

Recycling of discarded Li-Ion batteries (LIBs)



Nordic Recycling Day VIII
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Outline

- Introduction to Li-ion battery market
- Li-ion battery composition and recycling
- Project: Recycling of spent Li-ion batteries

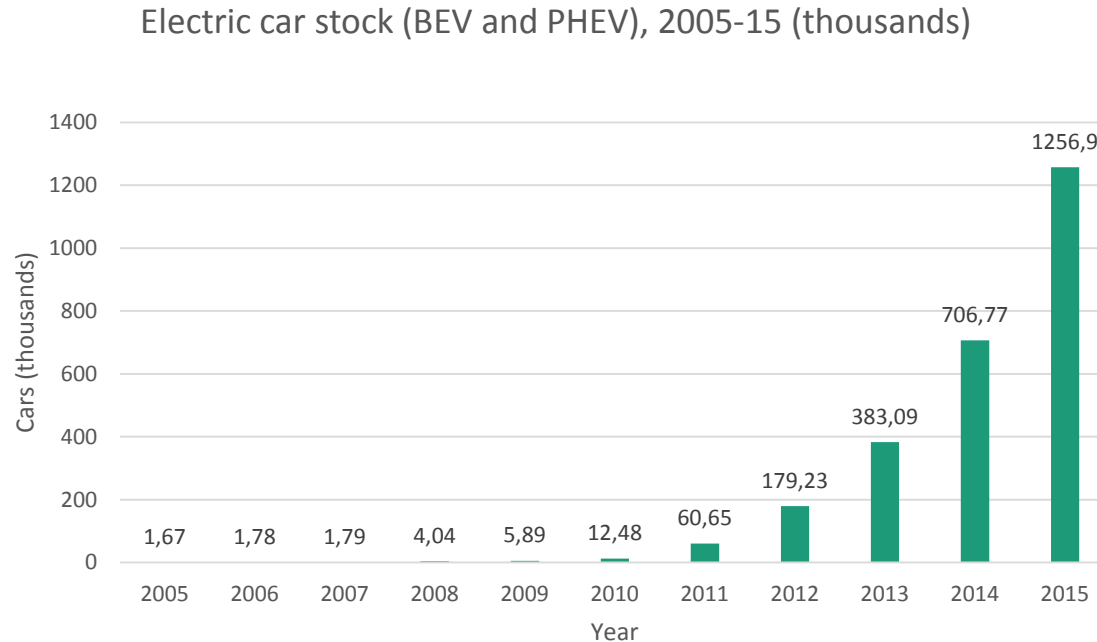
Introduction - Where are LIBs used?

- Li-ion batteries are used in many applications
- Increasing political and consumer focus on climate change
 - Increase electric vehicle (EV) production
 - Increased lithium-ion battery (LIB) production



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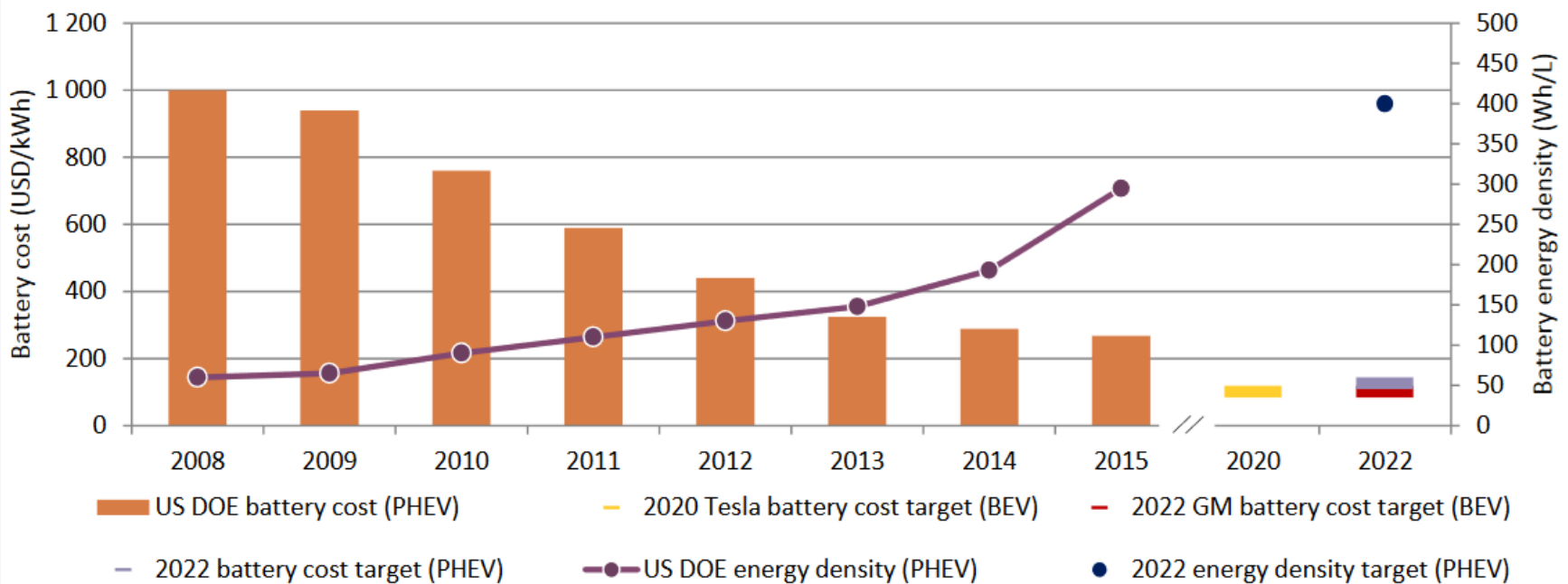


