Preliminary tests for lanthanum and cobalt recovery from waste SOFCs cathodes

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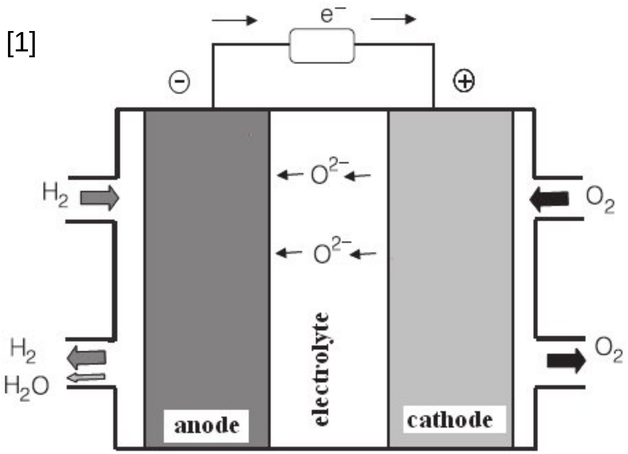
Solid Oxide Fuel Cells (SOFCs)

SustainaBlE SoluTions FOR recycling of end of life Hydrogen technologies

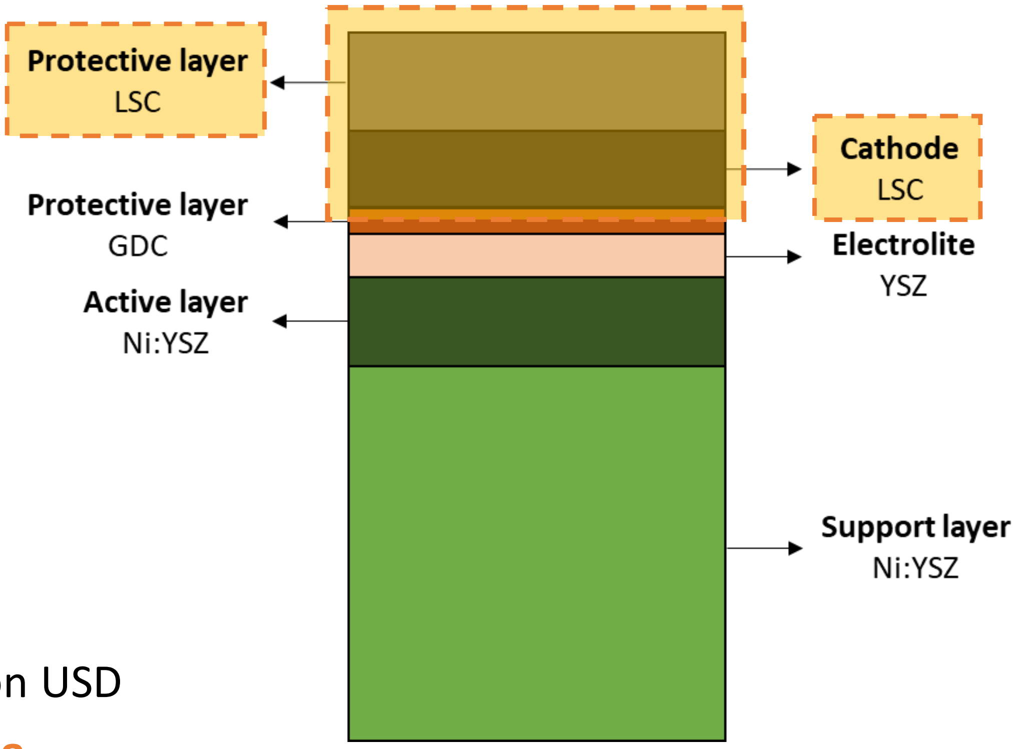
[1]



[2] Predicted SOFCs market growing:

1.09 billion USD → 5.31 billion USD

2021 → **2028**



Solid Oxide Fuel Cell (SOFC)

Lanthanum Strontium Cobaltite

$$La_{0,6}Sr_{0,4}CoO_3$$

GOAL

Hydrometallurgical recovery of lanthanum and cobalt from the cathodes of End of Life (EoL) SOFCs

[1] Taroco H, Santos J, Domingues R, Matencio T. Ceramic materials for solid oxide fuel cells. 2011.
[2] Solid Oxide Fuel Cell Market Size, Share & COVID-19 Impact Analysis, By Application (Stationary, Transport, Portable), ByEnd-User (Commercial, Data Centers, Military & Defense, and Others), and Regional Forecast, 2021–2028. Available online

