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Sustainable SoluTions FOR recycling of end-of-life Hydrogen technologies

Deliverable D4.3

Technical report on developed recovery technologies for LSC cathode materials

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Abbreviations

EoL	End of Life
SOCs	Solid Oxide Cells
SOFCs	Solid Oxide Fuel Cells
SOECs	Solid Oxide Electrolysis Cells
LSC	Lanthanum Strontium Cobaltite
FCs	Fuel Cells
%LE	Leaching Efficiency %
%RY	Recovery Yield %
XRF	X-Rays Fluorescence
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive X-ray Spectroscopy
XRD	X-ray Diffraction
BET	Brunauer-Emmer-Teller
SSA	Specific Surface Area
DLS	Dynamic Light Scattering
CRMs	Critical raw materials

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1 Executive Summary

The Deliverable 4.3 is a light version of D4.2, with some results accessible and public.

The main goal of WP4 is the development of a novel recycling technology for the cathodes of End-of-Life (EoL) Solid Oxide Fuel Cells and Electrolysis Cells (SOFCs and SOECs) at TRL3. Specifically, the focus was on lanthanum strontium cobaltite (LSC) cathodes, containing high amounts of critical raw materials (CRMs, as lanthanum and cobalt), which play a strategical role in the modern industry. The explored recycling technology was based on consequent phases (Figure 1), as follows. Firstly, the LSC have been detached from the EoL SOCs and prepared through a physic-mechanical process. Secondly, the LSC powders underwent different hydrometallurgical routes for the recovery of lanthanum (La) and cobalt (Co) through acid leaching based on different acids (sulfuric, nitric, citric, and oxalic) as alternatives. At M18 of the project, the third phase is starting. In details, the recycling perspectives for the recovered lanthanum La and Co will be explored considering closed-loop options (recycling in new SOCs after a synthesis of LSC materials from the recovered La and Co precursors); open-loop options for recycling will also be investigated, starting with a literature survey on the requirements of La and cobalt compounds for various uses. In the next months of the project, experimental tests on the direct recycling of EoL LSC materials will also be performed.

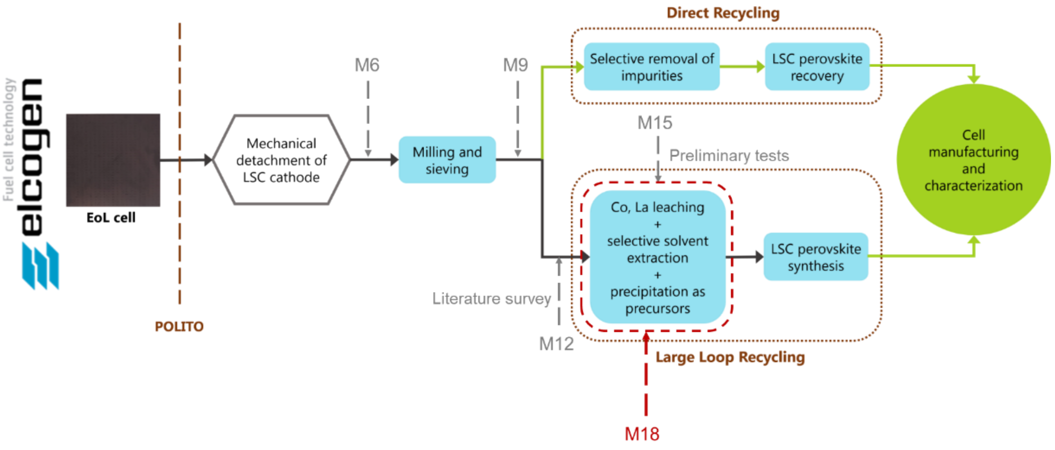

Figure 1 Outline of the activities within the WP4 from M1 toM18

Figure 1 provides an overview of the activities carried out between M1 and M18. The first 6 months have been dedicated to the optimization of the mechanical detachment of the LSC cathodes from the EoL cells provided by ELCOGEN. Then, ball milling and sieving processes were investigated to obtain LSC powders characterized by properties compliant with the acceptance criteria defined by ELCOGEN (see deliverable D4.1). The period between M9 and M12 was dedicated to the survey of the scientific literature on the leaching of lanthanum and cobalt from different EoL sources, as no literature specific for the

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recovery of La and Co from EoL SOCs is available. The literature survey was aimed at the investigation of the experimental parameters' ranges applied in previous studies. These ranges were investigated in the first experimental tests (carried out between M12 and M15). In M15-M18 the hydrometallurgical processes were further studied and optimized, to maximize the leaching efficiencies (%LE), the recovery yields (%RY) and the purities of the recovered La and Co products.