Almost
0.9% of
car
market

Introduction - Why LIBs?

- LIB is an important technology for electric vehicle (EV) – high specific power, energy density and lifetime
- Ongoing development of battery composition

Development of battery energy density and cost



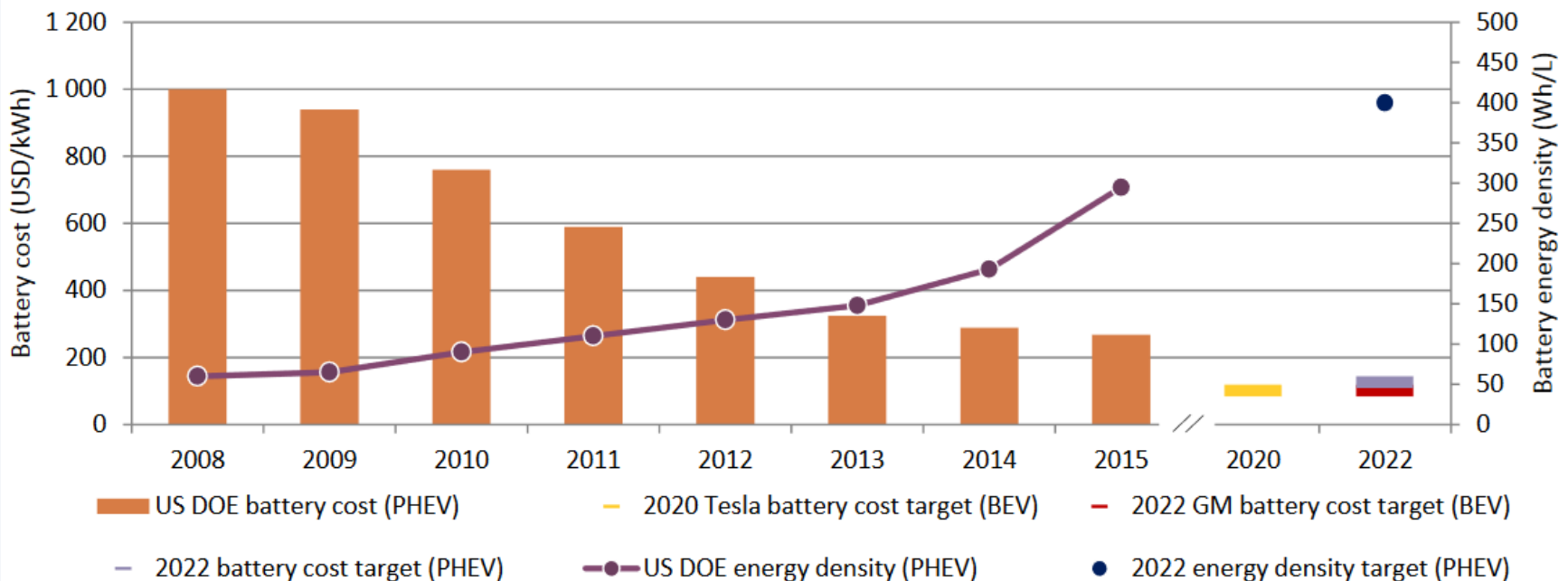
Source: © OECD/IEA 2016, *Global EV Outlook 2016*, IEA Publishing

Introduction - Why

Energy density:
30-50 Wh/kg Lead acid battery
110-160 Wh/kg Li-ion battery

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LIB composition – What's inside?

