

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



Deliverable D3.3

Pilot-scale plant (TRL5) based on two integrated
existing recycling technologies for SOFCs_PU

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Abbreviations

FCH	Fuel-Cell and Hydrogen
EoL	End of Life
SOFC	Solid Oxide Fuel Cells
NiO	Nickel Oxide
YSZ	Yttria-Stabilized-Zirconia
LSC	Lanthanum strontium cobaltite
PSD	Particle size distribution
SEM	Scanning electron microscopy
XRF	X-rays fluorescence
XRD	X-ray diffraction
ICP	Inductively coupled plasma
BET	Brunauer-Emmer-Teller
SSA	Specific surface area
DLS	Dynamic light scattering
GDC	Gadolinium-doped Ceria
HT	Hydrothermal
CRM	Critical raw materials
FESEM	Field-Emission Scanning Electron Microscopy



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Contents

1. Executive Summary	4
2. Introduction	4
3. Installation of pilot-plant reactor and safety operations	7
4. Scaling-up to TRL5: process optimization	9
5. Conclusions	18
6. References.....	19



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1. Executive Summary

The following deliverable focuses on the scaling-up to TRL5 of the procedure developed at lab-scale (TRL3) for the recovery of YSZ and Ni from exhausted electrode and electrolyte components of EoL SOFCs. The recovery pathway exploits the combination of hydrothermal and hydrometallurgical processes for enabling the disaggregation of the ceramic-metallic composite and the selective leaching of the metal for separating the ceramic phase (YSZ) and Ni.

The scaling-up of the process has been conducted on a pilot plant, consisting of a hydrothermal reactor equipped with a controller of temperature/stirring rate and enabling the continuous loading/unloading of the powder suspensions. The main goals of this scaling-up phase were: *i*) to combine **in a single step process** the hydrothermal disaggregation and the acid-leaching of Ni metallic phase and *ii*) to increase the amount of processed powder while minimising the energy/reagents consumption and the production of waste solution.

Once the reactor had been installed, several trials were conducted to highlight the effect of several process parameters on the process efficiency and on the physical-chemical properties (specific surface area, crystallinity, particle size distribution) of the recovered YSZ samples. In particular, temperature, duration time of the treatment, concentration of the acidic leaching solution and the solid: liquid ratio inside the reactor have been optimised for maximising the quantity of powder processed for each treatment and for minimising the energy consumption and waste production.

The powders and supernatant obtained after each trial have fully characterised and related results benchmarked against the specifications provided by the SOFC manufacturer.

2. Introduction

The lack of efficient, scalable, and cost-effective EoL strategies, enabling the management and valorisation of waste products derived from stacks operation, represents one of the major barriers to the full deployment of solid oxide fuel and electrolysis cell (SOFC/SOEC) technologies.

State-of-the-art materials mostly used in SOCs systems are Ytria-stabilized Zirconia (YSZ) as the electrolyte, Strontium-doped Lanthanum Manganite/Iron/Cobaltite (LSM/LSCF/LSC) as the oxygen electrode and NiO-YSZ cermet as the fuel/steam electrode and thick substrate, which undergoes reduction to Ni-YSZ during system operation. Currently, End-of-Life (EoL) strategies specifically conceived and implemented for the recovery and reuse of critical raw materials (CRMs) and also hazardous materials from exhausted SOCs are almost absent. A recent comprehensive study by Valente *et al.* [1] reviewed the overall consolidated and emerging technologies aiming at the recovery of valuable materials from Fuel-Cell and Hydrogen (FCH) technologies and concluded that no EoL processes are currently available for SOC components. Similarly, other authors [2] pointed out the need to address EoL recycling perspectives for hydrogen technologies and provided an overall classification of FCH materials based on related hazardousness, scarcity and cost. According to this classification, suitable recovery strategies for SOCs should be explored



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not only for Ni and LSC as CRMs but also for YSZ, due to its weight percentage in cells and related high economic value [3].

With this perspective and to provide a valuable contribution to target this urgent need, the BEST4Hy project aims to develop and validate recycling processes for EoL solid oxide cells dismantled from stacks. To this purpose, given the lack of well-established technologies for EoL SOFCs, the investigated recycling routes resulted from the combination and adaptation of existing recovery technologies, widely employed in other industrial sectors and applications, including the recovery of Rare-Earth Elements (RREs) and valuable metals from electronic-wastes, spent batteries and spent catalysts. The most common recovery strategies for CRMs, including Ni, Co and La among others, are based on hydrometallurgical approaches, which primarily consist of metal leaching by using inorganic acids such as HNO_3 , HCl and H_2SO_4 , at concentrations in the range of 1-2.5M, temperatures in the range of 60-80°C and duration time of 1-6 hours, achieving satisfactory (>95%) extraction efficiency in most cases. The leached metals are subsequently separated from the dissolution solutions by precipitation of insoluble compounds, such as salts or hydroxides. Besides the use of established hydrometallurgical methods, a pre-treatment using hydrothermal conditions has been considered to enhance the disaggregation and pulverization of the composite materials and the subsequent metal leaching. The hydrothermal treatment is widely used in the literature for several uses, including the synthesis of oxidic materials, the digestion of organic-derived compounds, and the disintegration of sintered bodies. Regarding the recovery of ceramic materials, such as zirconia, both at the proposal stage and later during the project deployment, the literature survey has revealed a few examples of recycling strategies. In the literature, only two contributions [5,6] focusing on the disintegration of sintered YSZ bodies into powdery particles have been found, and the reported process has been adapted for the composite Ni-YSZ powder derived from EoL SOFCs to implement a specific and efficient recycling process.