2 Introduction

Solid Oxide Fuel and Electrolysis Cells (SOFCs and SOECs) are efficient and clean power systems destined to be highly exploited in the next future, having a predicted market growing from 1.09 billion USD in 2021 to 5.31 billion USD in 2028 (*Solid Oxide Fuel Cell Market Size, Share & COVID-19 Impact Analysis, By Application (Stationary, Transport, Portable), By End-User (Commercial, Data Centers, Military & Defense, and Others), and Regional Forecast, 2021-2028*, 2021). According to the economic forecast, high amounts of Solid Oxide Cells (SOCs) will be produced in the next years; however, an efficient strategy for the management of waste SOCs still doesn't exist. In this context, Best4Hy project aims at the definition of an effective recovery strategy for valuable metals (i.e., lanthanum (La), cobalt (Co), nickel (Ni) from End-of-Life (EoL) SOCs to reduce the consumption of virgin raw materials, costs, and the environmental impacts of the production of new SOCs. In WP4, a sustainable process for the recovery of La and Co from the cathode of EoL SOFCs was investigated. Specifically, starting from EoL lanthanum strontium cobaltite (LSC) cathodes, four hydrometallurgical routes (based on sulfuric, nitric, citric and oxalic acids) for the recovery of La and Co were studied. Considering that both La and Co were included in the list of Critical Raw Materials (CRMs) in 2020, their recovery in the form of valuable compounds would be extremely interesting in the perspective of both open-loop and closed-loop recycling (European Commission, 2020). What is more, the development of an efficient and sustainable process for the management of waste SOCs would support the large-scale employment of FCs as alternatives to combustion technologies to produce electricity and ECs for massive hydrogen production and Power-to-X.

The studied experimental procedure that led to the selective recovery of compounds rich of La and Co involved several steps, summarized in Figure 2. First, the EoL LSC powders were prepared: mechanical detachment was carried out in wet conditions, to separate the cathodic materials from the protective layer of the SOC and the anodic phase. Once dried, the obtained powders were ball milled and sieved on 20 µm. The over-size powders underwent multiple milling/sieving cycles, until the target size (i.e., <20 µm) was reached. The prepared LSC powders were characterized through SEM-EDS, XRD, BET and DLS analyses, to evaluate the compliance with ELCOGEN acceptance criteria defined in

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Deliverable D4.1. The leaching process was then applied on the prepared LSC powders applying four different acidic lixiviants, inorganic and organic, as alternatives. The processes that employed inorganic acids (i.e., sulfuric, and nitric) applied a traditional approach to the hydrometallurgical recovery of valuable metals. More innovative routes were also investigated using organic lixiviants (i.e., oxalic, and citric acids), to evaluate the possibility of applying a process compliant with the Green Chemistry principles (Anastas & Warner John C., 2000). After the leaching step,La and Co have been recovered from the leachates obtained from all routes by adding oxalic acid as precipitating agents (in the oxalic acid process this step was not needed). The obtained lanthanum and cobalt oxalates were collected through centrifugation, washed and dried at 70°C. The characterization of the recovered powders was performed through XRD analysis, while SEM-EDS provided information about the morphology and the chemical composition. Lastly, the leaching efficiency and the recovery yield of the investigated processes were evaluated to compare the different routes.

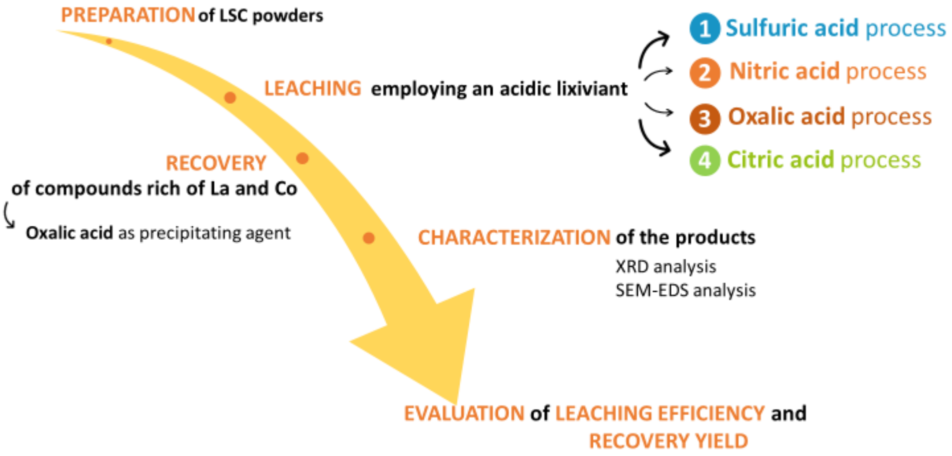

Figure 2 Overview of WP4 experimental activity performed in M1-M18

3 Literature review

The scientific literature was surveyed with the aim to explore the actual perspectives for the leaching (i.e., the first phase of a hydrometallurgical recycling process) of La and Co from waste materials.

While the recycling of fuel cells (FCs) has not been widely explored yet, numerous papers propose successful processes for La and Co recovery from other sources, e.g., spent NiMH batteries, mineral ores or spent cracking catalysts. In details, 70 papers were analyzed (46 related to cobalt recovery, 11 to rare earth elements (REEs)/lanthanum recovery, 13 to the recovery of both). Most references were published in the last decade, and the main interest

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concerned hydrometallurgical processes (Figure 3) based on inorganic (sulfuric, nitric, hydrochloric) and organic (citric, malic, tartaric) acids.