Experimental design

PREPARATION of LSC powders

LEACHING employing an acid lixiviant

- **1 Sulfuric acid** process
- **2 Citric acid** process

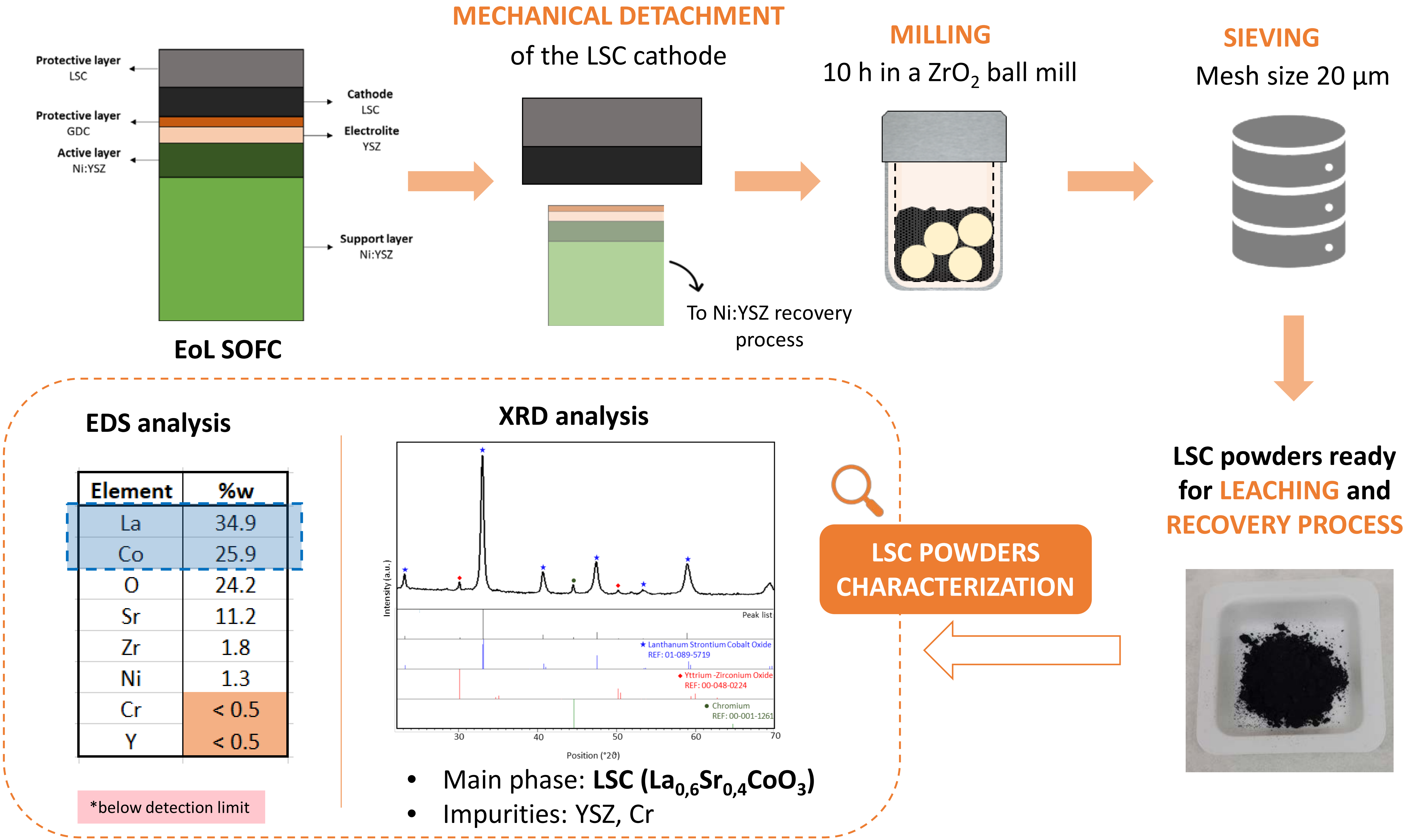
RECOVERY of compounds rich of La and Co

Oxalic acid was used as precipitating agent for both 1 and 2

CHARACTERIZATION of the products:

XRD analysis
SEM-EDS analysis

EVALUATION of LEACHING EFFICIENCY and RECOVERY YIELD of the two processes



MECHANICAL DETACHMENT
of the LSC cathode
MILLING
10 h in a ZrO_2 ball mill
SIEVING
Mesh size 20 µm
Protective layer
LSC
Cathode
LSC
Protective layer
GDC
Electrolite
YSZ
Active layer
Ni:YSZ
Support layer
Ni:YSZ
EoL SOFC
To Ni:YSZ recovery process
LSC powders ready for LEACHING and RECOVERY PROCESS
LSC POWDERS CHARACTERIZATION
EDS analysis
Element | %w
La | 34.9
Co | 25.9
O | 24.2
Sr | 11.2
Zr | 1.8
Ni | 1.3
Cr | < 0.5
Y | < 0.5
*below detection limit
XRD analysis
Intensity (a.u.)
Peak list
★ Lanthanum Strontium Cobalt Oxide
REF: 01-089-5719
◆ Yttrium -Zirconium Oxide
REF: 00-048-0224
● Chromium
REF: 00-001-1261
30
40
50
60
70
Position (°2θ)
• Main phase: LSC ($La_{0,6}Sr_{0,4}CoO_3$)
• Impurities: YSZ, Cr