In the frame of WP3, a multi-step recycling procedure has been developed *ad-hoc* to recover critical raw and hazardous materials from the anode components of EoL SOCs provided by ELCOGEN upon dismantling from stacks after long-time operation time (ca 10,000 hours). The figure below shows the schematic structure of the cells targeted in the frame of the project.

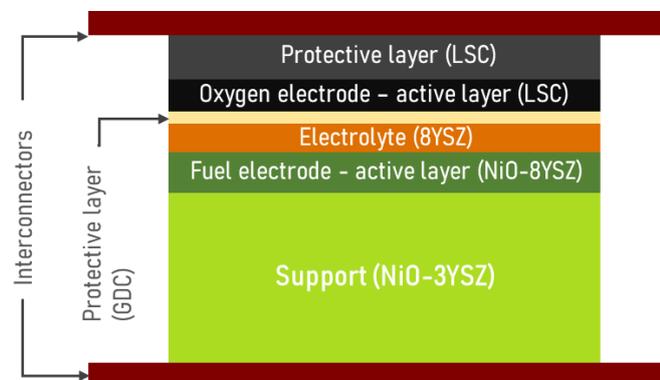


Figure 1: Schematic representation of ElcoCell™ structure



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POLITO, in strict collaboration with ELCOGEN, has developed a recycling process based on the combination and adaptation of HT and hydrometallurgical methods to recover both cost and supply risk (YSZ) and hazardous (Ni) materials from anode-supported electrolyte component of exhausted cells. The overall schematic processes for anode component recycling are reported in Figure 2 including the detachment of the top LSC layer, sequential milling, and HT treatments to disaggregate and pulverize the sintered ceramic-metallic (cermet) components, followed by oxidative selective leaching of Ni to recover the YSZ phase. The overall recovery pathway and related results have been recently published on a prestigious journal, testifying the novelty and soundness of the adopted approach [3].

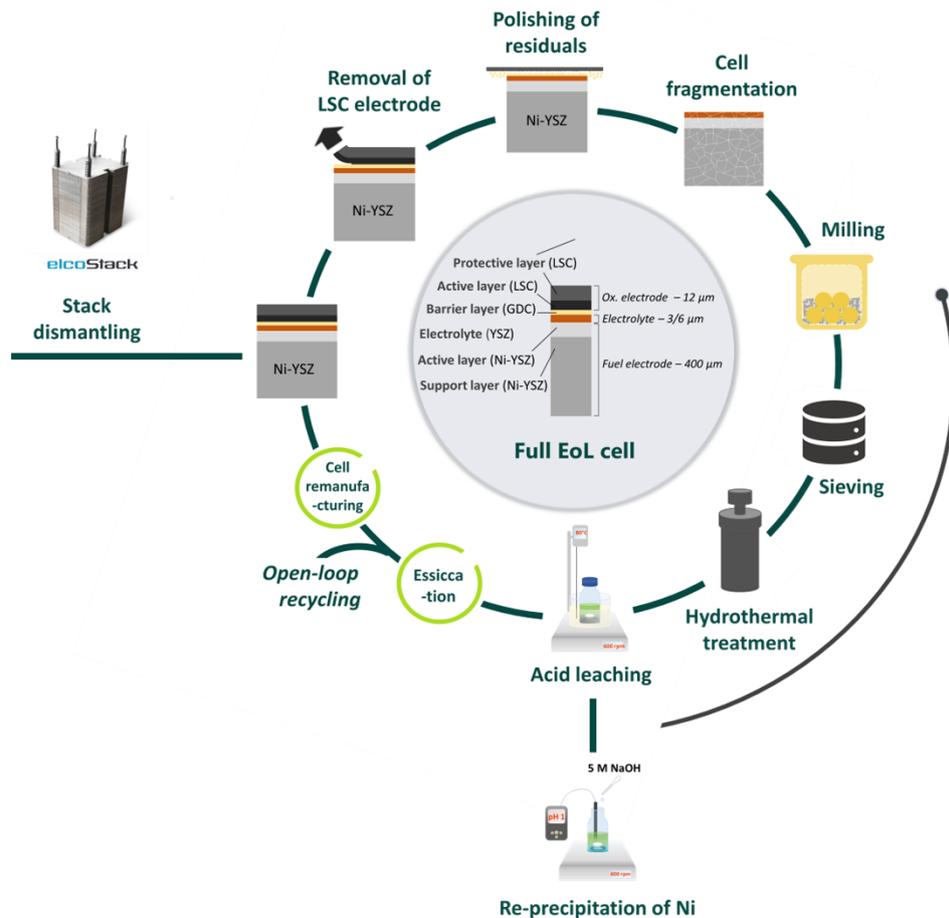


Figure 2: Schematic outline of the pathway followed for the recovery of YSZ and Ni in the form of NiO from EoL SOFCs.

Given the ultimate purpose of re-using the recovered YSZ and NiO for cell manufacturing, some specific acceptance criteria must be targeted by the obtained powders, with special focus on particle size distribution (PSD), specific surface area (SSA) and chemical purity. An extensive physical-chemical characterization of the powders after each step has been conducted by POLITO to define the most efficient process in terms of milling time and HT conditions (i.e. duration, temperature) and acidic leaching step, to guarantee the best results in terms of recovery yield and overall energy/chemicals consumption, in view of the scaling-up to TRL5.

3. Installation of pilot-plant reactor and safety operations

The BHM-2000 reactor with 2L maximum capacitance was received from Berghof Products (Germany) and successfully installed at Envipark as is shown in Figure 3. The different components necessary for the utilization of the reactor (Figure a-b) are 1) the electrical heating jacket to raise the temperature of the system to 300 °C; 2) a control unit that enables programming temperature and time for the treatment of the powder suspension; 3) a stainless steel cylinder with a capacity of 2.2 L, with an internal chamber covered with PTFE which reduces the volume to 1.8 L; 4) the lid of the reactor, which includes the valves for the liquid sample extractions, the pressure relief valve with a gauge up to 25 bars and the rupture disc security system up to 25 bars including a manometer for the control of the internal pressure of the reactor during operation, 5) stirrer drive to be assembled on top of the reactor and move the PTFE stirrer placed inside the chamber.