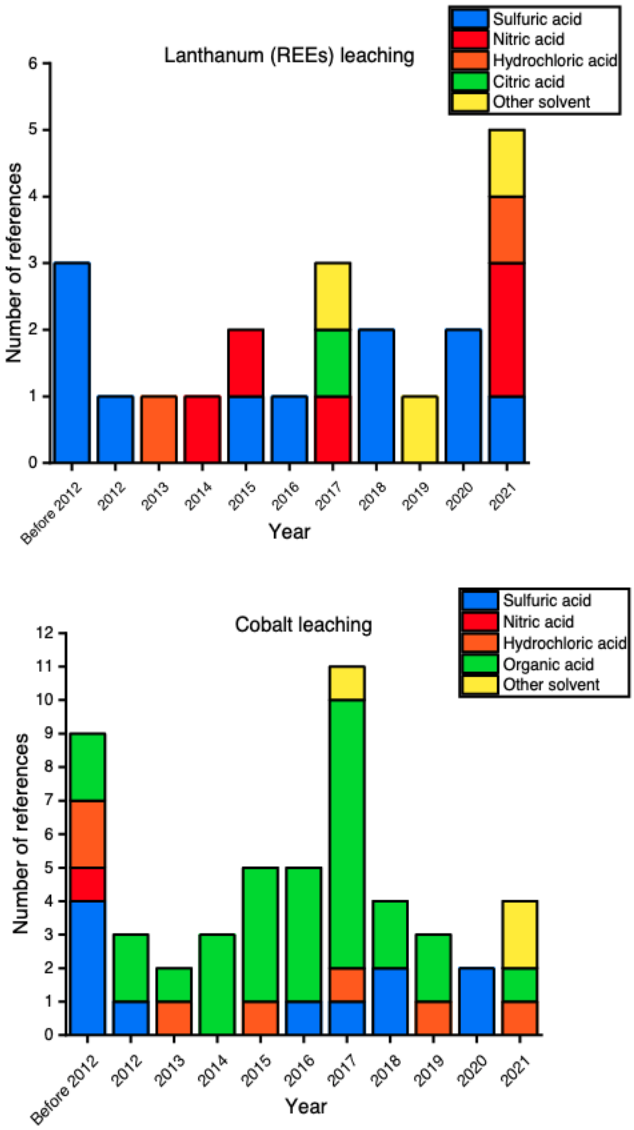

Figure 3 Overview of the literature studies investigating lanthanum/REEs and cobalt recovery through leaching.

Considering specifically the experimental conditions applied in the analyzed literature studies, the proposed ranges of the acid solvent concentration, solid/liquid ratio, temperature, and contact time are shown in Figures 4 and 5.

In the considered references, the only organic solvent adopted for lanthanum/REEs leaching was citric acid (Figure 4), which allowed to work with a more diluted chemical (median concentration 0.55 M) compared to the inorganic acids (median value 2 M). The leaching processes based on inorganic acids adopted concentrations ranging from 0.1 M to 12 M. The required solid to liquid ratio was higher in the processes that use citric acid

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(median value 200 g/L), while the median mass leached by 1 L of inorganic acid was 100 g. The experimental temperature range of La leaching didn't change significantly with the acid employed, staying in the range 45-75°C. Up to 72 hours can be required to complete the leaching process; the median value of the contact time was 3 hours for the inorganic acids and 4 hours for citric acid. In conclusion, using diluted organic acids, a higher amount of La can be leached at lower temperature, but at the same time extending the contact time.

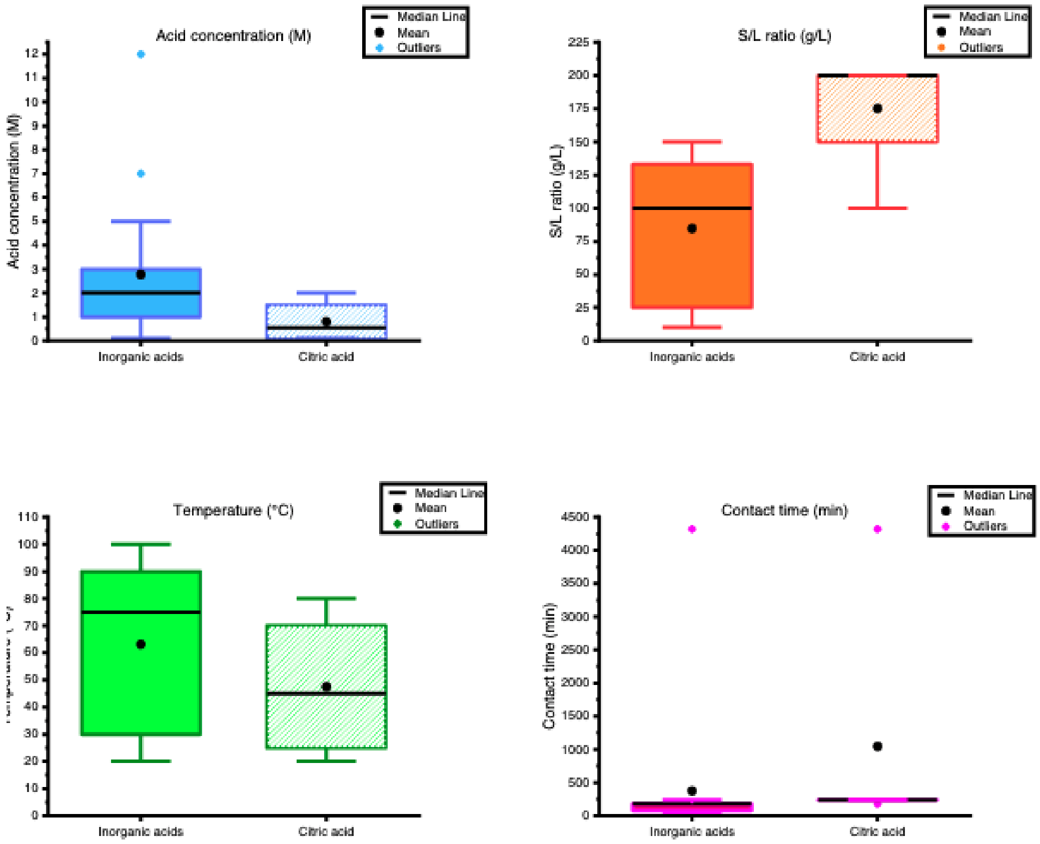

Figure 4 Overview of the experimental conditions reported in the considered literature studies investigating lanthanum/REEs leaching

