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PROJECT FINAL PUBLISHABLE SUMMARY REPORT

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1. Project Information

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Partners:

Deutsches Zentrum fuer Luft- und Raumfahrt e.V. - DLR	**D**
Commissariat à l'Energie Atomique – CEA	**F**
University of Sheffield – USFD	**UK**
Aerosol and Particle Technology Laboratory / Center for Research and Technology–Hellas/Chemical Process Engineering Research Institute	**GR**
Joint Research Center Petten – JRC	**B**
Ente per le Nuove tecnologie, l'Energia e l'Ambiente - ENEA	**I**
Eidgenoessische Technische Hochschule Zürich - ETHZ	**CH**
Empresarios Agrupados - EA	**E**
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Introduction

HycycleS, a project funded under the 7th Framework Programme of the European Commission, is a cooperation of nine European partners and further non-European partners and aims at the qualification and enhancement of materials and components for key steps of solar and nuclear powered thermochemical cycles for hydrogen generation from water. The focus of HycycleS is the decomposition of sulphuric acid which is the central step of the sulphur-based family of those processes, especially the hybrid sulphur cycle and the sulphur-iodine cycle. Emphasis is put on materials and components for sulphuric acid evaporation, decomposition, and sulphur dioxide separation. The suitability of materials and components is demonstrated by decomposing sulphuric acid and separating its decomposition products in scalable prototypes.

The key components, necessary for the high temperature part of the process, are a ceramic compact heat exchanger for solar or nuclear SO_3 decomposition, a receiver-reactor for solar H_2SO_4 evaporation and SO_3 decomposition and an oxygen separator that will on one hand separate the reaction products (i.e. SO_2 and O_2) and on the other hand will act as a promoter for SO_3 decomposition. One aspect essential for sufficient reaction rates is the development of dedicated catalyst systems, which is also part of HycycleS. The final aim is to bring thermochemical water splitting closer to realization by improving the efficiency, practicability and costs of the key components involved and by elaborating detailed engineering solutions.

Materials and catalysts

Firstly, candidate materials for the construction of the targeted key components of sulphur-based thermochemical cycles as well as for possible and promising catalyst/substrate combinations for the catalytic high temperature reduction of SO_3 have been reviewed.

As a consequence of this review, HycycleS' main development route was based on ceramic materials from the SiC family. Such materials seem to fulfil all necessary requirements for the solar absorbers of the planned receiver reactor, the plates of the planned compact heat exchanger and for the catalyst support. As base material for the SO_2-O_2 separation membranes Yttria-Stabilised Zirconia (YSZ) has been identified and selected.

A first phase of the long-term exposure of samples concerning different corrosive environments has already been carried out and completed. One kind of treatment are corrosion tests of samples facing temperatures above 800 °C and a chemical environment typical for SO_3 reduction applying a gaseous feed. A second kind of treatment is applied to investigate the stability of samples facing boiling concentrated H_2SO_4. Several of the examined materials and samples, in particular the SiC based materials, withstand the conditions and keep their structural integrity over a substantial period of time (1000 hrs).

Promising catalyst "families" have been identified exhibiting high and stable catalytic activity. Catalysts based on mixed metal oxides with substantially higher initial activity than the reference oxide material (i.e. Fe_2O_3) have been identified. A number of mixed oxides were synthesized and tested in the decomposition of sulphuric acid for the production of SO_2 and O_2. Materials such as Fe-Cr, Cu-Al, Cu-Fe and Cu-Fe-Al mixed oxides showed initial activity comparable to that of Pt/Al_2O_3, which is considered the most efficient material for this reaction so far. This indicates that such materials could provide promising alternatives to the precious-metal-based state-of-the-art catalysts. The reaction over these catalysts most likely proceeds via the formation of intermediate sulphate species and this requires that the temperature is sufficiently high in order to facilitate the rapid decomposition of these species.

An empirical kinetic law has been derived from experiments which enabled the refinement of reactor design and prototype development (see Figure 1). The first order kinetics probably indicates that the adsorption of the reactant on the catalyst is the rate limiting step of the reaction mechanism.

