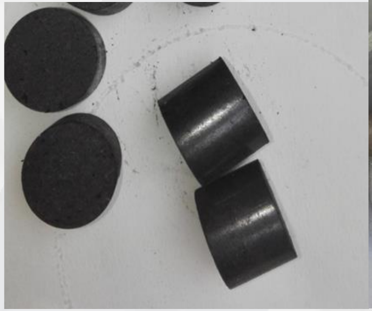
# 2h oxidation, BM



# Vacuum destillation

SWERIM



Before

After

Table 3. The chemical analysis of Mn-rich fraction

| Residues | Zn/% | Mn% | Ni% | Cd/% | C/% | Hg/% |
|---|---|---|---|---|---|---|
| 1000°C | 0.20 | 70.18 | 1.38 | ＜0.005 | 1.28 | ＜0.005 |
| 1200°C | 0.079 | 66.03 | 1.35 | ＜0.005 | 0.64 | ＜0.005 |

Table 4 The chemical analysis of condensed product

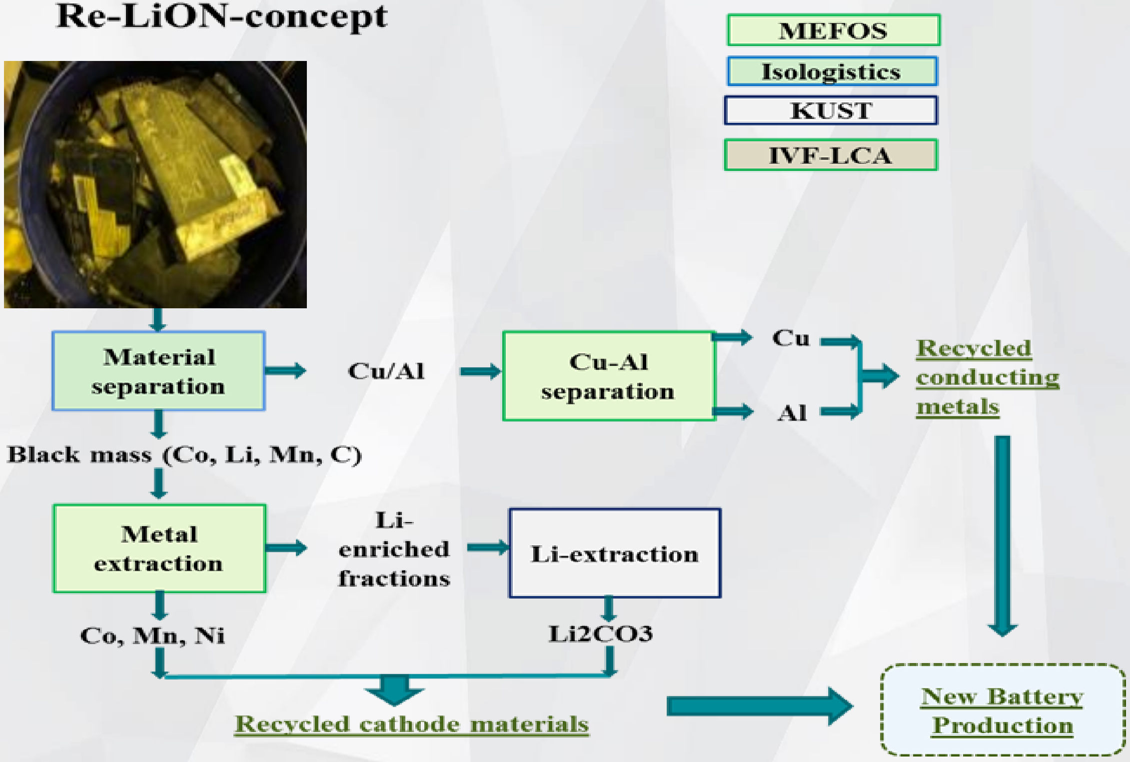
| Condense | Zn/% | Mn% | Ni% | Cd/% | C/% | Hg/% |
|---|---|---|---|---|---|---|
| 1000°C | 73.59 | 0.12 | ＜0.005 | 1.86 | 0.72 | ＜0.005 |
| 1200°C | 60.07 | 0.10 | 0.0054 | 1.19 | 0.93 | ＜0.005 |

**Kunming University of Science and Technology**

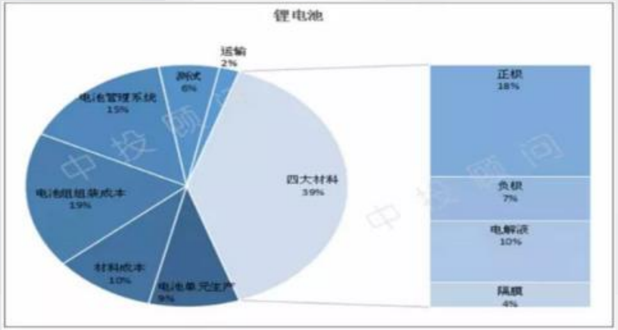
# The Re-Lion Project

SWERIM

## Re-LiON-concept




| Component | Composition (Mass %) |
|---|---|
| Casing | 25 |
| Cathode material LiCoO2 | 25 |
| Anode material graphite | 17 |
| Electrolyte | 10 |
| Copper electrode foil | 8 |
| Aluminium electrode foil | 5 |
| Separator | 4 |
| Others | Balance |



