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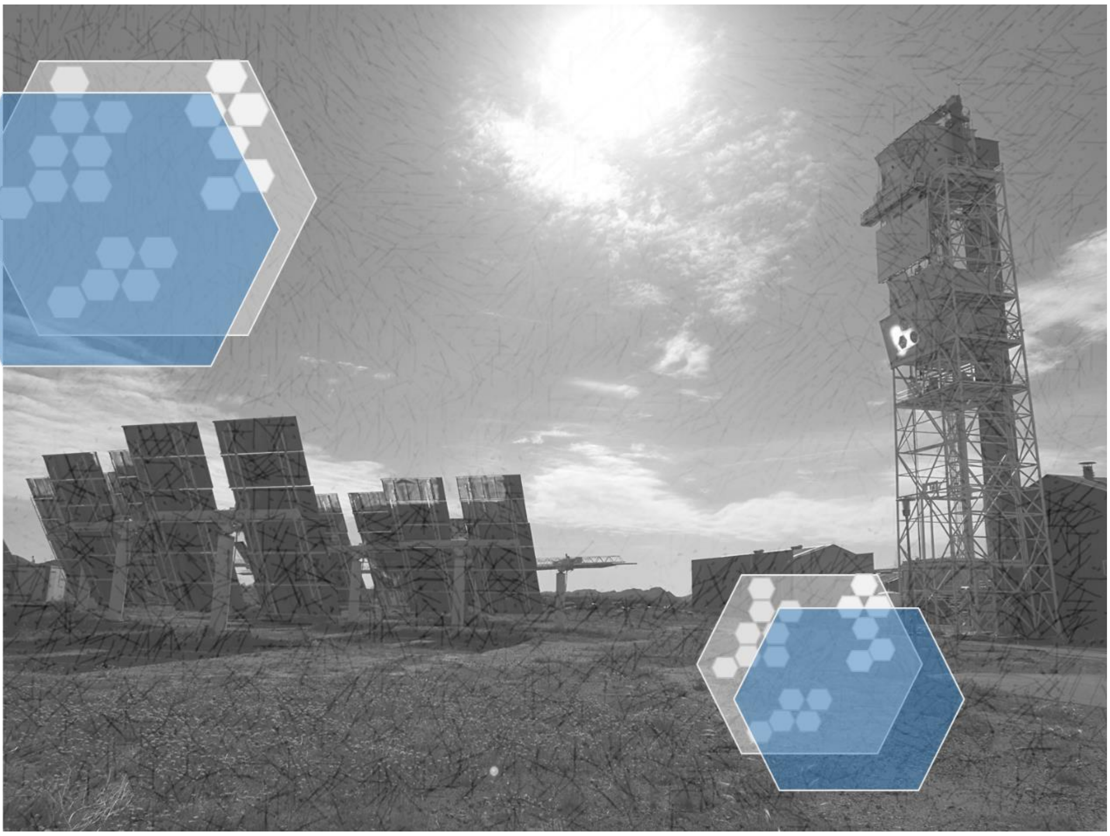

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Inert gas minimization-Publishable Summary Report

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Minimization of inert gas consumption

The HYDROSOL process is investigating the solar H_2 production from the thermochemical splitting of water via redox reactions is solar structured reactors that are based on metal oxides. The redox reactions involve thermal reduction of the metal oxide at high temperatures under oxygen poor atmosphere, e.g. with the use of inert gas as sweep gas, for the formation of oxygen vacancies in its lattice and its oxidation at lower temperatures where the material is oxidized from H_2O releasing H_2.

One of the main objectives of the HYDROSOL-beyond project is to develop concepts for the minimization of inert gas utilization during the solar two-step redox thermochemical cycles in the solar reactor with target the increase of the efficiency of the solar H_2 production process.

