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FINAL REPORT: PUBLISHABLE SUMMARY

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Project acronym: *RESTRUCTURE*

Project title: *Redox Materials-based Structured Reactors/Heat Exchangers for Thermo-Chemical Heat Storage Systems in Concentrated Solar Power Plants*

Funding Scheme: *Collaborative Project*

Period covered: *November 1st 2011 – January 31st 2016*

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Introduction

The RESTRUCTURE project was a 51-month undertaking, partially funded by the EC under the ENERGY Theme of FP7 programme, aiming at the exploitation of the thermal effects of reversible chemical reduction-oxidation (redox) reactions for the storage and on-demand controlled release of captured solar energy as heat. The new concept introduced by RESTRUCTURE was, instead of using packed or fluidized beds of the redox material as the heat storage medium, to employ monolithic structures, made entirely or partially from the redox active materials. The project's main scientific/technical objectives were:

- The development of suitable redox systems with thermochemical heat storage (THS) and release capability quantified via fast reduction and re-oxidation kinetics, and prolonged lifetime as well as constant activity and cyclability.
- The design of new structured honeycomb/foam reactors/heat exchangers with enhanced transport, thermal and heat recovery properties, also incorporating a high amount of redox material per volume.
- The shaping of the redox powders above into heat storage structures with sufficient thermomechanical properties.
- The demonstration of the structured reactor/heat exchangers for cyclic heat storage/release operation, within the operating temperature range of future high temperature solar tower plant designs.
- The manufacture of a pilot-scale structured reactor/heat exchanger, its coupling to an existing solar tower facility (Solar Tower Jülich/STJ research platform) and the on-site validation of the technology by demonstrating heat storage/release capability during on-sun and off-sun operation respectively, reaching energy storage density levels of at least 400 kJ/kg and storage capability for seven days.
- Identification of investment and operational cost of a 70.5 MWe commercial plant incorporating the particular THS system and comparison to the EU targets of: (a) Thermal Energy Storage Cost of 18 €/kWhe, (b) a levelized electricity cost (LCOE) of 0.10 €/kWh and (c) a storage efficiency higher than 90%.
- Presentation of a suitable strategy for the introduction of the technology into the market within a reasonable period of 5-10 years after the end of the project.

The project comprised 8 workpackages (WP) and involved 6 partners from 5 EU countries. The participants were:

- The Aerosol & Particle Technology Laboratory of the Centre for Research & Technology Hellas (APTL/CERTH)-Greece(*Coordinator*). Website: http://www.apt.cperi.certh.gr/index.php?lang=en
- The Institute of Solar Research of the German Aerospace Centre (DLR)-Germany. Website: http://www.dlr.de/sf/en/
- AEIFOROS Metal Processing S.A.-Greece. Website: http://www.aeiforos.gr/en/
- Molycorp Chemicals & Oxides (Europe) Ltd-UK. Website: http://www.molycorp.com/
- LiqTech International A/S-Denmark. Website: http://www.liqtech.dk/

- Abengoa Solar New Technologies-Spain. Website: http://www.abengoasolar.com/web/en/
- General Atomics (GA)-USA. Website: http://www.ga.com/ GA was involved in the project as an International non-funded partner. Its involvement was on the basis of exchange of information and identification of opportunities for further collaborative efforts in the field, both in the US and in Europe. The starting point for this collaboration was a previous DoE project run by GA involving fundamental studies on candidate redox materials for thermo-chemical storage (TCS) application.

The main purpose of this document is to provide an overview of the main results and achievements of the project by making evident the specific advancements per key aspect of the proposed technology, the challenges identified in the duration of the project and the proposed roadmap for further development of the RESTRUCTURE technology via follow-up R&D activities. The structure of the document is as follows:

- Overview of main results/achievements/challenges identified per workpackage.
- Main conclusions and summary of required additional work in the framework of future follow-up activities in order to further develop the technology defined and validated in the framework of RESTRUCTURE.
- Outline of main socio-economic impact of RESTRUCTURE.

WP1: Synthesis of oxide redox materials & evaluation of their thermochemical heat storage capacity (project month 01-18)

The main objective of this WP was to develop, characterize and evaluate the performance of redox metal oxide compositions, in-principle suitable for the purposes of the project. The aim was to shortlist materials via thermodynamic and experimental studies, so that those would be used for the subsequent more thorough studies in the course of the project and ultimately for the needs of scaled-up production activities. Key performance indicators for the evaluation of compositions developed in the framework of WP1 included:

- The cyclability (i.e. cycle-to-cycle stable reduction-oxidation) of compositions.
- The redox kinetics and the effective temperature windows for reduction and oxidation reactions. Preferably, sufficiently fast kinetics, similar rates between reduction-oxidation and relatively narrow effective redox temperature windows were targeted.
- Sufficient reaction extent to achieve energy density of at least 400 kJ/kg redox (quantitative target of the project and milestone no 1).

Initial thermodynamic calculations for 8 redox systems and also taking into account the reported findings of a previous US DoE project (DE-FG-36-08GO18145, 2009-2012) operated by General Atomics and in which DLR was also involved, revealed that the in-principle suitable redox systems were the Co_3O_4/CoO, MnO_2/Mn_2O_3/Mn_3O_4 and BaO_2/BaO. Those were assessed as capable of providing energy densities in the range of 350-880 kJ/kg redox material. Initial experimental evaluation under proof-of-principle thermogravimetric analysis (TGA) conditions indicated that the BaO_2/BaO system was characterized by irreversibility (i.e. no repeatable cycle-to-cycle redox activity in the course of few cycles) and thus was disqualified from further studies. According to similar studies for the manganese oxide system, only the Mn_2O_3/Mn_3O_4 cyclic transition was assessed as practical and despite the fact that its energy density potential was lower that the project target (i.e. approx. 220 vs. 400 kJ/kg) and its oxidation kinetics were found to be considerable slower cf. reduction, it was decided that further studies should be conducted. The Co_3O_4/CoO pair was characterized by excellent cyclability, stoichiometric conversion under TGA conditions, reduction and oxidation reaction rates were comparable, its redox window (i.e. temperature difference between start of oxidation and start of reduction) was quite narrow (i.e. about 30-35^{o}C) and the maximum energy density potential could be as high as 880 kJ/kg. Thus, this system was assessed as the most promising one.

Since RESTRCUTURE concept was dedicated to structured redox reactors/heat exchangers, in the framework of WP1 small scaled structured bodies (i.e. perforated pellets), made entirely from cobalt oxide and manganese oxide, were prepared and tested under cyclic redox conditions in lab-scale experimental setups. For benchmarking purposes, comparison to the respective powder formulation under identical reaction conditions was performed for the case of cobalt oxide. The main findings of those studies can be summarized as follows:

- Contrary to the case of TGA studies, conversion of Co_3O_4 to CoO at such larger scale and for a standard commercial cobalt oxide grade was limited to about 60%. In-lab synthesized cobalt oxide powders were capable of achieving higher conversions, but still far from stoichiometric (i.e. close to 70%). This corresponded to a decrease of maximum energy storage potential of the material to values in the general range of 500-600 kJ/kg (depending on the grade of cobalt oxide employed).

- Small structured bodies showed approximately the same, if not slightly better overall redox performance cf. the respective powders. Thus, no negative effect due to material formulation was identified and in fact a measurable favourable impact was detected from the case of small structured body during oxidation (Figure 2).
- Pellets prepared entirely from the redox material suffered from loss of thermo-mechanical stability, even in the course of 5-10 redox cycles (Figure 1). This was attributed to stresses developed by the cyclic phase changes (i.e. between Co_3O_4 and CoO and Mn_2O_3 and Mn_3O_4) involved in the cyclic transformation of the materials, which resulted in fragmentation along grain boundaries. Thus, based on this finding it was made evident that such redox structures needed to be stabilized with additives that would provide sufficient structural stability in the course of as many cycles as possible, but at the same time without detrimentally affecting reactivity and consequently stored energy density potential. Such additives were chosen to be refractory ceramics of relatively low cost and high availability (e.g. iron oxide from metallurgical wastes/by-products, alumina, silicon carbide, zirconia, ceria, magnesia, silica etc.). Composite formulations were evaluated in the framework of WP3 (see relevant section).
- In confirmation to preliminary TGA findings, manganese oxide was proven problematic in terms of its oxidation kinetics. Fine-tuning of redox temperatures and applied heating/cooling rates mitigated this phenomenon, however practicability of applying such fine-tuning measures under real operating conditions were assessed as questionable (see Figure 3).

Figures 1-3 provide photographs and indicative experimental results from the preliminary evaluation studies of perforated pellets and powders of commercial cobalt oxide and manganese oxide grades.