- Cathode
 - Lithium metal oxide, LiMeO_2 , graphite and PVDF binder on **Al-foil**
 - Metals used: i.e. **Co, Ni, Mn, Al, Fe**
- Anode
 - Carbon and PVDF binder on **Cu-foil**
- Electrolyte
 - Li salts and organic solvents (flammable).
- Casing
 - Steel (Fe, Cr, Ni), Al
- Complex material to recycle

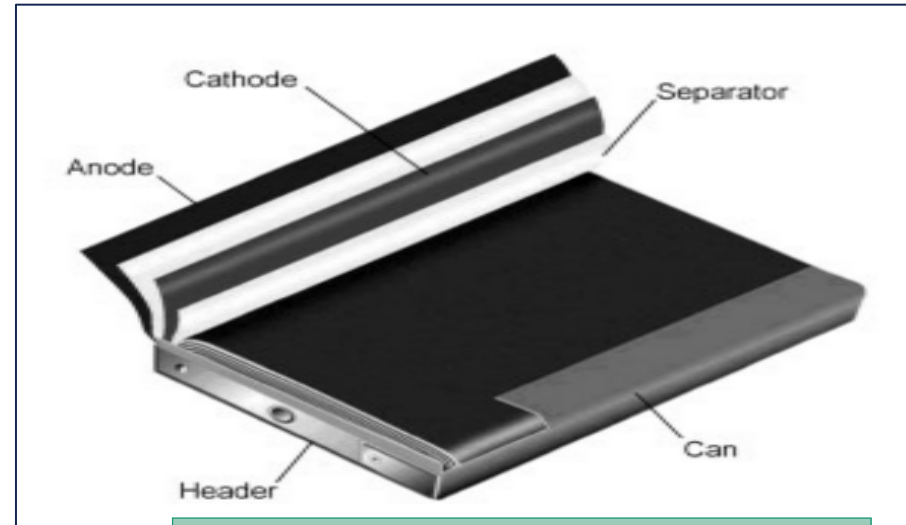
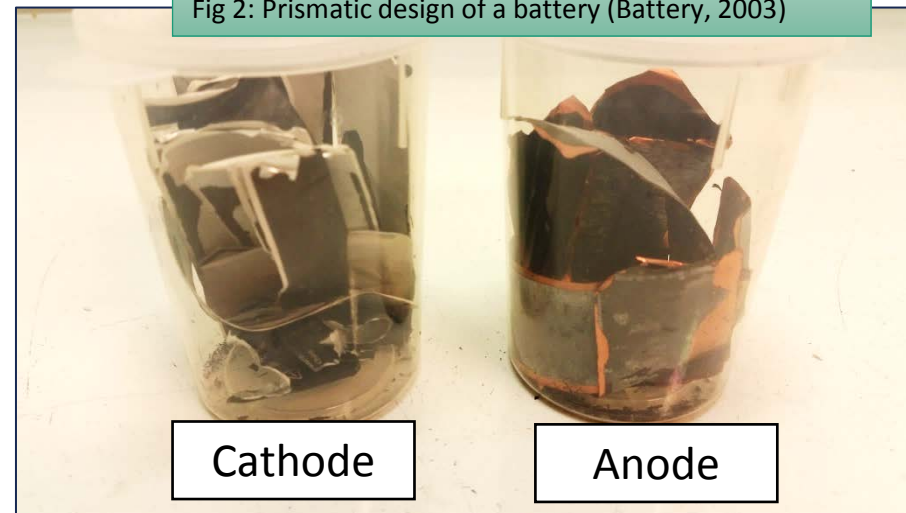


Fig 2: Prismatic design of a battery (Battery, 2003)



LIB recycling – challenges!

- Existing high temperature recycling process
 - Based on Co and Ni recovery
- Short circuiting / thermal runaway
 - Need of pre-treatment
- Battery chemistries
 - Development of cathode active material
 - What to recycle in the future?

System Electrodes	NCA Graphite	LFP(phosphate) Graphite	MS (spinel) Graphite
Positive (Cathode)	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	LiFePO_4	LiMn_2O_4

Recycling of spent LIBs project

Recap:

- Increasing volumes of end of life LIBs
- Ongoing development of battery chemistry
- Recycling in existing processes

Aim:

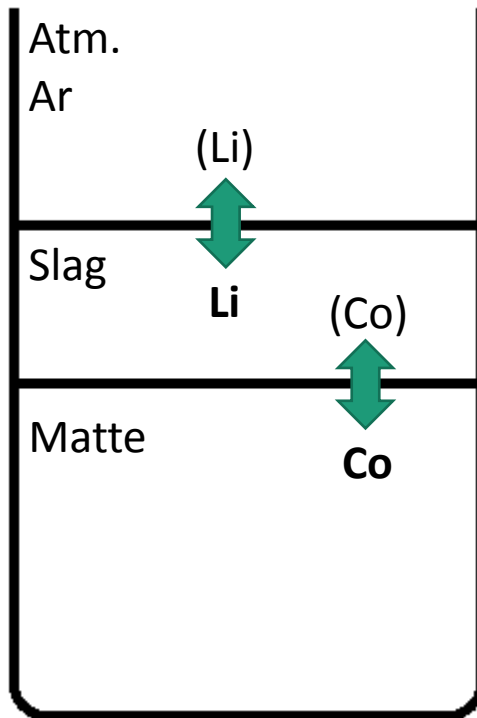
- **To investigate thermochemical feasibility of the processes – FactSage**
- **To recycle spent LIBs in copper pyrometallurgical process**
 - Distribution of Li and Co between phases



Cu-system

- Slag: $\text{Fe}_2\text{SiO}_4 + (\text{CaO})$
- Matte: Cu_2S
- Metal: Cu

FactSage results



Li to gas phase:

- T increase $>1300^{\circ}\text{C}$
- CaO addition
- $<\log\text{PO}_2 (-10)$

Co to matte phase:

- CaO addition
- $<\log\text{PO}_2(-10)$

Validation with experimental work!