1 SULFURIC ACID process (1/2)

2 LEACHING STEPS at different temperatures:

Co solubility **increases** with temperature

EoL LSC powders

High T LEACHING STEP

2 M H_2SO_4

150 g/L; 80°C; 3h

Co-rich liquor

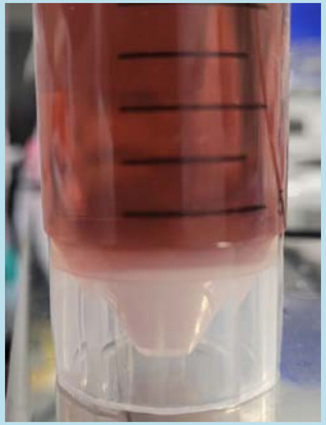
pH 0.5

La-rich solid

Low T LEACHING STEP

10 M NaOH

RECOVERY #1



1 **1st precipitate**

pH ≤ 1.5

Equilibrium pH 1.5
adding **10 M NaOH**

RECOVERY #2

1 M $H_2C_2O_4$

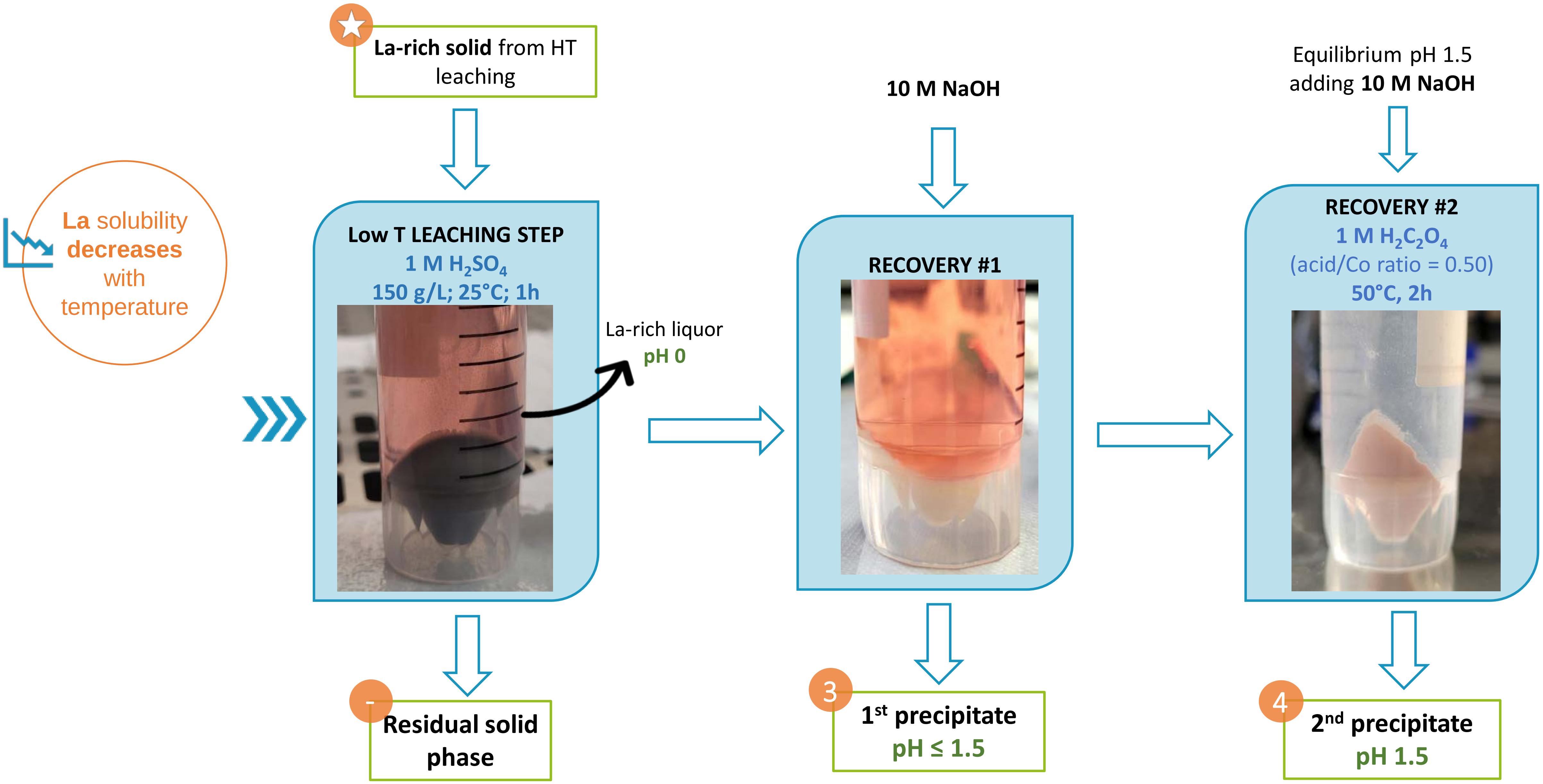
(stoichiometric for Co)