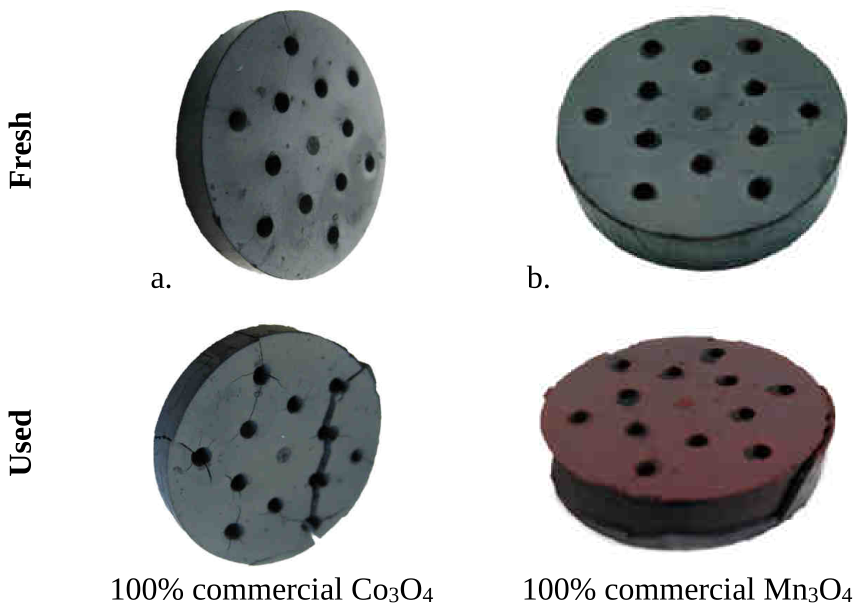


Figure 1: Perforated pellets from: a) commercial cobalt oxide and b) commercial manganese oxide in their fresh and used (i.e. after 10 redox cycles) state. The pellets had a diameter of approx. 30 mm and thickness of approx. 5 mm.

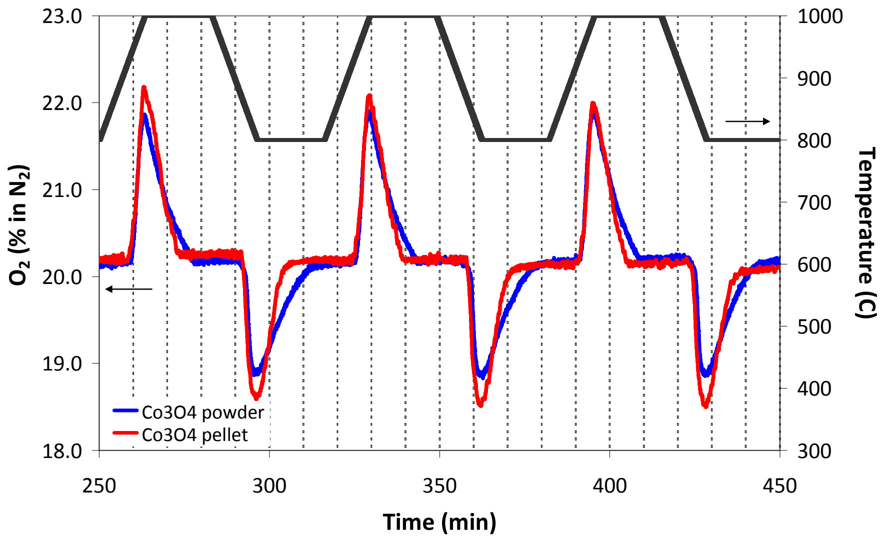


Figure 2: Redox evaluation of powder and pellet formulations prepared entirely from a standard commercial cobalt oxide grade. The plot depicts cycle #3-#5 out of 10 performed in total. Curves show the evolution of O_2 during reduction and oxidation. Temperature swing between 1000°C and 800°C at a heating/cooling rate of 15°C/min and employed air flow of 2 l/min (std).

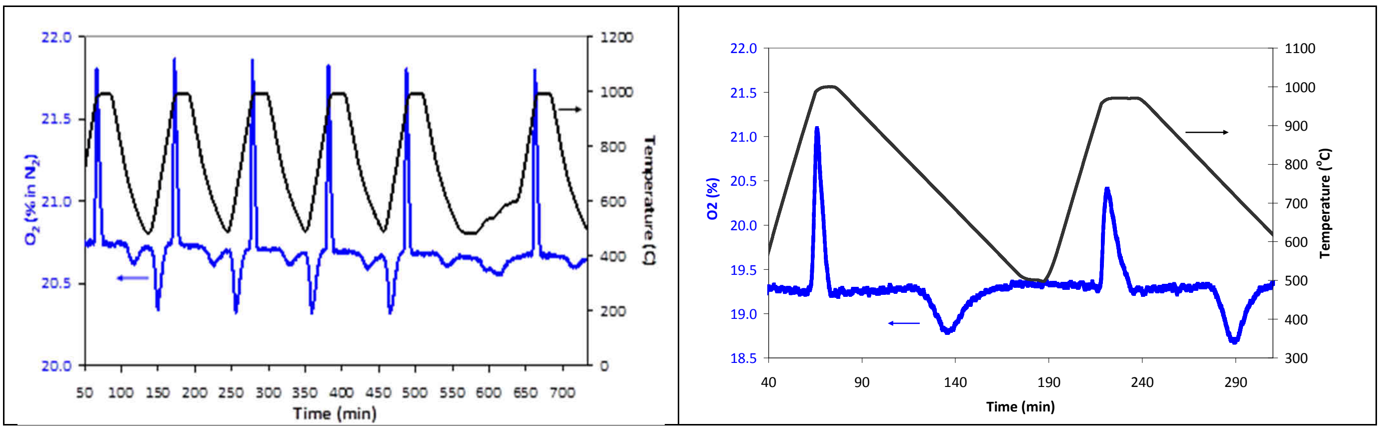


Figure 3: Initial (left) and improved via precise temperature tuning (right) redox behaviour of pure manganese oxide pellet. O_2 evolution profiles in the left plot indicate fast reduction and very slow re-oxidation taking place in two steps. By applying very slow heating and cooling rates (right plot) reduction becomes slower and oxidation becomes faster and occurs in one step. In both cases, temperature swing of as high as > 300°C is required.

Based on the outcome of WP1 studies, it was decided that qualified compositions after project month 18 would be cobalt oxide based.

WP2: Conceptual and final design of structured thermochemical storage reactor / heat exchanger (project month 1-24 & 37-51)

The main objective of WP2 was to initially define the general specifications of the pilot redox thermochemical storage (TCS) system to be implemented at the STJ research platform and to setup a first version of an overall reactor model in order to provide guidelines for the possible operating strategies and the preparation of the monolithic building blocks of the final structured assembly. At a later stage, this model was validated and refined by pilot-scale experimental data and was also used for the design and parametric studies for a commercial scaled-up system, providing also input for WP6 studies (please refer to the relevant section). The feedback loop between this WP and experimental data at lab- and pilot-scale level was continuous. Key aspects of WP2 studies included:

- Minimisation of parasitic losses of the system (i.e. pumping & heating losses) with respect to the geometry of the reactor and its building blocks, also including benchmarking with powder formulations.
- Definition of important design components to avoid notable air flow/temperature inhomogeneity and under-utilisation of the active material.
- Implementation of a phenomenological/global kinetic model generated by experimental data in the overall reactor numerical model.
- Definition and parametric studies on important operating parameters of the process (i.e. inlet air temperature, effect of air flow recirculation, effect of O_2 partial pressure).

Initial WP2 studies confirmed the advantages of monolithic/honeycomb reactor/heat exchangers assemblies vs. powder fixed beds, as the former were confirmed to offer substantially lower parasitic losses during operation and notably higher flexibility in terms of reactor geometry. In order to avoid unacceptably high parasitic losses, a hypothetical powder fixed bed reactor would need to be of very flat shape (i.e. very low height to length). This would correspond to high heat losses and notable challenges with respect to air flow distribution over its inevitably very high cross-sectional area. Moreover, the range of honeycombs' channel width to wall thickness ratio to ensure minimization of pressure drop losses was determined and this data was used as input to WP3 studies (see next section). The next step included the setup of the continuous flow design (CFD) reactor model. An indicative example of the temperature and Co_3O_4 mapping during reduction (i.e. storage system charging) mode, as generated from the first version of this model, is provided in Figure 4 below.

The next step was to use experimental data to derive a kinetic model for the reactor design. The form of this model is provided in Figure 5, which also includes its comparison to an indicative redox cycle, as obtained from WP1 studies for a pure cobalt oxide perforated pellet. Evidently, there is very good agreement between the model and the experiment for both reduction and oxidation. It is noted that p_1, p_2, K_i, K_{io} and E_i (where i = reduction or oxidation) are fitting parameters of the model and y is the fraction of Co_3O_4 transformed to CoO at any given time of reaction. The reaction kinetics equation, as provided in Figure 5, is valid for both reduction and oxidation.

