

## **HYTHEC : AIMS AND FIRST ASSESSMENTS OF AN EC FUNDED PROJECT ON MASSIVE SCALE HYDROGEN PRODUCTION VIA THERMOCHEMICAL CYCLES**

**Alain LE DUIGOU – Jean-Marc BORGARD – Bruno LAROUSSE – Denis DOIZI – F. WERKOFF -** Commissariat à l’Energie Atomique (CEA – F) (i) / [aleduigou@cea.fr](mailto:aleduigou@cea.fr)

**Ray ALLEN, Bruce C. EWAN, Geoff H PRIESTMAN, Robin DEVONSHIRE, Rachael ELDER, Manu MINOCHA, Victor RAMOS -** University of Sheffield (USFD – UK) (ii) / [r.w.k.allen@shef.ac.uk](mailto:r.w.k.allen@shef.ac.uk)

**Giovanni CERRI, Coriolano SALVINI, Ambra GIOVANNELLI, Giovanni DE MARIA, Sergio BRUTTI, Claudio CORGNALE -** Università degli studi – Roma tre (DIMI – I) (iii) / [cerri@uniroma3.it](mailto:cerri@uniroma3.it)

**Martin ROEB, Nathalie MONNERIE, Mark SCHMITZ, Adam NOGLIK, Christian SATTLER-** Deutsches Zentrum für Luft und Raumfahrt (DLR – D) (iv) / [Martin.roeb@dlr.de](mailto:Martin.roeb@dlr.de)

**Alfredo ORDEN MARTINEZ, Daniel de LORENZO MANZANO, Jorge CEDILLO ROJAS**Empresarios Agrupados (EA – SP) (v) / [ddm@empre.es](mailto:ddm@empre.es)

**Stephane DECHELOTTE, Olivier BAUDOIN -**PROSIM (F) (vi) / [olivier.baudouin@prosim.net](mailto:olivier.baudouin@prosim.net)

- (i) Département de Physico-Chimie – Commissariat à l’Energie Atomique / Saclay – 91191 Gif-Sur-Yvette Cedex – FRANCE
- (ii) The University of Sheffield - Firth Court, Western Bank - S102TN Sheffield, UNITED KINGDOM
- (iii) Università degli Studi ROMA TRE - Via della Vasca Navale 79 – 00146 Roma – ITALY
- (iv) Deutsches Zentrum für Luft-und Raumfahrt e.V. - Linder Höhe – 51147 Köln – GERMANY
- (v) Empresarios Agrupados Internacional, S.A. – Magallanes 3 – 28015 Madrid – SPAIN
- (vi) ProSim SA – Stratège Bâtiment A – F-31312 Labège - FRANCE

---

### **ABSTRACT**

The objective of HYTHEC - Hydrogen THERmochemical Cycles - is to investigate the effective potential for massive hydrogen production of the S\_I thermo-chemical cycle, and to compare it with the hybrid S Westinghouse (WH) cycle. The project aims to conduct flow-sheeting, industrial scale-up, safety and costs modeling, to improve the fundamental knowledge and efficiency of the S\_I cycle H<sub>2</sub> production step, and to investigate a solar primary energy source for the H<sub>2</sub>SO<sub>4</sub> decomposition step which is common to both cycles. Initial reference flow-sheets for S\_I and WH cycles have been prepared and compared. First data and results are available now on the coupling of S\_I cycle with a Very High Temperature Nuclear Reactor, scale-up to industrial level and cost estimation, improvement of the knowledge of the H<sub>2</sub>x mixture (S\_I cycle) and membrane separation, splitting of sulphuric acid using a solar furnace, and plant concepts regarding the WH process. This project is funded by the European Community - Sixth Framework Program Priority [6.1] - Sustainable Energy Systems, Medium to Long Term –(contract number : 502704).

**KEYWORDS:** HYTHEC, hydrogen production, thermochemical, Sulphur Iodine cycle, Hybrid-Sulphur cycle

---

## 1. INTRODUCTION

Today, Hydrogen is mainly produced from fossil resources. In the long term, given the prospect of an increasing energy demand (+20% by 2020, expected to double by 2030, with a possible threefold increase by 2050), a lack of fossil resources and limitations on the release of greenhouse gases, only water and biomass are viable, long term candidate raw materials for hydrogen production. The two processes that have the greatest likelihood of successful massive hydrogen production from water are electrolysis and thermo-chemical cycles. The thermo-chemical cycles are processes where water is decomposed into hydrogen and oxygen via chemical reactions using intermediate elements which are recycled. As the heat can be directly used, these cycles have the potential of a better efficiency than alkaline electrolysis. The required energy can be either provided by nuclear energy or by solar energy, and, since the production requires a continuous supply of heat, hybrid solutions including solar and nuclear energy input are conceivable and desirable.