50°C, 2h

2 **2nd precipitate**

pH 1.5

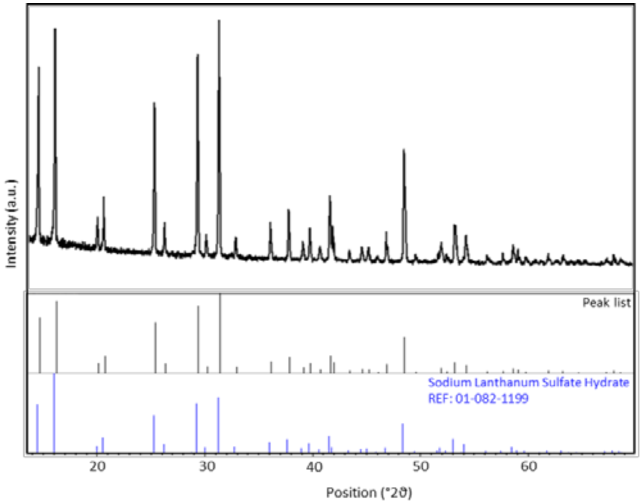
SULFURIC ACID process (2/2)



SULFURIC ACID process: characterization of the solid phases

Products from **HIGH T** leaching step

1 **1st precipitate**
pH ≤ 1.5

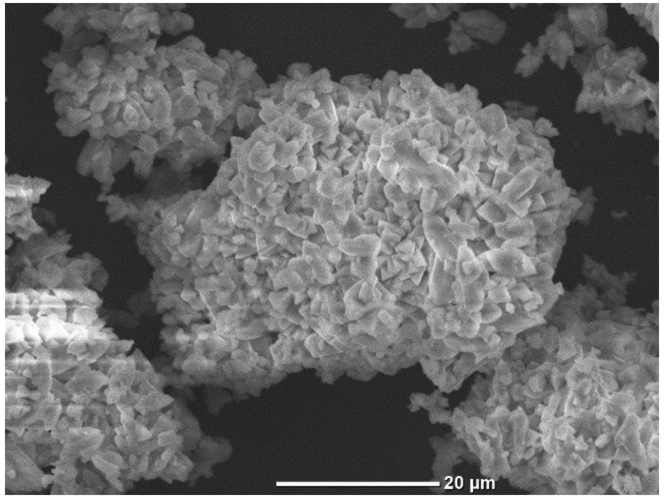


EDS: Average composition

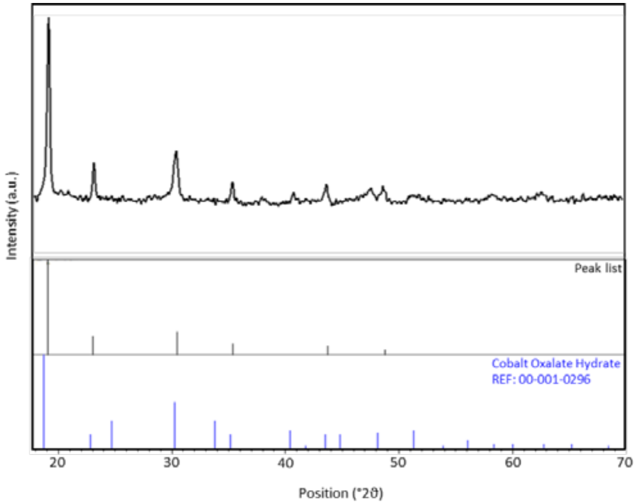
Element	%w
La	40.9
O	37.6
S	12.4
Na	6.6
Co	0.7
Y	< 0.5
Sr	< 0.5
Cr	< 0.5
Ni	< 0.5
Zr	< 0.5

Sodium lanthanum sulfate hydrate

$NaLa(SO_4)_2 \cdot 2H_2O$



2 **2nd precipitate**
pH 1.5

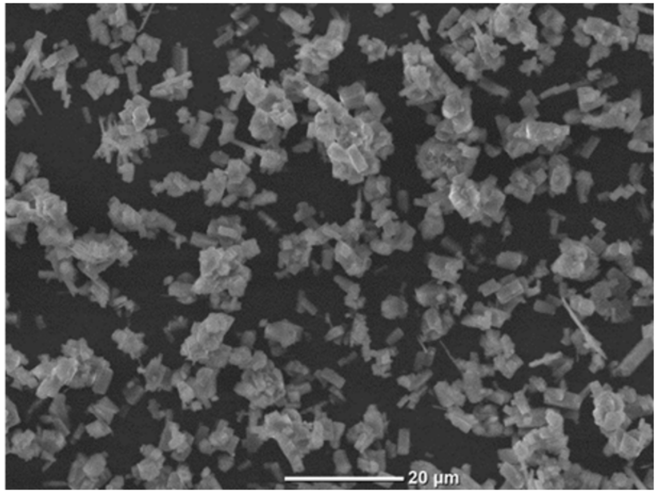


EDS: Average composition

Element	%w
O	50.7
Co	32.6
C	12.1
Ni	4.0
La	< 0.5
Na	< 0.5
Cr	< 0.5
Zr	< 0.5
Sr	< 0.5
Y	< 0.5
S	< 0.5