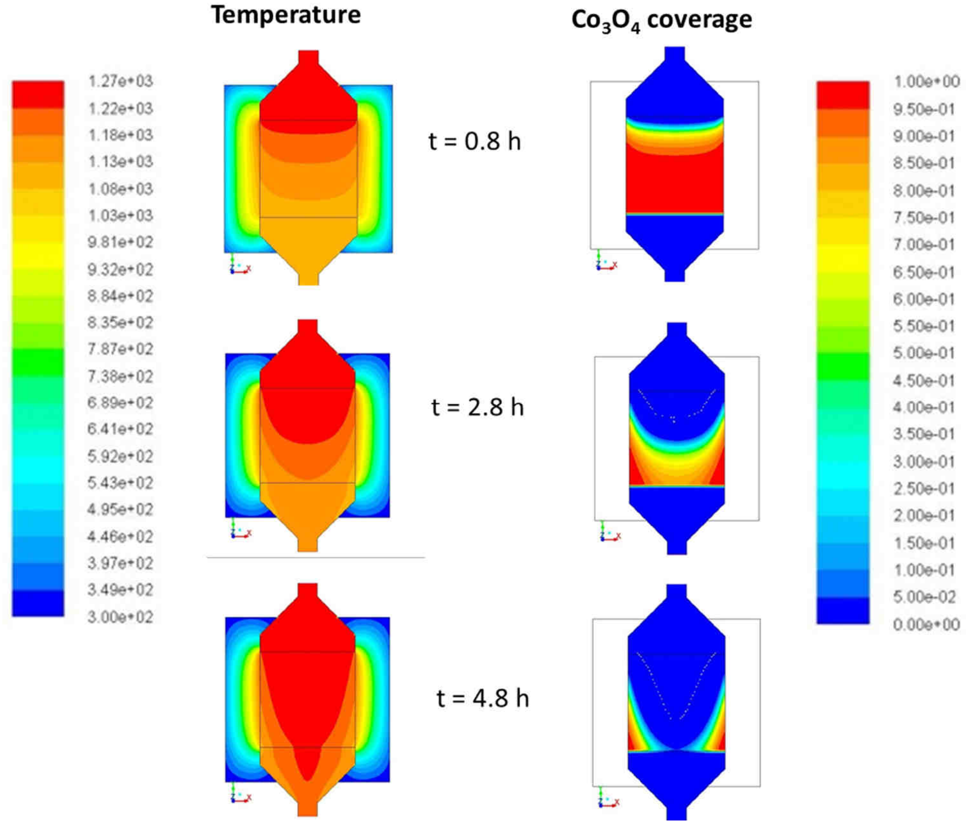


Figure 4: Evolution of reactor temperature and Co_3O_4 over time, as calculated from the CFD reactor model

$$\frac{dy}{dt} = R\,,\quad R = K\left(1 - \frac{y}{y_{eq}}\right),\quad y_{eq} = \left(1 + \frac{p_1}{T} e^{p_2/T}\right)^{-1} \quad K_i = K_{io} \cdot \exp\left(\frac{-Ei}{T}\right)$$

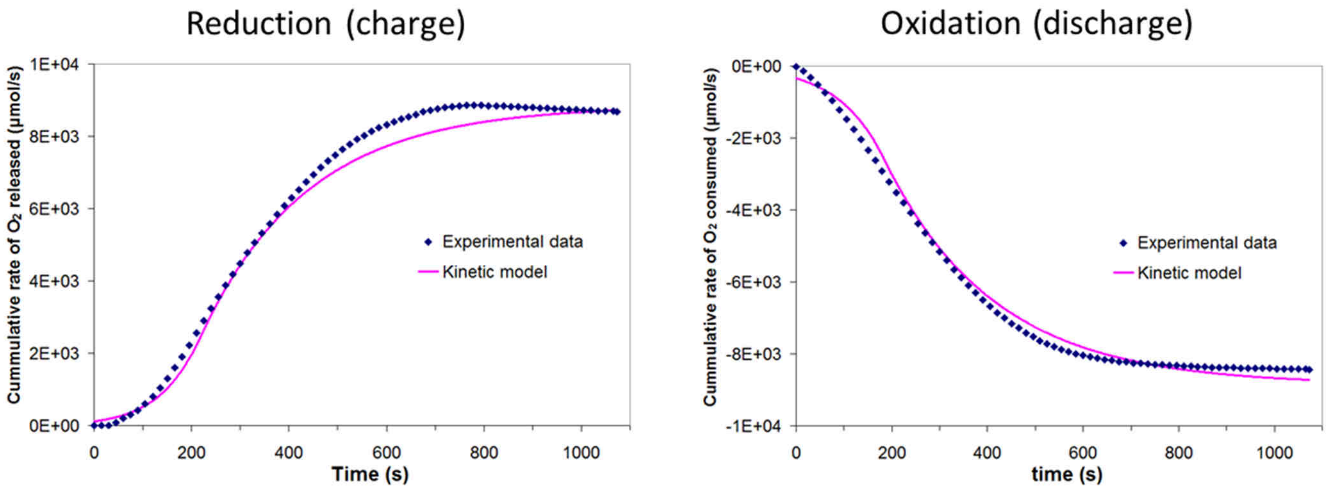


Figure 5: General form of the kinetic model (top) and comparison to experimental data during one redox cycle.

Several runs and preliminary parametric studies confirmed the feasibility of the concept proposed by RESTRCUTURE, while the incorporation of design optimisation aspects, as briefly discussed above, confirmed the favourable effect of the latter. The overall design of the reactor is provided in Figure 6 below. It was envisaged as a two-chamber system to allow higher flexibility and the potential for testing different formulations simultaneously under identical operating conditions.

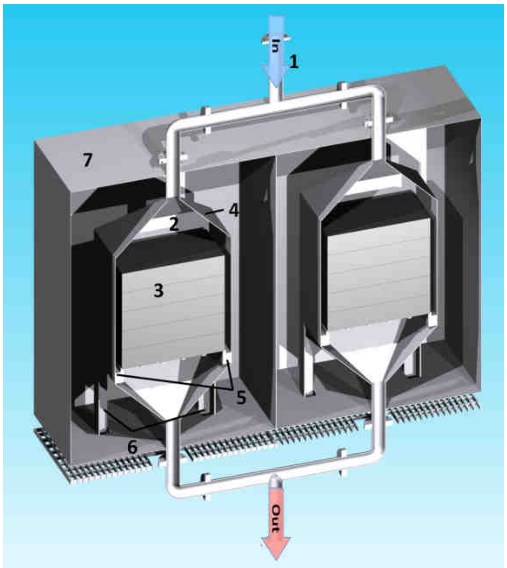


Figure 6: Overall pilot reactor of RESTRUCTURE

During the final period of the project, the above briefly described model was validated with experimental data and refined to ensure realistic evaluation of various parametric studies. The comparison of the model with experimental data corresponding to an indicative cycle is shown below. Evidently there is good agreement between the experiments and the predictions of the model.

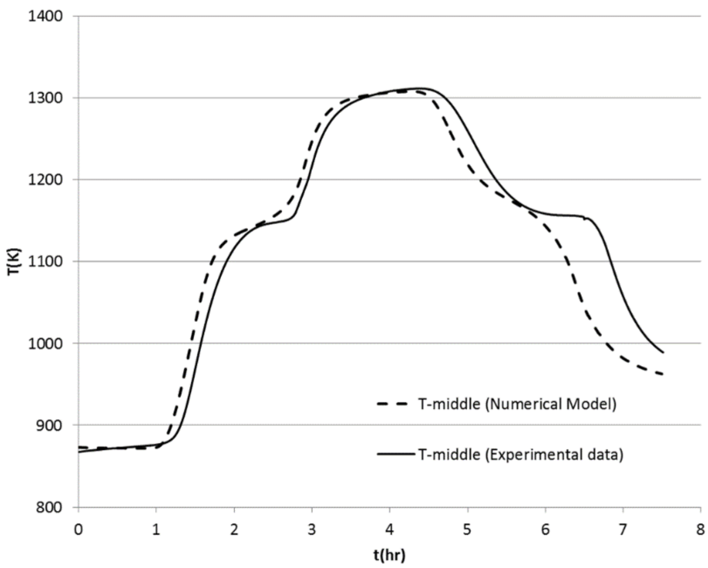


Figure 7: Comparison of experimentally measured temperature in the middle of the pilot rector with the relevant prediction of the refined overall reactor model.