Considering the leaching of cobalt (Figure 5), the concentration of the organic acids was lower (median concentration 1.4 M) compared to the inorganic acids (median concentration 2M). The solid to liquid ratio was higher for the inorganic acids (median value 50 g/L) than for the organic acids (median value 20 g/L). The temperature range was between 75°C (median value for the inorganic acids) and 87.5°C (median value for the organic acids). The median contact time needed with the inorganic acids was 75 minutes, and 85 minutes for the organic acids (but it can last up to 6 hours).

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The literature survey provided useful hints for the definition of the type of agents and the operative parameters that were then employed in the preliminary experimental tests.

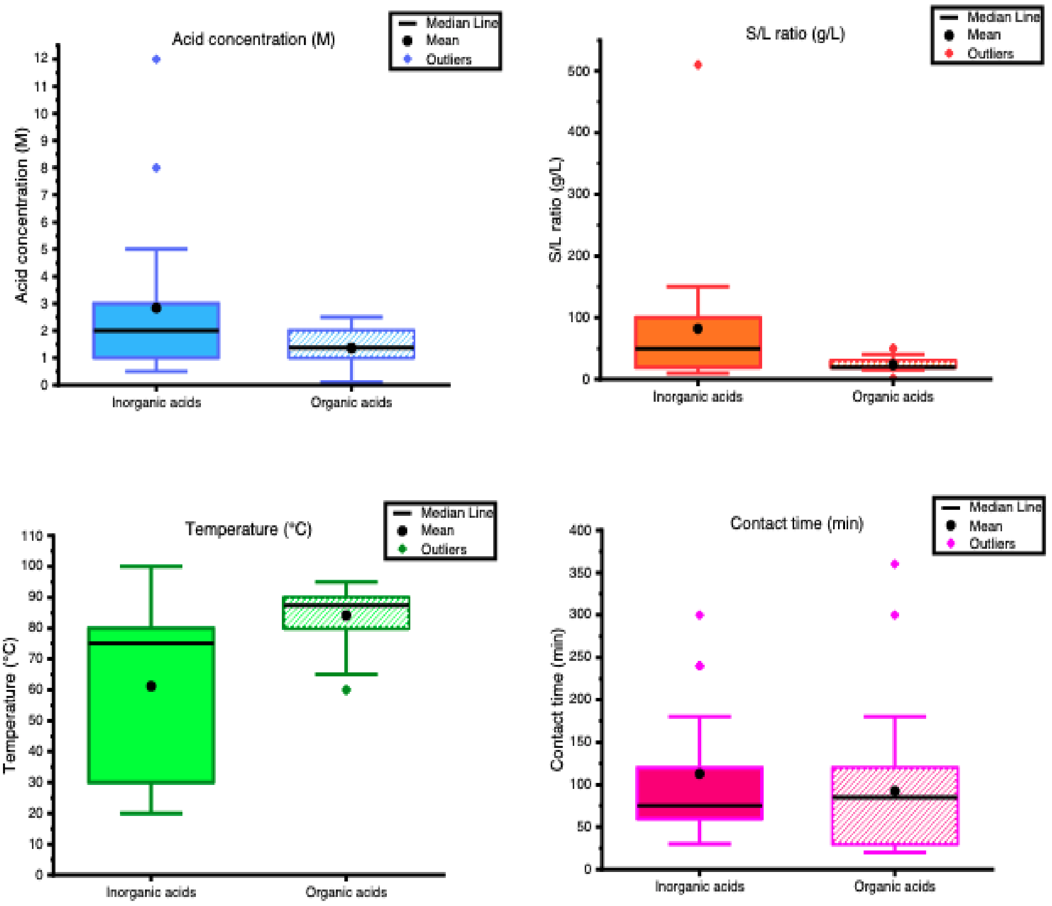

Figure 5 Overview of the experimental conditions reported in literature studies investigating cobalt leaching

4 Experimental procedures

4.1 Preparation of the LSC powders

The mechanical detachment protocol has been optimized in the period M1-M5, obtaining a mass recovery equal to 86%. During the period M7-M12 the experimental activities were focused on the further steps (e.g., milling and sieving) of the mechanical treatment of the cathode active materials. The XRD analyses of the obtained powders proved that the LSC crystalline phase was preserved after up to 10 hours of milling (Figure 6). The SEM and particle-size (BET, DLS) analyses (Figure 8) demonstrated that Elcogen specific acceptance criteria for the recycling of LSC perovskite powders were successfully targeted after 10 hours of milling.