Cobalt oxalate hydrate

$CoC_2O_4 \cdot 2H_2O$

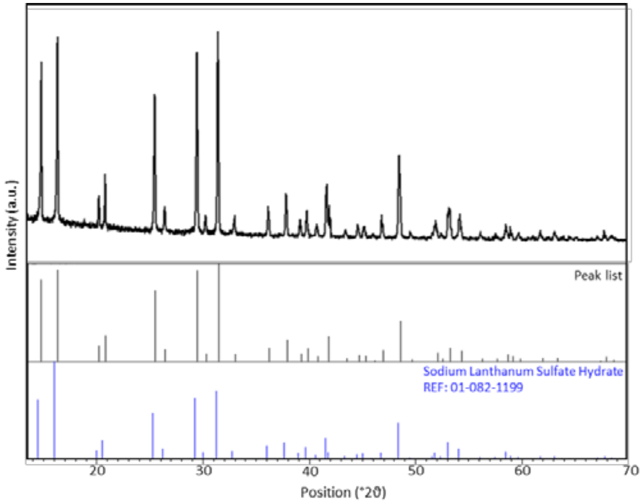


SULFURIC ACID process: characterization of the solid phases

Products from **LOW T** leaching step

3

1st precipitate
pH ≤ 1.5

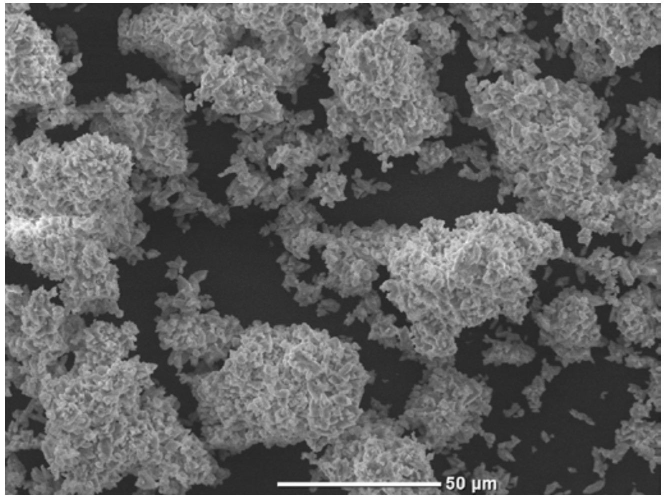


EDS: Average composition

Element	%w
La	44.0
O	34.9
S	12.4
Na	6.8
Cr	0.9
Ni	< 0.5
Co	< 0.5
Y	< 0.5
Sr	< 0.5
Zr	< 0.5

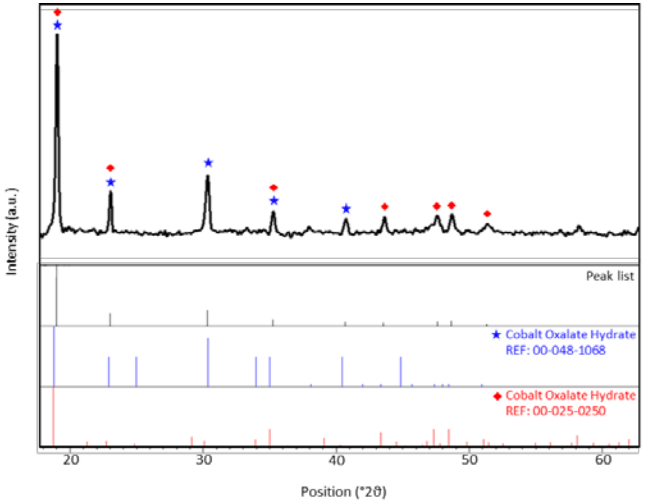
Sodium lanthanum sulfate hydrate

$NaLa(SO_4)_2 \cdot 2H_2O$



4

2nd precipitate
pH 1.5

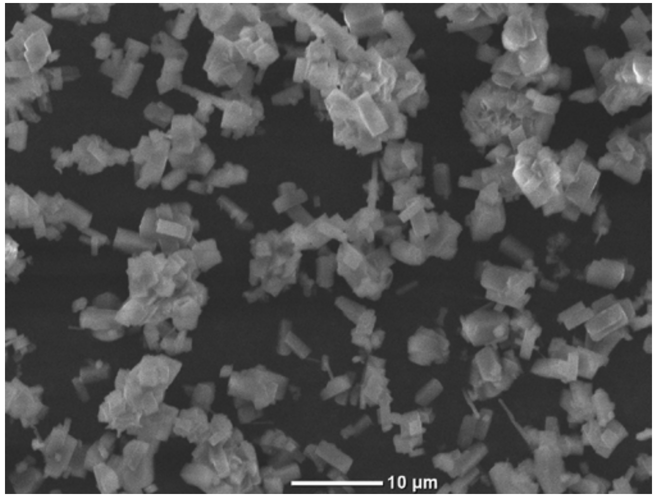


EDS: Average composition

Element	%w
O	46.5
Co	31.0
C	11.7
Ni	5.3
La	2.0
Sr	1.6
Na	1.0
S	< 0.5
Zr	< 0.5
Y	< 0.5
Cr	< 0.5

