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CROCODILE

The use of Deep Eutectic Solvents in the context of CROCODILE H2020 project

11th MAY 2022

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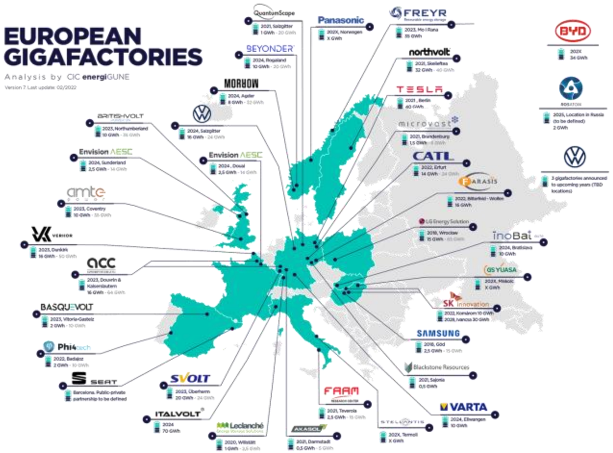
Introduction: The need

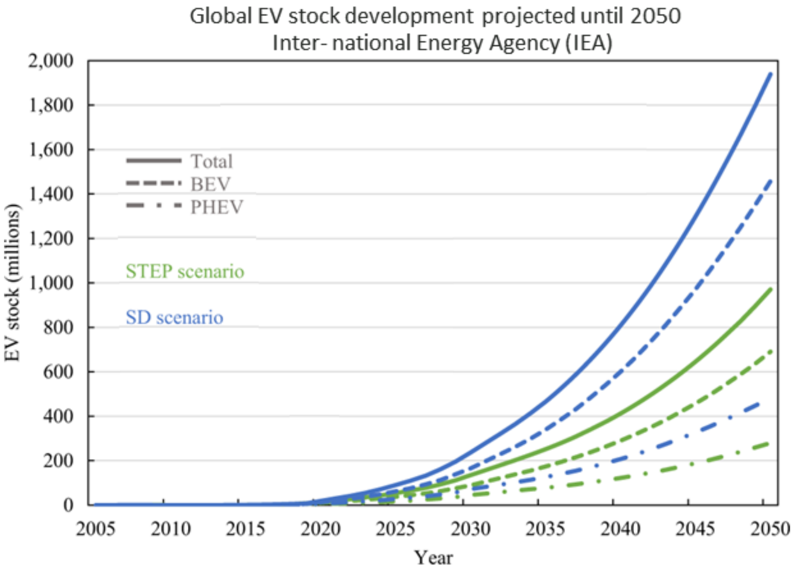
- Batteries are essential for energy storage in the electronics used in our everyday lives:
  - Small portable electronic devices (cell phones and laptops)
  - Medical devices
  - Electric vehicles

- Their use is continuously growing:

30 Initiatives projected for producing Li-Ion Battery cells in Europe



- For 2050, exponential growth is projected



BEV: battery electric vehicle
PHEV: plug-in hybrid electric vehicle

STEP: Stated Policies scenario
SD: Sustainable Development scenario

Introduction: The problem

- The expansion of EV market lead to a fast growth of battery residues

Millions of electric car batteries will retire in the next decade. What happens to them?

The quest to prevent batteries – rich in raw materials such as cobalt, lithium and nickel – ending up as a mountain of waste

▲ Batteries at a factory in Nanjing in China's eastern Jiangsu province, which makes lithium batteries for electric cars. Photograph: STR/AFP via Getty Images

- Residues containing Critical Raw Materials

- Materials scarce in Europe that lead to a great dependence of non-EU countries.
- Extraction and refining in third countries leads to high socio-economic and environmental impact.