Experimental tests carried out at pressure higher than 1 atm (up to 4 bar) indicated that SO_3 decomposition kinetics is relatively unaffected by operating pressure in the 1-4 atm range. Absorber monoliths coated with Fe_2O_3 and CuO catalyst were exposed to typical reaction environment for 100 hours without significant reduction of catalytic activity (Figure 1) and therefore qualified as the reference catalyst systems of choice for the first experimental campaigns with the solar receiver-reactor. Other catalysts with even higher initial activity were developed and qualified and exhibited a stability comparable to that of Fe_2O_3 or even better. Based on the systematic studies on the quantitative evaluation of the catalytic activity, durability and stability of the candidate catalysts investigated as well as on the conclusions drawn from the ex-situ post-characterization activities, it was concluded that a Cr-Fe mixed oxide ($Fe_{0.7}Cr_{1.3}O_3$) is the most promising material among the ones examined.

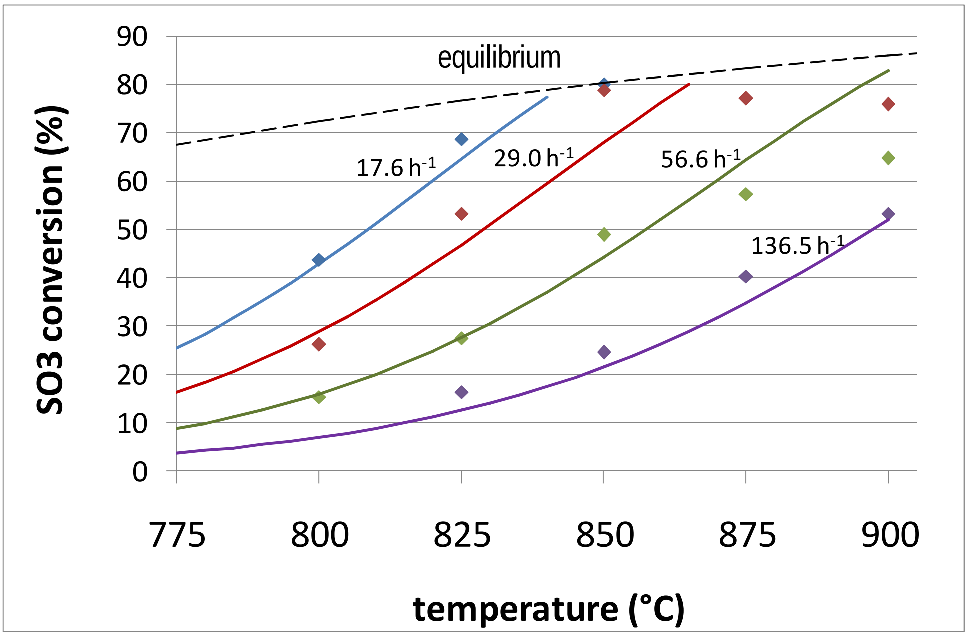

Figure 1: comparison between experimental data and the proposed kinetic model for a SiSiC substrate coated with Fe0.5Cu0.5AlOx

Heat exchanger reactor

The development and use of high temperature heat exchangers are essential for the accomplishment of hydrogen production by high temperature processes powered by concentrating solar systems or high temperature nuclear reactors.

Those heat exchangers have to withstand high temperature and, at the same time, have to operate as reactors. In the case of the present sulphur based thermochemical cycles they, therefore, have to resist in very corrosive environment. Only ceramics can match these specifications. A shell-and-tube concept of SiC heat exchangers does not achieve the compactness required to reach the thermal efficiency aimed at. Therefore, a decision to develop a compact SiC plate heat exchanger was made.

The assembly of a plates stack is a key technological point for such a component. The heat exchanger will exhibit a large number of joints and some of them will have a large surface but at the same time all requirements related to tightness, corrosion and mechanical resistance must be satisfied. In terms of achieving an efficient assembly of the plates, brazing was regarded as the most promising solution.

The development and construction of a heat exchanger prototype has to take into consideration the possibilities and limitations of the specific fabrication process and therefore it was supported by modelling of different design options as well as by the fabrication and testing of manufacturability, tightness and structural integrity of smaller mock-ups representing crucial parts of the prototype.

The final aim of this development was the qualification of a pilot-scale heat exchanger as H_2SO_4 decomposition reactor. The main research challenge is to implement a large scale plate heat exchanger with a thermal efficiency of more than 85%.