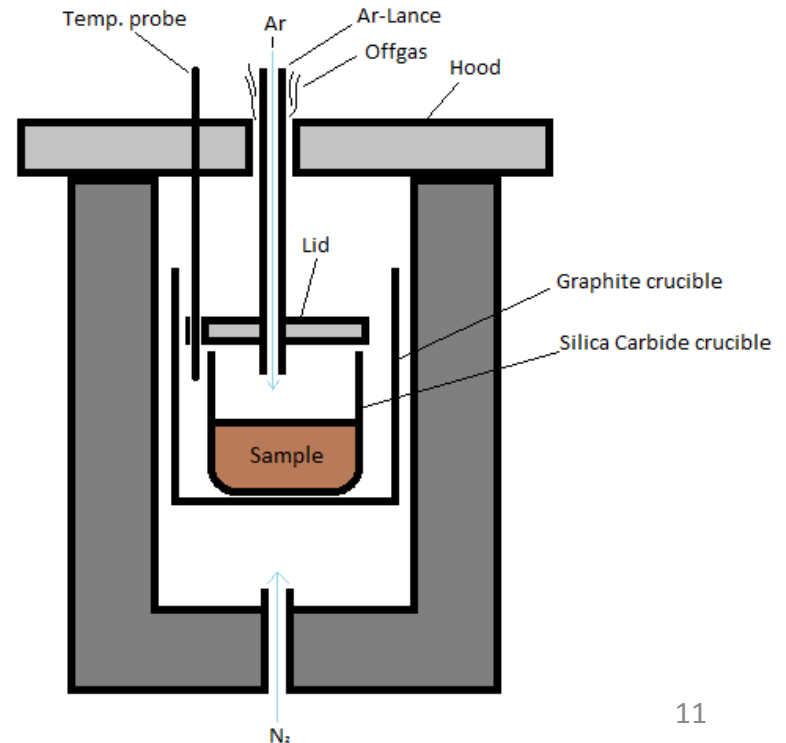
Experimental method

Parameter	Low value	Middle value	High value
Temperature	1250°C	1350°C	1450°C
Fe/SiO ₂	1	1.3	1.6
CaO addition	0 wt.%	5 wt.%	10 wt.%

- Inert atmosphere

Sample

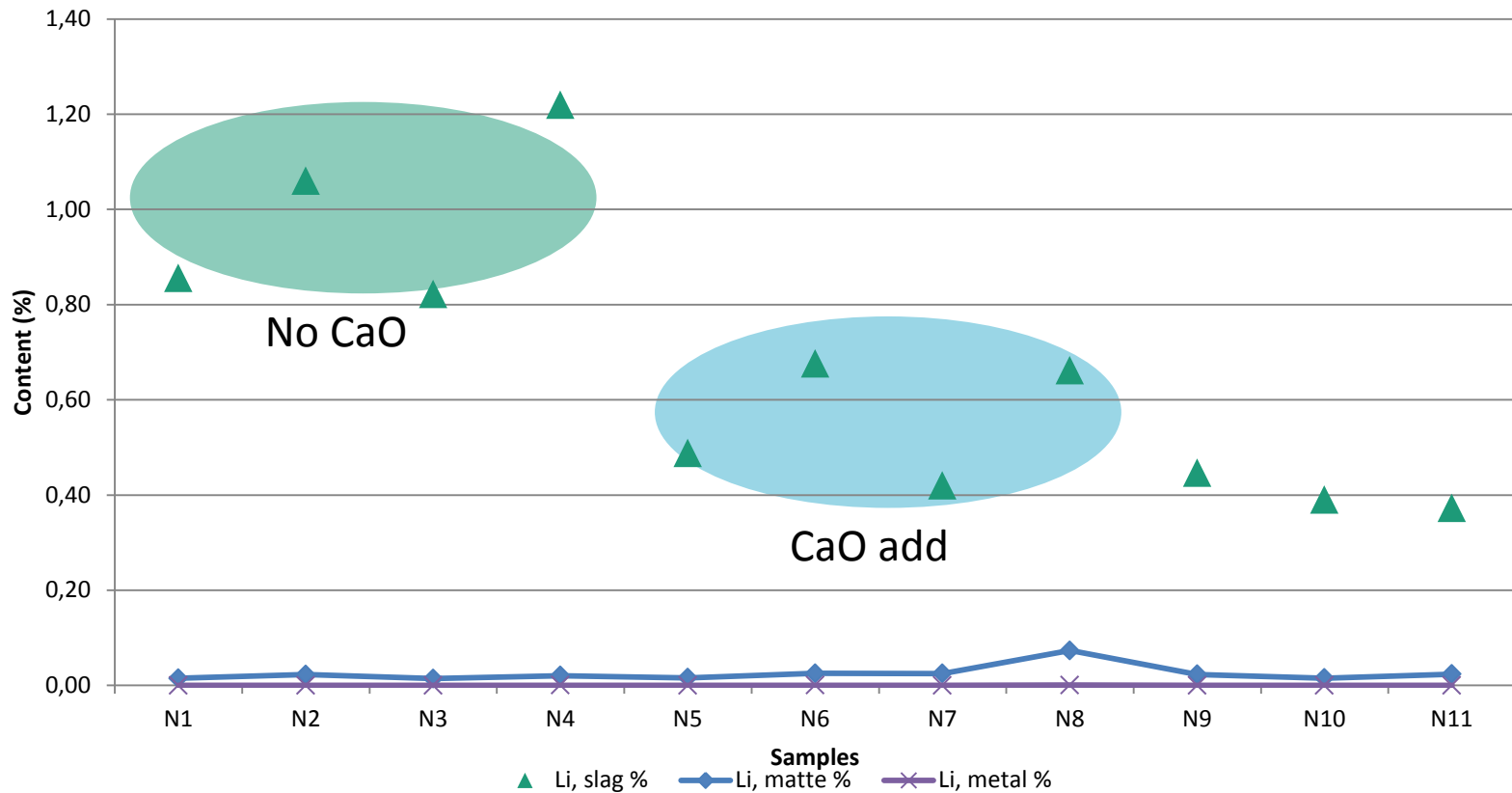
- Slag, Fe₂SiO₄ 50g
- Matte, Cu₂S 75g
- Metal, Cu 25g
- 5% LiCoO₂ (constant)
- CaO addition