For example for the Co :

- At least, 50% of the cobalt comes out of the mines in the Democratic Republic of the Congo
- 43% of refined cobalt is produced in China

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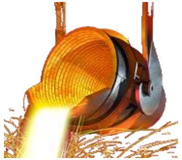
Introduction: The problem

Some of the challenges faced in current recycling SOA technologies:

- High environmental impact
- High energetic cost
- Low recovery yields
- Not all metals are recovered from batteries
- High generation of waste (slag and gas emissions)



- High CAPEX (limits the generation of new recycling companies)

- Use of strong inorganic acids

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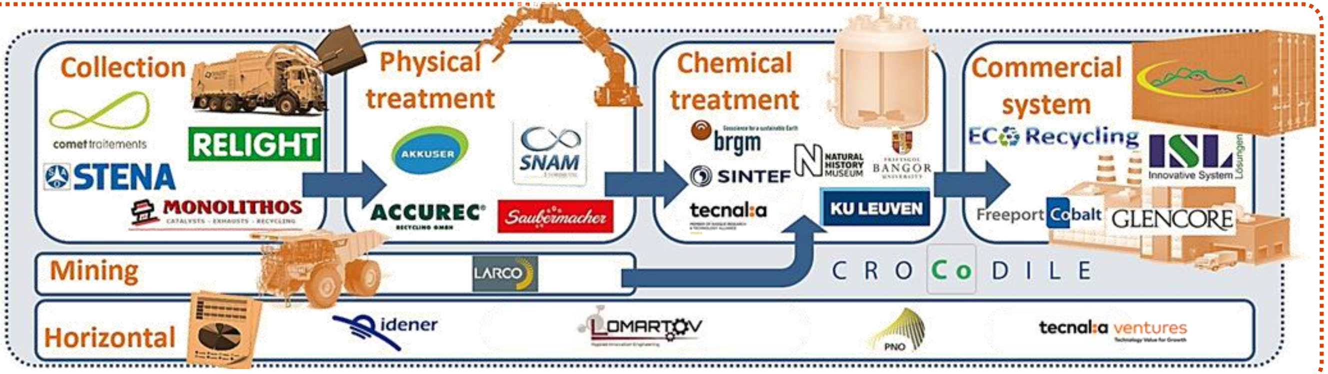
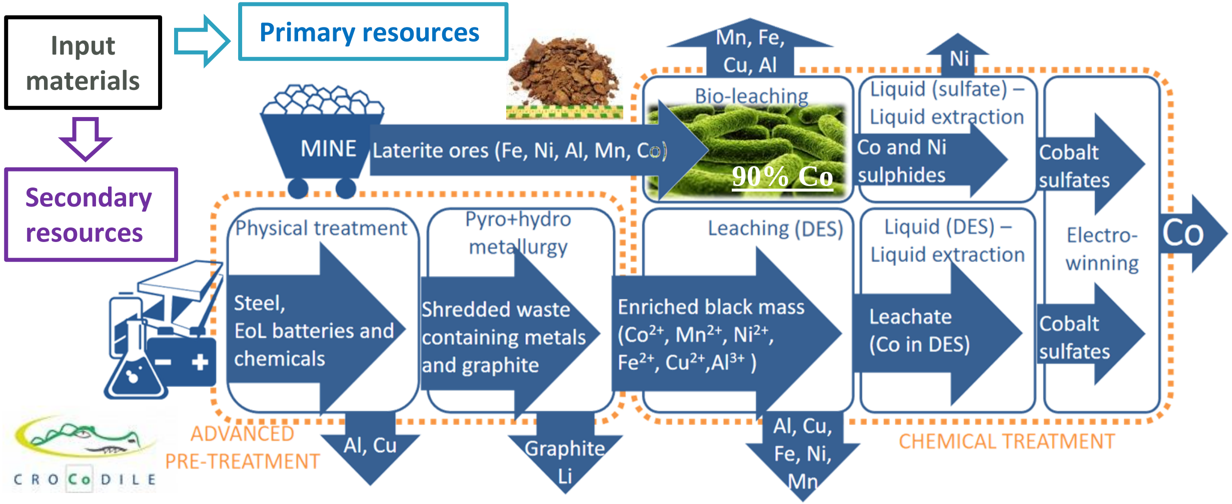
Grant Agreement No 776473

Coordinator: TECNALIA (Spain)





- **Scale-up** innovative integrated systems and technologies considering waste side streams
- Develop a **system** capable of producing cobalt metal in an environmental friendly way
- Build a **strong value chain**