From the beginning of the project, an optimized design has been proposed (about 800mm x 300mm x 200mm) taking into account kinetic and thermo-hydraulic correlations, chemical engineering approach for the modeling and possibility to braze the final prototype. For the hot source plates, wavy channels (so-called herringbone pattern, Figure 2 - left) were used to improve the local heat transfer coefficient and ensure turbulent flow regime compared to straight channels. For the reaction plates, large straight channels filled with catalyst and meandering inside plates are used to ensure satisfactory reaction efficiency with a sufficient residence time for the reactive fluid (Figure 2 - right). The main characteristic of this so-called “catalyst bed” exchanger-reactor design is that it consists of permanent thermal exchange and chemical reaction areas.

Figure 2: SiC channelled plates of the prototype: heat source plates (left) and a reaction plate with one large meandering channel (right).

The full-size prototype has been manufactured, which is probably one of the largest SiC heat exchanger ever made in the world (Figure 3). It was successfully tested in the first months of 2011.

Figure 3: SiC prototype on the thermal test rig (before being thermally insulated).

Solar receiver-reactor

As a concept for a direct coupling of concentrated solar radiation into the process, a multi-chamber reactor was chosen which allows adaptation of each part of the reactor to the requirements of both evaporation and decomposition reactions so that these two sub-processes are performed separately (Figure 4). In particular, such a concept is advantageous when considering a future up-scaling for a solar tower application. On the receiver of a solar tower, there are typically regions with high heat flux in the center while significantly less solar radiation reaches the outer part of the receiver. Consequently, a multi-chamber reactor with two different temperature levels can exploit the energy input on a solar tower more efficiently than a single-chamber requiring a more uniform heat flux distribution.
The reactions in the two chambers have different reaction enthalpies and require different operating temperatures:

Evaporation: $H_2SO_{4(aq)} \rightarrow H_2SO_{4(g)} \rightarrow SO_{3(g)} + H_2O_{(g)}$ T = 350-400 °C

SO_3 reduction: $SO_{3(g)} \rightarrow SO_{2(g)} + \frac{1}{2}O_{2(g)}$ T = 800-1000 °C

Consequently, the conditions needed for the evaporator and the decomposer differ considerably. Therefore, the reactor design for a prototype solar receiver-reactor includes two different chambers operating at different conditions: one for the evaporation of the acid, the second for the SO_3 reduction.

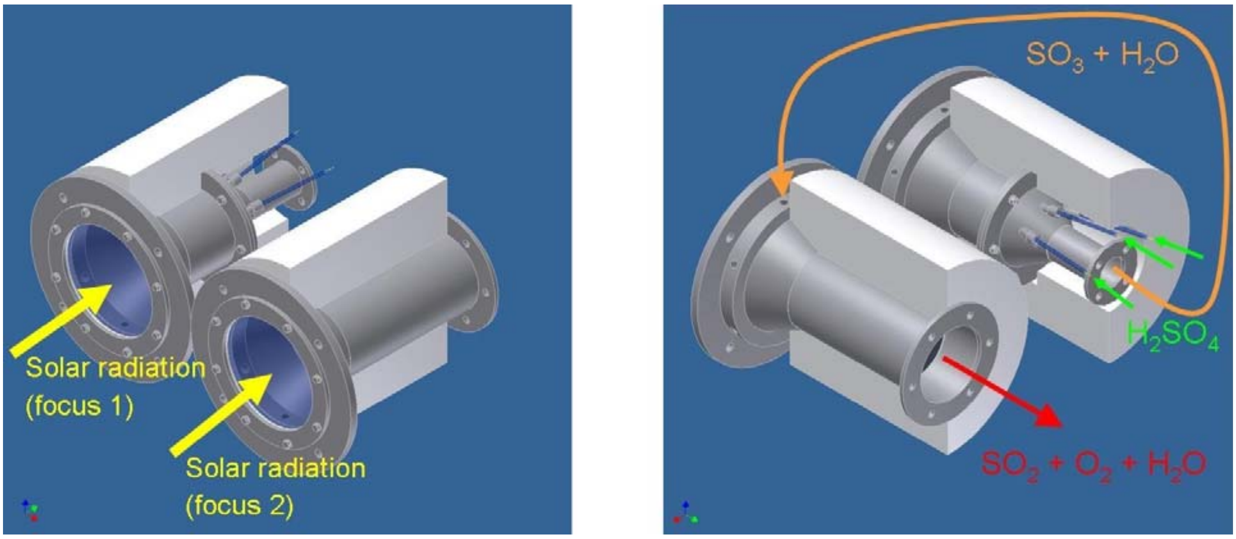

Figure 4: Front (left) and rear view (right) of the HycycleS multi-chamber solar reactor: focus 1 – evaporator; focus 2 – decomposer.