The refined model was used to define the boundary conditions of the operation of such a redox TCS system. It was confirmed that oxygen content did not play a significant role on reactor performance during discharge over a very broad range of concentrations (i.e. 1- 21%). The intended operation in under air flow during both charge and discharge and thus only minor O_2 variations due to reduction and oxidation are expected. However, employing air recirculation during charging may significantly affect the final O_2 content. Moreover, it was confirmed that discharge of the system can be performed quite efficiently, when employing air inlet temperatures that are typical of power cycles, in-principle compatible to the RESTRUCTURE concept (i.e. Rankine and in particular Air-Brayton cycles). A clear preference towards Air-Brayton cycle was identified (i.e. storage system air inlet temperature at 673 K). As for the case of Rankine cycle (i.e. 423 K) a measurable, albeit not detrimentally high, amount of material was found to be non-reactive. The model also confirmed that varying the air inlet flow rate can quite effectively control the system discharge pattern (i.e. duration/power of stored energy discharge).

Finally, the model was used for the design of a scaled-up reactor to achieve 6 and 13 h of storage for a 70.5 MWe solar tower commercial CSP plant. The main parameters used as limiting factors were the pressure drop and the estimated heat losses of the system. Specific limits, based on realistic operation data from existing systems, were defined and it was identified that for the 6 h case, the overall reactor would be necessary to be split into at least 4 modules while for the 13 h case the required reactor modules would be at least 8.

The outcome of WP2 studies provided further confidence in the validity of the redox TCS concept proposed by RESTRUCTURE and its flexibility from a technical feasibility point-of-view.

WP3: Shaping, evaluation & testing of small-scale structured reactors/heat exchangers (project month 13-24)

The main objective of WP3 studies included the definition of all important process parameters for the preparation of small scale structured honeycomb-shaped redox bodies to be used as compact reactors/heat exchangers for high temperature TCS applications. Of high importance were also the necessary evaluation and detailed characterization activities aiming at: a) the proof-of-concept lab-scale validation and preliminary TCS performance evaluation of the RESTRUCTURE concept; b) the identification of strategies for the mitigation/elimination of structural stability issues due to redox cycling, already assessed as highly important in the framework of WP1 and c) the detailed physico-chemical characterization of such structured bodies.

Activities started with the continuation of perforated pellets preparation and their evaluation (typically 10 redox cycles) but this time several additives were used together with cobalt oxide, in order to identify compositions that would ensure adequate structural stability upon redox cycling while at the same time not detrimentally affecting the good redox characteristics of cobalt oxide. It is noted that in order to achieve successful preparation of extruded structures substantial developmental efforts were required and the achievement of this important milestone constituted one of the main innovations of RESTRUCTURE as manufacturing of such structures had been never reported in the past. Based on evaluation and post-characterization studies, two composite structures were found to be very good compromises between structural stability and overall redox performance and therefore were qualified for further studies: cobalt oxide/alumina and cobalt oxide/iron oxide. The iron oxide source was a steelmaking industry by-product produced inside the consortium. Moreover, the inert honeycomb substrate coated with high loading of cobalt oxide was also favourably evaluated by such preliminary studies.

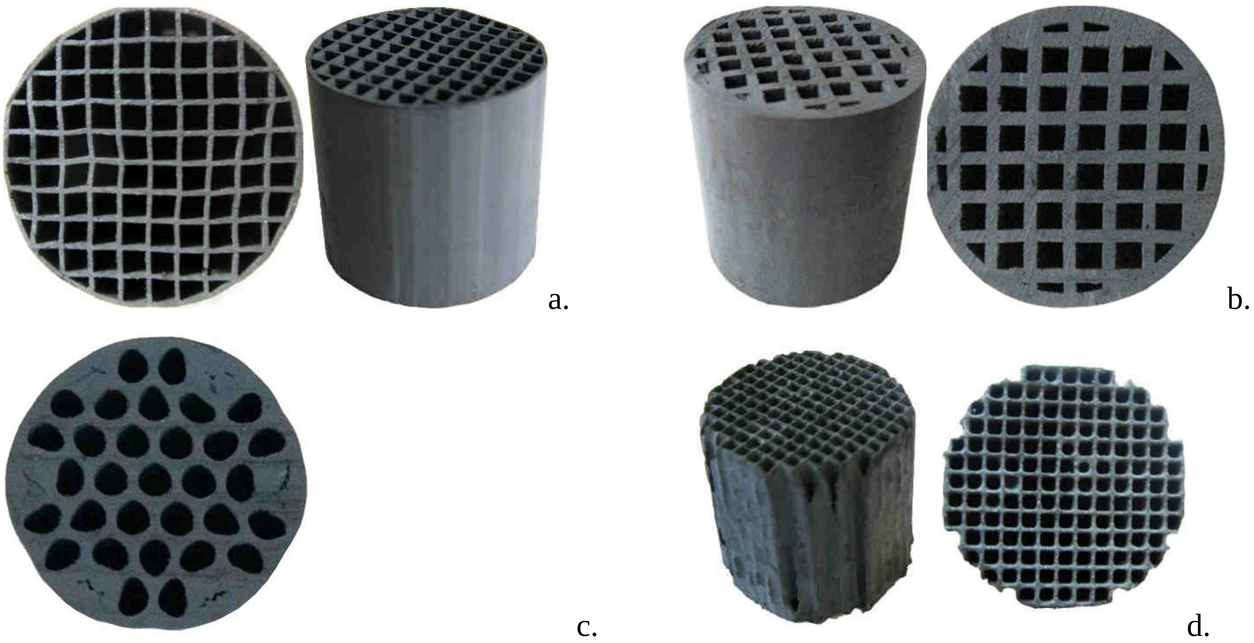


Figure 8: Indicative photographs of extruded honeycombs of different geometries (a. – c.) and a coated inert honeycomb substrate (d)

Following the above preliminary shaping activities and definition of shortlisted compositions, WP3 proceeded with the preparation of more complex, small-scale honeycomb-shaped structures (Figure 8) that could ensure relatively low pressure drop as well as higher gas-solid contact area and therefore more efficient heat exchange between the redox reactor/heat exchanger and the working fluid (air). Such structures were prepared by 2 parallel approaches: a) extrusion of high content cobalt oxide based structures and b) coating of inert honeycombs with pure cobalt oxide. The cobalt oxide used was a commercial grade as scaled-up production of in-lab synthesized powders at quantities required by the pilot system (i.e. > 100 kg) was not favourably assessed. Qualified composite structures were subjected to multi-cyclic redox evaluation (i.e. up to more than 100 cycles) during which the proof-of-concept heat dissipation from/to air flow to/from the redox reactor/heat exchanger was evaluated with the aid of a specially designed and constructed experimental setup. Figure 9 shows the profiles of O_2 evolution and the effect of reduction and oxidation reactions on the flowing air temperature at the reactor outlet ($T_{air,out}$) during one indicative redox cycle. Air is clearly cooled down or heated up due to the occurrence of the endothermic (i.e. charging – reduction) and exothermic (i.e. discharging – oxidation) reactions respectively. This constituted the proof-of-concept validation of the core objective of the project at small-scale level.

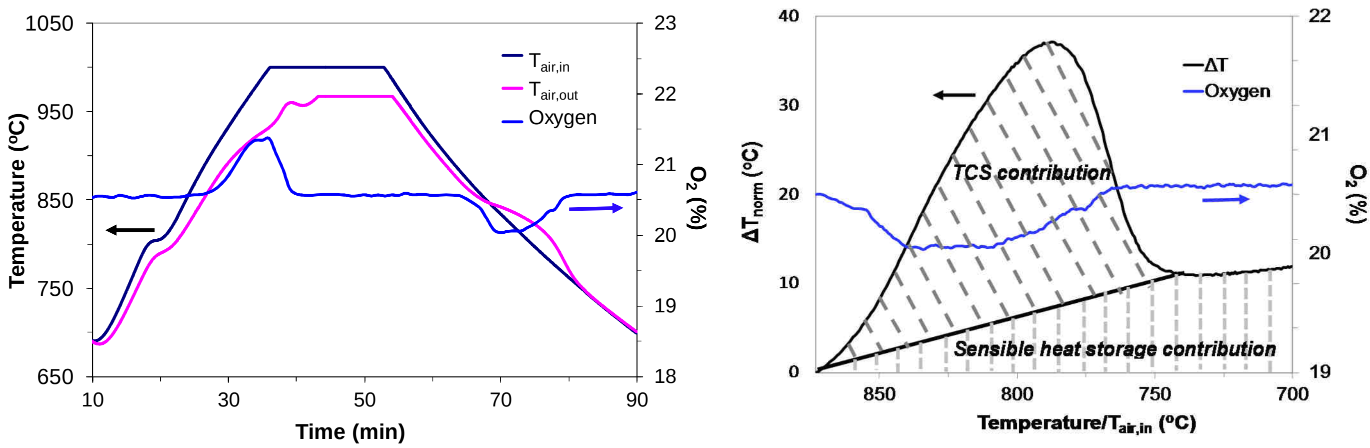


Figure 9: Left: indicative redox cycle showing the effect of redox reactions on the reactor outlet temperature of air passing through the small-scale honeycomb redox reactor/heat exchanger. Right: Normalised temperature difference between air inlet and outlet temperatures with a simplified sketch indicating the contribution of thermochemical reaction and sensible heat storage during oxidation (discharge) and how temperature difference increase coincides with the evolution of the exothermic reaction.