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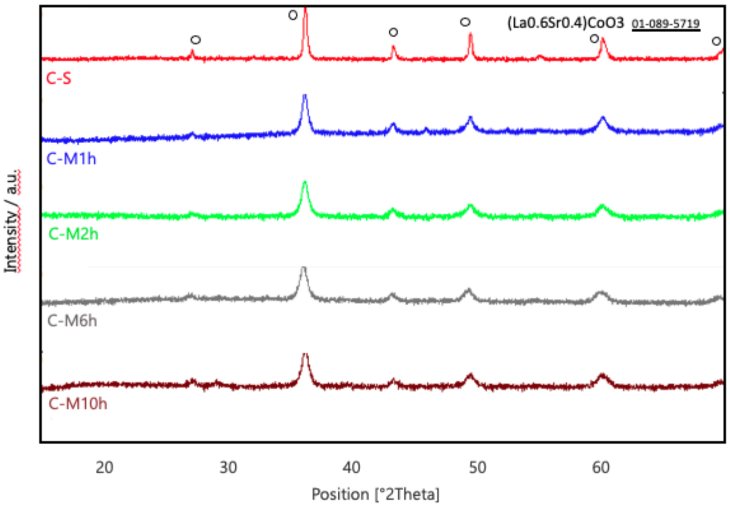
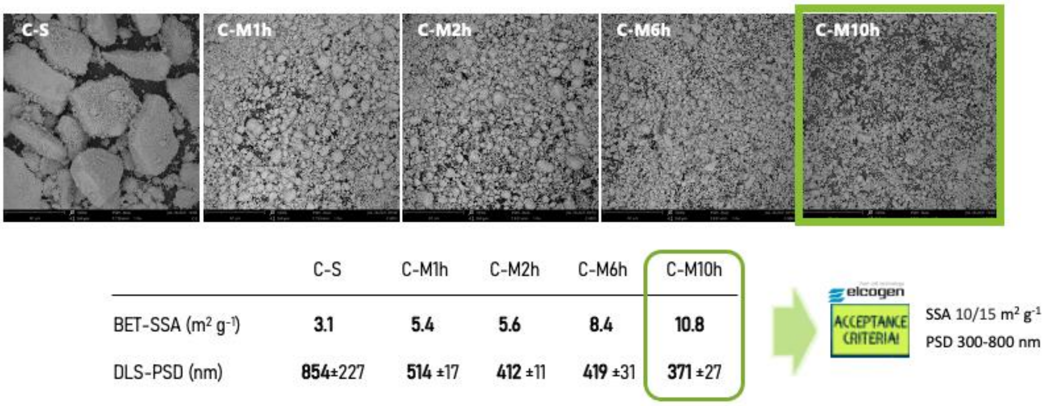


Figure 6 XRD characterization of the cathode active materials after scratching (S) and milling (M) for different times



	C-S	C-M1h	C-M2h	C-M6h	C-M10h
BET-SSA ($m^2\ g^{-1}$)	**3.1**	**5.4**	**5.6**	**8.4**	**10.8**
DLS-PSD (nm)	**854±227**	**514 ±17**	**412 ±11**	**419 ±31**	**371 ±27**

Figure 7 SEM and particle-size (BET, DLS) characterization of the cathode active materials after scratching (S) and milling (M) for different times

4.2 Leaching and recovery tests

The behavior of four different acids (both inorganic and organic) as lixiviants for La and Co recovery from the cathodes of EoL SOCs was analyzed. According to the literature review, the investigated agents were nitric acid, sulfuric acid, oxalic acid, and citric acid. For each process, leaching and precipitation conditions were optimized to maximize the recovery yield and the purity of the resulting products.

Both in the processes with inorganic acids and in the citric acid process, oxalic acid dihydrate ($C_2H_2O_4$•2 H_2O) was added to the ions-rich liquor (resulting from the leaching step) as precipitating agent. The amount of acid was calculated considering the moles of

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$(C_2O_4)^{2-}$ required for the precipitation of La oxalate ($La_2(C_2O_4)_3$) and Co oxalate (CoC_2O_4), assuming that the whole amount of La and Co present in EoL LSC powders was lixiviated. Lastly, the leaching efficiency (%LE) and the recovery yield (%RY) of each process were evaluated according to equations (1) and (2), respectively.

$$\%LE_i = \frac{m_{i\ EoL\ LSC} - m_{i\ residual\ solid\ phase}}{m_{i\ EoL\ LSC}} * 100 \qquad (1)$$

$$\%RY_i = \frac{\sum_n^N m_{i\ in\ the\ n-precipitate}}{m_{i\ EoL\ LSC}} * 100 \qquad (2)$$

Where $i = La, Co$ and $n = 1, 2 \dots N$ ($N = total\ number\ of\ precipitates$).

4.2.1 Nitric acid process

The leaching process on EoL LSC powders (size < 20 μm) was carried out (Figure 8) based on operative conditions reported by literature (Lee & Rhee, 2003; Sposato et al., 2021).