Evaporator
The solar radiation enters the reaction chamber through a quartz window held by a flange construction. The vaporization of the sulphuric acid is carried out in a cylindrical absorber made of SiSiC foam. The acid is fed to the interior of the foam by tubes. The product gases, primarily consisting of sulphur trioxide, water vapour and the carrier gas nitrogen, leave the reaction chamber through an exhaust pipe and are subsequently directed to the second chamber for the decomposition of SO_3.

Decomposer
The decomposer is powered by focus 2. The flange construction supporting the quartz window is the same as in the case of the evaporator. The inlet gas coming from the evaporator enters the decomposer through three inlets in the flange. The splitting of sulphur trioxide takes place on a SiSiC honeycomb structure coated by the catalyst material. Product gases of the decomposer are sulphur dioxide, unreacted sulphur trioxide, oxygen, water vapour and carrier gas. After leaving the second chamber, the gas is spectrometrically analyzed at the reactor outlet and subsequently neutralised in a gas washing unit.

The reactor has been constructed and installed at DLR’s solar furnace in Cologne (see Figure 5). Several series have already been carried out. The tests proved the practicability and suitability of all reactor components. Moreover, sulphuric acid was successfully decomposed to provide the required SO_2 product with yields of up to 90 % of the respective thermodynamic value and with reactor efficiencies of up to 40 %.

Figure 5: Solar H_2SO_4 decomposer receiver-reaction in operation in a solar furnace.

Design activities and experimental series are accompanied and supported by different methods of reactor and process simulation: on the one hand the high temperature chamber for SO_3 decomposition was modelled and simulated, on the other hand the SiC foam used for the evaporation chamber was analysed in depth. The accurate knowledge of its effective heat/mass transport properties is crucial for the optimal design and operation of the solar reactor. Structure and dimensions of the foam must allow for an efficient evaporation while avoiding reduced heat transfer at the Leidenfrost point.

The heat and mass transfer properties of the foam were determined. Computer tomography in conjunction with numerical techniques were used to determine the morphological characteristics and the effective transport properties of the foam, namely: extinction coefficient, scattering phase function, thermal conductivity, interfacial heat transfer coefficient, permeability, Dupuit-Forchheimer coefficient, tortuosity and residence time distributions as well as the dispersion tensor. These effective transport properties have been incorporated in a continuum reactor model developed by spatial averaging the governing equation in the fluid and solid phases. This allowed for treating the distinct phases as interpenetrating continuum, where the effective properties account for the complex pore-level structure (Figure 6, left).

The two model applied were used to provide recommendations on properties of the porous ceramics (porosity, size, inlet of the liquid acid) optimised with respect to the performance of the evaporation and decomposition process. The dynamic behaviour of the decomposer was simulated to develop control strategies for the operation of the solar reactor (Figure 6, right).

