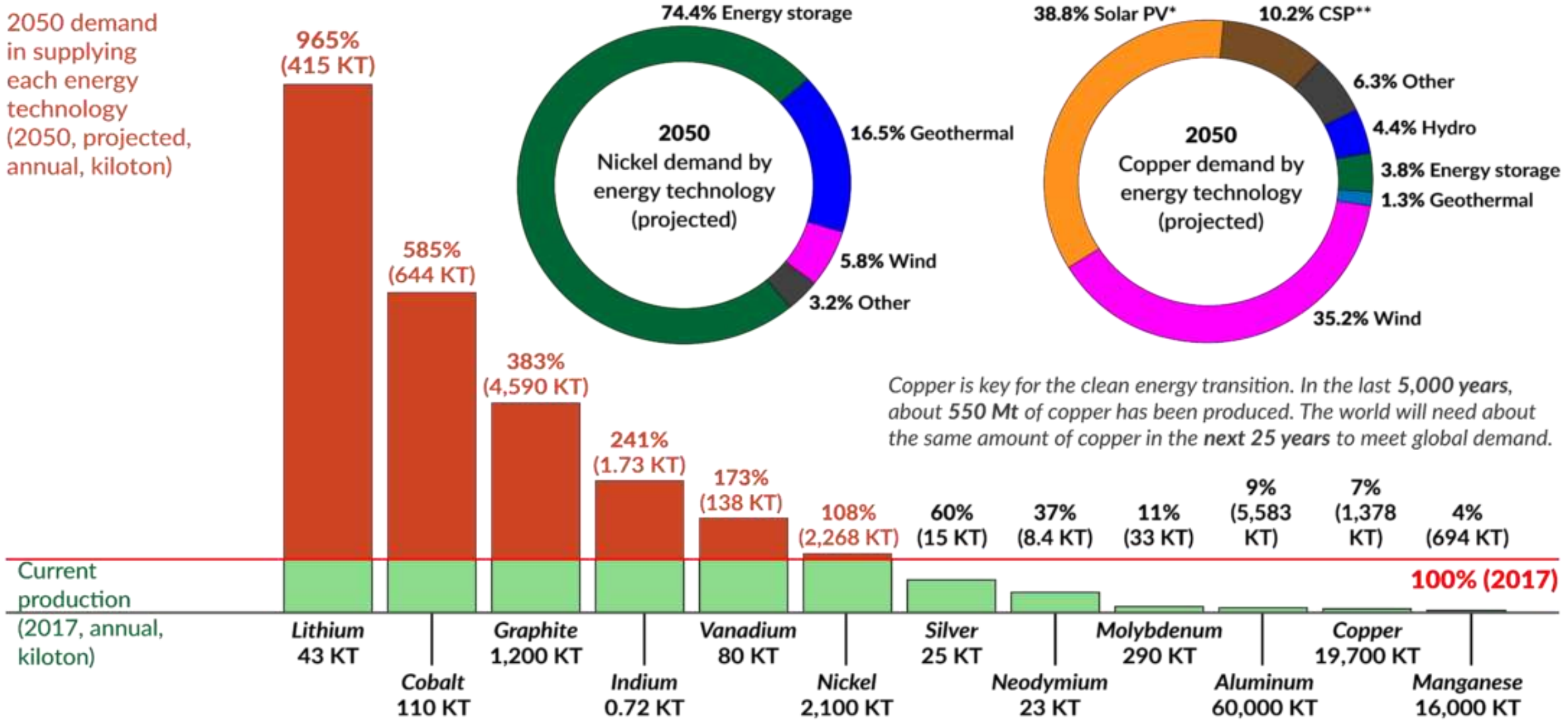
Il progetto Cariplo TECH4LIB: nuove tecnologie basate sull'utilizzo di microonde per il recupero di metalli in batterie al litio esauste

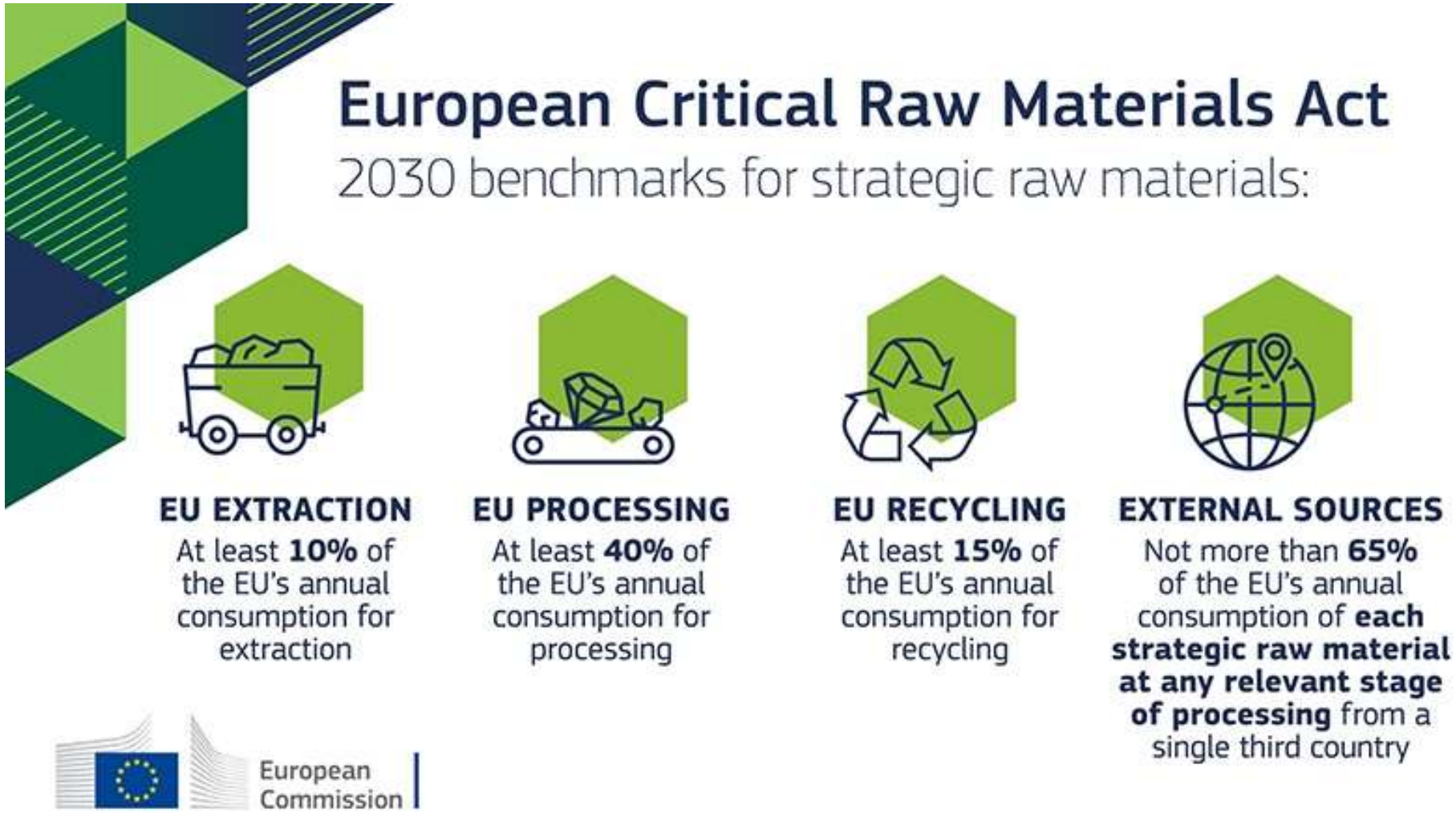
Elza Bontempi
elza.bontempi@unibs.it

The alternative energy megatrend, as the demand for some metals and rare earth elements