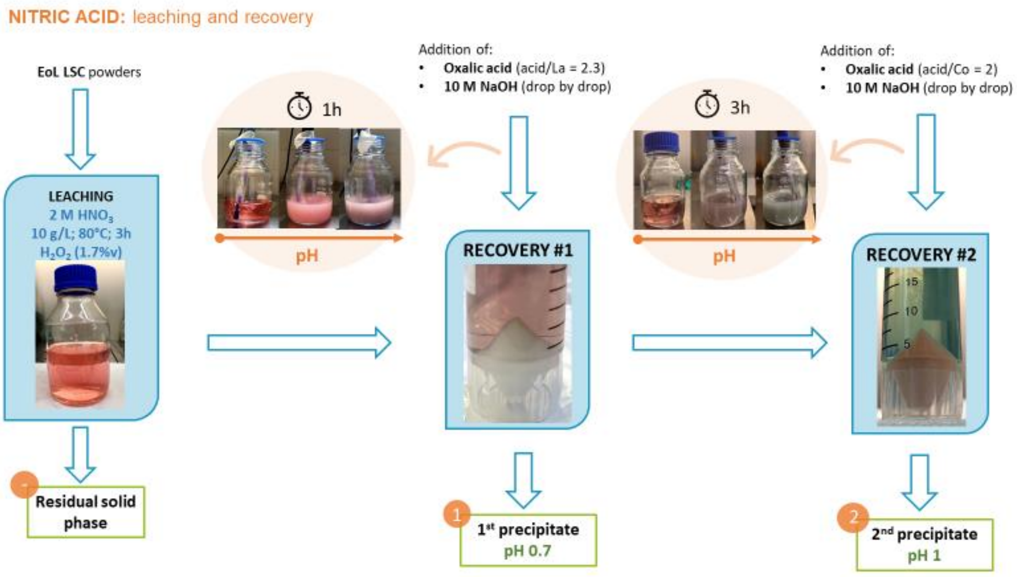

Figure 8 Nitric acid process: leaching and recovery of La and Co

4.2.2 Sulfuric acid process

With the aim of optimizing the recovery of lanthanum and cobalt, the process with sulfuric acid consisted of two sequential leaching steps (Figure 9): the first at high temperature to maximize cobalt solubility, the second at room temperature (where lanthanum solubility is higher) (Innocenzi & Vegliò, 2012).

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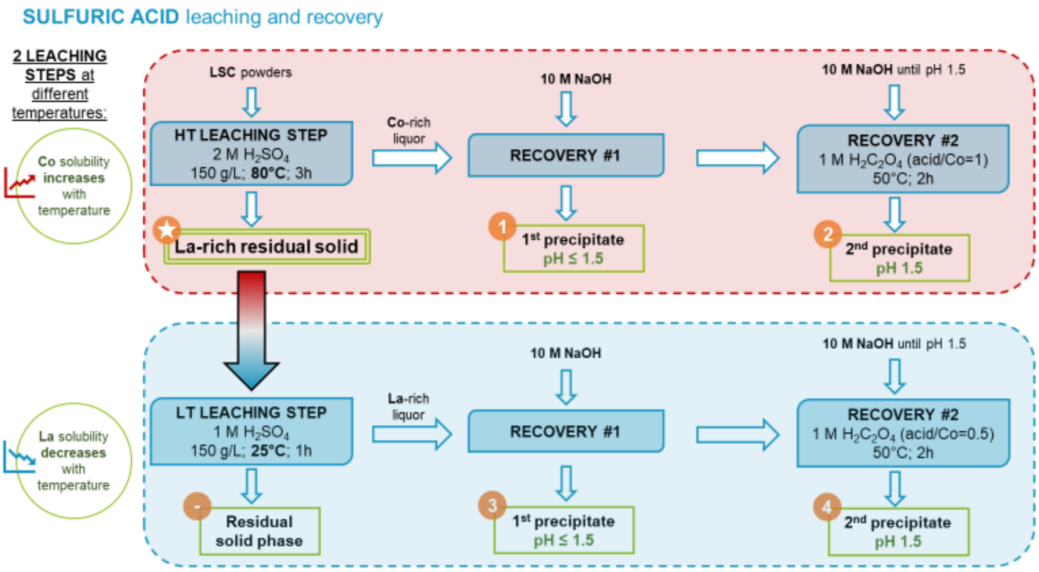

Figure 9 Sulfuric acid process: two leaching steps and recovery

4.2.3 Oxalic acid process (preliminary test)

The leaching process with oxalic acid was carried out (Figure 10) according to the operative conditions reported by literature (Sun & Qiu, 2012).

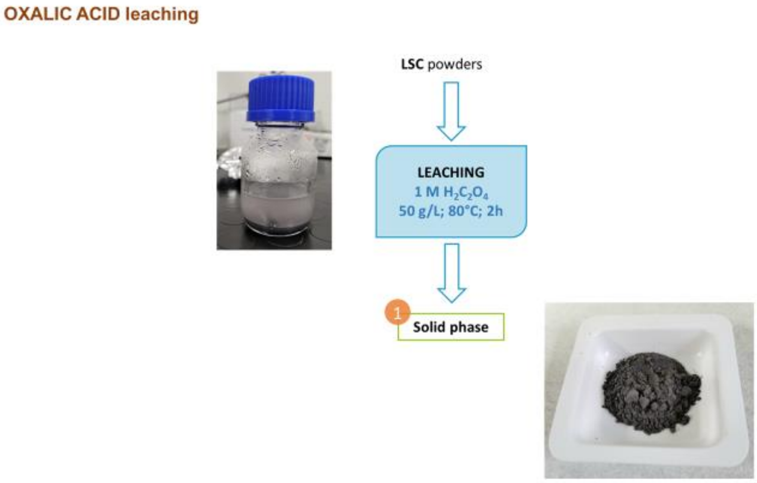

Figure 10 Oxalic acid process: one-step leaching and recovery

The recovered powder was a mixture of the unreacted residual solid phase and the precipitates (generated by the interaction of the solubilized ions and the oxalate anions in

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solution). A simple and efficient way to separate the compounds was not found, therefore the evaluation of the leaching efficiency and the recovery yield was not possible.

4.2.4 Citric acid process

The optimized leaching process with citric acid (Figure 11) was carried out according to the operative conditions reported by literature (Chen et al., 2015; Petrus et al., 2019).