Figure 3: Reactor components (a) before the installation. Reactor system after the installation (b) ready to use.

The reactor was used for a first test by applying the experimental conditions (T, time, S:L ratio) identified at the lab scale. This TRL5 configuration allows the hydrothermal treatments of 20 g instead of the lab scale reactor which could process no more than 2 g at a time.

The temperature of the reactor has been raised to 200 °C and an internal pressure of ≈ 15 bars has been measured. 300 rpms have been maintained with the stirrer system to ensure the proper distribution of the powders inside the chamber.

Figure 4a shows the lifting system of the lid to facilitate the work of the operator during the insertion of the Ni-YSZ powders inside the chamber of the reactor. Moreover, a metal fixed tube was used for the way out of the rupture disc security system as a safety measure.

Figure 4b shows a different view of the lifting system of the reactor.

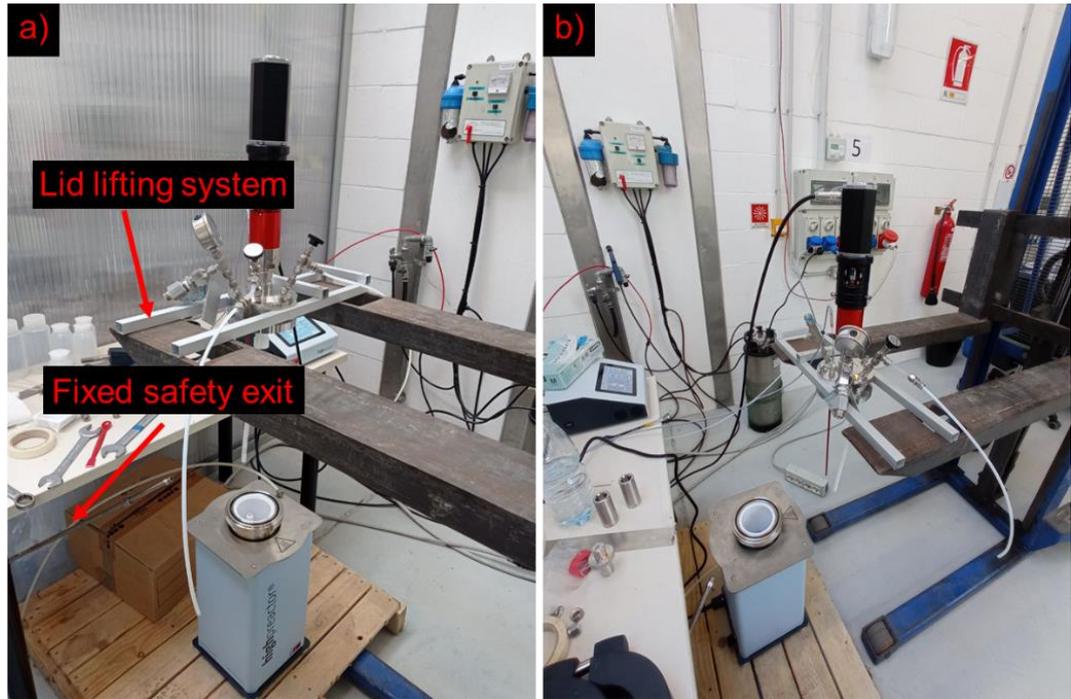


Figure 4: Digital image of the reactor opened with the lifting system and of the fixed safety exit (a), different point of view of the reactor opened (b)

The reactor was then moved to its final position to allow the use of the acidic solution under safety conditions (Figure 5). As extra safety measure, the team installed a tank filled with water for the ways out of both the pressure relief valve with a gauge up to 25 bars and the rupture disc security system up to 25 bars, so that in case of leakages from the reactor from the valve and the rupture disk, the powder suspension in HNO_3 would be immediately neutralised. Moreover, aiming to use the automatic sampling system of the reactor, a tube to flow N_2 inside the chamber of the reactor was installed.

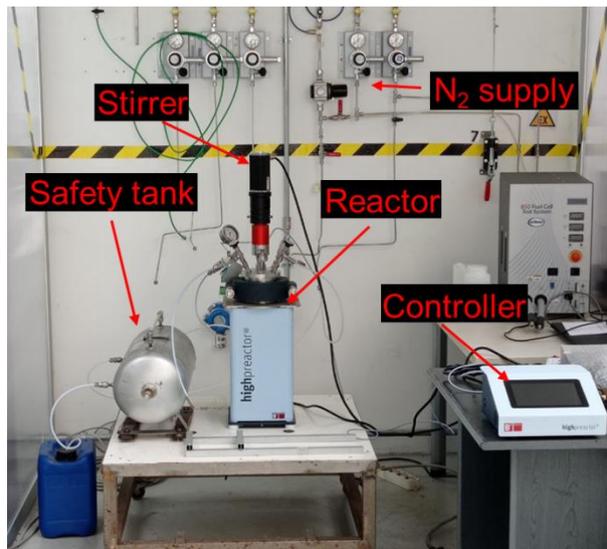


Figure 5: Reactor in its final configuration.

The procedure (Figure 6) to recover safely the acid solution of leached Ni and the YSZ powders, after the hydrothermal treatment, consisted of the following operations: i) once

the HT is finished, the suspension is left without stirring overnight to allow the sedimentation of the powder, ii) the nitric solution is recovered flowing N_2 inside the reactor, iii) Deionized water is pumped inside the reactor, iv) the stirring is brought to 600 RPM for 20 minutes and subsequently the suspension of deionized water and YSZ is recovered flowing N_2 inside the reactor chamber. With this procedure, both the nitric acid solution of leached Ni ions and the YSZ suspension are recovered without opening the reactor for the safety of the operator. Once the suspension of water and YSZ is recovered the reactor can be opened for cleaning and maintenance.