# The Cu-Al foil fraction

As received

Manual separation

58.13% 23.93% 17.95%

Smelting

Unmelt powder fraction<0.5 mm

With quite high C content

Coarse fraction, >0.5 mm

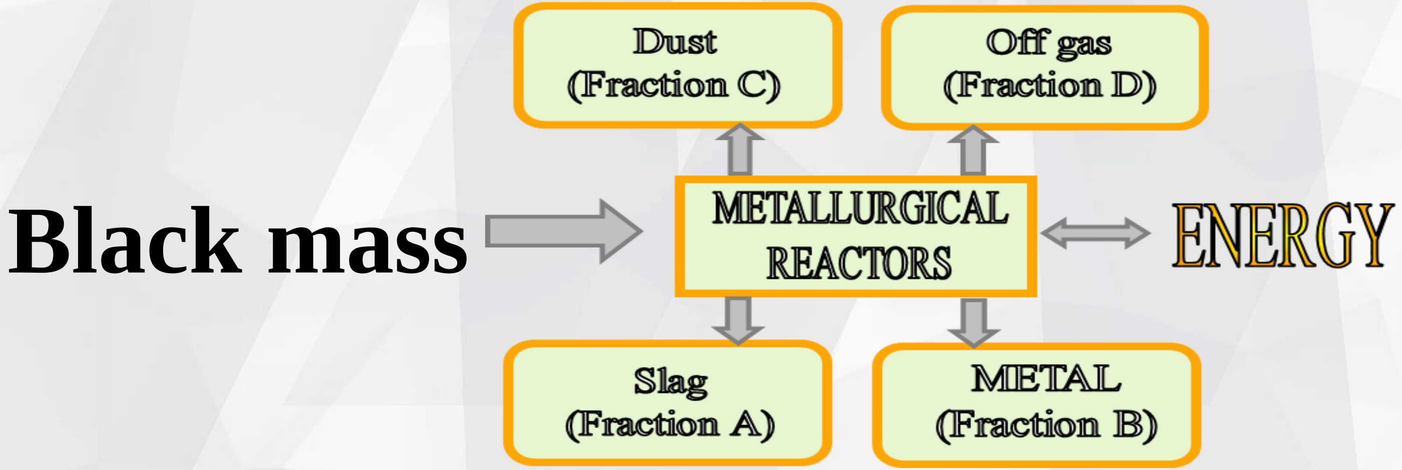
Remelting

73%Cu
9.3%Fe
8.7%Al
3.25%Ni
1.73%Co
1.78%Cr

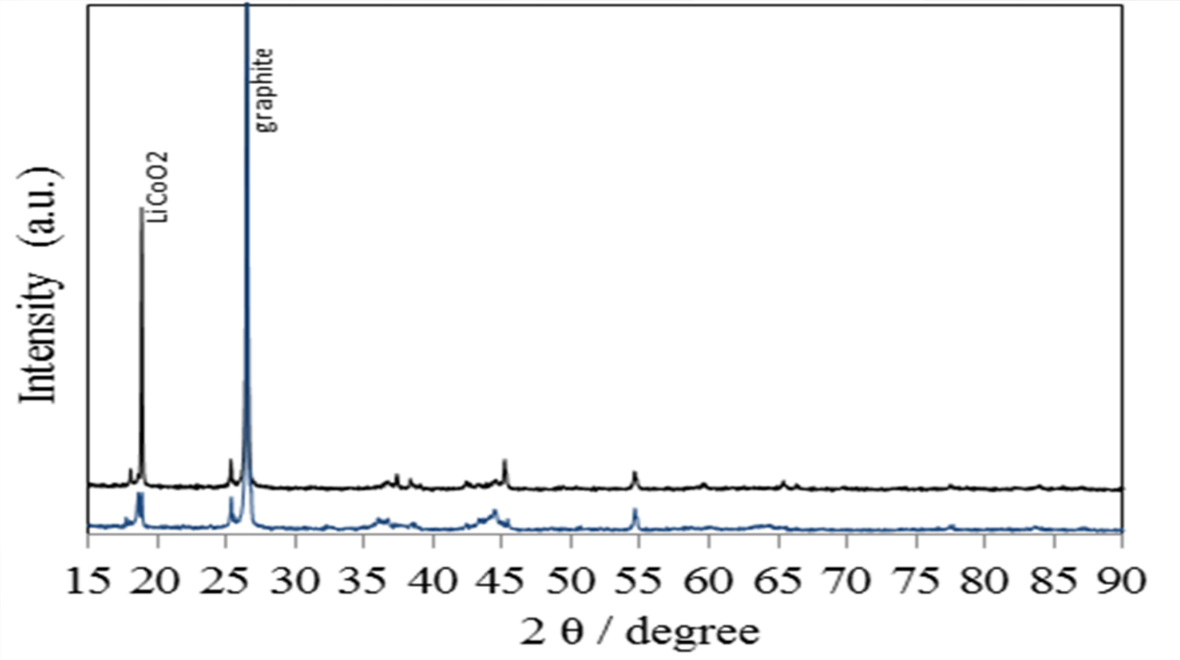
# Black mass, chemical analysis

| | Co | Cu | Ni | Fe | Mn | Al | Si | Li | C | F | Cl |
|---|---|---|---|---|---|---|---|---|---|---|---|
| BM ALS-Poland | 22.40% | 0.74% | 2.49% | 0.90% | 1.93% | 2.03% | 0.34% | 3.91% | 43.30% | 1.10% | 0.07% |
| BM ALS-High | 21.30% | 0.83% | 4.87% | 0.38% | 1.93% | 0.76% | 0.75% | 3.86% | 45.10% | 1.10% | 0.03% |
| BM ALS-Low | 2.62% | 1.56% | 4.43% | 1.26% | 1.88% | 1.57% | 3.88% | 4.15% | 47.80% | 2.10% | 0.02% |

**B-fraction** **A-fraction** **D-fraction**



# XRD - blackmass




- Confirm the high content of graphite
- The other dominating mineral phase is $LiCoO_2$

**Because of the high C content it was decided to remove some C first before the smelting test**

# Black mass before and after decoking

| | 01 BM | 02 BM | 03 BM |
|---|---|---|---|
| C | 45.10% | 47.80% | 43.30% |
| Co | 21.30% | 2.62% | 22.40% |
| Ni | 4.87% | 4.43% | 2.49% |
| Mn | 1.93% | 5.84% | 1.93% |
| Li | 3.86% | 4.15% | 3.91% |
| Al | 0.76% | 1.57% | 2.03% |
| Si | 0.75% | 3.88% | 0.34% |
| Ca | 0.03% | 0.11% | 0.04% |
| Cu | 0.84% | 1.56% | 0.74% |
| Fe | 0.38% | 1.26% | 0.90% |
| Na | 0.13% | 0.12% | 0.08% |
| P | 0.48% | 0.93% | 0.63% |
| S | 0.11% | 0.13% | 0.06% |
| F | 1.10% | 2.10% | 1.10% |

| | 01 BM | 02 BM | 03 BM |
|---|---|---|---|
| C | 0.04% | 0.15% | 0.02% |
| Co | 39.52% | 5.88% | 41.13% |
| Ni | 9.04% | 9.94% | 4.57% |
| Mn | 3.58% | 13.10% | 3.54% |