Among the different compositions and honeycomb geometries evaluated, the cobalt oxide/alumina composite having the geometry depicted in Figure 8b and the coated honeycomb were the ones that showed sufficient thermo-mechanical stability in the course of > 100 cycles. Both formulations showed stable redox performance and appreciable heat effects during their long-term exposure. A direct comparison between fresh and used extruded honeycombs of pure cobalt oxide and of the aforementioned cobalt oxide/alumina composite is shown in Figure 10. The detrimental effect of redox cycling on the structural stability of the pure cobalt oxide honeycomb is evident, while the composite structure retains its integrity and its main geometrical characteristics.

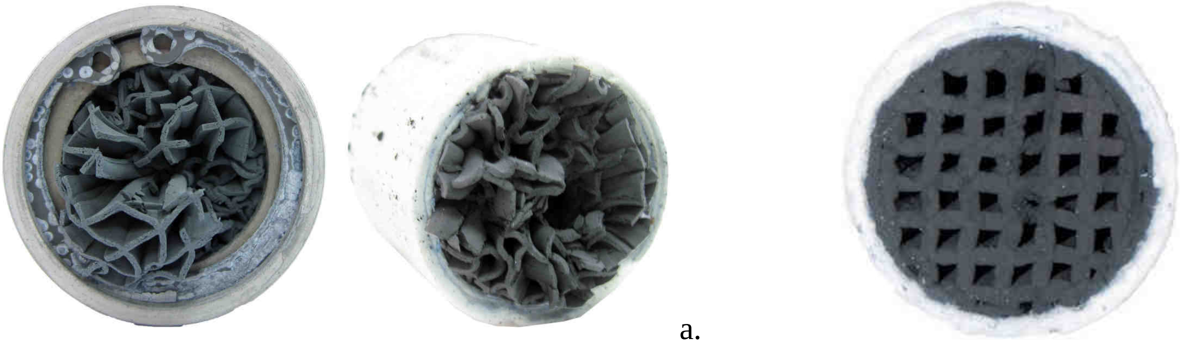


Figure 10: Extruded honeycombs after their multi-cyclic evaluation: a. pure cobalt oxide after 52 cycles; b) cobalt oxide/alumina composite after 104 cycles.

Extensive SEM, mercury porosimetry and in-situ dilatometry studies on most evaluated formulations revealed that this effect was due to net structure swelling causing fragmentation along grain boundaries and notable increase in the porosity of the bodies. Evidently, the high temperature involved (up to 1000^{o}C) was not enough to mitigate this unfavourable phenomenon via structural sintering, which one would normally expect to play an important role. Naturally, this phenomenon was caused by cyclic phase changes between CoO and Co_3O_4 and alumina addition was found to substantially supress this, albeit not eliminate it. As a conclusion of the main WP3 studies, the two stable formulations were qualified for scaling-up in the framework of WP4 activities.

Finally, with these two qualified structures some preliminary calculations on the sizing and envisaged energy density of the pilot system to be installed and operated at STJ (WP5) were conducted. According to conservative estimations, for the case of the extruded bodies, stored energy density values in excess of 100kWh/m^3 on the basis of chemical reaction only were derived. Naturally, such a value could be double or even higher upon consideration of sensible heat storage and depending on the operating temperature range.

WP4: Pilot-scale structured redox thermochemical reactor/heat exchanger prototype manufacturing (project month 25-44)

This WP focused on the procurement of necessary raw materials and scaled-up production of the building blocks of the pilot redox TCS reactor/heat exchanger. Based on the findings of previous WPs, the preferred option was the extrusion of cobalt oxide/alumina composites. The strategy of coating inert honeycomb substrates with cobalt oxide was also considered as fallback option. For practical reasons and also taking into account the design/sizing of the pilot reactor as derived from WP2, the shape of the honeycombs was chosen to be parallelepipedic and the channel/wall geometry would be kept similar to that presented in Figure 8b. As stated before, commercial metal oxide powders were purchased and used for the production of the structured bodies.

Following some initial preparatory activities (i.e. pre-treatment of raw powders, definition of optimum rheology properties of pastes, choice of more suitable extrusion method etc.), stable and defect-free green bodies were produced and dried (Figure 11a, 11b). In total, approx. 500 kg of honeycomb logs were produced which were later cut to smaller segments and according to the pilot reactor specifications. However, subsequent calcination of the structures was proven very challenging, as despite the development of numerous different heating protocols no stable honeycombs were obtained (see indicative Figure 11c). This result was surprising, particularly when taking into account the stable calcined bodies obtained for the case of small-scale honeycombs prepared in WP3. Based on thorough research, it was concluded that the main reason for this notable discrepancy was the detrimentally high cross-sectional area of the full-scale honeycombs. Certain measures were taken to decrease this size until stable calcined structures were obtained, however sufficient stability was achieved at cross-section sizes that would be non-practical for the pilot system. At this point, it became evident that radically new approaches would be needed to overcome this problem and therefore it was decided to follow the fallback option.

Regarding the coating activities, those were based on the successful lab-scale studies of WP3 but the recipe needed to be optimized so that maximum exploitation of the active material would be achieved (as most of it had been consumed in extrusion), while the amount of active material per unit mass/volume of honeycomb needed to be sufficiently high. The produced coated structures were stable enough to be used for the needs of the pilot system. An indicative photograph of a prepared honeycomb is provided in Figure 12. The coated honeycombs were prepared in several different shapes to ensure maximum exploitation of the dual chamber reactor volume. Moreover, an adequate number of uncoated/inert honeycomb substrates of identical shapes to the coated ones were prepared to be used for 'blank'/reference studies in the pilot. Due to limited availability of cobalt oxide, the total amount incorporated into the honeycomb substrates was approx. 90 kg (i.e. substantially lower cf. the case of extruded ones). The activities in the framework of WP4 were concluded with the shipment of the prepared coated bricks to the solar platform.