Three approaches are investigated in the project:

1. Thermal reduction under lower inert gas flow rate
2. Coupling of the water splitting reactor with an oxygen trap for the removal of oxygen from the inert gas stream during the thermal reduction step and potential recycling of oxygen free gas
3. Reverse Pressure Swing Adsorption for the purification of the inert gas stream

1 Reduction of inert gas flow rate during the thermal reduction step

The thermal reduction of the redox material is improved in low oxygen partial pressure. Therefore, such a reaction would benefit either from vacuum or from high N_2 flow rates. The latter is the case of the HYDROSOL process where a significant amount of inert gas is used to facilitate the removal of O_2 from the redox material at high temperatures.

The high N_2 requirements, however, are negative for the overall efficiency of the process and its footprint. In the current project, one approach was to investigate the effect of the reduction of the N_2 flow rate during the thermal reduction of the redox material on its water splitting activity, i.e. removal of O_2 from H_2O at the water splitting step, in the long-term.

In this direction, a $NiFe_2O_4$-coated ZrO_2-foam was used for the lab scale evaluation. This is the standard redox structured body that was previously developed (HYDROSOL-Plant project, GA325361), has been extensively investigated at the laboratory scale and is the structure that is currently used at full scale in one of the directly irradiated solar cavity reactors at the HYDROSOL platform at Plataforma Solar de Almeria.

A high temperature laboratory testing rig was used to perform a series of thermal reduction and water splitting cycles. It was observed that there was no significant effect on the H_2 production with the reduction of the N_2 flow rate to half of the original flow rate during the thermal reduction step. These results are positive and indicate that the O_2 that was adsorbed by the redox material during the water splitting step can be sufficiently removed with a lower inert gas flow rate. However, the number of cycles is not very high to reach a safe conclusion that the low flow rate has no significant effect on the extent of the regeneration of the material in the long-term. The stability of the material performance can only be evaluated through multiple cycles and long-term exposure to low inert gas flows, since inadequate amount of N_2 may not suffice to sweep the O_2 produced during the regeneration of the redox material.

2 Development of an oxygen trap (O-trap) based on redox material

In parallel, another approach that was investigated involved the utilization of a redox material as an O-trap sub-unit for the removal of the O_2 that is released in the N_2 stream during the thermal reduction step, i.e. coupling of the HYDROSOL process with a technology that was developed in a previous project (RESTRUCTURE GA283015)[1] for the storage of thermal energy based on redox reactions.

This technology is based on multi-valent metal oxides, such as Cobalt oxide (CoO/Co_3O_4) that have the ability to consecutively absorb and release oxygen atoms out of their lattice without destroying their inner structure (similar behavior with the redox materials used for the thermochemical water splitting). A significant advantage of this method is that it requires lower temperatures than the thermal reduction step of the H_2 solar reactor and therefore there is no energy penalty induced for the separation of the mixture stream to its constituents.

The high-temperature effluent stream can be directly introduced to the O-trap sub-unit for the removal of the oxygen. Furthermore, there is no need of additional sweep gas because of the ability of these redox materials (e.g. cobalt oxide) to regenerate under an oxygen-rich atmosphere (e.g. air) with the increase of temperature, simplifying the requirements of the process.

Another important benefit is the high-temperature of the exit stream. The purified N_2 stream exits the O-trap at moderately high temperatures (~600°C compared to the almost ambient temperature of a Pressure Swing Adsorption unit which can be used for the purification of the N_2 stream), thus the extra energy needed for the re-circulation of the stream back to the process is quite small.

The two-step reaction scheme for the case of cobalt oxide is shown below:

$3CoO + 0.5O_2 \rightarrow Co_3O_4$	T = 900°C(endothermic)
$Co_3O_4 \rightarrow 3CoO + 0.5O_2$	T = 600°C (exothermic)

Preliminary experiments have been performed in a laboratory test rig (Figure 1) for the proof of concept of the proposed method. The material employed for the abovementioned campaign was $NiFe_2O_4$ coated ZrO_2 foam for the water splitting mode, while for the O-trap an all-redox honeycomb monoliths of cobalt oxide was used (previously developed during the RESTRUCTURE project[2]).