Experiment results – Li - CaO add

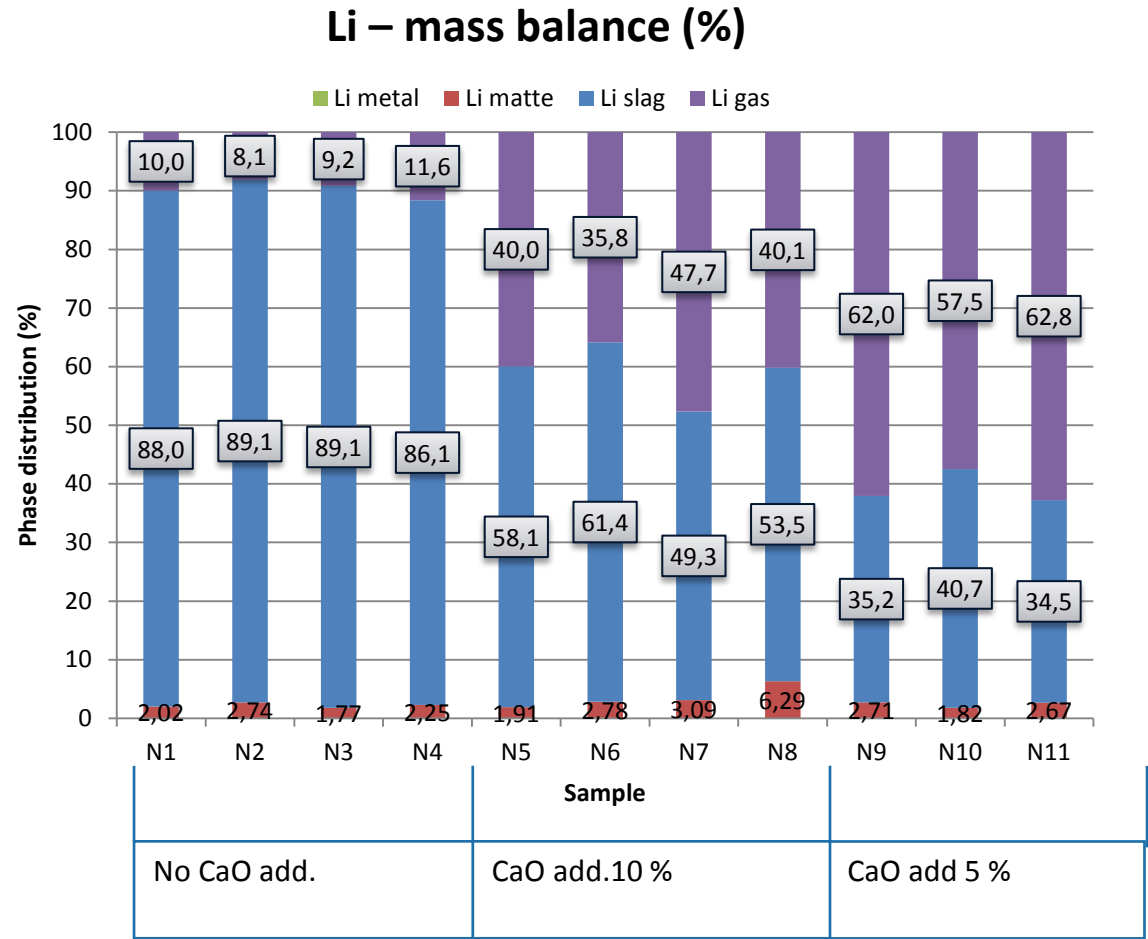
Lithium in slag phase

Li-content (wt.%)



Experimental results – Li mass bal.