| Li | 7.16% | 9.31% | 7.18% |
| Al | 1.42% | 3.52% | 3.73% |
| Si | 1.40% | 8.70% | 0.62% |
| Ca | 0.06% | 0.26% | 0.08% |
| Cu | 1.55% | 3.50% | 1.36% |
| Fe | 0.70% | 2.83% | 1.65% |
| Na | 0.24% | 0.26% | 0.14% |
| P | 0.89% | 2.08% | 1.16% |
| S | 0.12% | 0.06% | 0.02% |

# 120-gram-scale smelting trials in the tamman furnace

SWERIM

- ‘Black mass + graphite’ in MgO crucible without slag forming materials
- Ar atmosphere;
- 10 $^{o}$C/min to 1575 $^{o}$C.

# The obtained metal and slag samples


01 black mass (metal)


03 black mass (metal)


02 black mass (metal)


03 black mass (metal)

No slag formed from the smelting of 01 black mass and 02 black mass.

# Chemical analysis of the obtained metal samples

SWERIM

| Element | 01 black mass | 02 black mass | 03 black mass |
|---|---|---|---|
| C | 0.69 % | 2.49 % | 0.81 % |
| Si | 0.01 % | 1.1 % | 0.04 % |
| Mn | 5.81 % | 30.7 % | 4.07 % |
| P | 0.90 % | 3.1 % | 0.49 % |
| S | 0.001 % | 0.045 % | 0.002 % |
| Cr | 0.327 % | 0.47 % | 0.155 % |
| Ni | 14.389 % | 25.8 % | 7.292 % |
| Mo | 0.005 % | < 0.002 % | < 0.001 % |
| Ti | 0.003 % | 0.31 % | 0.009 % |
| Nb | 0.002 % | 0.03 % | 0.004 % |
| Cu | 3.78 % | 5.3 % | 4.43 % |
| Co | 69.1 % | 13.4 % | 73.0 % |
| W | 0.01 % | < 0.005 % | < 0.01 % |
| V | 0.009 % | 0.04 % | 0.002 % |
| Al | 0.005 % | 5.0 % | 0.47 % |
| Fe | 3.27 % | 4.7 % | 7.46 % |
| Zr | 0.012 % | 0.03 % | 0.020 % |

# Conclusion

- Pyrometallurgy provides a wide range of possibilities for efficient recovery and/or enrichment of valuables from spent batteries

- A hybrid flexible system with Pyro- and Hydrometallurgy is foreseen to be the future option for efficient recycling of spent batteries

SWERIM