UNIVERSITÀ DEGLI STUDI DI BRESCIA

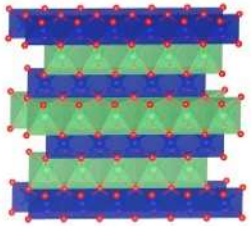
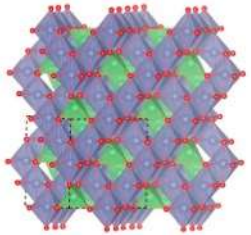
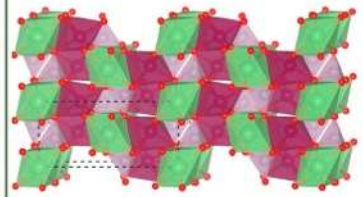
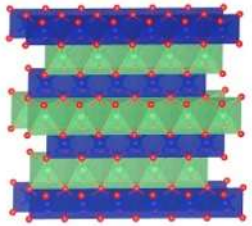
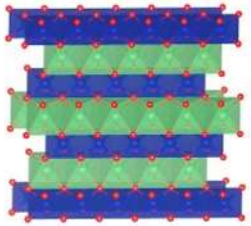
Member States will need to adopt and implement national measures to improve the collection of critical raw materials rich waste and ensure its recycling into secondary critical raw materials



The proposed Regulation will be discussed and agreed by the European Parliament and the Council of the European Union before its adoption and entry into force.
The Critical Raw Materials Act will equip the EU with the tools to ensure the EU's access to a secure and sustainable supply of critical raw materials

16 March 2023

Cathode materials from the most commonly used commercial LIBs

Cathode types	LCO	LMO	LFP	NCA	NCM
Chemical formula	$LiCoO_2$	$LiMn_2O_4$	$LiFePO_4$	$LiNi_xCo_yAl_zO_2$	$LiNi_xCo_yMn_zO_2$
Structure					
Market share	Dumped	Small	Growing	Steady	Main force
Typical use	Portable electronic devices	Power tools and electric bikes	Electric bikes, large EVs and power tools	Panasonic batteries for Tesla EVs	Portable electronic devices and EVs
Comments	Low safety, high cost, medium performance	Medium safety, low cost, medium energy density, low lifetime	Good safety, low cost, high thermal stability, medium energy density	Medium safety, medium cost, higher energy density	Medium safety, medium cost, higher energy density, high lifetime

UNIVERSITÀ DEGLI STUDI DI BRESCIA

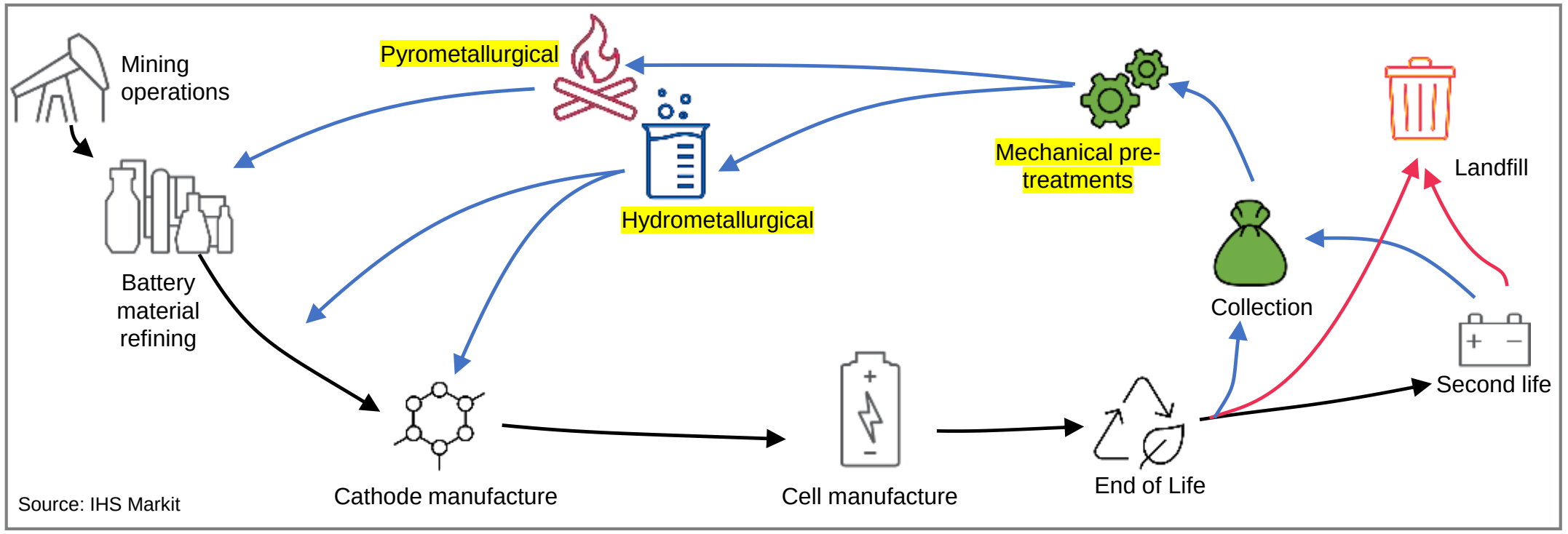
Journal of Cleaner Production 340 (2022) 130535

Li-ion battery recycling possibilities

UNIVERSITÀ DEGLI STUDI DI BRESCIA

Overview of LIBs battery recycling treatments

The already established recycling processes are mainly based on pyrometallurgy and hydrometallurgy.