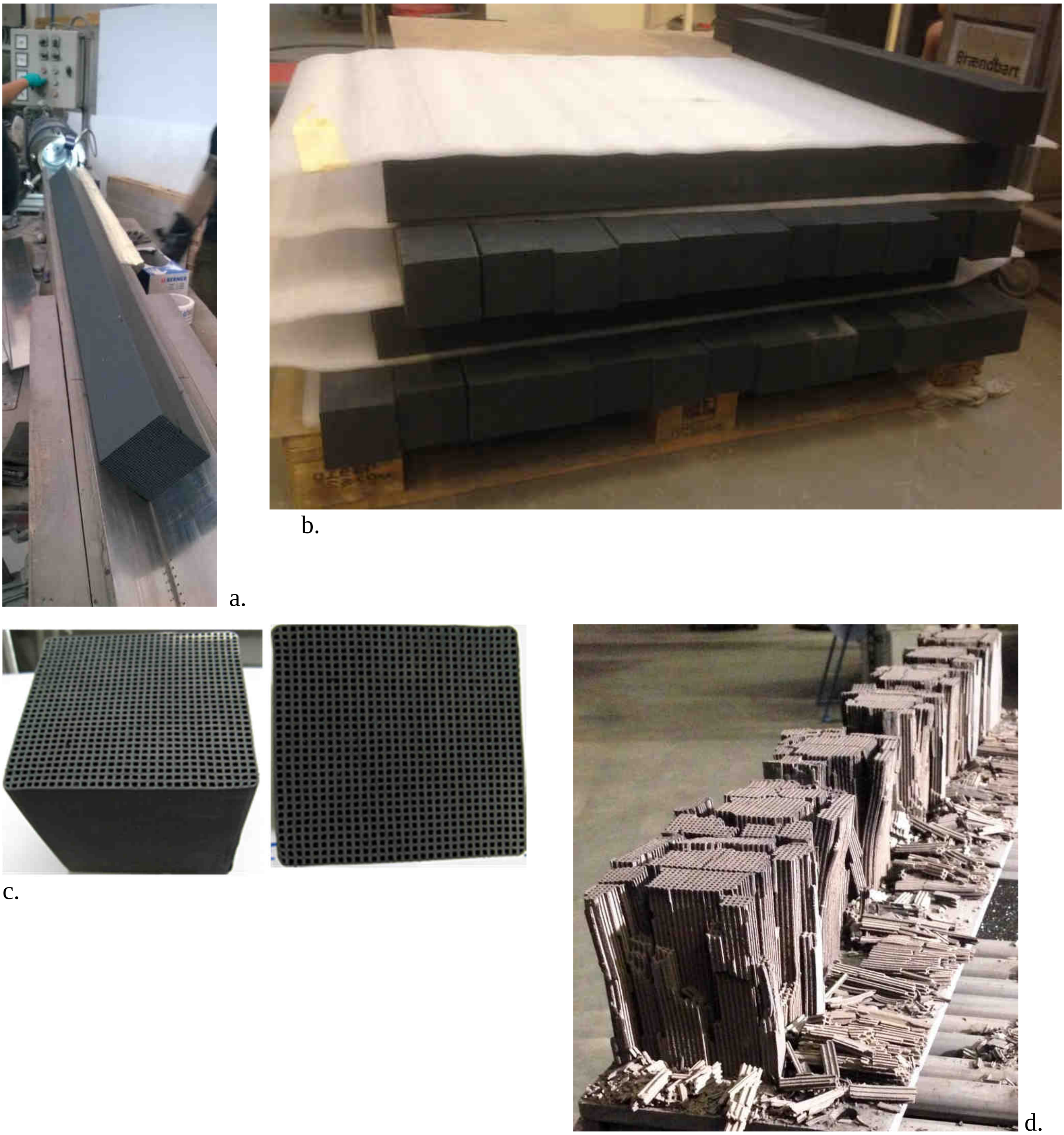


Figure 11: a. Extrusion of cobalt oxide/alumina composite honeycomb; b. Assembly of dried extruded green honeycomb logs prior to their cutting into smaller bricks; c. Indicative photograph of cut honeycombs after their unsuccessful calcination

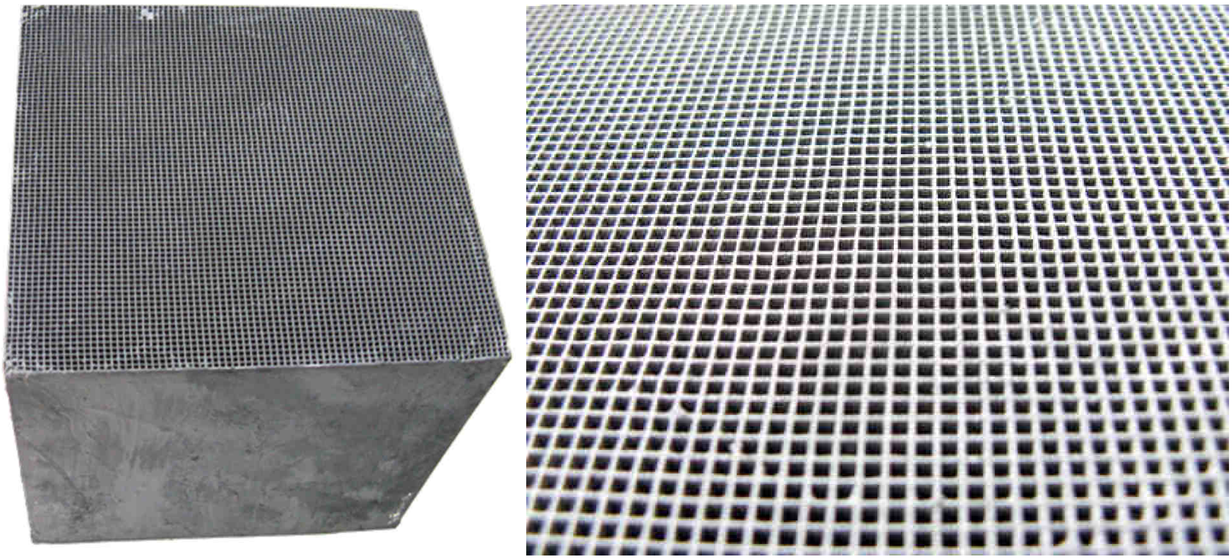


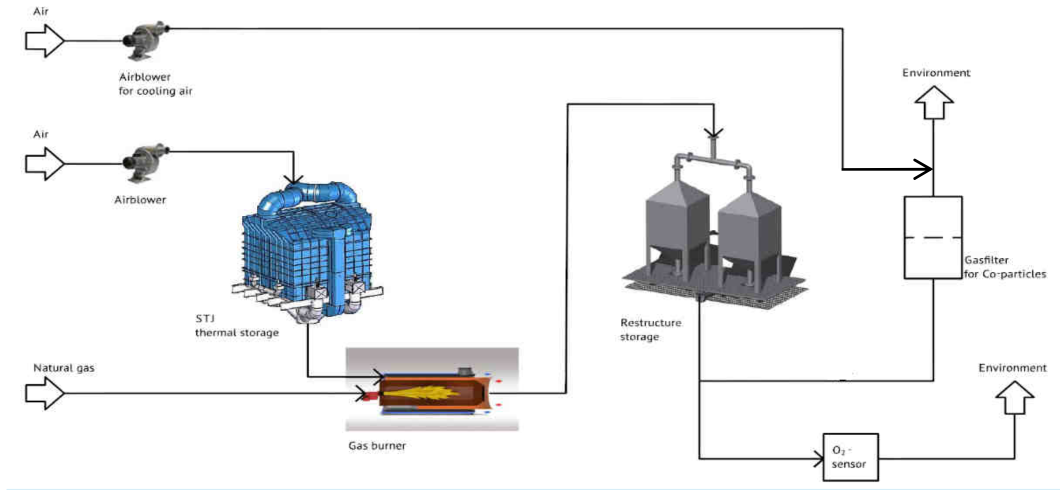
Figure 12: Coated honeycomb (left) and photograph of the coated honeycomb channels (right)

WP5: Pilot-scale reactor/heat exchanger prototype installation in solar tower platform and test operation (project month 34-51)

The objective of WP5 was to construct, operate and evaluate the experimental campaigns at the pilot scale structured reactor/heat exchanger at the solar platform of STJ. The ultimate aim was to proceed one step beyond the WP3 studies and validate the proof-of-concept of RESTRUCTURE at higher scale and under nearly realistic operating conditions.

The 'heart' of the system was the close-packed honeycomb assembly of coated monoliths produced in WP4. The reactor comprised 2 chambers (see also Figure 6), occupying a total volume of approx. 0.36 m^3. The system was equipped with all necessary peripherals: mass flow controllers for the regulation of air flow during charge/discharge, oxygen sensors for in-line measurement of oxygen concentration during redox cycling, various thermocouples installed at 3 different levels of the reactor chambers (i.e. top, middle and bottom of the assembly) and also along the cross section of each assembly, pressure transducers, a filter for the collection of potentially entrained particles by imposed air flow, high temperature insulation, requisite in-house developed software for the control of the system and data acquisition etc. The system was operated by tapping a small side stream of air available at 150-600^{o}C from the existing sensible storage system of STJ (1.5 MW_e), which was subsequently heated up by a burner to be able to reach the high temperature required by the system charging (i.e. Co_3O_4 reduction) step. It is noted that such a stream simulates air available from the next generation air-operated high temperature (i.e. $\geq$ 1000^{o}C) solar tower CSP systems, which is a technology currently under development. Indicative photographs of the reactor, as installed and operated at the solar platform, are provided in Figure 13.

The system was operated successfully for a total number of 28 cycles. An indicative charge/discharge (i.e. reduction/oxidation) cycle is shown in Figure 14. The plots show the evolution of average temperature profiles, as recorded/calculated at the 3 different height levels (T_{top}, T_{middle} and T_{bottom}) of the honeycomb assembly. The clear plateaus identified for the case of T_{middle} are evidence for the occurrence of the chemical (redox) reactions. For the T_{top} sensors, the plateaus corresponding to the occurrence of charge/discharge reactions are barely visible because the active material on top of those thermocouples was very thin, while for T_{bottom} the insulation was insufficient to overcome the high heat losses, which resulted to inability of the system to reach the high temperatures required by the charging step. The main conclusion from the T_{middle} plot vs. time is the clear proof-of-concept validation of RESTRUCTURE approach.



a.

b.

c.

Figure 13: The RESTRUCTURE pilot reactor/heat exchanger installed at the research solar platform at STJ: a. Sketch showing a simplified flow chart of the operational system; b. Photograph during construction; c. One reactor chamber ready for operation.