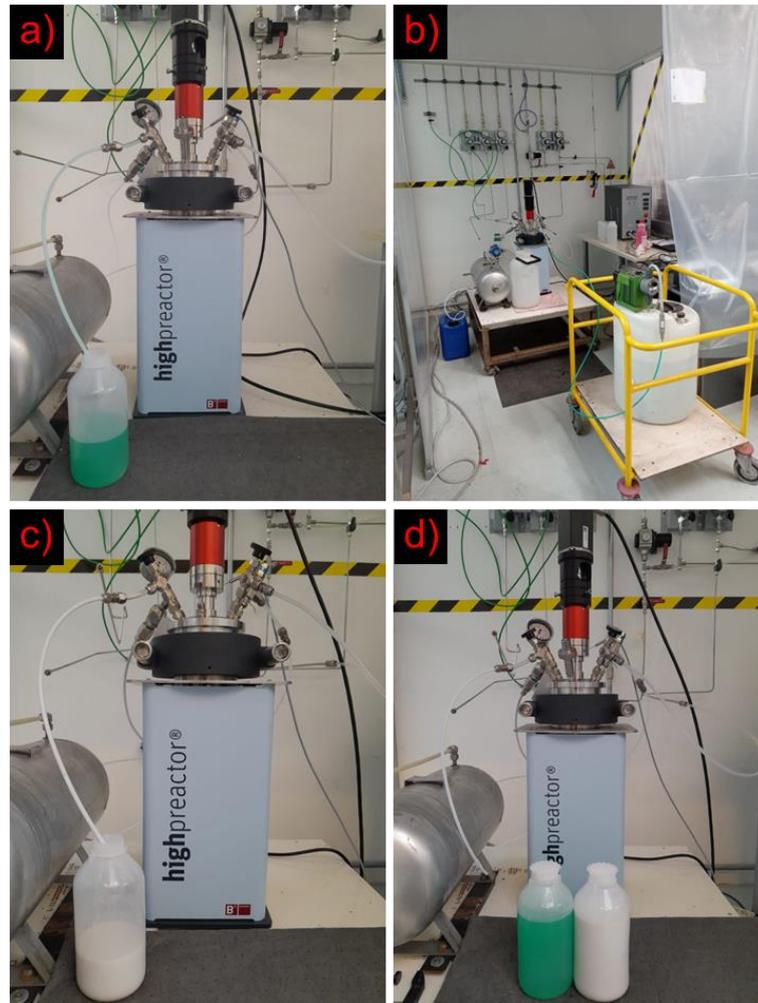


Figure 6: Images of sequential recovery operations the samples recover operation. N_2 is flown inside the reactor chamber to recover the nitric acid (a), then deionized water is pumped and the stirrers is watched on (b). The suspension of water and YSZ is recovered increasing N_2 pressure inside the chamber (c). The separated samples in front of the reactor(d).

4. Scaling-up to TRL5: process optimization

Different processing conditions had been investigated for selecting the best-performing conditions in terms of yield and energy consumption and providing materials meeting some acceptance criteria, defined under the guide of ELCOGEN (SOFC manufacturer) for their effective use in new cell re-manufacturing.



The scaling-up phase focused on the hydrothermal treatment of the sintered composite Ni-YSZ powders inside the hydrothermal reactor (described in section 3). The hydrothermal treatment (HT) plays a key role in the efficiency of the overall recovery process, as it enables efficient disaggregation of the milled Ni-YSZ composite powders and the surface exposure of the nickel metallic phase for the subsequent extraction by the acidic solution. At TRL3 the HT disaggregation step was carried out in a lab-scale reactor containing water at 200 °C with a weight solid/liquid (S/L) ratio of 1:50 and resulted efficient in increasing the specific surface of the milled powders and in the overall reduction of the average particle size. Recovered YSZ resulted suitable for the manufacturing of new fuel electrodes, while Ni could be re-precipitated from the supernatant in the form of a precursor and then converted to NiO through calcination.

For scaling-up the process to TRL5, POLITO aimed at combining the hydrothermal disaggregation and the following metal leaching inside the hydrothermal reactor, developing an optimized **single-step recovery process** at the pilot scale as schematically outlined in Figure 7:

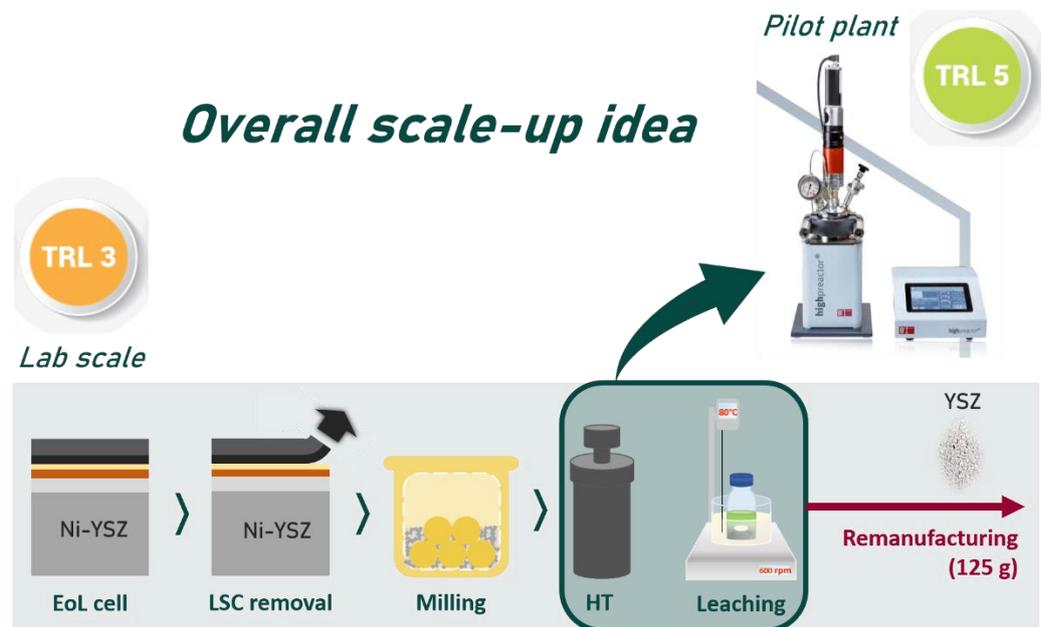


Figure 7 Schematization of TRL5 scaling-up developed at POLITO for the validation of the recovery process. The scale-up aims at combining two key steps of the process, i.e. hydrothermal treatment and leaching, in view of validating and optimizing an efficient single recovery process.

The combination of these two steps consisted of conducting the hydrothermal treatment in the presence of acidic solution (dilute HNO₃ solutions) instead of water to promote the metal phase removal while avoiding the degradation of the ceramic phase (YSZ) due to the concurrent effects of acidic and hydrothermal conditions.



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Based on the conditions identified at TRL3 for the two separate steps (Figure 8), POLITO aimed at identifying the process parameters (T, time, S/L, acid concentration) to maximize both the efficacy and efficiency of the overall recovery strategy at TRL5 enabling to: i) reduce the powder loss thanks to the elimination of one processing step; ii) reduce the overall energy consumptions due to the hydrothermal treatment (the most energy-consuming according to the initial LCA evaluations) iii) maximize the efficiency of Ni extraction and, therefore, the purity of the recovered YSZ, while still targeting the reference acceptance criteria defined by ELCOGEN.

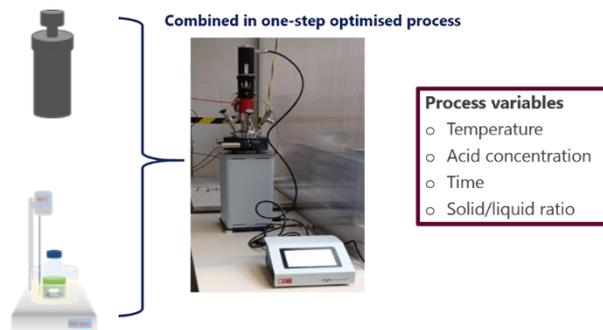


Figure 8 Schematization of the operating conditions identified at TRL3 for the separate hydrothermal treatment (HT) and leaching combined at TRL5. Identification of the variables (i.e. T, time, acid concentration and S:L ratio) investigated for the single-step process.

The attempt to combine the two separate treatments had already been tackled at TRL3, however the results were not satisfactory in term of nickel removal, most likely due to mass transfer limitation inside the HT reactor. Based on the results of the conducted preliminary test, it was found that: i) compared to the leaching carried out as a separate step in batch, the effect of increasing acid concentrations proved to be a critical factor since at 200 °C an extensive degradation of YSZ was found ii) Ni residues were above 1%mol., evidencing not satisfactory removal of the metallic phase. It was therefore concluded that to keep the temperature at 200 °C and ensure the disaggregating effect on the composite powders while avoiding the degradation of YSZ, the HNO₃ solution should not exceed a critical concentration of 1 M. Moreover, stirring (not available for the reactor at TRL3) was found to be essential to ensure a good mass transfer and to promote efficient Ni extraction.

Based on these considerations, and with the final aim to properly optimize the processing parameters, a Design-of-Experiments (DoE) approach was adopted. DoE is a systematic and statistical approach that allows to study of the variation of one or more responses (or output variables Y) of a process as a function of input factors (or input variables X) [4]. In particular, DoE aims to explore, map and model the behaviour of the response/responses across multiple factors simultaneously, by varying all variables at once according to a predefined experimental matrix. The behaviour is studied within a given reaction space, defined by the combined ranges of all factors involved.

As previously mentioned, the input variables of our process are temperature (T), time (t), S/L ratio and acid concentration. For all the experiments, the T was fixed at 200 °C, since based on the available literature, this temperature is required to induce an efficient disaggregating effect on the composite powders. The disaggregation is induced by the high pressure generated inside the reactor as a result of the increased vapour pressure of the



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liquid at high temperatures. A reduction in temperature would lead to a decreased pressure, with the risk of compromising the disaggregating effect of the treatment.

The concentration of the HNO₃ acidic solution was also fixed, since according to the technical data sheet provided by *Berghof*, the reactor can safely withstand a solution with a maximum concentration of 1.0 M at the working T of 200 °C.

As a result, the two input variables targeted for the optimization of the recovery process at TRL5 were the time (duration of the treatment) and the S:L ratio. To decrease the treatment time while concurrently increasing the quantity of treated powders, the final aim was to maximize the overall efficiency of the recycling process, delivering the highest amount of YSZ powders with the lowest consumption of energy and chemicals.