CROCODILE project

Secondary resources → **DES**

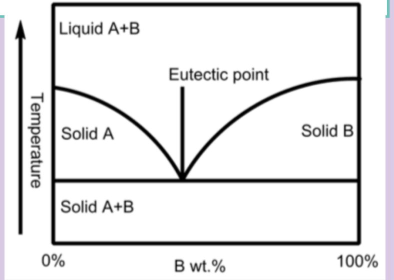
1. **Co-bearing scraps**


2. **Spent NiCoMo catalyst**

3. **EOL Co containing batteries**

New leaching process using Deep Eutectic Solvents (DES)

DES: Systems formed from a eutectic mixture of Lewis or Brønsted acids and bases (hydrogen bond donor + hydrogen bond acceptor). They are classified as types of ionic solvents with special properties: eutectic with a melting point much lower than either of the individual components.



- Low toxicity
- Low cost
- No flammable
- Reduced environmental impact
- High recovery yields
- Reusable

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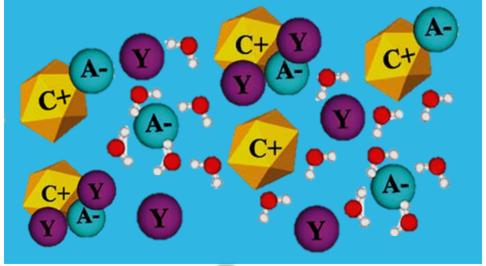
CROCODILE project

Secondary resources

DES (Hydrogen bond donor
+ Hydrogen bond acceptor)
+ H_2O & additives



+

Cobalt-bearing residues

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DES leaching
(Reductive/ Oxidative)

Solid residue

+

Leachate

Impurities:
Ni, Li, Mn, Cu, Al,
Fe, Zn, Mg

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Secondary resources

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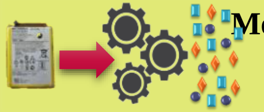
Pre-treatment

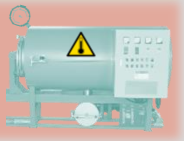
Input residues

Pyro-thermal

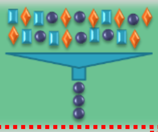
Mechanical



Vacuum-thermal



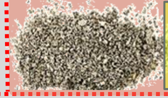
Dry / wet sorting



Metals:

Carbon:

Enriched residue



BM
7-37% Co

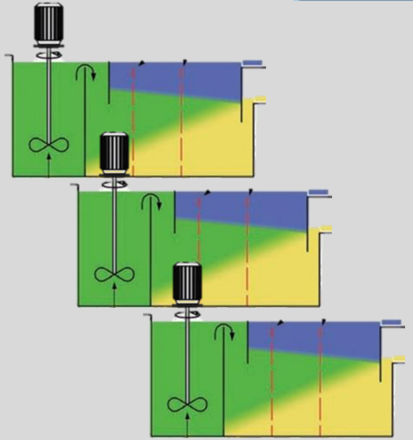
DES leaching

Leachate

Co + Impurities: Ni, Li, Mn, Cu, Al, Fe, Zn, Mg

Extraction of > **90% Co** from pre-treated residues in 3h

Liquid-liquid extraction



Co Sulphate

Transfer of >90% Co of the leachate to EW

Co metal E-winning

High value pure metal

High current density
High current efficiency

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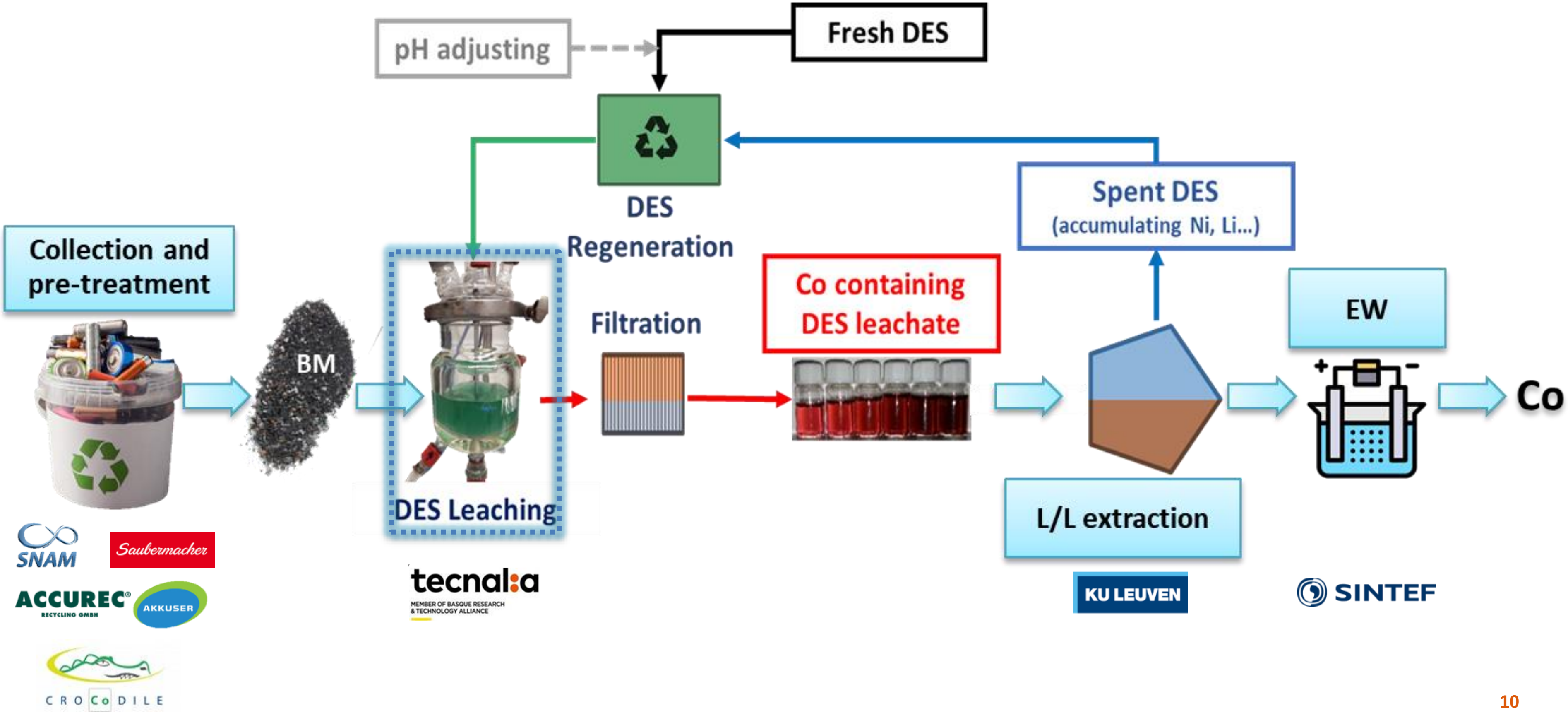
Secondary resources



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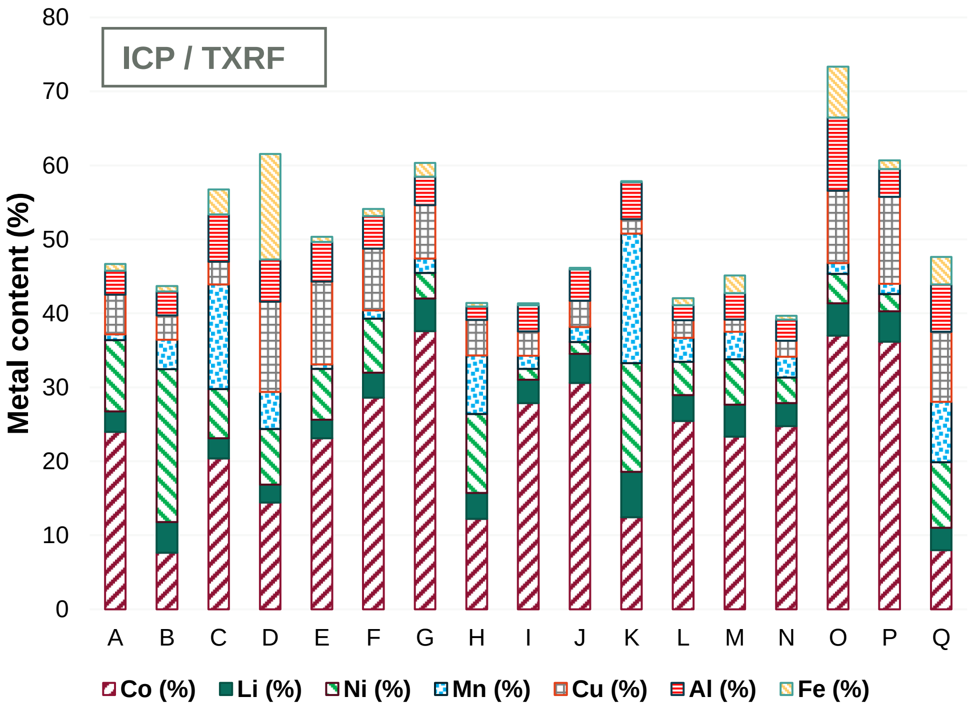
Experimental: Input sample analysis