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[1] https://cordis.europa.eu/project/id/283015

[2] Karagiannakis G., Pagkoura C., Halevas E., Baltzopoulou P., Konstandopoulos A.G. (2016) "Cobalt/Cobaltous Oxide Based Honeycombs for Thermochemical Heat Storage in Future Concentrated Solar Power Installations: Multi-cyclic Assessment and Semi-quantitative Heat Effects Estimations", Solar Energy, 133, pp. 394-407

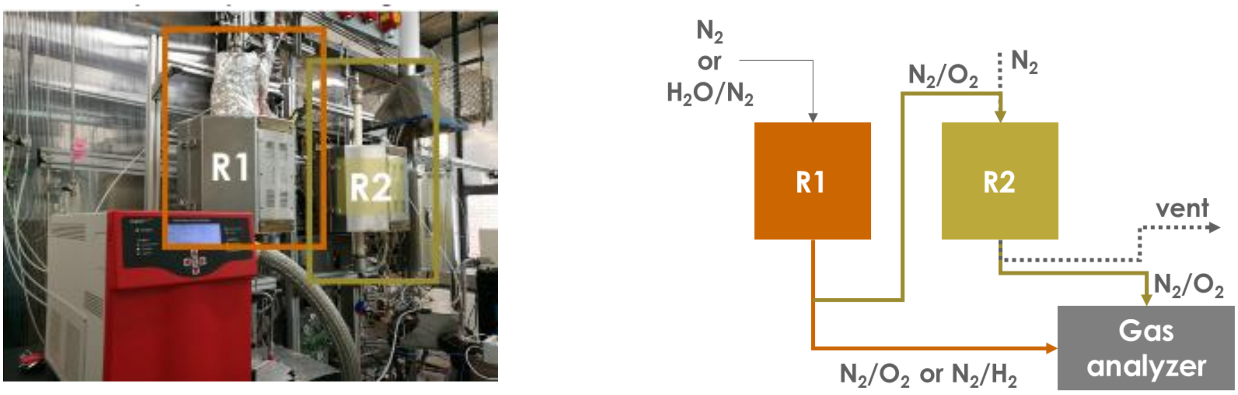

Figure 1. The coupled experimental tests rig (HYDROSOL reactor coupled with the O-trap reactor)

The stream from the exit of the Water splitting/Thermal reduction reactor (R1) was passed through the O-trap reactor (R2). The result was that O_2 that was originally released from the R1 reactor during the thermal reduction step under N_2 flow was not detected at the exit of the R2 reactor that contained the O-trap material (Figure 2). Under the specific conditions (O-trap storage mode) O_2 was removed from the N_2 stream and pure N_2 exited the R2 reactor. This stream could potentially at a next step be used for the reduction in another "R1 type reactor" (i.e. reactor containing the water splitting material) which is under thermal reduction mode.