End-of-life treatments: black mass (BM)

Hydrometallurgy

Pyrometallurgy

https://www.duesenfeld.com
Vecteezy

Carbothermic reduction

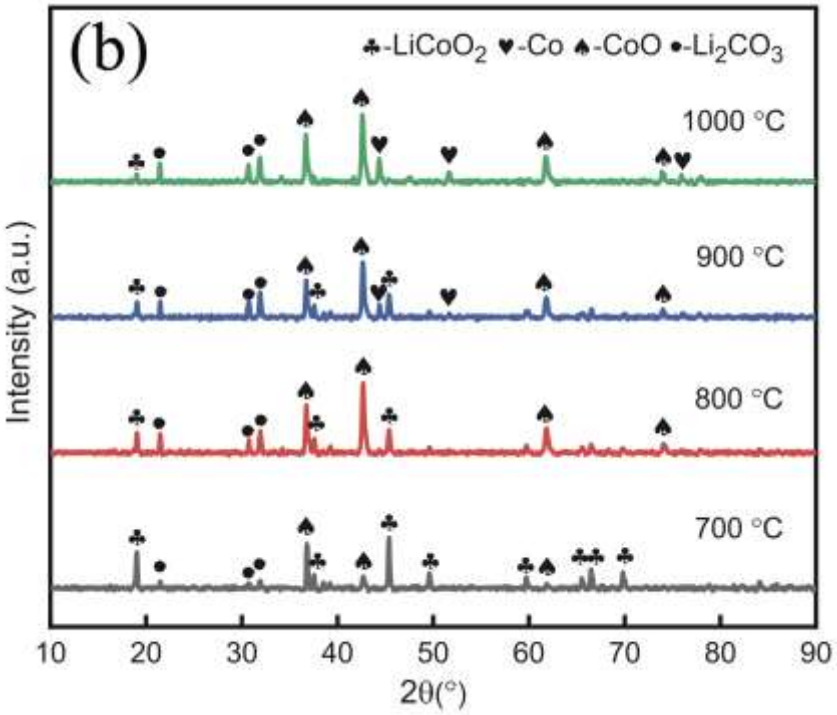
Electrode material $LiCoO_2$ decomposes at above 900°C

$4LiCoO_2 \rightarrow 2Li_2O+4CoO+O_2$

During the high-temperature treatment of the mixture of $LiCoO_2$ and graphite in air

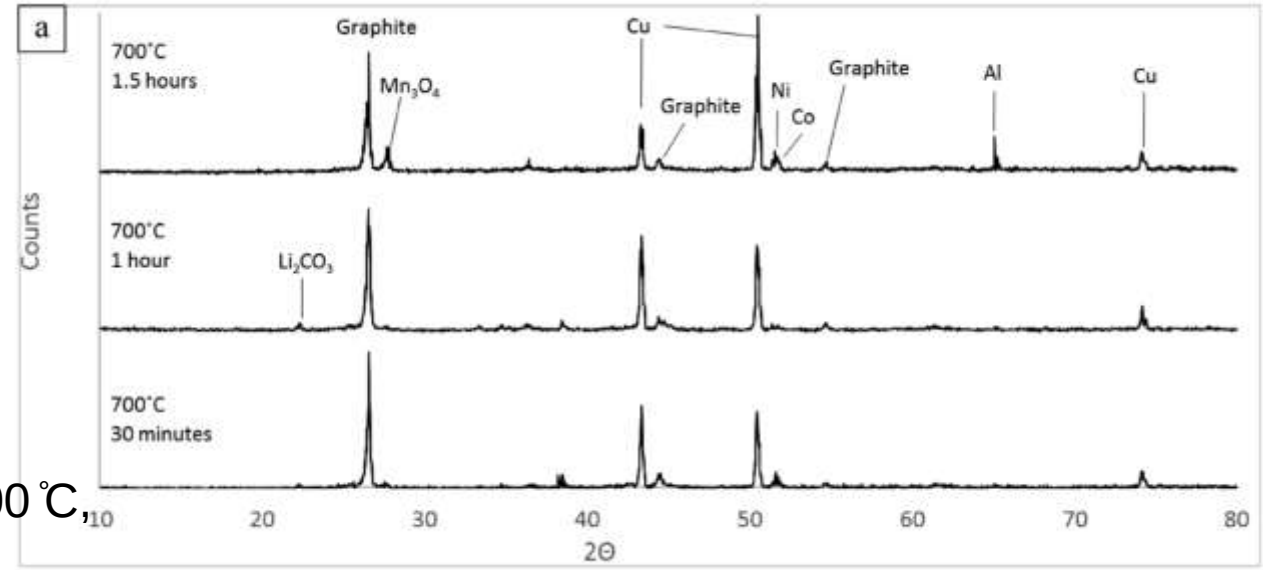
$2LiCoO_2+3CO \rightarrow 2Co+Li_2O+3CO_2$

XueFeng She , Kewei Zhu, JingSong Wang and QingGuo Xue, Journal of Chemical Research 2022



The increasing of the temperature and time of treatment promotes the carbothermic reduction and the removal of graphite and organic components. It was observed that at 700 °C after 1.5 h of treatment the cathode active material is completely decomposed.

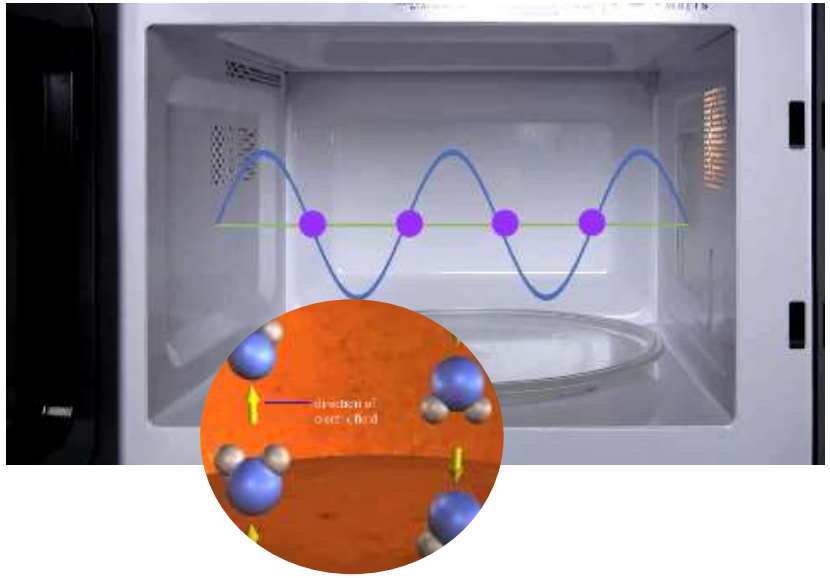
ACS Sustainable Chem. Eng. 2019, 7, 13668−13679