- Broad type of samples were characterized: ICP/TXRF, XRD, SEM-EDS.



Metal	Content range (%)
Li	2-6%
Co	8-38%
Ni	1-21%
Mn	1-17%

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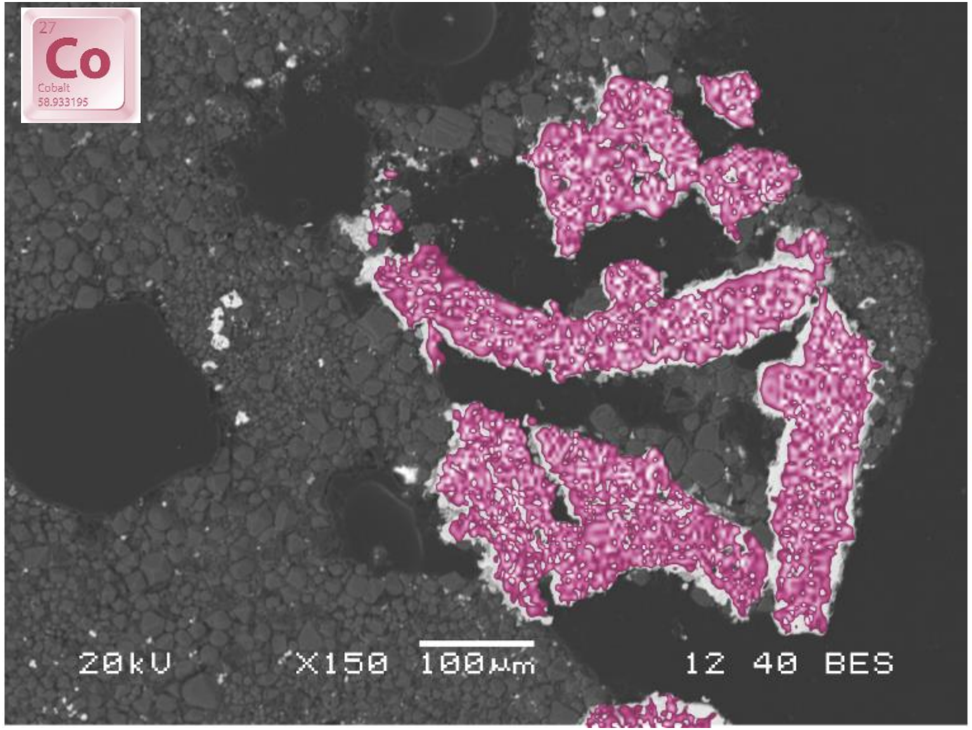
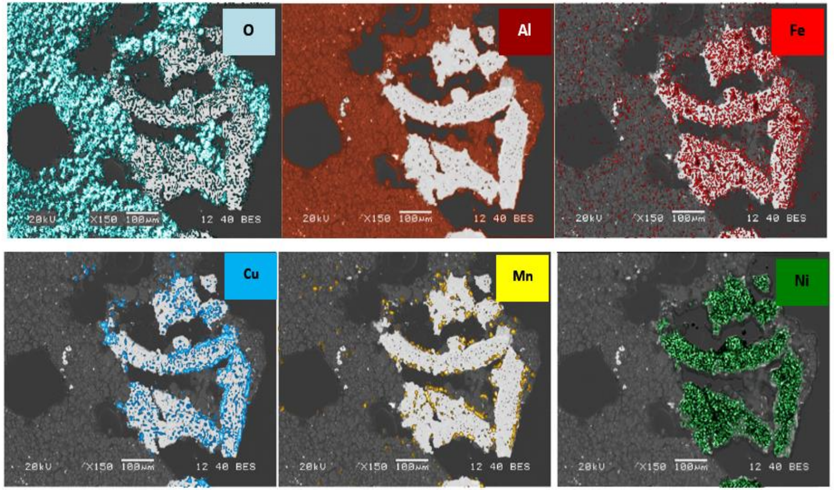
Experimental: Input sample analysis