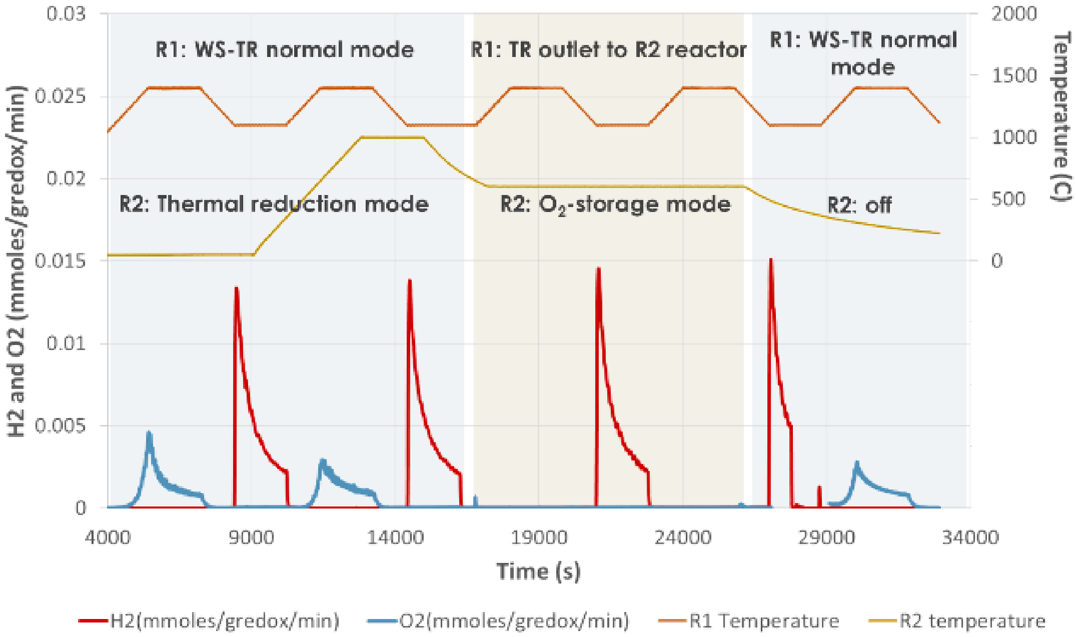

Figure 2. Experimental results of the coupled operational mode.

The results were very encouraging and novel architectures of the materials was decided to be tested in order to evaluate their performance. For the prototyping of these structures the geometry was designed, dimensioned and printed through additive manufacturing in a polymer material, similarly to the case of the water splitting redox materials (replica technique or Schwarzwalder method). The printed polymeric models served as template structures (sacrificial polymeric templates impregnated in a ceramic slurry) for the ceramization process that gave the desired morphology to the final prototype.

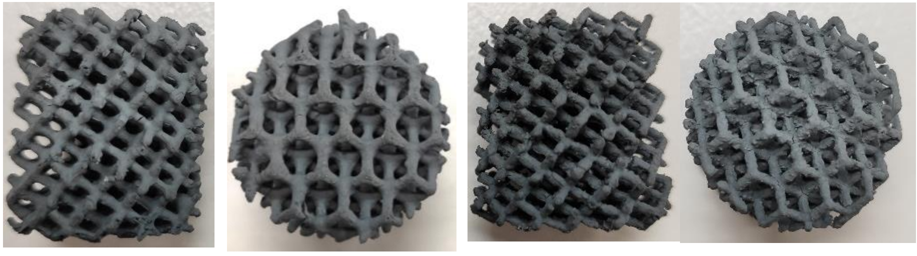

Figure 3. 2nd batch of all-redox cobalt oxide lattice structures delivered to APTL.

All samples were initially tested with the aid of thermogravimetric analysis (TGA) under air. The testing protocol involved cycling of the material under air within a temperature window and measuring the weight loss and gain that corresponds to oxygen removal (reduction of material) and uptake (oxidation of material) respectively.

The structure that qualified based on its cyclability and oxygen trapping capacity (weight gain during the oxidation step) was the "medium cell size" cobalt oxide lattice structure that was chosen for further testing in the coupled laboratory experimental test rig in series with the redox water splitting reactor.

3 Reverse Pressure Swing Adsorption (reverse PSA)

Another approach that is investigated for the purification and potential recycling of the inert gas is the Pressure Swing Adsorption. The stream that exits the solar reactors during the thermal reduction step consists of nitrogen and oxygen that should be appropriately treated in order for the clean nitrogen to re-enter into the process. The employment of an effective PSA system, similar to the one used for the product (H_2) purification could provide a viable solution to inert gas consumption minimization.

Within the HYDROSOL-beyond project the option to use Pressure Swing Adsorption (PSA) technology to purify the regeneration gas stream consisting of nitrogen with up to 2.5% oxygen to pure nitrogen. By using the PSA in a different manner, i.e. using what is normally the off-gas as the purified gas stream, the contaminated nitrogen stream is cleaned. In the "normal" way to operate a PSA, the gas species that is least strongly adsorbed, is purified. In this case the most strongly adsorbed gas is produced as a purified stream. To be able to separate oxygen from nitrogen a special sorbent material will be used.