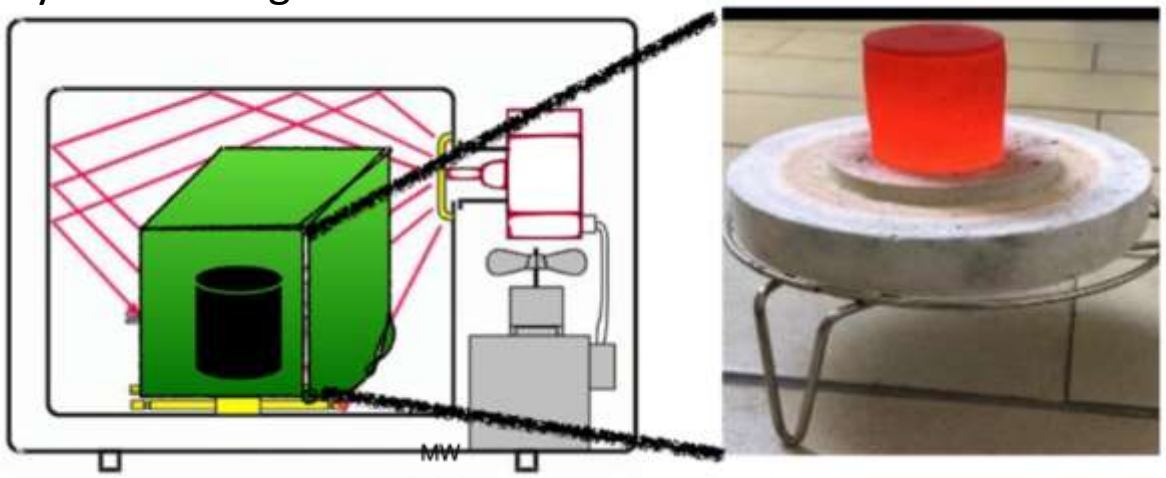
The chemical reactions became spontaneous at ≥ 600 ℃, because their Gibbs free energy became negative

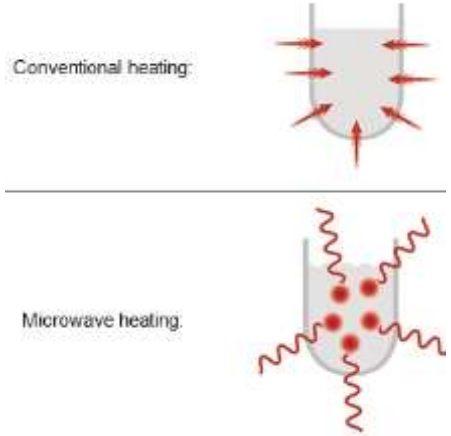
Chemical Engineering Journal 435 (2022) 135165

Microwave (MW)-based heating technology

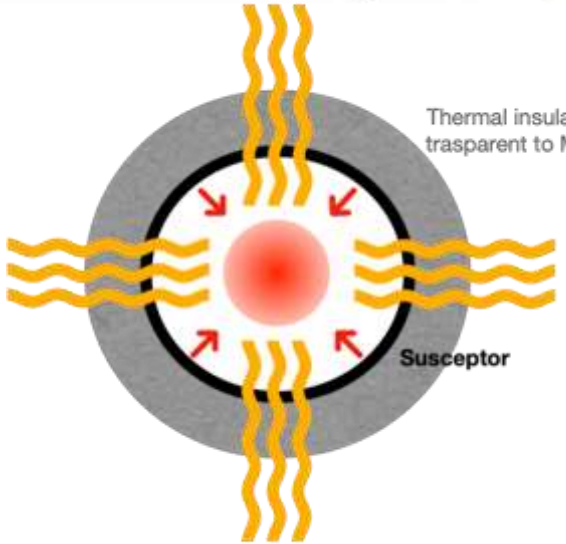


hybrid heating mechanism





When a susceptor is excited by MW radiation it rapidly increases his temperature.
The effect of hybrid heating reduces heat loss and results in more uniform heating of the material.