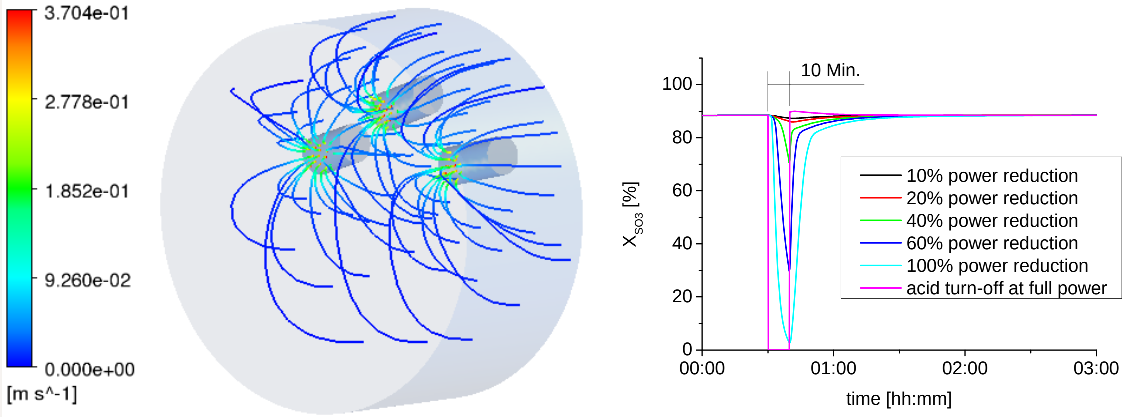

Figure 6: **left**: simulated stream lines starting at the acid inlets in the ceramic foam. The colour indicates the velocity magnitude in m/s. **right**: simulation of SO_3 conversion during/after reduction of insolated power to the ceramic honeycomb.

SO_2-O_2 separation

The decomposition of SO_3 to SO_2 is thermodynamically favoured at temperatures above 800°C in order to produce a sensible equilibrium conversion. Le Chatelier’s principle suggests that oxygen removal will shift the equilibrium in favour of increased decomposition. Identifying suitable methods for carrying out this separation is complicated by the lack of membrane materials able to withstand the severe process conditions involved. Therefore dense oxygen transport membranes, made from novel and complex ceramics, are investigated to evaluate their stability and suitability to the H_2SO_4 decomposition section. This may enable a highly pure oxygen product stream to be produced without the need for a further oxygen separation step in the process. Alternatively, such a membrane could be used to reduce the maximum temperature required, enabling the use of a wider range of heat sources for the thermochemical cycle.

Calculations were performed to evaluate the process stability of candidate materials. As a result, YSZ is considered to be a good candidate material and is being investigated further. Experimental stability and permeation testing of the membranes is carried out using a high temperature membrane cell held within a furnace. It was found that at an operating temperature of 850 °C, the oxygen flux through the membrane reaches a pseudo-steady state of approximately 20% of the original flux after eight hours of exposure to SO_2/O_2 mixtures. Work has been concentrated on maximising the flux during that pseudo steady state.

Like shown in Figure 7, YSZ conducts O_2 in the presence of SO_2 at 800-900 °C, however a degradation in performance is observed when SO_2 is introduced into the feed stream. This degradation mechanism has been identified as adsorption of SO_2 on to platinum electrodes which reduces the oxygen flux. Variation of the applied voltage only partially regenerates the performance. Fluxes through the membranes tested are low for practical purposes and thinner membranes are required. The technology has promise, however improved performance is required and this relies on improved production processes.

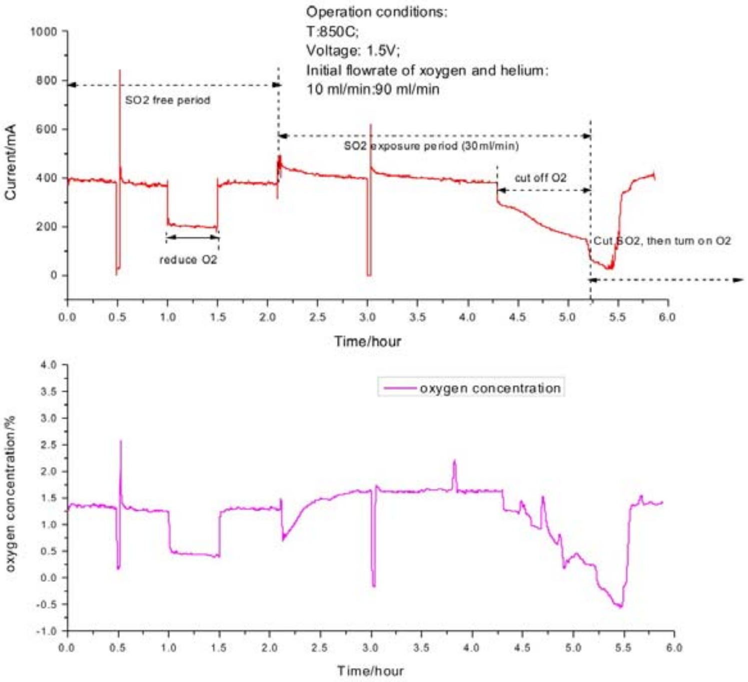

Figure 7: Current and oxygen concentration changes using the YSZ tube at 850 °C

In order to make commercial progress in the near future, it will be necessary to proceed with a detailed design of a conventional oxygen separator. The necessary materials information, in terms of reliable thermodynamic data on the equilibrium between oxygen and the solutions of SO_3 and SO_2 downstream of the decomposition reactor, do not exist in the literature and yet represent a major obstacle to the immediate design of an operating cycle. Thus, multi-component equilibrium data for SO_2, oxygen and water are being measured and models to allow prediction of the relevant properties are being developed. The data are being measured using a separate and independent apparatus which already exists in prototype form.