PSA model calculations have been done using special in-house developed software tools. For the calculations the following specifications were used:

Feed Flow N_2: 20 kg/h

O2 concentration: ~2.5%

Required purity: < 0.001%. O_2

Operating pressure: 1.45 bar

Off-gas pressure: 0.1 bar

It is assumed that the feed stream is cooled down to room temperature. A blower is to be used, to get the pressure up to 1.45 bar. A higher feed pressure can increase the performance of the PSA, but is chosen to be below the PED-limit. A vacuum pump is used to extract the off-gas. A vessel size of 20 litre is taken for the calculations. The nitrogen yield and the oxygen concentration are calculated for different cycle times and operation modes. Indicative results are shown in Figure 4.

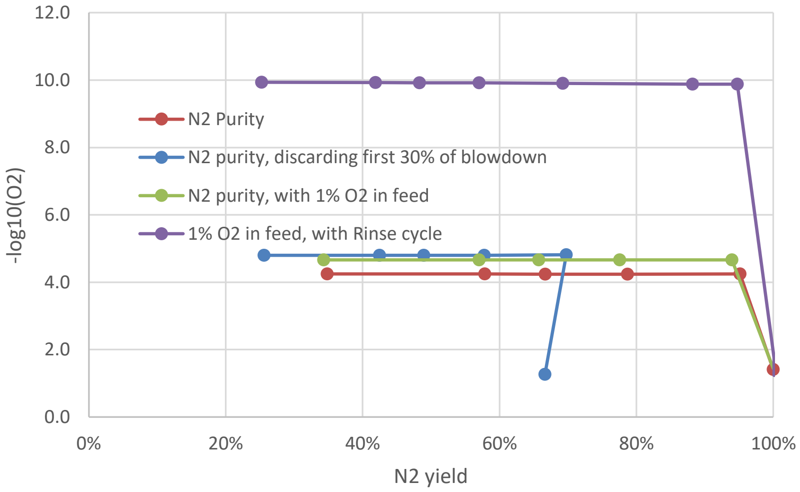

Figure 4. Indicative results from the PSA model.

The model calculations indicate that high yields can be achieved, while reaching the purity specifications. The purity also depends on the feed concentration: 1% O_2 gives better results than 2.5% O_2. Adapting the mode of operation can result in higher purity. It is clear that a flow of 100 kg/h of nitrogen would result in larger vessels.

An existing PSA test rig has been modified and adapted to test the nitrogen purification option. The P&ID of the test system is shown below. The feed flow is made by mixing nitrogen with air. A sample line is present to measure the gas composition of the purified nitrogen.

Figure 5. PSA test rig: 4-vessel PSA (right part of picture), vacuum pump and storage vessel (left part of image)

During operation there is the possibility that the oxygen concentration can peak to values above 25%, of course depending on the inlet oxygen concentration. Such high concentrations are considered dangerous. For the studied 2.5% case, high oxygen concentrations can occur, mainly inside the PSA vessels. At the normal product side higher concentrations may occur, but using a buffer vessel will eliminate peaks.

A stream with a 2% oxygen content is fed to the test setup by mixing an air and nitrogen flow (MFC_Air and MFC_N2 in the plot). The first results show that the oxygen concentration at the impure side (AI_QECO2) increases above 2% when reducing the cycle time, whereas the concentration at the outlet nitrogen stream is below 2%, indicative of the purification of the nitrogen stream. The operation parameters are further adjusted to achieve deep purification of the raw nitrogen stream.

4 Conclusions

Minimization of the inert gas can be achieved either by lowering the inert gas flow rate, provided that sufficient reduction extent of the redox water splitting material can be achieved, or by introducing concepts of recycling of the inert after its purification. For the latter two approaches were investigated based (i) on oxygen-trapping on redox materials and (ii) on reverse Pressure Swing Adsorption (PSA). A novel concept of an oxygen-trapping redox system based on cobalt oxide structured bodies that is coupled with the water splitting reactor and can remove oxygen from the inert gas stream that exits the water splitting reactor was successfully tested at the laboratory scale in a dual reactor testing rig and under consecutive cycling mode, providing a promising and attractive new technological approach to the purification and recycling of N_2. In the case of the reverse PSA a modified experimental set-up was used to investigate the applicability of the concept. The technology, although mature for its application in its conventional operation, it has still some issues to resolve in its reverse mode especially at peak O_2 concentrations.