Having defined the two input variables/factors of our system (*i.e.* treatment time and S:L ratio), a Full Factorial Design (FFD) approach was adopted. An FFD is a factorial experiment whose design consists of all possible combinations of the chosen factors and levels (the values that each factor can take on). Effects of all factors (main effects) and interactions among them are considered in this design, making it a potent tool that provides the most comprehensive insight into the system's behaviour. If all input factors k have the same number of levels n , the total number of runs r is equal to n^k .

$$r = n^k \quad [1]$$

By increasing the number of factors and levels, the number of experimental runs grows hugely. Having assigned two levels (-1,1) to each of our variables (t and S:L), our experimental model (Fig. 9a) was constituted by a total of 2² (4) runs. The level 0 (halfway between -1 and 1) was considered for this purpose, allowing us to work in the centre (0,0) of our experimental space and to obtain a symmetric model. Therefore, exp. n° 5 was added to the model, and two repetitions (n° 6 and n° 7) were added in the same conditions to evaluate the experimental error and define a confidence interval for the validation of the model. The overall experimental matrix constituted by a total of 7 experimental runs is shown in Figure 9a. After defining the values to be assigned to each level (Fig. 9b) of the two factors X1 and X2, the final matrix displaying the experimental conditions for each run could be obtained (Fig. 9c).



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(b)

	X1 t (h)	X2 s/l ratio	[X2 powders (g)*]
-1	1	1:50	20
1	4	1:20	50
0	2	1:35	28.6

* in 1L of acidic solution (HNO₃ 1M)

(a)

Exp. n°	MODEL					VALIDATION	
	1	2	3	4	5	6	7
X1	-1	-1	1	1	0	0	0
X2	-1	1	-1	1	0	0	0

(c)

Exp. n°	MODEL					VALIDATION	
	1	2	3	4	5	6	7
t (h)	1	1	4	4	2	2	2
s/l ratio [powders (g)]	1:50 [20]	1:20 [50]	1:50 [20]	1:20 [50]	1:35 [28.6]	1:35 [28.6]	1:35 [28.6]

Figure 9 Results of a Full Factorial Design (FFD) approach for a system constituted by 2 input factors each one evaluated on 2 different levels, for a total of 22 (4) experimental runs. Three additional experimental runs (one as part of the model, two as a validation) were planned in centre (0,0) of the experimental space with the aim to collect more information on the behaviour of the system and define a confidence interval. The figure shows the experimental matrix before (a) and after (c) having defined the factors X1 and X2 and their related levels (b). The factor X2 can be referred to either “S:L ratio” or “grams of powders in 1L of HNO₃ acidic solution”.

The YSZ powders recovered after each treatment have been fully characterized in terms of crystalline phase, specific surface area, particle size distribution, morphological features and amount of residual Ni after leaching. Specifically, the crystalline structure of powders was examined through X-ray diffraction (XRD, Panalytical, Xpert3 MRD) analysis using Cu K α radiation at a voltage of 40 kV and a current of 40 mA, to evaluate any possible structural change or degradation induced by the combined HT+leaching.

Moreover, N₂ adsorption-desorption isotherm analyses were conducted by using an ASAP2020 Micromeritics analyser at a temperature of -196 °C to evaluate the specific surface area (SSA) after each treatment. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area (SSA_{BET}) from the adsorption isotherm in the 0.04–0.2 relative pressure range. The same powders were also analyzed through dynamic light scattering (DLS) analysis, with a Zetasizer nano ZS90 (Malvern Instruments Ltd., Malvern, UK) at RT to assess their average particle size distribution (PSD).

Field Emission Scanning Electron Microscopy (FESEM, Jeol, JCM-6000Plus, Benchtop SEM) was performed in high vacuum conditions and at a voltage of 5kV to evaluate the morphological features of the recovered powders. The concentration of residual Ni in the recovered YSZ was measured through Inductively Coupled Plasma Atomic Emission Spectrometry Technique (ICP-AES) (ICP-MS, Thermoscientific, Waltham, MA, USA, ICAP Q) after acidic digestion of the powders. ICP analysis was used also to measure the concentration of Ni, Y and Zr in the supernatants recovered after the treatments and to evaluate the yield of Ni extraction and the possible degradation of YSZ.



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The recovered YSZ powders were first characterized through XRD analysis to evaluate the crystalline phase retention of zirconia after being exposed to acidic leaching at high temperatures inside the hydrothermal reactor. According to XRD results, the crystal structure of YSZ was fully retained even after prolonged treatment times (up to 4h) and for all investigated S:L ratios. As a result, none of the two variables, time and S:L ratio appeared to significantly affect the crystalline structure of the recovered YSZ powders within the investigated experimental space (*i.e.* t: 1-4; S:L ratio: 1:50-1:20).

The physical-chemical features of the recovered powders were also evaluated and compared with the reference acceptance criteria terms of SSA (12-20 m²/g) and PSD (100-600 nm). According to the results listed in Table 1, most samples recovered after the combined (HT + leaching) process satisfied these criteria.

Table 1 Specific surface area (SSA) and particle size distribution (PSD) values of the recovered YSZ powders, evaluated through the Brunauer–Emmett–Teller (BET) equation from the corresponding adsorption isotherms and through dynamic light scattering (DLS) analyses, respectively.

Exp. n°	SSA _{BET} (m ² /g)	PSD* (nm)
1	17	404 ± 166
2	23	388 ± 161
3	18	358 ± 124
4	18	437 ± 194
5	19	322 ± 114
6	18	357 ± 129
7	20	327 ± 100

*derived from distribution % volume

FESEM analysis evidenced (Fig. 10) that, overall, the recovered powders were constituted by a fraction of fine powders with a size of about 400±150 nm based on DLS analysis, together with a fraction of larger aggregates with an average size of about 10 μm,