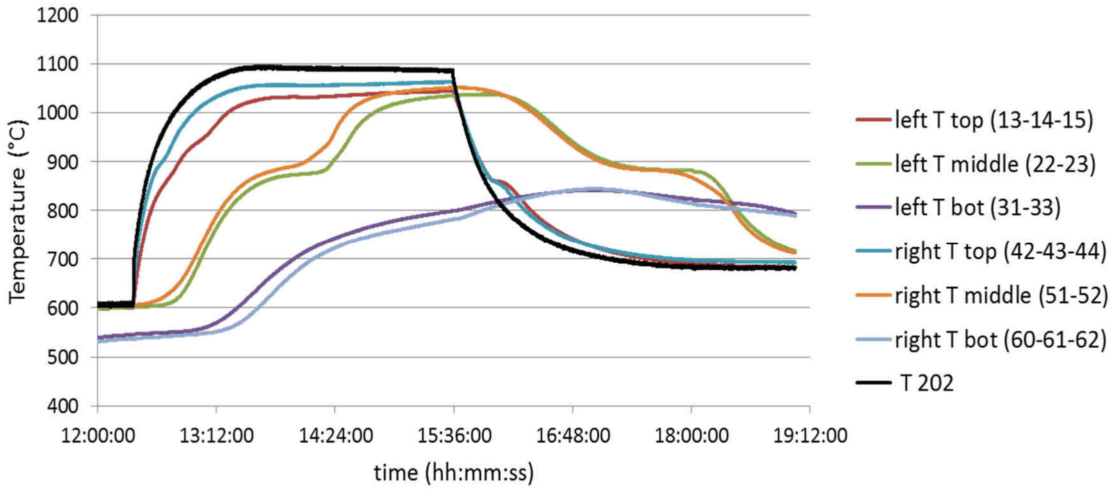


Figure 14: Evolution of recorded temperatures over time during one indicative redox thermochemical cycle of the system (left and right indications refer to the 2 chambers of the reactor, which were simultaneously operated). T_{202} refers to imposed air flow temperature at the reactor inlet.

On the basis of all thermochemical redox cycles performed and also taking into account 'blank'/non-reactive tests performed under identical operating conditions with the chemical ones but with uncoated honeycombs assembled in one of the two reactor chambers, the following main conclusions were drawn:

- An overall energy density of 135-205 kWh/m^3 was estimated for the case of the pilot RESTRUCTURE system (depending on the temperature difference). It must be noted that the respective value for the case of the existing sensible storage system at STJ is only 71 kWh/m^3 (i.e. at least 2 times less). Moreover, potential successful manufacturing of such a system from scaled-up extruded redox bodies (i.e. similar to the ones unsuccessfully calcined in WP4) via future follow-up efforts would have the ability to increase the aforementioned estimated energy density by at least a factor of 2-3, as such a formulation would incorporate substantially more active material per reactor volume.
- Comparing the blank with the chemical tests, it was demonstrated that thermochemical contribution increased the energy density by a factor of at least 2.
- It was proven that imposed air flow regulation can provide an effective means of precise tuning of the discharge pattern of the system, thereby providing energy release and/or storage in a flexible/on-demand way.

Of high importance were also the following findings:

- Based on relevant experimental evidence, the charged system could be discharged even by feeding air at ambient temperature. Naturally, discharge time was faster under such mode of operation however this finding is indicative to the flexibility that such system can offer.
- The used honeycombs, as proven by detailed physico-chemical ex-situ post analysis, did not suffer from any notable structural deformation or particle entrainment issues. Naturally, more cycles will need to be performed, e.g. in the framework of follow-up research activities, to be able to further elaborate on this important issue.

WP5 results were of key importance for the validation and further development of the detailed numerical model on reactor/heat exchanger operation of WP2 and also provided confidence for the validity of calculations (i.e. techno-economic evaluation) in the framework of WP6.

WP6: Evaluation of up-scaling to commercial scale and of technical and economic potential (project month 37-51)

WP6 aimed at the assessment of the RESTRUCTURE technology from a technical and economic perspective. Those studies were conducted considering commercially relevant environment and by proceeding with the necessary analysis of all associated key components and processes for the incorporation of the proposed redox TCS system into a CSP plant. To this respect results produced from all other technical WPs (and primarily WP2 and WP5) were used.

The analysis started by choosing an appropriate installation site (mainly on the basis of sufficiently high DNI, availability of auxiliaries and distribution network for produced energy) and define a relevant electrical production capacity of a CSP plant incorporating the RESTRUCTURE technology. Those were defined to be Tonopath-Nevada and 70.5 MWe respectively. Subsequently, the most efficient (i.e. optimized) system configuration was chosen and the system was assessed for two different storage duration periods; i.e. one able to provide delayed intermediate load (6 h storage) and one operating in base load mode (13 h storage). The qualified system was an air-operated Solar Tower, having the RESTRUCTURE TCS system in series with the power block. The latter was defined to operate with the Air Brayton Combined Cycle, which ensures very high efficiency among commercially available power cycles and also lies in the broader operating temperature range of the TCS system proposed by RESTRUCTURE. A sketch showing the general configuration of the system is shown in Figure 15. All inlet-outlet temperatures of key-components were chosen on the basis of WP2/WP5 studies and knowledge of standard operating conditions of the power block.

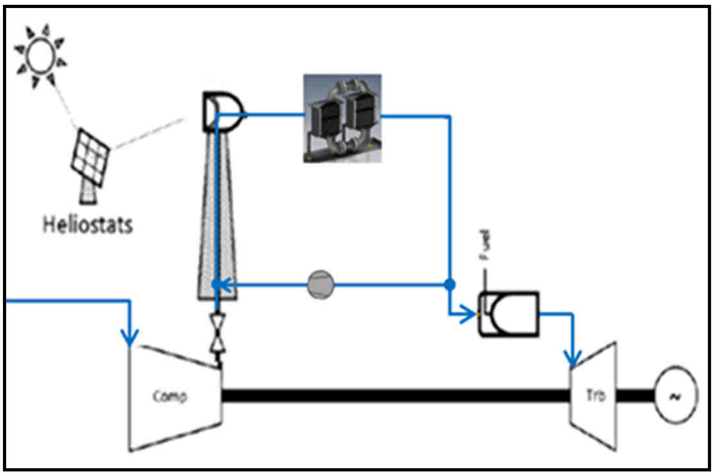


Figure 15: Qualified overall configuration of CSP system incorporating the RESTRUCTURE redox TCS

Due to the fact that results produced in the framework of WP6 have not been published yet and also due to a certain degree of confidentiality regarding calculated cost and other technical figures, such specific results cannot be presented here. The overall conclusions of WP6 studies can be summarized as follows:

- Overall LCOE estimations for a CSP plant incorporating the TCS storage system proposed by RESTRUCTURE corresponded to values of at least 20% lower than the respective maximum cost figure target published by the US DoE Sunshot initiative (i.e. < 0.15 €/kWh_{th}). Thus, the potential of the technology was assessed as promising (see also next bullet). Naturally, the potential future efficient addressing of main cost drivers involved (see also 3rd bullet) will further increase its competitiveness.
- LCOE values for both cases studied fall well within maximum and minimum reference values for Combined Cycle Power plants (IEA, 2015). Such reference values vary in the range of ~ 0.07 – 14.5 €/kWh and strongly depend on geographical aspects and natural gas price fluctuation.
- The main cost drivers for the case of the TCS system were found to be the high temperature blower required for air recirculation during charge and the active material itself (cobalt oxide). In terms of the former, there is relatively large uncertainty as such blowers are not widespread commercially while for the active material case, this highlights the need to continue with materials screening and development so that high performance alternatives will be identified. However, the cost of cobalt oxide is not prohibitively high and the potential inability to identify cost effective materials with equal to cobalt oxide performance is not considered detrimental for the RESTRUCTURE technology. Moreover, the potential creation of a market for high temperature blowers (high temperature TCS systems could contribute to this) is expected to lead to mass production of such components, thereby decreasing cost per unit substantially.

As a general conclusion from WP6 studies and also from the overall project activities, the RESTRUCTURE concept at the end of the project was assessed as technically feasible, conceptually and practically simple and therefore in-principle readily applicable to future high temperature air-operated CSP installations. Moreover, it has the potential to generate significant impact on the industrial sectors involved (i.e. CSP, materials synthesis and shaping into compact structures, metallurgy) and also on society due to the fact that it can be the first step towards to an 100% renewable energy production technology by offering a novel, compact and high energy density system capable of tackling the challenge of solar energy intermittency. An important prerequisite to achieving these goals is the continuation of the development of the technology via follow-up Research & Innovation collaborative efforts. There is still substantial work to be performed regarding identification of high performance and identifying materials more cost-effective than cobalt oxide, long-term stability studies under near realistic conditions to secure robustness of the technology and further examination of parametric experimental studies on certain operating conditions (e.g. to assess the performance of such a concept at pressure higher than 1 bar to ensure better compatibility with the Air-Brayton power cycle).

WP7: Administrative management and international cooperation (project month 01-51)

This WP was dedicated to project management activities and to the cooperation/interaction of the RESTRUCTURE consortium with the project's international partner. In this section only some general information regarding international collaboration will be provided.