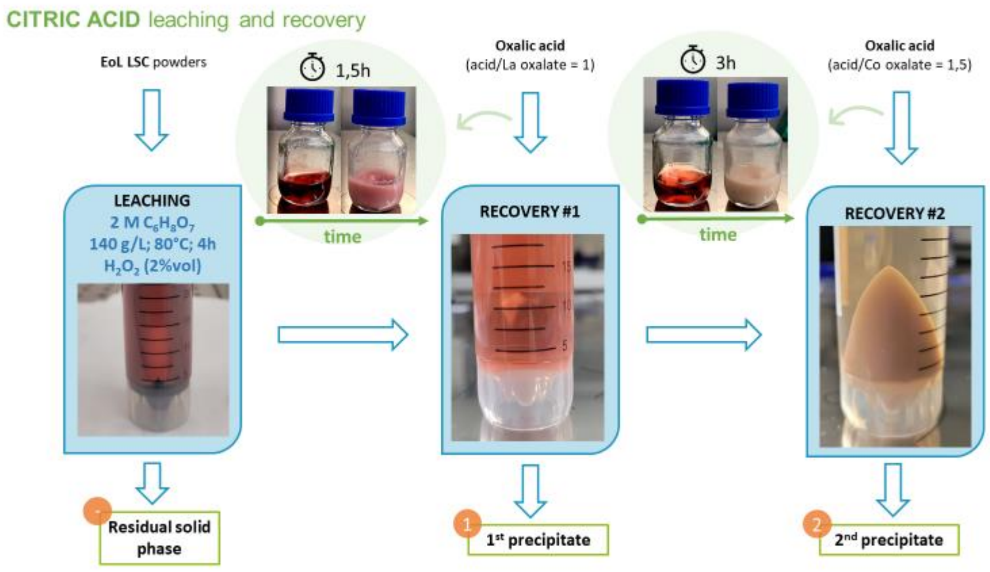

Figure 11 Citric acid process: leaching and recovery

4.3 Characterization of the solid phases

Phases identification was carried out analyzing the XRD spectra of the powders. EDS analysis was performed both on the residual solid phases (resulting from the leaching processes) and on the precipitates. The obtained information was employed for the evaluation of the leaching efficiency and the recovery yield of the investigated processes. The morphology of the recovered precipitates was investigated through SEM analysis.

4.3.1 Nitric acid process

The XRD pattern of the solid phase obtained from the process with nitric acid showed that the powder consisted of zirconium yttrium oxide and zirconium oxide. EDS analysis confirmed that the residual amounts of La and Co were low: the elements of interest have been effectively lixiviated.

The XRD pattern of the first precipitate obtained from the nitric acid process showed that lanthanum oxalate hydrate was recovered. Starting from the composition provided by EDS

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analysis, the amount of impurities was estimated as 1.5%-wt. According to the XRD analysis, the second precipitate was identified as cobalt oxalate hydrate with 4.8%-wt of estimated impurities.

4.3.2 Sulfuric acid process

The residual solid phase from the sulfuric acid leaching consisted of strontium sulfate, with low amounts of lanthanum and cobalt. The XRD spectra and the SEM-EDS analysis of the first powders precipitated from the liquor resulting from the high temperature leaching step showed that they were made of sodium lanthanum sulfate hydrate (0.7%-wt of impurities). The second precipitate consisted of cobalt oxalate hydrate with 4%-wt of impurities. The XRD spectrum and EDS composition of the first precipitate from the low temperature leaching showed sodium lanthanum sulfate hydrate (with 0.9%-wt of impurities). The second precipitate consisted of cobalt oxalate hydrate (9%-wt impurities).

4.3.3 Oxalic acid process (preliminary test)

According to the results of the XRD and EDS analyses, the powder recovered from the oxalic acid process was a mixture of unreacted LSC, cobalt oxalate hydrate, lanthanum oxalate hydrate and lanthanum cobalt oxalate hydrate. In the oxalic acid process, selective precipitation did not happen and a simple and sustainable method for the separation of the La-rich and Co-rich compounds from unreacted LSC and impurities (mainly Sr and Ni) was not found. Therefore, after some preliminary tests, the oxalic acid process was discarded.

4.3.4 Citric acid process

The XRD analysis showed that the residual solid phase from the citric acid leaching mainly consisted of zirconium yttrium oxide and zirconium oxide. However, as previously observed, lanthanum leaching efficiency had strong variability. The first precipitate was a mixture of lanthanum oxalate hydrate and cobalt oxalate hydrate. The second precipitate was a mixture of cobalt oxalate hydrate, strontium hydrogen oxalate hydrate and lanthanum oxalate hydrate. Selective precipitation was not observed in the citric acid process: the obtained powders were mixtures of compounds.

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5 Conclusions

Considering that the oxalic acid process was discarded (due to the need of additional complex procedures for the separation of the compounds of interest from the unreacted powders), a comparison between the three more interesting processes is reported in Figure 12. It was observed that nitric acid was the best lixiviant for both lanthanum (La) and cobalt (Co), but sulfuric acid provided good leaching efficiencies as well. Citric acid was proved to be an excellent lixiviant for Co, while the average leaching efficiency of La was lower and affected by a huge variability. Concerning the recovery yields, the highest amounts of La and Co were recovered through the nitric acid process. More than the 80% of La and Co present in the EoL LSC powders were recovered when sulfuric acid was employed as leaching agent. The organic acid provided lower recovery yields, but more than the 70% of both (La,Co) the CRMs was recovered.