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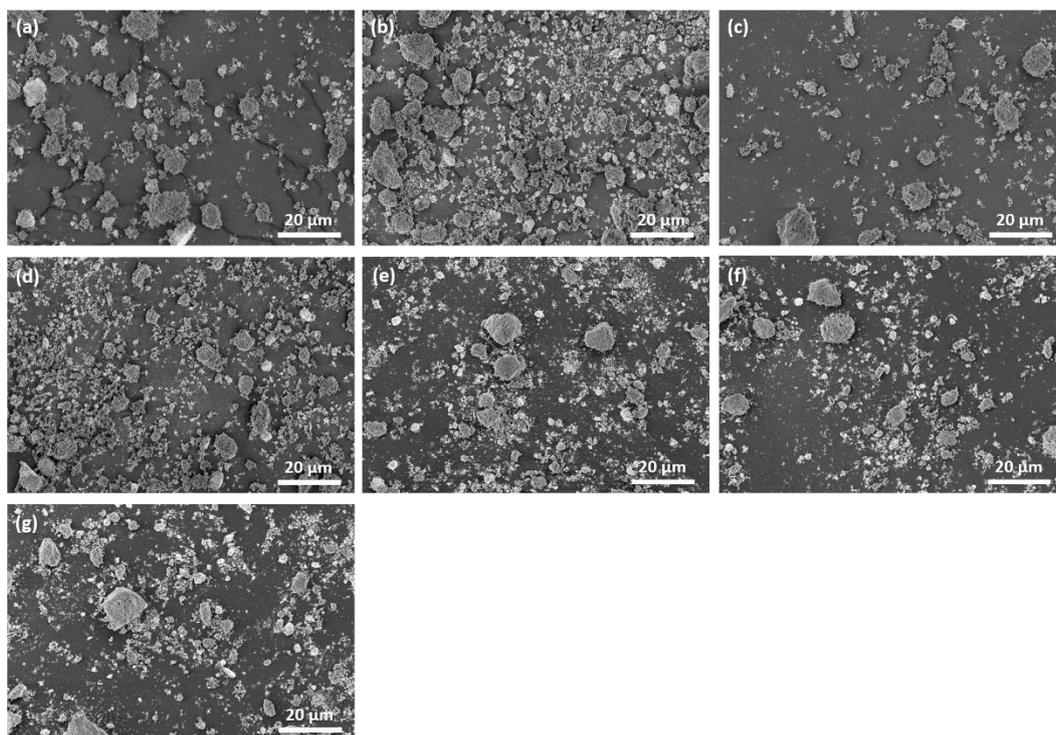


Figure 10 FESEM images of the YSZ powders recovered after the experimental runs detailed in Fig. 5c. Figures (a)-(g) correspond to experiments 1-7.

Together with the structural and physical features of the recovered powers, the amount of residual Ni plays a key role on the overall success of the recovery process, especially in view of demonstrating the possible re-use of the powders in an *open-loop* scenario. To this purpose, the powders were acid-digested to evaluate the % wt of Ni residuals after each treatment and determine the efficacy of extraction.

According to the values, an overall residual amount of Ni comprised between 0.15 and 0.20 %wt was detected. However, in view of a closed-loop recycling and according to ELCOGEN, a residue of ~ 0.3 % wt is acceptable. Therefore, the experimental conditions corresponding to exp. n°2 can be considered the most satisfactory in terms of the overall efficacy of Ni extraction and efficiency of process (considered as the highest amount of powders treated in the shortest time possible with the lowest related energy consumptions and while targeting the reference acceptance criteria for re-manufacturing).

The increased efficacy of Ni extraction at TRL5 could be easily stated (qualitatively) based on a visual inspection of the powders (Fig. 11).



Figure 11 Visual aspect of the powders recovered (left) after acidic leaching carried out in the reactor at the laboratory-scale, (right) after acidic leaching carried out in the pilot-scale reactor at TRL5 (200 °C, HNO₃ 1.0 M, stirring 650 rpm) (c).

ICP analysis was eventually carried out on the supernatants retrieved after each experimental run to determine the concentration of Ni²⁺ and Zr⁴⁺ leached out during the processes, as a further confirmation of the previous characterizations. Results showed the lowest concentrations of Ni for exp. n° 1 and 3, corresponding to a S:L ratio of 1:50 in both cases and to 1h and 4h treatment times, respectively. The highest concentrations (triplicated compared to 1 and 3) were instead observed for exp. n° 2 and 4, with a S:L ratio of 1:20 and 1h and 4h treatment times, respectively. Importantly, the amount of Zr in solution was negligible in all the retrieved supernatants, confirming that YSZ is not degraded (not even after prolonged treatment times) when exposed to HNO₃ 1.0 M at 200 °C, confirming the XRD results discussed above.

The results presented and discussed so far have been analysed also as part of the DoE defined in Fig. 9. The analysis was carried out by use of the chemometric software CAT – Chemometric Agile Tool. Considering X1 (time, h) and X2 (S:L ratio) as the input variables, and X1*X2 as their linear interaction, Fig. 12 (a-c) shows the plots of the resulting coefficients (b₁, b₂, b₁₂) corresponding to the outputs (Y), specifically Y1 (Specific Surface Area, SSA, m²/g), Y2 (Residual Ni, %wt) and Y3 (Particle Size Distribution, PSD, nm), according to the following correlation:

$$Y = b_0 + (X_1) + b_2(X_2) + b_{12}(X_1 X_2) \quad [2]$$

where b₀ is the value of Y when X₁=X₂=0, i.e. the value at the centre of the experimental space. The red histograms indicate the values of the coefficients related to the variables X₁ and X₂ and their interaction X₁*X₂. The green bars represent instead the experimental uncertainty derived from the measurements. Being the values of the coefficients smaller than the experimental uncertainty according to Fig. 12 (a-c), none of the two variables and neither their interaction significantly affects the final responses of our system in the experimental space considered for the study. As previously observed in the above discussion, in fact, none of the powder features among SSA, Ni residues and PSD were significantly varied as a result of changing the treatment time or S:L ratio. This does not mean that these two factors do not have an impact by any means, but rather that they do not have a significant impact within the investigated ranges of variation (time: 1-4h; S:L



ratio: 1:50-1:20). By considering lower/higher treatment times and/or S:L ratios the impact would probably become more remarkable.