In the beginning of the project, GA provided detailed reports on findings of their past DoE-funded redox TCS project previously mentioned (see Introduction section). Those reports provided useful guidance on the work performed in the initial stages of the project and particularly in the framework of WP1 regarding materials screening. The RESTRUCTURE consortium, mainly via its coordinator, maintained a frequent communication and exchange of information with GA regarding the progress and main achievements of the project in the course of its 51-month duration. Capitalizing on the encouraging results of the projects, as presented above, several attempts were made to generate spin-off activities such as bilateral and collaborative projects both in the US and in Europe. Despite the fact that none of such efforts was successfully evaluated, the communication between selected key partners of RESTRUCTURE (e.g. APTL/CERTH, DLR, LiqTech) and GA will continue as the identification of efficient TCS (redox or other) processes and concepts lies well within the interests of these organizations.

WP8: Research and technological development coordination, dissemination and exploitation activities (project month 01-51)

WP8 was dedicated to projects results dissemination and exploitation with the aim of making the main achievements of RESTRUCTURE known to the scientific community, to the industry and also to the greater public. Tables 1-3 below provide an overview of such activities (scientific publications, organization of events, participations in conferences and workshops, training activities etc.).

Table 1: Overview of presentations related to the RESTUCTURE project in International Conferences

No	Conference	Partner(s) involved	Title & nature of presentation
1.	13th Conference on the European Ceramic Society (ECERS 2013), June 23-27, 2013, Limoges-France	APTL	Cobalt Oxide Based Materials for Thermochemical Heat Storage in Concentrated Solar Power Plants (*poster presentation*).
2.	SolarPACES 2013 conference, September 17-20, 2013, Las Vegas-USA	DLR	Thermochemical solar energy storage via redox oxides: materials and reactor/heat exchanger concepts (*oral presentation*)
3.	SolarPACES 2013 conference, September 17-20, 2013, Las Vegas-USA	APTL	Monolithic ceramic redox materials for thermochemical heat storage applications in CSP plants (*poster presentation*)
4.	SolarPaces 2014 conference, September 16-19, 2014, Beijing-China	APTL	Co_3O_4 based honeycombs as reactors / heat exchangers for redox thermochemical heat storage in future CSP plants (*oral presentation*)
5.	SolarPaces 2014 conference, September 16-19, 2014, Beijing-China	DLR, APTL	Design of a thermochemical storage system for air-operated solar tower power plants (*oral presentation*)
6.	EUROTHERM SEMINAR No. 98, July 4-5 2013, Vienna-Austria	DLR	Thermochemical Reactions for Solar Energy Storage and Fuel Production, Concentrating Solar Energy Systems (*oral presentation - invited*)
7.	International CAE conference, October 27-28, 2014, Pacengo del Garda (Verona)- Italy	DLR	Thermochemical heat storage for solar power plant. Design through CFD modelling (*oral presentation)*
8.	ICAE2015, March 28-31, 2015, Abu Dhabi-United Arab Emirates	DLR	Numerical model to design a thermochemical storage system for solar power plants (*oral presentation)*
9.	14th International Conference of European Ceramics Society (ECerS 2015), June 23-25, 2015, Toledo-Spain	APTL	Cobalt oxide based honeycomb monolithic structures as compact reactors/heat exchangers for redox thermochemical heat storage (*oral presentation)*
10.	SolarPACES 2015 conference, October 17-20, 2015, Cape Town-S. Africa	APTL	Co_3O_4-Based Honeycombs as Compact Redox Reactors/ Heat Exchangers for Thermochemical Storage in the Next Generation CSP Plants (*oral presentation*)

11.	MRS Fall Meeting, November 29-December 4 2015, Boston, Massachusetts	DLR	Thermochemical Heat Storage for Baseload Concentrated Solar Power Generation (*oral presentation*)
12.	6th International Congress on Ceramics (ICC6), August 21-25, 2016, Dresden-Germany	APTL, DLR	High temperature redox thermochemical storage based on structured reactors/heat exchangers: from lab studies to semi-pilot scale validation (*submitted & awaiting decision*)

Table 2: Overview of RESTRUCTURE-related manuscripts published or awaiting publication in scientific journals

No	Authors, Title of publication	Journal & publication details	Partner(s) involved
1.	Karagiannakis G., Pagkoura C., Zygogianni A., Lorentzou S., Konstandopoulos A. G. ‘‘*Monolithic ceramic redox materials for thermochemical heat storage applications in CSP plants*’’	Energy Procedia 49 (2014) 820 – 829	APTL
2.	Tescari S., Agrafiotis C., Breuer S., Oliveira L., Neises-von Puttkamer M., Roeb M., Sattler C. ‘‘*Thermochemical solar energy storage via redox oxides: materials and reactor/heat exchanger concepts*’’	Energy Procedia 49 (2014) 1034 – 1043	DLR
3.	Pagkoura C., Karagiannakis G., Zygogianni A., Lorentzou S., Kostoglou M., Konstandopoulos A.G., Rattenburry M., Woodhead J.W. ‘‘*Cobalt oxide based structured bodies as redox thermochemical heat storage medium for future CSP plants*’’	Solar Energy 108 (2014) 146–163	APTL, Molycorp
4.	Pagkoura C., Karagiannakis G., Zygogianni A., Lorentzou S., Konstandopoulos A.G. ‘‘*Cobalt oxide based honeycombs as reactors/heat exchangers for redox thermochemical heat storage in future CSP plants*’’	Energy Procedia 69 (2015) 978 – 987	APTL
5.	Tescari S., Breuer S., Roeb M., Sattler M., Flucht F., Schmücker M., Karagiannakis G., Pagkoura C., Konstandopoulos A.G. ‘‘*Design of a thermochemical storage system for air-operated solar tower power plants*’’	Energy Procedia 69 (2015) 1039 – 1048	DLR, APTL
6.	Agrafiotis C., Tescari S., Roeb M., Schmücker M., Sattler C., ‘‘*Exploitation of Thermochemical Cycles based on Solid Oxide Redox Systems for Thermochemical Storage of Solar Heat. Part 3: Cobalt Oxide Monolithic Porous Structures as Integrated Thermochemical Reactors/Heat Exchangers*’’	Solar Energy, 114 (2015) 459–475	DLR
7.	Tescari S., Lantin G., Lange M., Breuer S., Agrafiotis C., Roeb M., Sattler C. ‘‘*Numerical Model to Design a*	Energy Procedia 75 (2015) 2137-2143	DLR

	Thermochemical Storage System for Solar Power Plant''		
	Pagkoura C., Karagiannakis G., Halevas E., Konstandopoulos A.G. *''Co_3O_4-Based Honeycombs as Compact Redox Reactors/ Heat Exchangers for Thermochemical Storage in the Next Generation CSP Plants''*	AIP Proceedings, *Article In Press*	APTL
8.	Karagiannakis G., Pagkoura P., Halevas E. , Baltzopoulou P., Konstandopoulos A.G. *''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 (2016) 394–407	APTL

Table 3: Additional RESTRUCTURE-related dissemination activities

No	Title and nature of activity	Link (if available)	Partner(s) involved
1.	*''Science delivers vault for clean energy''*, EU Research & Innovation magazine-Horizon, Date of publication: 05/10/2015	http://horizon-magazine.eu/article/science-delivers-vault-clean-energy_en.html	APTL (interview)
2.	*''Novel honeycomb design for better thermochemical energy storage capabilities''*, CORDIS (Community Research & Development Information Service), Date of publication: *pending*	*http://cordis.europa.eu/news/rcn/124820_en.html*	APTL (interview)
3.	*Collaborative Workshop on Thermo-Chemical Heat Storage: TCS-Power, StoRRe & RESTRUCTURE projects*. September 9, 2015, DLR-Cologne, Germany. Audience: 42 persons	-	All partners
4.	Tescari S., *Lecture on solar thermochemical storage and the RESTRUCTURE project in a high school conference (Programma Eccellenze all'istituto Boscardin)*, January 15, 2014, Vicenza, Italy.	-	DLR
5.	Roeb M., *State-of the-Art and Trends of Solar Fuel Generating Processes*, International Kick-off Symposium for Energy Materials Chemistry, June 23, 2014, Kumamoto University, Kumamoto, Japan (invited keynote lecture).	-	DLR

Table 4: PhD and MSc theses in the framework of the RESTRUCTURE project

Name	Title	Partner responsible
Mr. Lantin Gunnar (*Master thesis in Sustainable Energy Technology*)	*Numerical investigation of heat and reaction propagation in a thermochemical heat storage for Concentrated Solar Power applications*	DLR
Mr. Alexander Ulcyfer (*Master thesis in Mechanical engineering*)	*Directly irradiated rotary kiln for thermochemical heat storage*	DLR
Mr. Nikolaos Tsongidis (*Chemical Engineer – undergraduate student*)	*Small-scale cobalt oxide-based monolithic structures for redox thermochemical heat storage applications / Date of defense: 14-11-2013*	APTL
Mrs. Danai Tasioula & Sofia Petrou (*Chemical Engineers – undergraduate students*)	*Preparation and evaluation of ceramic porous structures for environmentally friendly energy applications / Date of defense: 15-07-2014*	APTL