E.g. thermodynamic modelling of the binary SO_2-H_2O and multi-component SO_2-H_2O-O_2 systems has already been accomplished. Equations to describe the vapour liquid equilibrium of sulphur dioxide in water have been developed. These equations were then solved and the results were compared with own experimental data and with data from the literature. The resulting average error between the calculated and experimental solubility at the range of temperatures studied was in the region of ± 1.5 %.

An experimental apparatus was designed to provide data points to verify the thermodynamic models created. A photo of the apparatus, shown without insulation for illustration, is given in Figure 8a.

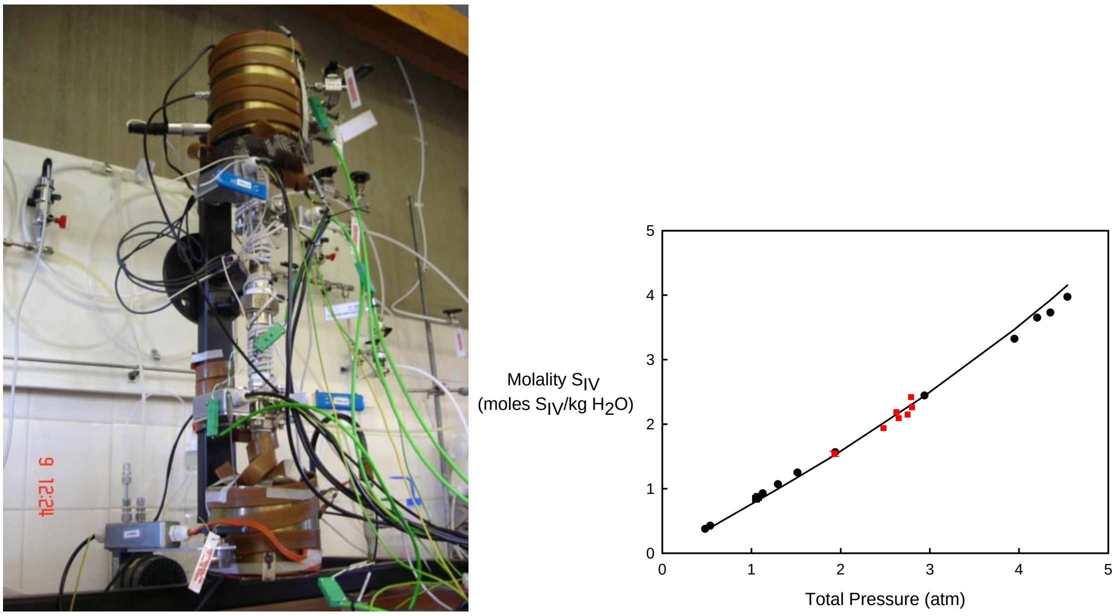

Figure 8: a) photo of the equilibrium still; b) Comparison of values for sulphur dioxide solubility at 40 °C.

Results obtained for the SO_2-H_2O system show very good agreement with both the model and the literature data, as shown in Figure 8b. The deviation is generally lower than 5%. This finding was taken as strong indication that equilibrium can be measured using the apparatus. Another test rig has been developed and was used to measure the oxygen solubility in multi-component mixtures.

Techno-economics

The main parameters that crucially influence the investment costs of a high temperature hydrogen production plant are the components costs mainly based on the obligatory choice of quite expensive materials. In the majority of cases, these are the only ones which are able to withstand the extreme conditions of the sulphur-based thermochemical cycles. HycycleS evaluates the impact of the key alternatives concerning the choice of materials, manufacturability, reliability etc. both on investment cost and on the production cost of hydrogen. An analysis is carried out in order to assess the critical aspects regarding component costs, reliability, maintenance that greatly influence the hydrogen production cost.