Fig. 12 (d-f) shows on the other hand the contour plots of Y1, Y2, Y3 in the experimental domain set for the DoE (X1, X2). A contour plot displays a two-dimensional view of the outputs in which points that have the same response value are connected to produce contour lines, enabling to determine the settings of X1 and X2 that will maximize (or minimize) the response variables or that will result in hitting some pre-determined target values. The blue contour lines indicate the output response values of Y1, Y2, Y3, while the red contour lines underneath indicate the associated experimental error. The green areas represent instead the range of values that target the acceptance criteria of the recovered powders for each output, as a function of the variables X1 (time, h) and X2 (S:L ratio). As shown in Fig. 12 (d-f) and according to the previous discussion on the results, the acceptance criteria for Ni residues and PSD are satisfied in the entire experimental domain, while the conditions on SSA are satisfied in a narrower area.

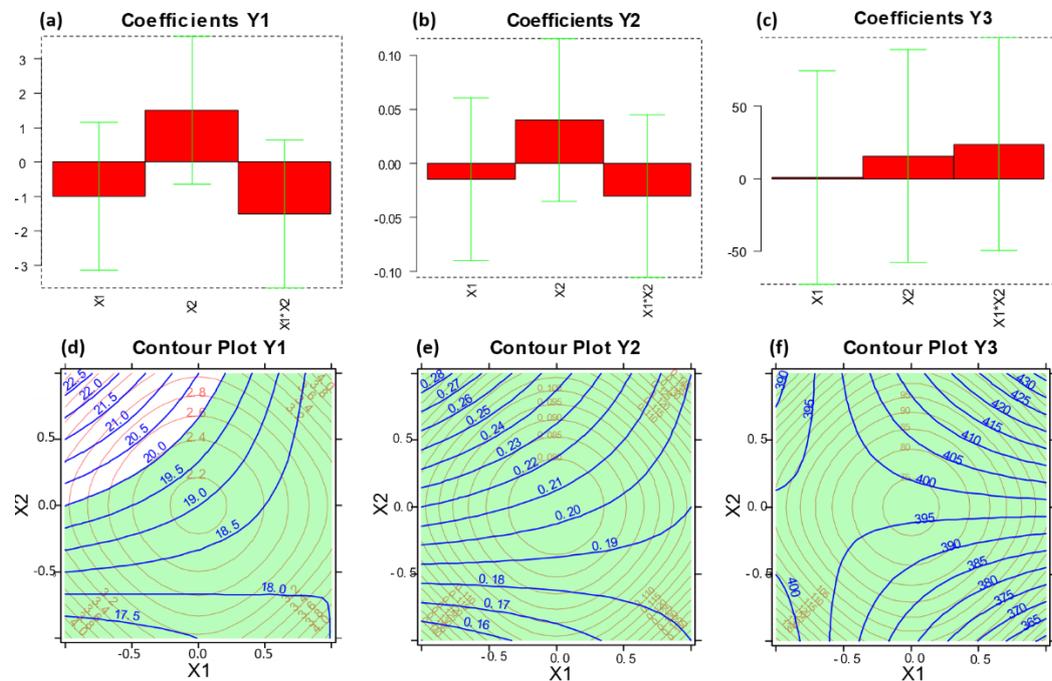


Figure 12 Above: plots of the coefficients of the model corresponding to the outputs (a) Y1 (SSA, m²/g), (b) Y2 (Residual Ni, %wt), (c) Y3 (PSD, nm). Below: contour plots (blue contour lines, each one indicating the same response value) of (d) Y1, (e) Y2, (f) Y3 in the experimental domain set in the DoE. The green areas represent the range of values that target the acceptance criteria of the recovered powders for each output, as a function of the variables X1 (time, h) and X2 (S:L ratio). The red contour lines underneath indicate the experimental error. The crossing between the blue and the red contour lines corresponds to the value \pm error.



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Overall, thanks to the DoE approach, the optimal processing conditions in the investigated experimental domain could be identified. The acceptance criteria at TRL5 were targeted despite increasing the quantity of powders (50g in 1L, i.e. S:L=1:20) and decreasing the treatment time (1h) compared to the process defined at the laboratory scale (1:50 and 4h).



5. Conclusions

The recovery process of YSZ and Ni in the form of Ni^{2+} solution has been successfully scaled up from a lab-scale to a pilot hydrothermal reactor, enabling the control of T, stirring and the measure of the generated internal pressure. The reactor has been installed at Envipark to operate safely, and the final setting allowed the loading and unloading of the powder and the acidic solution without risks to the operators.

A single-step process has been optimised at TRL5 by treating the composite powder inside the reactor filled with diluted HNO_3 solution. This combination was already attempted at the lab scale but the results were unsuccessful since the leaching of nickel was not satisfactory, mostly due to mass transfer limitation inside the reactor (not stirred).

At variance, the combined process carried out on the pilot-plant reactor proved to enable both the disaggregation of the composite powders and the complete leaching of the nickel phase. By exploiting a DoE approach seven trials were identified out by fixing the T (200°C) and the concentration of the acidic solution (1M) and by varying the duration time as well as the S:L ratio.

Based on the obtained results the optimal processing conditions in terms of S:L and duration time were respectively S:L = 1:20 (50g in 1L) and the treatment time of 1h, which allowed to target a significant increase in the process efficiency compared to the lab scale (S:L 1:50 and duration time of 4h), enabling a ten-fold increase in the amount of powders treated in each experiment.

The recovered YSZ powders after each trial were fully characterised, showing the retention of the crystallinity, the appropriate specific surface and particle size, and chemical purity according to the specifications provided by ELCOGEN, and proving their suitability for re-using in the manufacturing of novel SOFCs.



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6. References

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