Hybrid MW heating with susceptor

PCT
METHOD FOR RECOVERING MATERIALS FROM WASTE OR SCRAPS THROUGH AN IMPROVED CARBOTHERMAL PROCESS

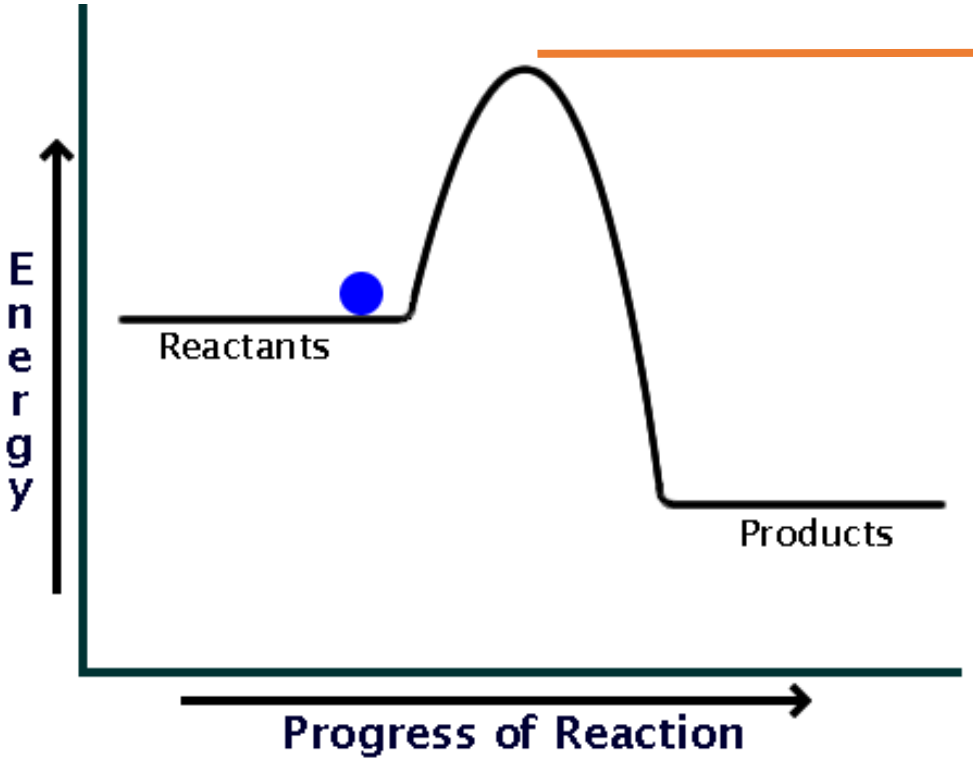
UNIVERSITÀ DEGLI STUDI DI BRESCIA

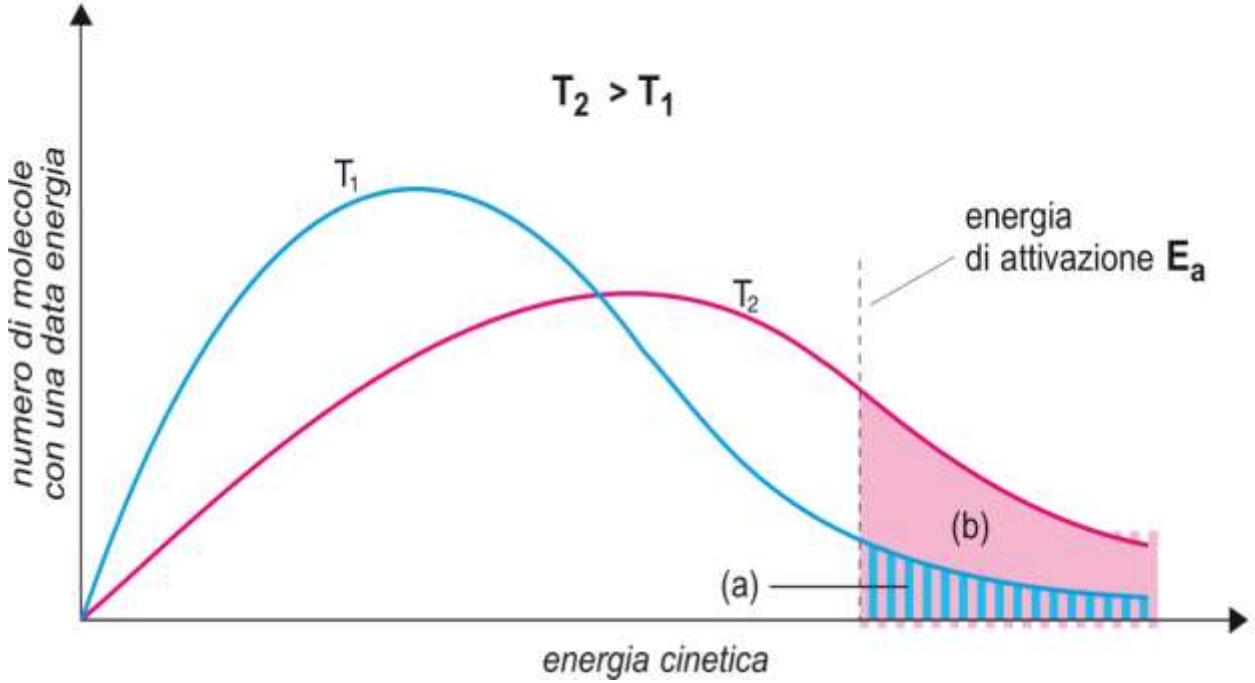
Co-funded by the Horizon 2020 programme of the European Union

ERA-MIN 2

RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

Activation energy



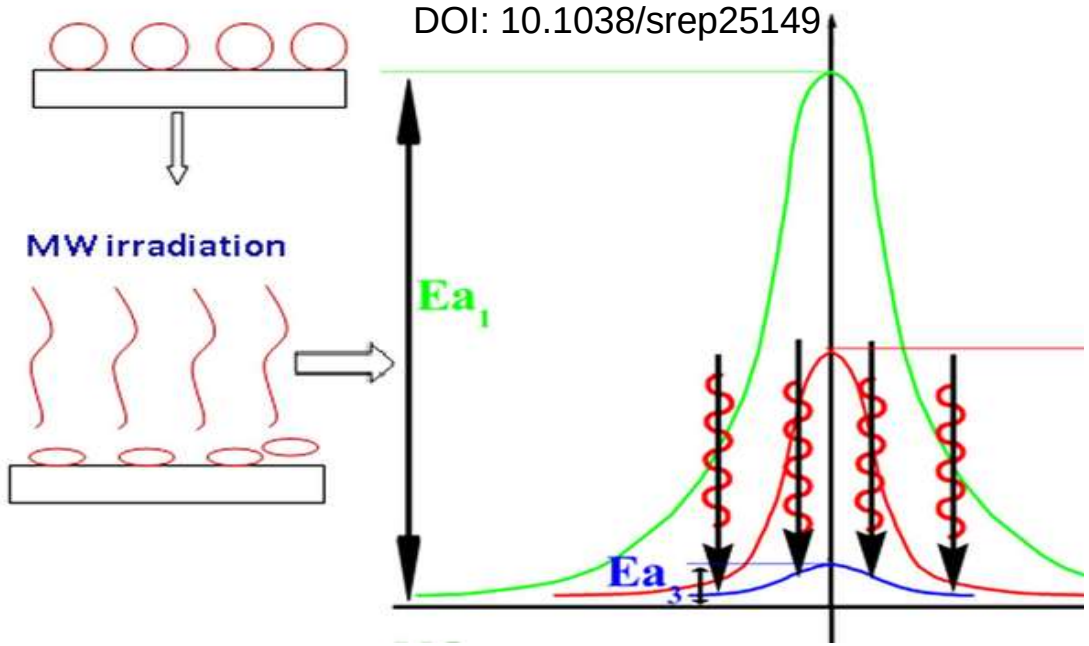


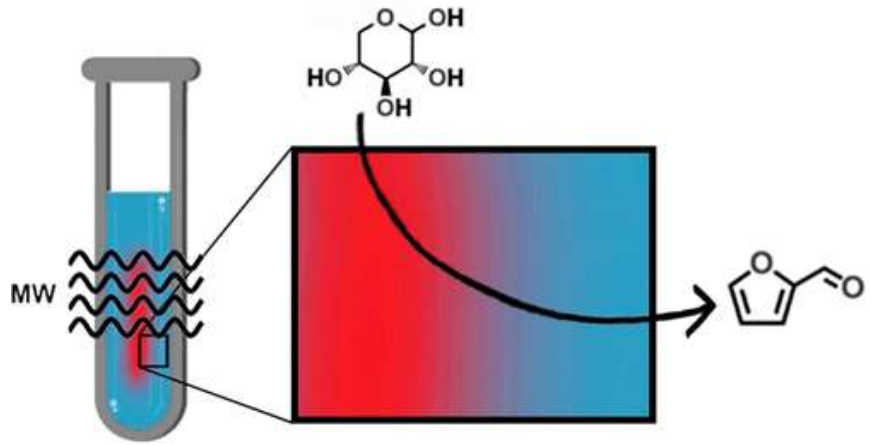
UNIVERSITÀ DEGLI STUDI DI BRESCIA

Microwave non thermal effects

Nonthermal effects may result from a direct interaction of the electric field with specific molecules in the reaction medium. This results in an enhancement of reactivity by lowering the activation energy

DOI: 10.1038/srep25149





DOI: 10.1021/acssuschemeng.9b03580

MW irradiation energy can cause a change in the molecular rotational energy level, which leads to a decrease in the Activation energy (Ea) for reactions involving a polar transition state