SEM - EDS



SEM-EDS mapping shows the metal distribution in the particles



Experimental: Input sample analysis

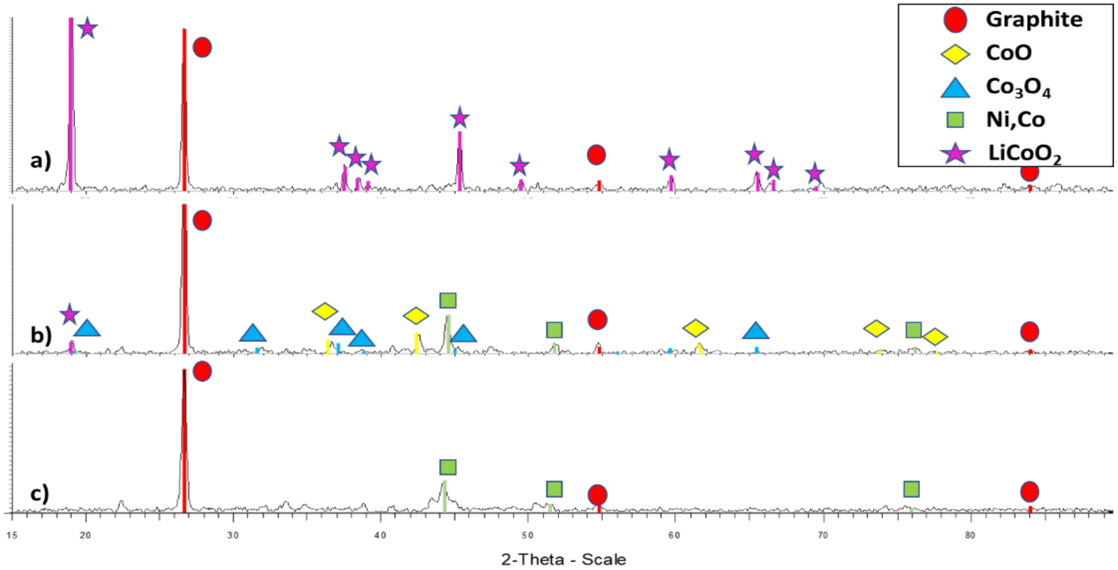
XRD

Different predominant mineralogical species were found by XRD, depending on the BM sample and pre-treatment processes performed:

$LiCoO_2$

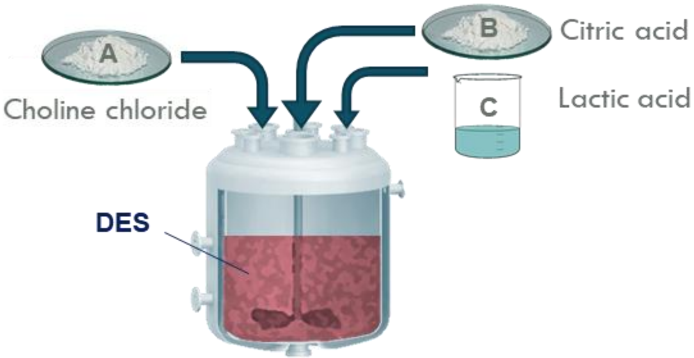
Co oxides (CoO, Co_3O_4)