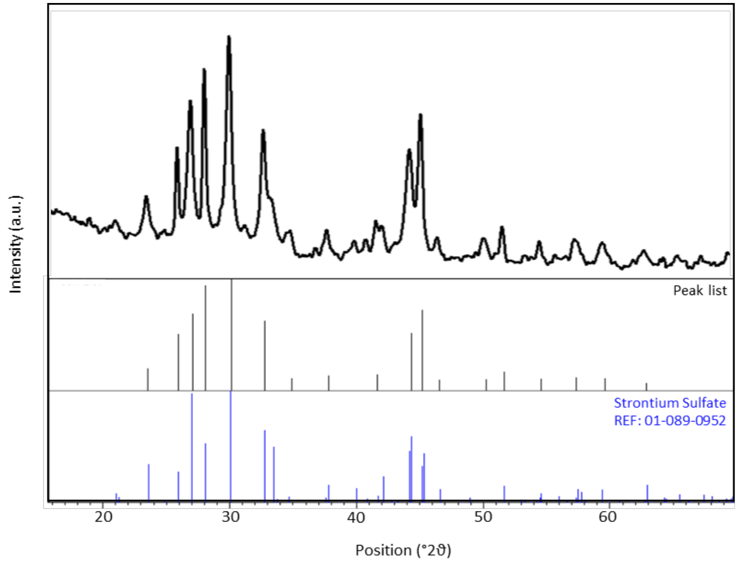
Cobalt oxalate hydrate

$CoC_2O_4 \cdot 2H_2O$



SULFURIC ACID process: characterization of the solid phases and evaluation of the process efficiency

Residual solid phase



Strontium sulfate

$SrSO_4$

EDS: Average composition

Element	%w
O	47.0
Sr	27.4
S	9.8
La	8.3
Zr	4.5
Co	1.5
Y	1.0
Ni	< 0.5
Cr	< 0.5

PROCESS EFFICIENCY:

Leaching Efficiency %

$\%LE_{La}$: **90** ± 2

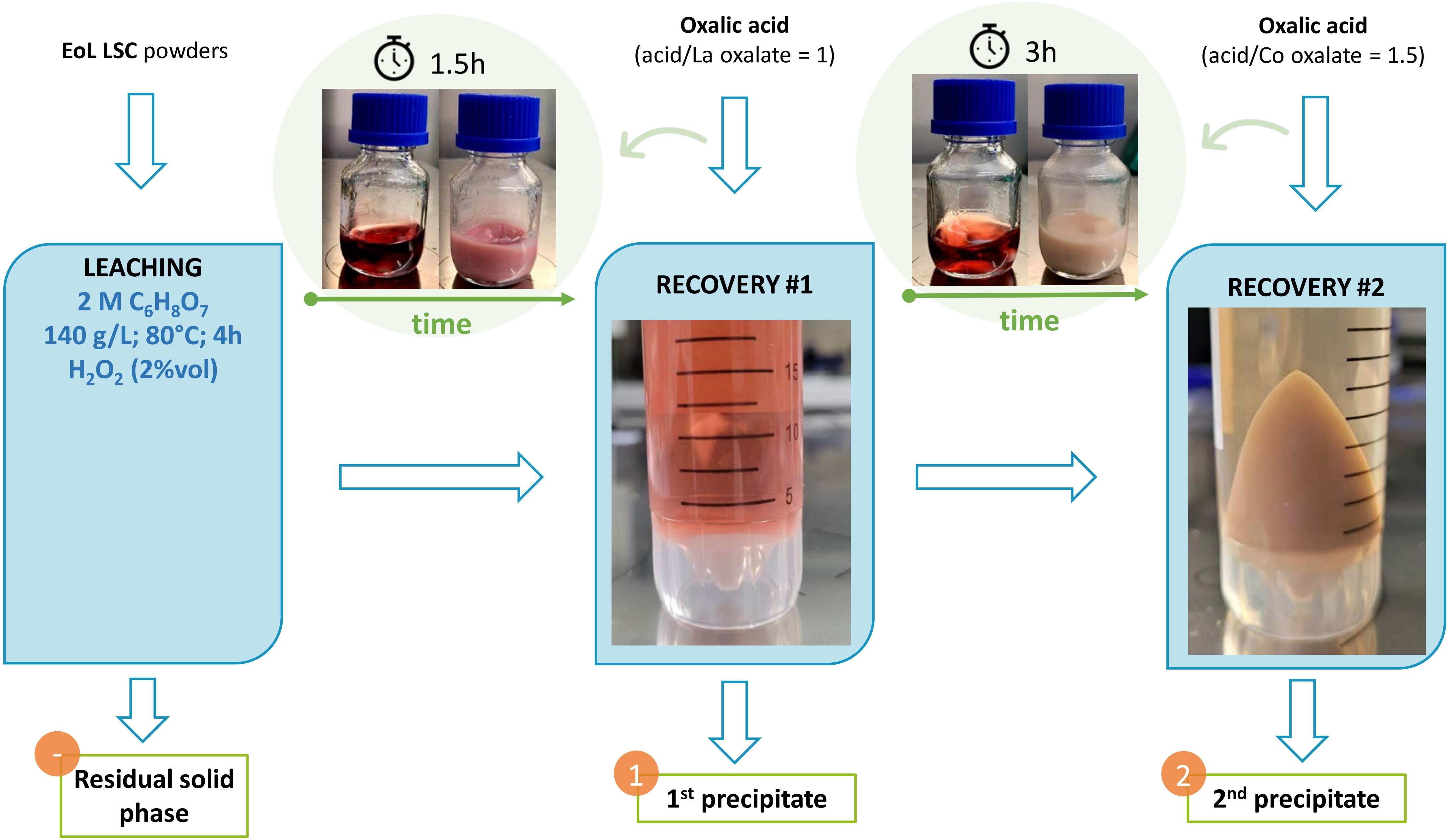
$\%LE_{Co}$: **98** ± 1

Recovery Yield %

$\%RY_{La}$: **83** ± 2

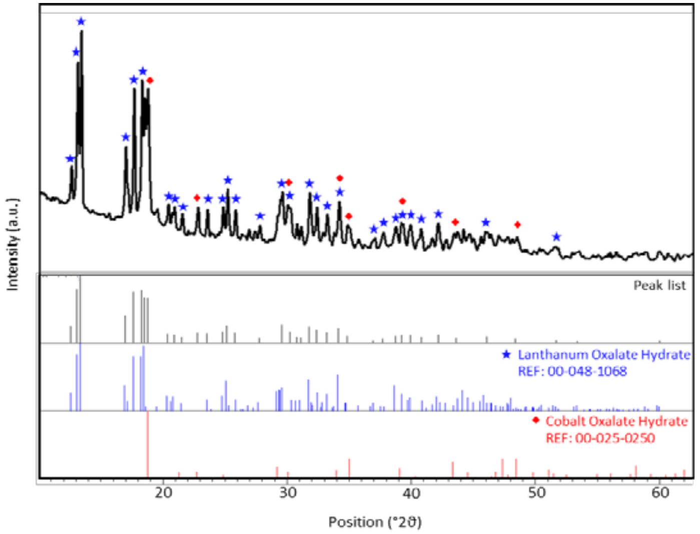
$\%RY_{Co}$: **93** ± 2

2 CITRIC ACID process



CITRIC ACID process: characterization of the solid phases

1 — 1st precipitate

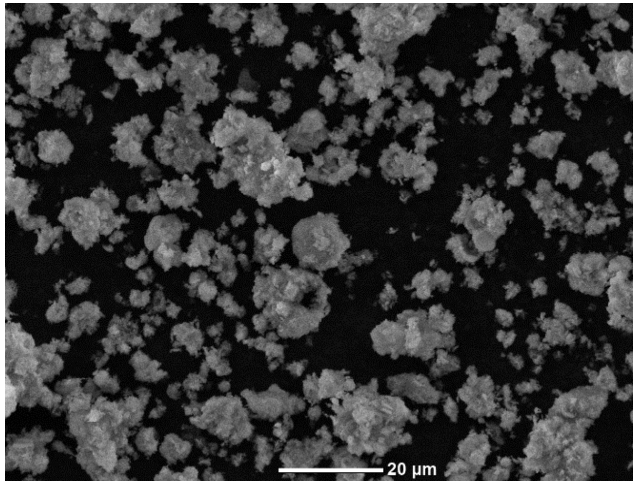


EDS: Average composition

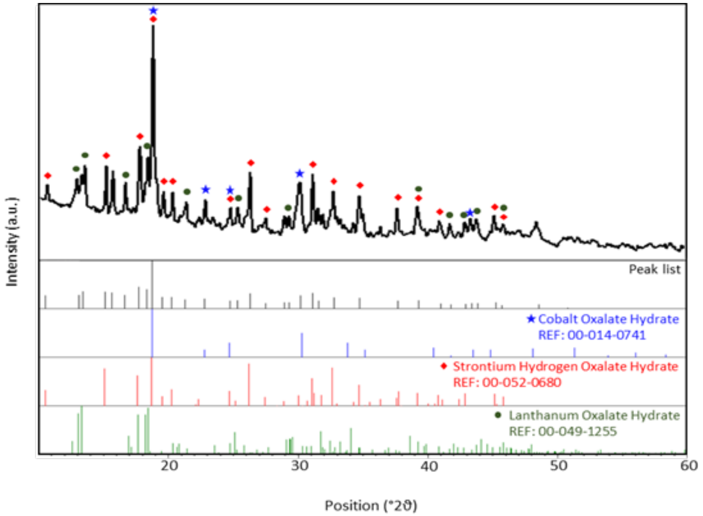
Element	%w
O	47.4
La	16.8
C	15.6
Co	15.1
Sr	4.0
Ni	0.5
Zr	< 0.5
Cr	< 0.5
Y	< 0.5