- No CaO addition
 - 88% Li in slag
- CaO addition 10%
 - 35% Li loss
- CaO addition 5%
 - 56% Li loss
- No/small effect of Fe/SiO₂ ratio



Experimental results – Li

- Middle-point samples N9-N11

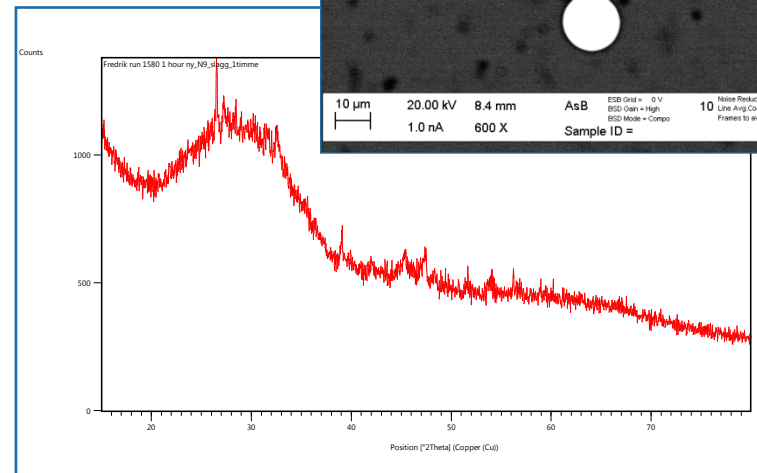
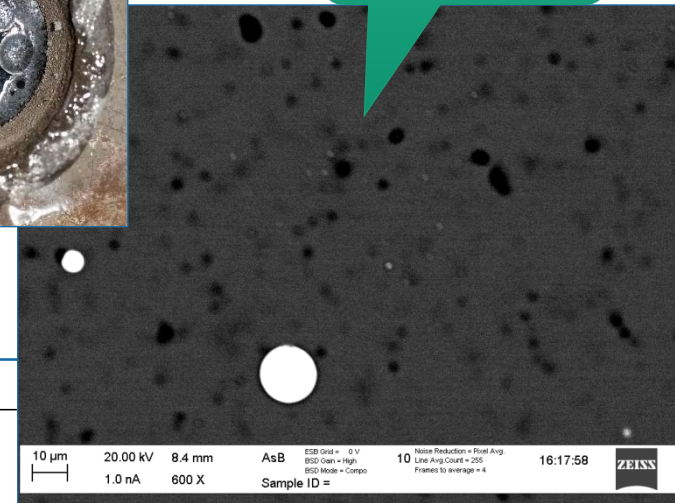
Conditions

- T 1350°C
- Fe/SiO₂ 1.3
- CaO add 5%

- Glassy amorphous slag
- Verified by XRD and SEM
- Consistent for all 3 samples
- Most of Li reported as loss (58-63 mass%)