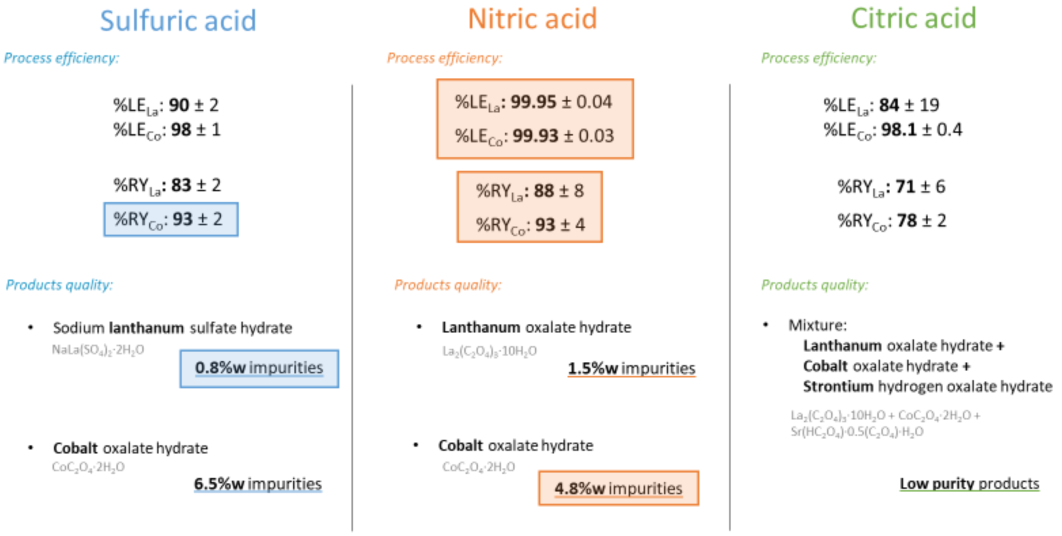

Figure 12 Comparison between the studied leaching and recovery processes

A highly pure La-rich compound (sodium lanthanum sulfate hydrate, <0.8% of impurities) was recovered from the sulfuric acid process. The lanthanum oxalate hydrate obtained from the nitric acid process had low amounts of impurities as well. This compound could be easily converted into lanthanum oxide through calcination, generating a suitable precursor for the preparation of novel LSC from recovered materials.

In all the investigated processes, Co was recovered as cobalt oxalate hydrate. The product with the highest purity was generated by the nitric acid process. Thanks to the high content of Co, this compound is suitable for both open-loop and closed-loop recycling (after a simple calcination step). The mixture of oxalates recovered in the process with citric acid

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could be converted into a mixture of oxides through calcination, but in order to re-synthesize LSC a stochiometric adjustment of La, Sr and Co is required.

In Figure 13 is reported the comparison between the average leaching efficiencies of La and Co of the new proposed routes with the ones of the processes described by the previous literature. The %LEs of all the processes involved in the literature survey were included in the calculation of the average leaching efficiencies (in black in the graphs). It is interesting to observe that the proposed processes with inorganic acids provide higher leaching efficiency for both (La ,Co) with respect to previous studies. The %LE of La obtained from the process with citric acid must be further optimized, while the leaching efficiency of Co is already high and has a good repeatability if compared with the processes found in literature.

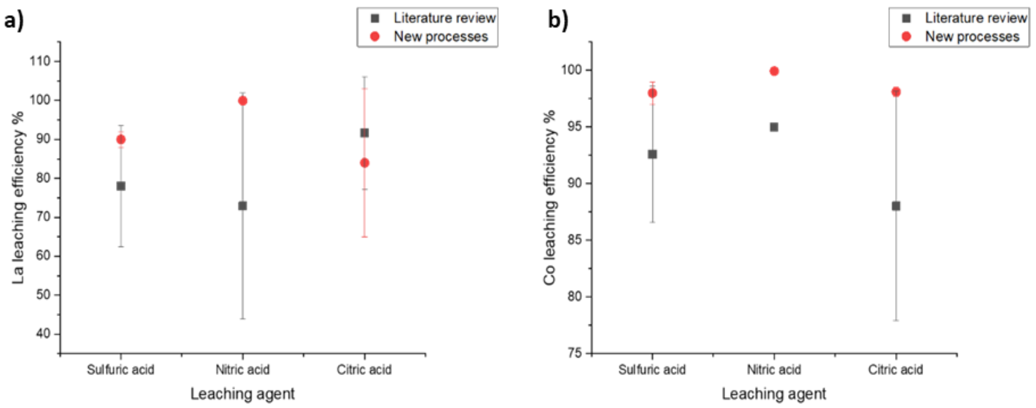

Figure 13 Comparison of the leaching efficiencies of the Best4Hy "new" processes and the results of literature review

6 Dissemination activities

A literature review about the leaching of lanthanum and cobalt from different sources was published in March 2022 on MDPI *Sustainability* (Benedetto Mas et al., 2022).

The preliminary results of the experimental tests of the leaching and recovery of La and Co from the EoL LSC cathodes (sulfuric acid and citric acid routes) were presented at the 9th International Conference on Sustainable Solid Waste Management in Corfù, Greece.

The latest experimental results will be included in a scientific paper in preparation.

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