Cobalt oxalate hydrate
Lanthanum oxalate hydrate

$CoC_2O_4 \cdot 2H_2O$
$La_2(C_2O_4)_3 \cdot 10H_2O$



2 — 2nd precipitate

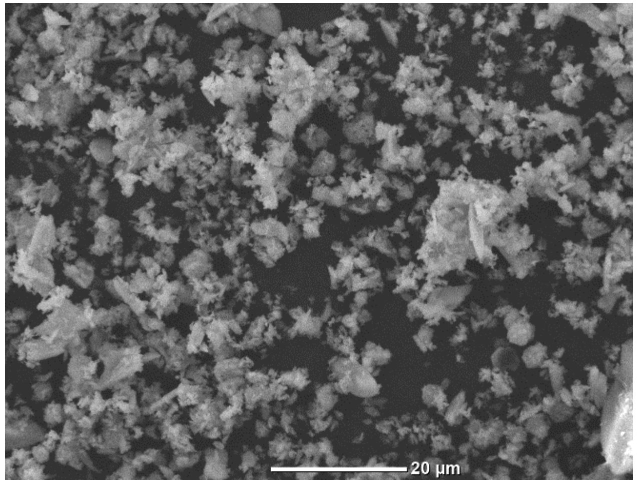


EDS: Average composition

Element	%w
O	45.9
La	16.5
C	16.3
Co	12.7
Sr	5.9
Ni	1.3
Y	0.7
Cr	< 0.5
Zr	< 0.5

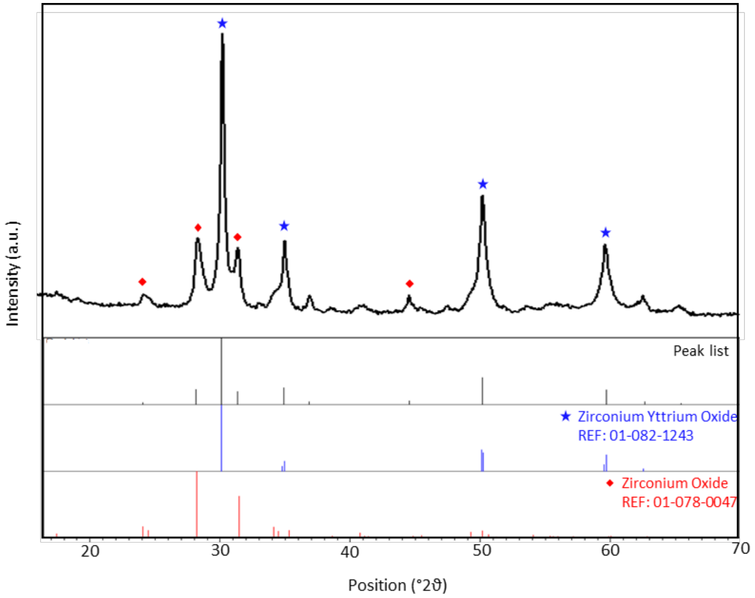
Cobalt oxalate hydrate
Lanthanum oxalate hydrate
Strontium hydrogen oxalate hydrate

$CoC_2O_4 \cdot 2H_2O$
$Sr(HC_2O_4) \cdot 0.5(C_2O_4) \cdot H_2O$
$La_2(C_2O_4)_3 \cdot 10H_2O$



CITRIC ACID process: characterization of the solid phases and evaluation of the process efficiency

Residual solid phase



Zirconinum yttrium oxide
Zirconinum oxide

$Zr_{0.86}Y_{0.14}O_{1.93}$
ZrO_2

EDS: Average composition

Element	%w
O	45.6
La	23.0
C	19.3
Co	8.4
Sr	1.6
Ni	0.9
Zr	0.9
Cr	< 0.5
Y	< 0.5

PROCESS EFFICIENCY:

Leaching Efficiency %

$\%LE_{La}$: **84** ± 19
$\%LE_{Co}$: **98.1** ± 0.4

Recovery Yield %

$\%RY_{La}$: **73** ± 7
$\%RY_{Co}$: **80** ± 1

Conclusions

- **Citric acid** process involves a **single** leaching step, but requires a **reducing agent**
- **Sulfuric acid** process provides higher **%LE for La**
- **Cobalt** is effectively leached by **both the acids**
- **> 80%** of La and Co were recovered in the **sulfuric acid** process
- **High purity** products are obtained with the **sulfuric acid** process

Sulfuric acid

Process efficiency:

$\%LE_{La}$: **90** ± 2
$\%LE_{Co}$: **98** ± 1

$\%RY_{La}$: **83** ± 2

$\%RY_{Co}$: **93** ± 2

Products quality:

- Sodium **lanthanum** sulfate hydrate
  $NaLa(SO_4)_2{\cdot}2H_2O$
  0,8%w impurities
- **Cobalt** oxalate hydrate
  $CoC_2O_4{\cdot}2H_2O$
  6.5%w impurities

Citric acid

Process efficiency:

$\%LE_{La}$: **84** ± 19
$\%LE_{Co}$: **98.1** ± 0.4

$\%RY_{La}$: **71** ± 6

$\%RY_{Co}$: **78** ± 2

Products quality:

- Mixture:
  Lanthanum oxalate hydrate **+**
  Cobalt oxalate hydrate **+**
  Strontium hydrogen oxalate hydrate

$La_2(C_2O_4)_3{\cdot}10H_2O + CoC_2O_4{\cdot}2H_2O + Sr(HC_2O_4){\cdot}0.5(C_2O_4){\cdot}H_2O$

Low purity products

Sulfuric acid process is more efficient and reliable, providing higher quality products

Thank you for your attention!

Politecnico di Torino

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