Co-funded by the Horizon 2020 programme of the European Union

ERA-MIN 2

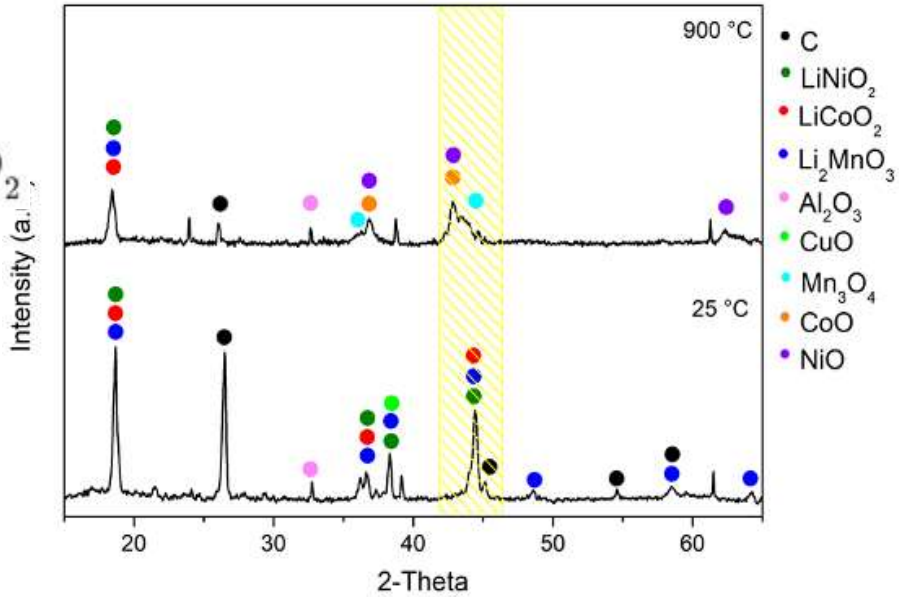
RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

Examples of the treatment procedure

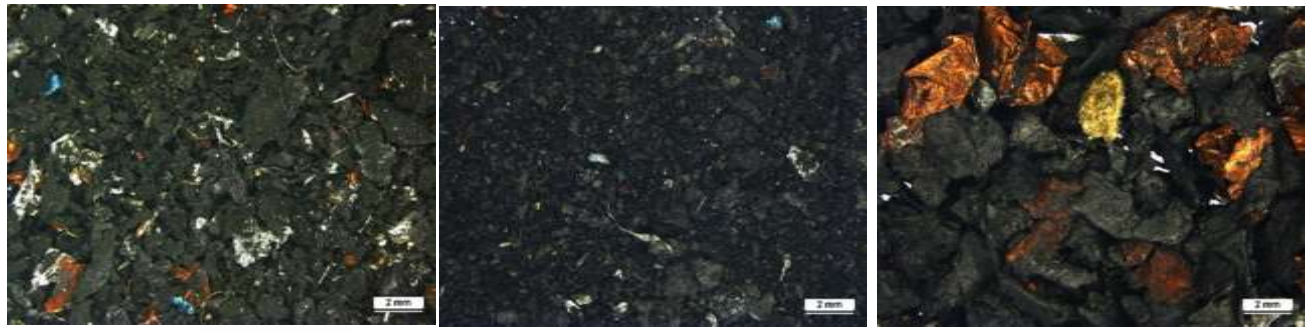
Mixed LIBs waste typologies:
LNO – $LiNiO_2$
LMO – Li_2MnO_3
LCO – $LiCoO_2$

The mixed powder begins to decompose at a temperature higher than 500 °C and forms the corresponding metal oxide.
The reaction formula is as follows:

$$LiNi_xCo_yMn_{1-x-y}O_2 = \frac{1}{2}Li_2O + xNiO + yCoO + 1\text{-}x\text{-}yMnO_2 + \frac{1}{2}(x+y-\frac{1}{2})O_2$$



Bulk | Φ<1mm | Φ>1mm

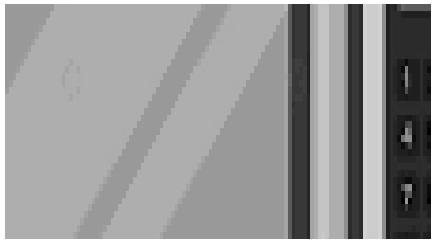


- Cu and Al removal for safety of microwave treatment

Black mass (BM)

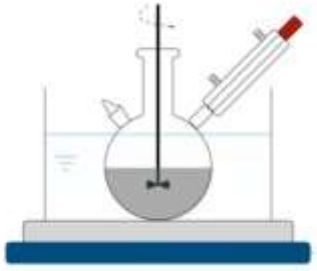
- Sieving

Mechanical sieving



Microwave treatment

- Air Atmosphere
- No chemicals addition
- Target weight loss (volatile C)