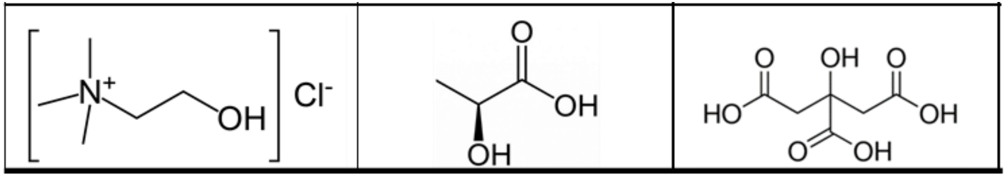
Metallic (Co, Ni)



Experimental: Leaching conditions

➢ Ternary Deep Eutectic Solvent mixture





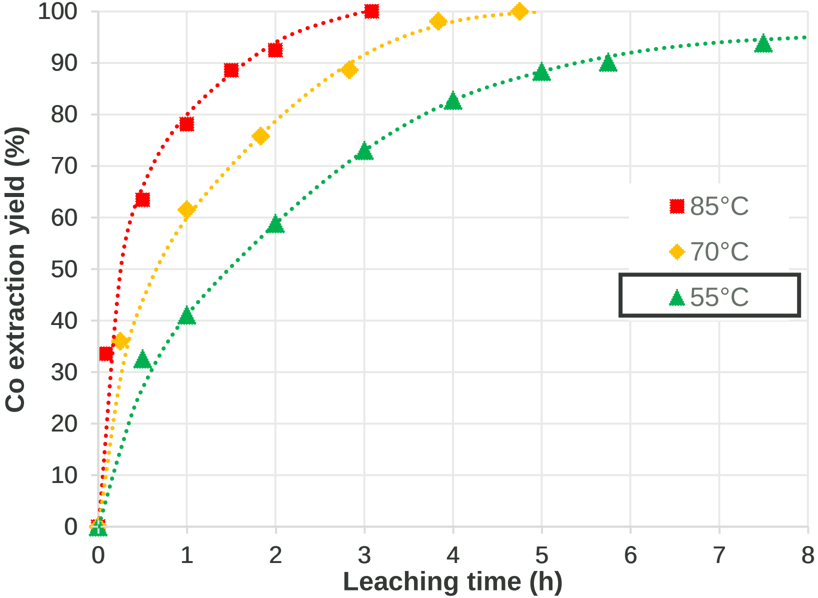
Choline Chloride	Lactic Acid	Citric Acid
Hydrogen bond acceptor	*Hydrogen bond donors*	

➢ Parameters studied

- Time [0-24h]
- Temperature [55-85°C]
- BM:DES:Water ratios
- Additives

Experimental: Leaching results

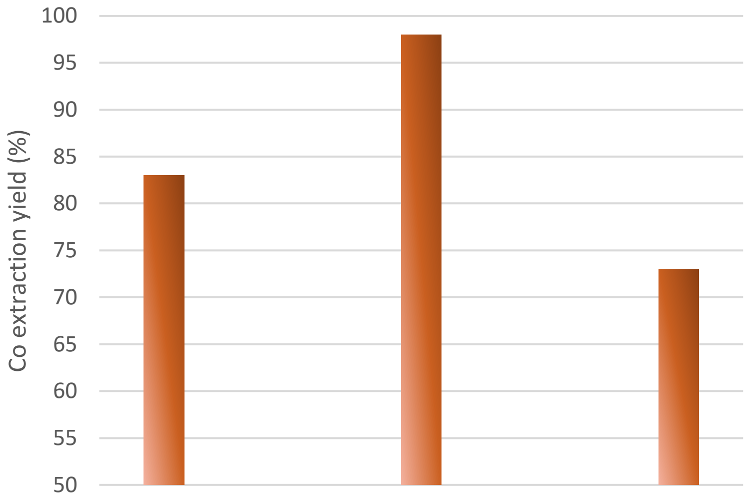
- Temperature



BM:DES 1:50

- BM:DES:water ratio

Tª: 55°C
t: 3h



(BM:DES)	Low DES	Optimized conditions	High DES
(DES:Water)	High dilution		Low Dilution