A general calculation method and a procedure of assessing the process have been developed. Data from the experimental parts of the project including choice of materials, plant and components design and sizing, efficiencies and chemical yields were used to be fed into the model to calculate investment costs, operation and maintenance costs and consequently hydrogen production costs. For a nuclear powered HyS process hydrogen production cost of 6.3 €/kg have been determined. Sensitivity studies revealed a potential range between 3.5 and 13 €/kg. For a HyS plant integrated in a solar tower system the base case hydrogen production cost were calculated to be 7.8 €/kg.

A solar powered hybrid sulphur cycle process could well be an attractive route to convert solar power into chemical energy. Further reductions in conceptual hydrogen production costs would be needed for the process scheme to find widespread acceptance. Ultimately, if shown to be a viable option for solar energy conversion, the solar hybrid sulphur cycle could eventually even be explored as a process route for the generation of clean hydrogen as a fuel source of the future. A demonstration scenario has been depicted which foresees the multiplication of individual receiver-modules in an area-wide arrangement and the integration of the main parts and of most components of a HyS chemical hydrogen production plant into the housing of dedicated solar tower system (see Figure 9).

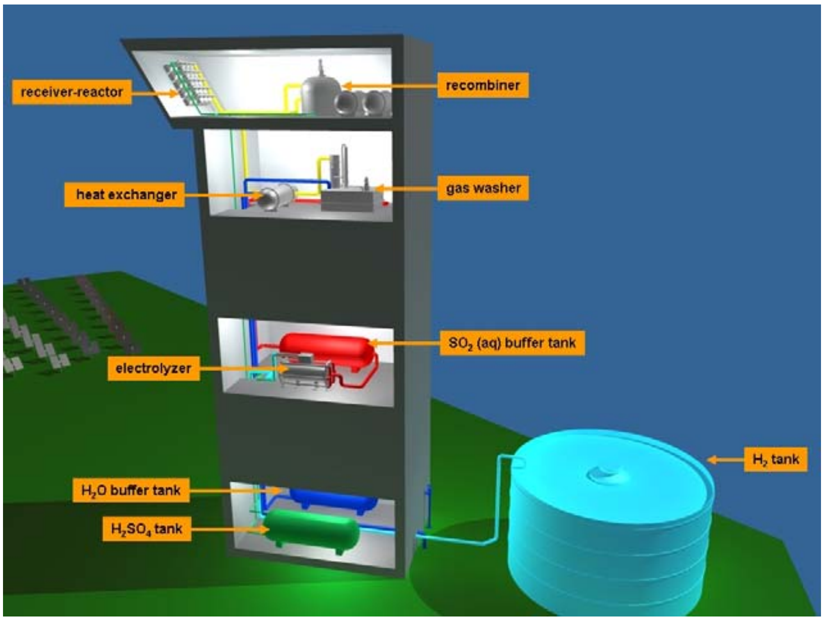

Figure 9: Unit operations of solar HyS process integrated into tower the structure of a solar tower system.

Summary

The project HycycleS identified potential construction and catalyst materials for the targeted key components of solar and nuclear powered sulphur based thermo-chemical cycles and for the catalytic high temperature reduction of SO_3 as one of the crucial steps of those processes.

HycycleS' main development route was based on ceramic materials from the SiC family – to be used as construction materials for sulphuric acid decomposers of two different configurations: on the one hand a solar receiver reactor and on the other hand a compact heat exchanger. The base material to be employed as O_2 separation membrane from the SO_3 decomposer reactor outlet mixture is YSZ. SiC turned out as the material of choice for those components of the process facing the highest temperatures and most corrosive environments. Specific oxides were qualified as catalyst for the SO_3 decomposition with significantly higher activity and higher stability than the reference materials.

Mock-ups of sub-units and prototypes of the mentioned decomposers have been developed and tested. Laboratory test rigs for different purposes such as corrosion tests, catalyst development, catalyst stability tests and selectivity of separation membranes - have been built and used to qualify materials and to prepare and accompany the prototypes' test operation. E.g., one of the largest SiC heat exchanger ever made could be realized. The solar receiver-reactor turned out practicable and suitable for scale-up purpose by multiplying the module on top of a solar central receiver system. The experimental data from lab testing and prototype testing have been used to refine models of components, process units, and of the process as a whole to enable the evaluation of plant and hydrogen production costs and to enable the elaboration of potential scale-up scenarios.