40 g/L
80°C
30 min

Water and organic acid (1,2M) leaching treatment

Co-funded by the Horizon 2020 programme of the European Union

ERA-MIN 2

RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

BM microwave treatment of few minutes

BM water leaching to recover Li

Vecteezy

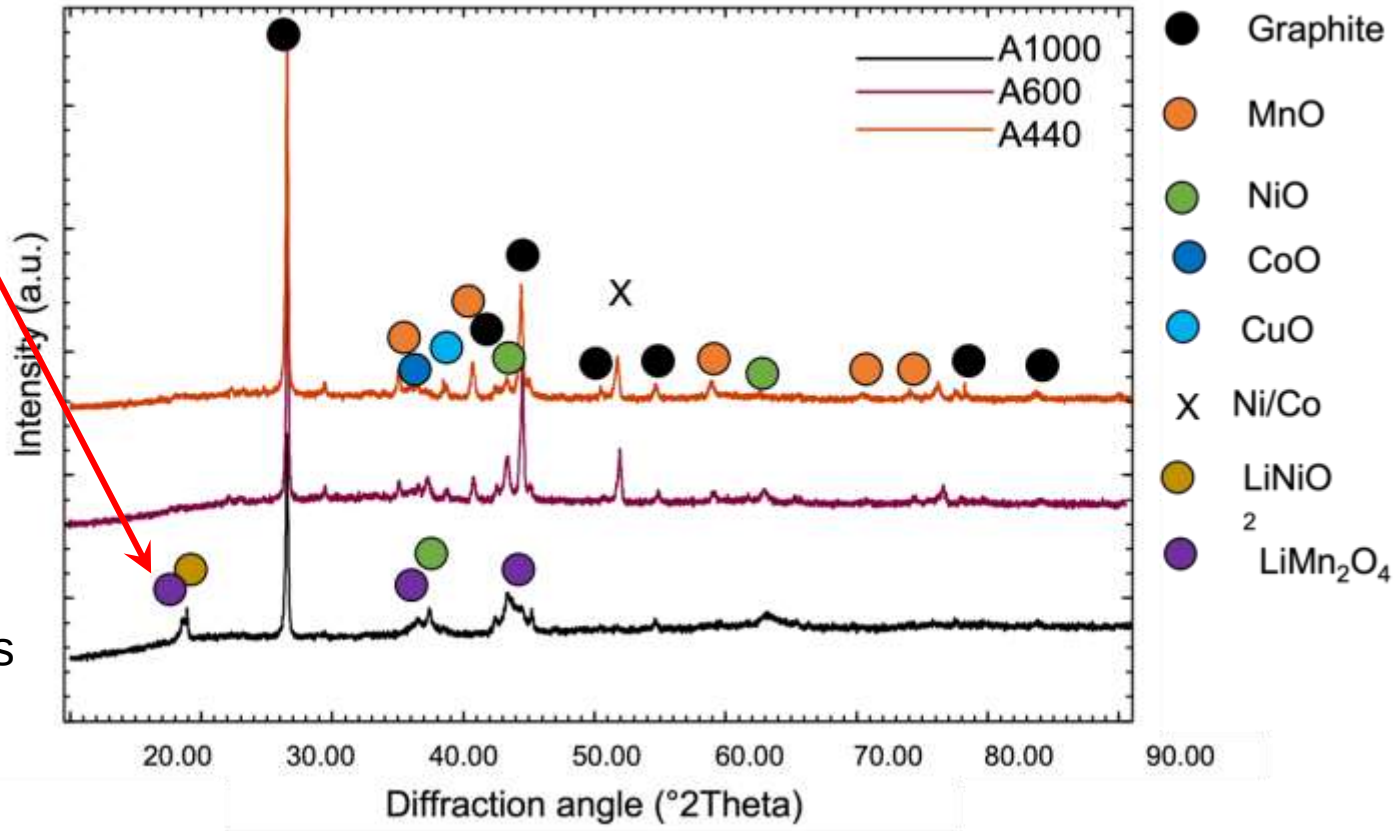
Results: after MW treatments and water leaching (with the inset)

Li-mixed oxides are still present only in this sample

A440: 440 W for 12 minutes

A600: 600 W for 8 minutes

A1000: 1000 W for 4 minutes



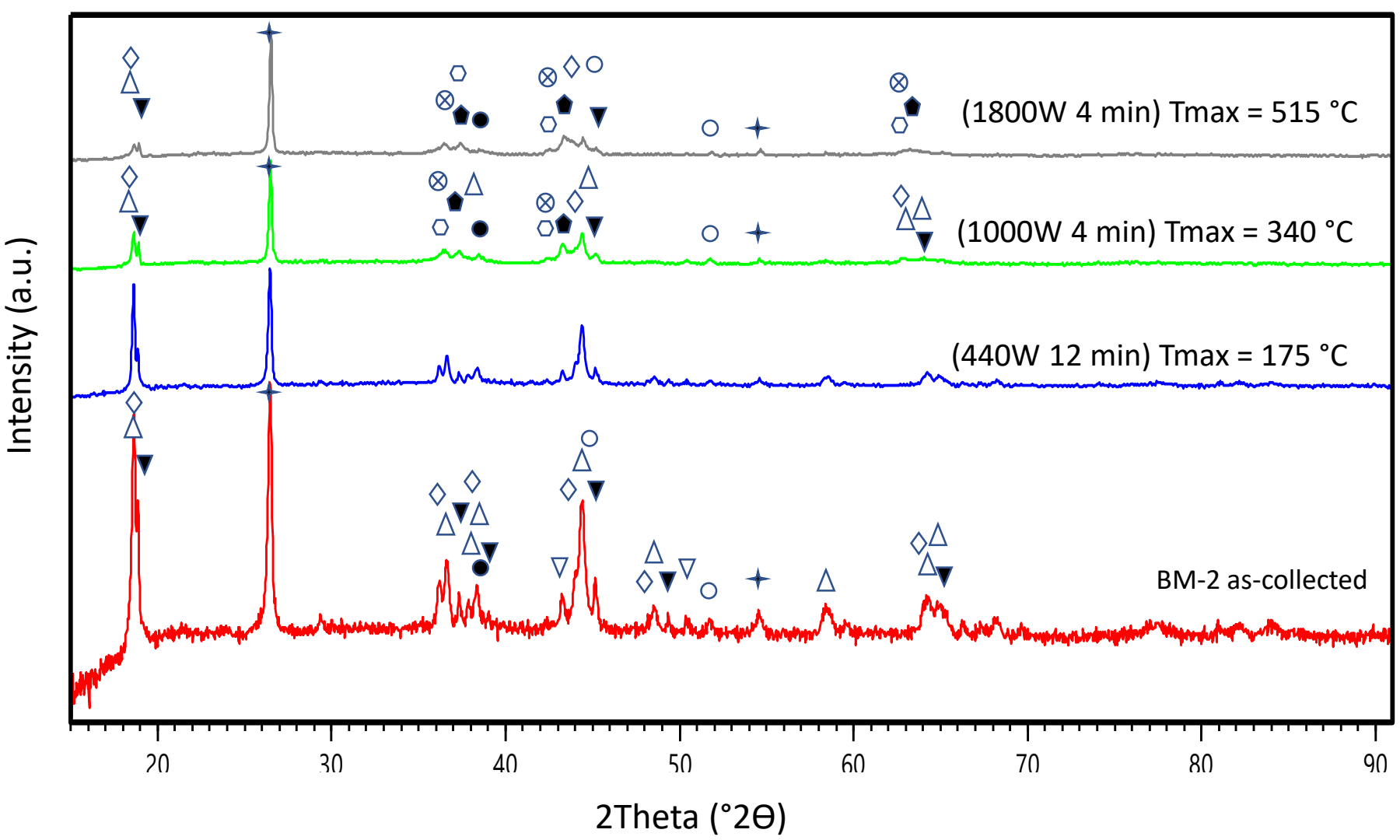
Considering that cathodic material Li(Ni-Co-Mn) oxides, having oxidation properties and graphite, having reduction properties, are both present in the BM a typical carbothermic reaction was occured.

Co-funded by the Horizon 2020 programme of the European Union

ERA-MIN 2

RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

Results: after MW treatments and water leaching (without the inset)



- Graphite – C
- Nickel – Ni
- Copper – Cu
- Aluminum - Al
- Lithium Cobalt Oxide – $LiCoO_2$
- Lithium Manganese Oxide – $LiMn_2O_4$
- Lithium Nickel Oxide – $LiNiO_2$

Phases found only in 1000-1800 W treated samples:

- Cobalt Oxide – CoO
- Nickel Oxide - NiO
- Copper Oxide – Cu_2O

440W sample shows the same XRD diffraction pattern of BM-2 as-collected.