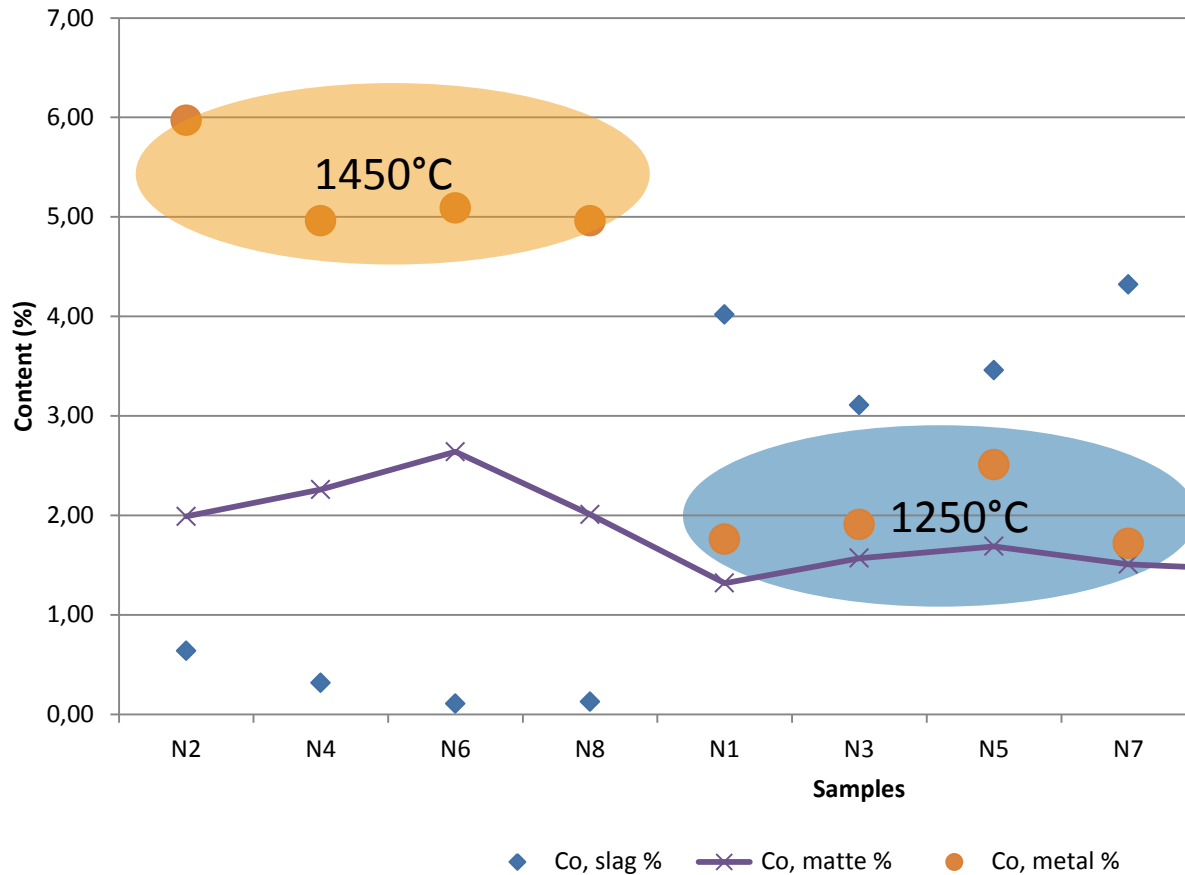


Homogeneous phase



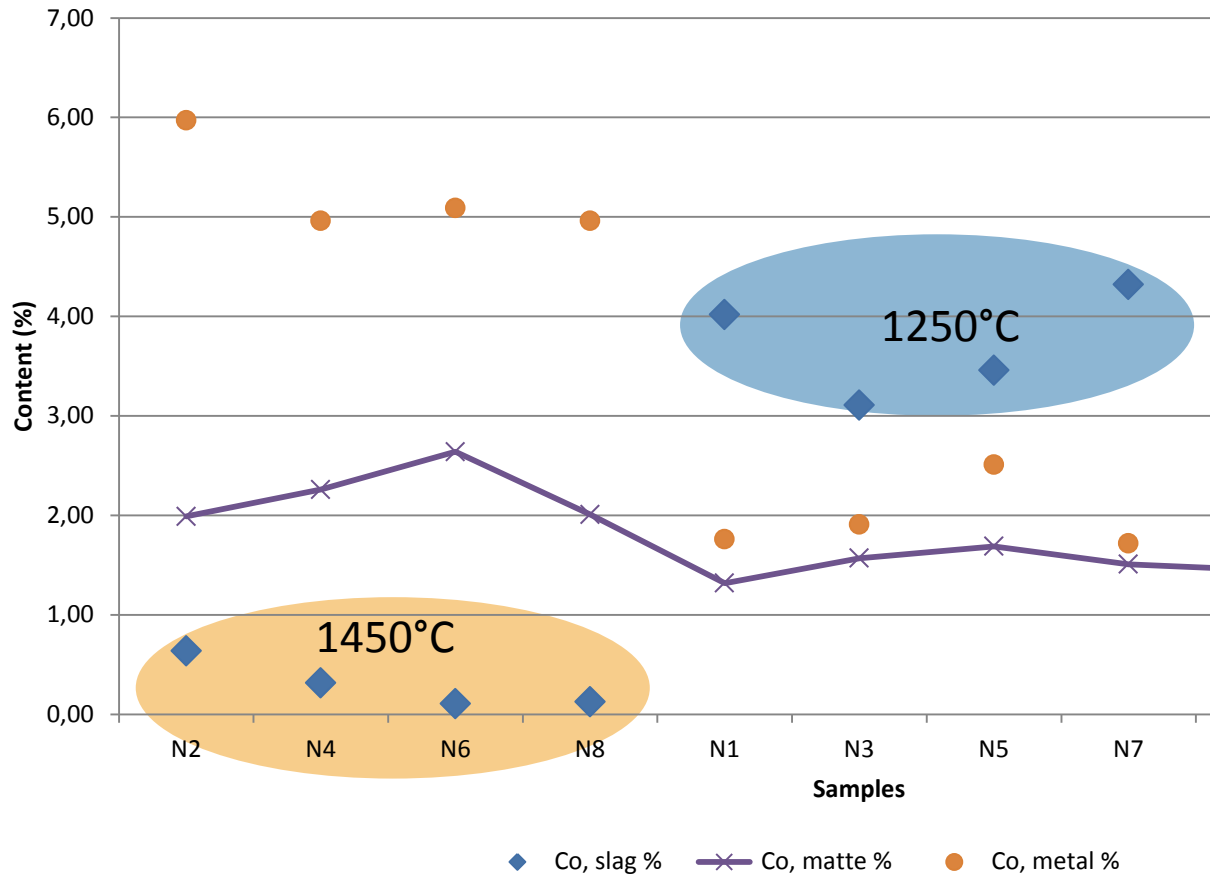
Experiment results – Co - Temp

Cobalt in metal phase



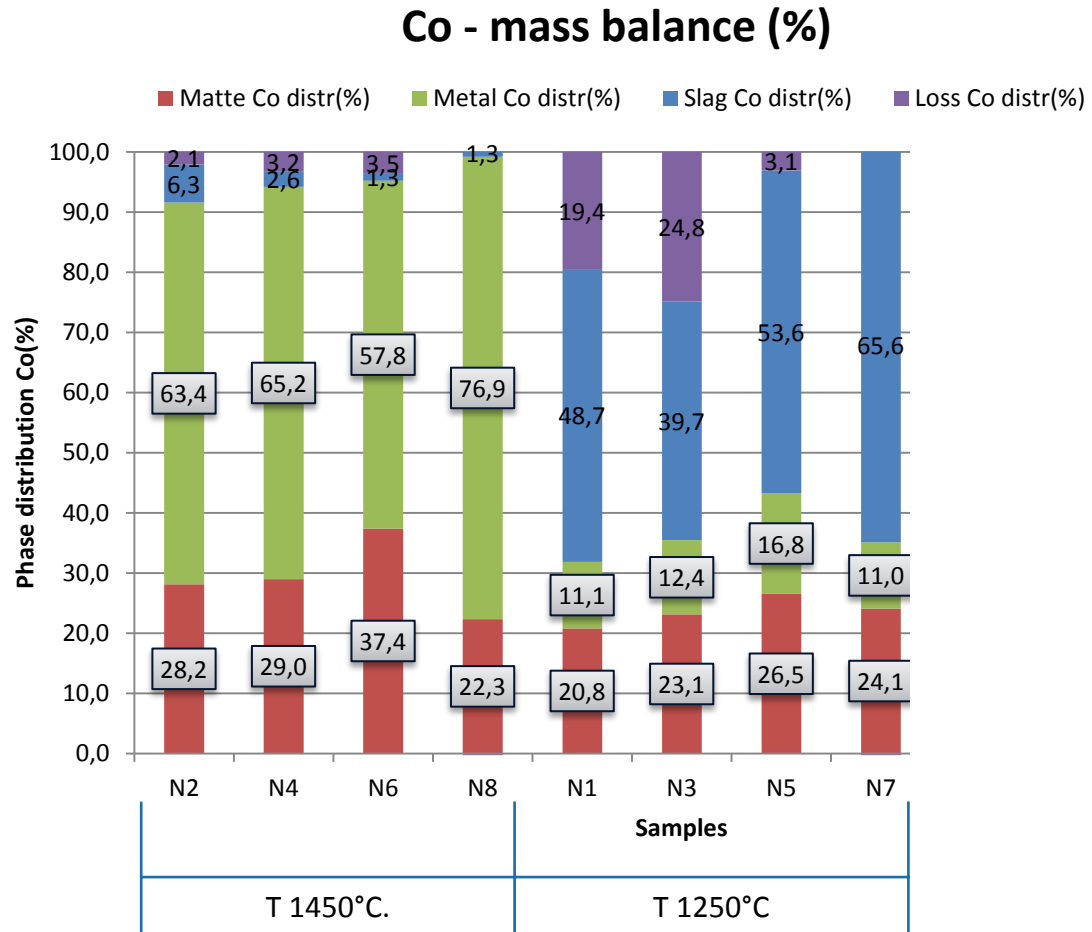
Experiment results – Co - Temp

Cobalt in slag phase



Experimental results – Co mass bal.

- 1450°C
 - 66% Co in metal
- 1250°C
 - 52% Co in slag
- No/small effect of Fe/SiO₂ ratio and CaO add



Summary

- Li is distributed between slag and gaseous phases (loss)
 - CaO addition reduces the amount of Li reported to the slag phase
- Co is distributed between slag, matte and metal(mainly) phases
 - Co is at 1250°C dissolved into the main slag phase
 - Co is at 1450°C in the metal phase and as diffused metal droplets in the slag and matte phase
- Co in matte phase as inclusions (metal droplets) – no dissolution.

Further work

- Investigate the influence of adding other metals as Al, Mn, Ni to the system
- Further investigation with spent LIBs instead of LiCoO_2 addition to the Cu-system
- Pre-treatment of batteries, physical separation

Thank you for your attention!

Project partners:
Stena Recycling AB
KTH
Chalmers