Low leaching agent

Diffusion limited by high viscosity

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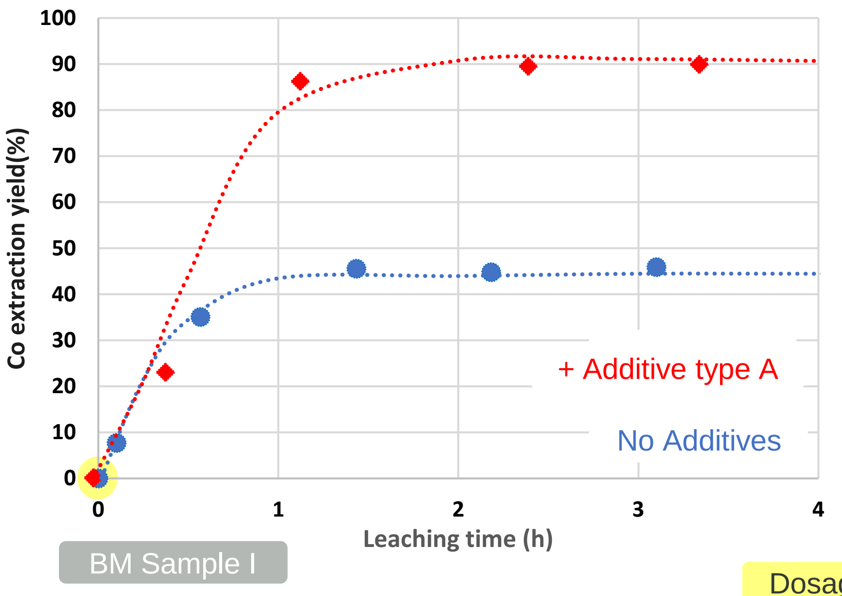
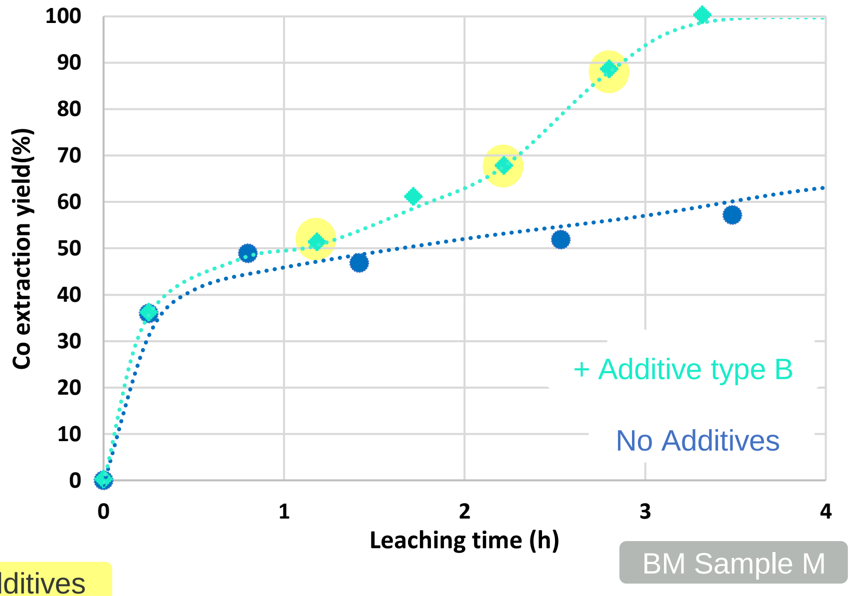
Experimental: Leaching results

➤ Additives: dosage of external additives





Dosage of additives

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Conclusions

DES Leaching

- It has been proved the viability of leaching most of the Co present in BM residues from LIBs in about 3 h and at low working temperature (55ºC) by using DES
- The obtained results indicate that the use of additives may be necessary for some type of BM
- Knowledge of the nature of the black mass to select the adequate operating conditions of the treatment is required

L/L extraction	Achieved transfer of >90% Co of the DES to EW	EW	High current density High current efficiency

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Thank you for your attention

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CROCODILE website: https://h2020-crocodile.eu/

Research group : https://www.linkedin.com/showcase/tecnalia-waste-valorisation

This project has received funding from the European Union's EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No 776473

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