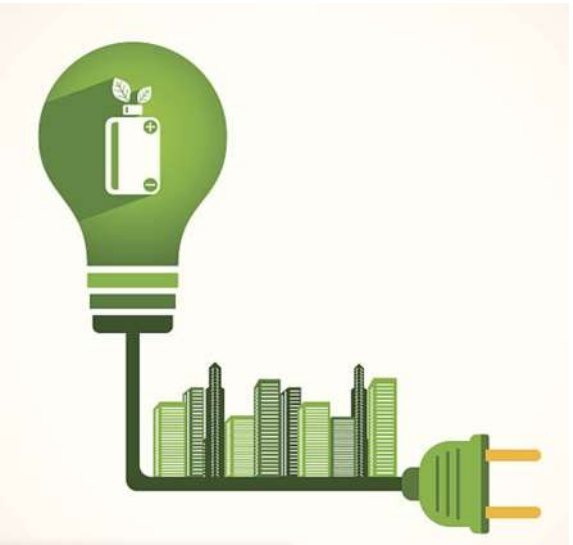
BM acid leaching to recover the other metals

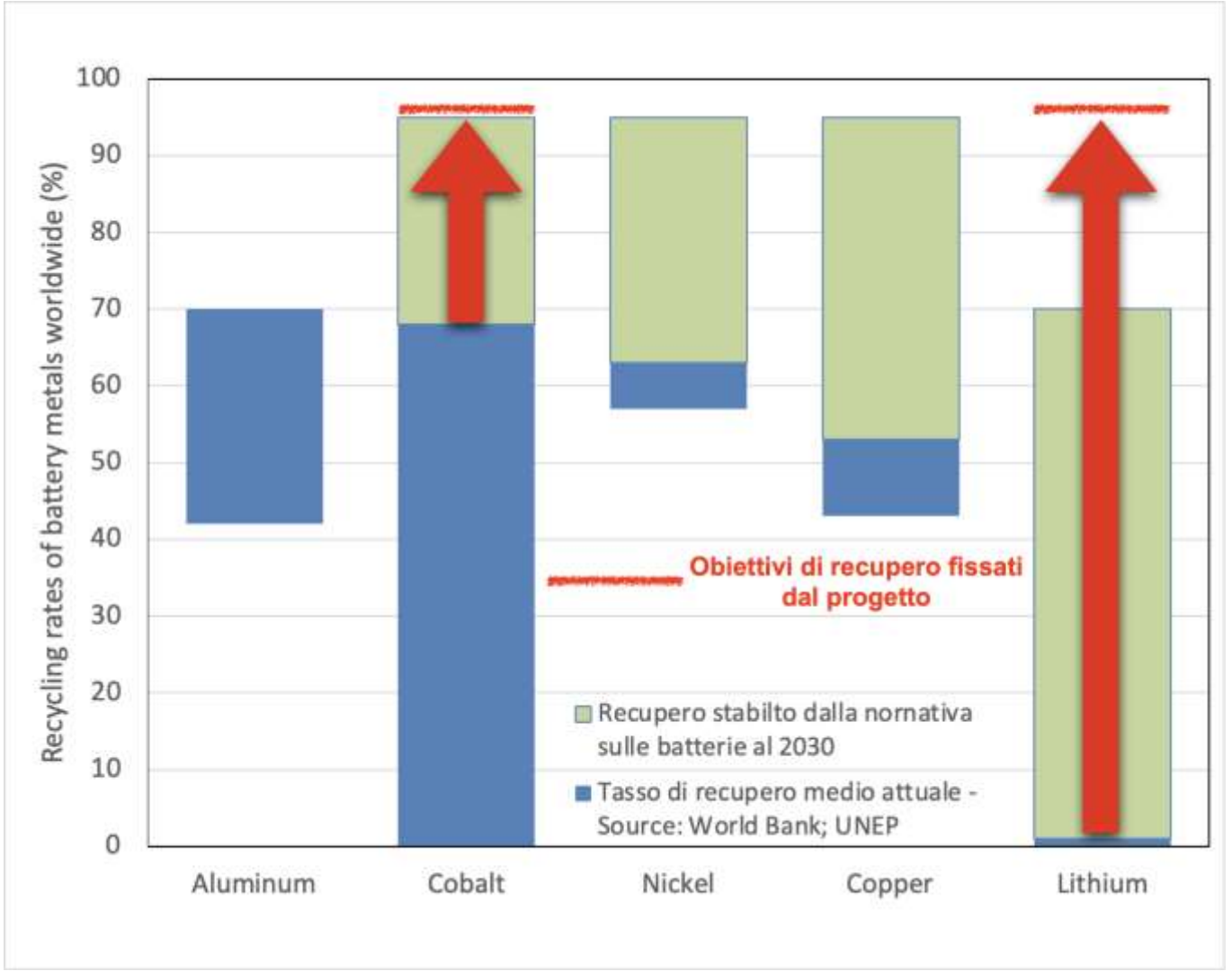
Vecteezy

Regulation constrains

In December 2020, the European Commission published the proposed Regulation on Batteries and Waste Batteries

Recovery target on 2030





Project results:
Lithium > 90%
Cobalt > 90%
Manganese > 90%
Nickel > 70%
Aluminum > 50%

Co-funded by the Horizon 2020 programme of the European Union

ERA-MIN 2

RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

$MO\ (s) + CO(g) \Rightarrow M(s) + CO_2\ (g)$

M = metal

Recovery of Lithium

Cobalt

Manganese

Nickel

Iron

Aluminium

Copper

Vecteezy

Conclusion and technology advantages

- This treatment induces a unique transformation of BM, which cannot be achieved either with conventional treatment or simple MW heating
- The method is very flexible, requires minimum treatments and reduced quantities (near to zero) of commercial chemicals
- It allows the use of organic acids (which may be obtained from food waste) instead of their inorganic counterpart
- Preliminary energy evaluation allows us to conclude that the method is more sustainable in comparison to standard pyrometallurgical treatments
- The treatment, based on carbothermic reactions, can be applied to all cathodic Li materials, also on mixed batteries waste
- The method is flexible, then it can be suitable to treat also future batteries made on mixed metals oxides, and then it is suitable to be extended

Possible improuvments

- Due to the presence of residual graphite, it would be possible to propose also graphite partial recovery, for example by flotation
- The carbon dioxide generated by carbothermic reduction could be recovered to promote lithium-ion carbonation and the recovery of the Li_2CO_3 phase
- The safety aspect connected with gas production must be investigated in detail in the next future

Thanks to EIT Raw Materials for selection

A sustainable future for batteries

Vecteezy

Research founded by
Fondazione Cariplo
(Tech4lib project) and
PNRR (3°-Italy project)

elza.bontempi@unibs.it

Laboratorio di Chimica per le Tecnologie

Grazie per l'attenzione

UNIVERSITÀ DEGLI STUDI DI BRESCIA

Fondazione CARIPLO

MICS