## 2. HYTHEC: THE SEARCH FOR AN EFFICIENT HYDROGEN PRODUCTION ROUTE FROM RENEWABLES

The Sulfur-Iodine (S\_I) cycle (Figure 1) was extensively studied by the General Atomics Company [1]. Japan has recently built a small pilot plant of this process [2]. Thus, the S\_I cycle seems to be the best known, internationally leading candidate, as a promising thermo-chemical option. Beyond that, the Hybrid-Sulfur (WH) process (Figure 2) which offers a combination of electrolysis and thermo-chemical reactions is also the focus of much international attention. The objective of HYTHEC is to investigate, and compare, the effective potential of those two leading candidates, which have in common the high temperature process step: the  $H_2SO_4$  decomposition reaction. These thermo-chemical options can only be considered viable if they meet two major criteria: demonstrated large scale technical feasibility, and competitive cost.

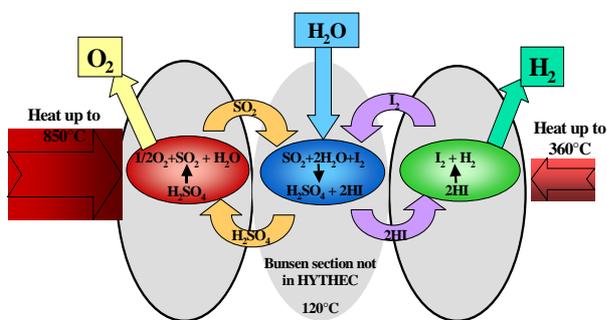


Figure 1 : The Sulphur\_Iodine (S\_I) cycle

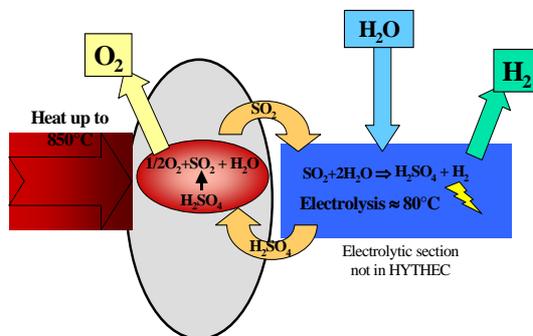
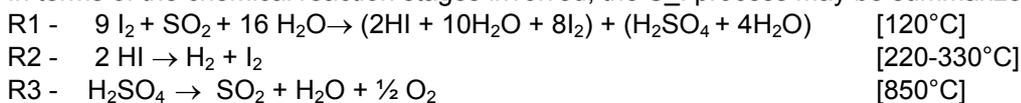


Figure 2 : The Hybrid-Sulfur (WH) cycle

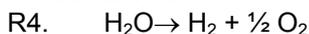
## 3. BASIC KNOWLEDGE AND NEEDS FOR S\_I AND WH THERMO-CHEMICAL CYCLES

### The S\_I cycle :

In terms of the chemical reaction stages involved, the S\_I process may be summarized as follows:



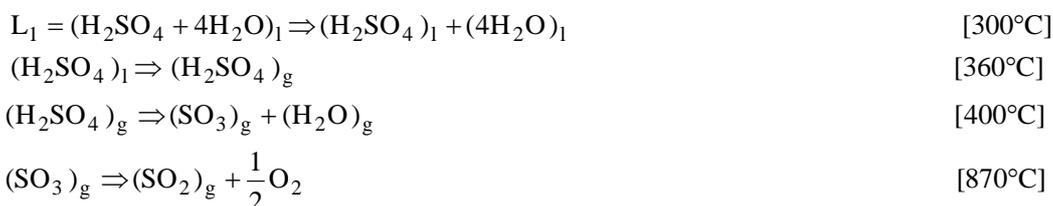
These sum to:



The first reaction, called the Bunsen-reaction, proceeds exothermically in the liquid phase and produces two immiscible aqueous acid phases whose compositions are aqueous sulfuric acid and a mixture of hydrogen iodide, iodine and water named  $HI_x$ . These acids are concentrated and the excesses of water and

iodine are recycled in R1. HI and H<sub>2</sub>SO<sub>4</sub> are then decomposed according to reactions R2 and R3. Reaction R2 is the HI decomposition step with little endothermic heat of reaction. Reaction R3 is the major endothermic reaction releasing water, oxygen and sulfur dioxide. It takes place in the vapor phase in a catalytic reactor at about 900°C. The concentration by distillation of the two acids HI and H<sub>2</sub>SO<sub>4</sub> involves significant energy consumption, which has a direct influence on the efficiency of the cycle. One of the major challenges of this cycle is to reduce these excesses of water and iodine or to find separation processes that consume less energy than distillation. Among all options available for the HI<sub>x</sub> section (extractive distillation using phosphoric acid, electrodialysis and so on), HYTHEC is focusing on the reactive distillation concept as proposed by Knoche et al. [3]. Their approach allows this step to be done in one reactor so it seems to have the highest efficiency potential. An improved version has already been proposed in [4]. However necessary vapor-liquid equilibrium data and energy integration calculations are not available so that it is difficult to develop a reliable conceptual design. On the other hand, we propose to investigate the use of membranes in the distillation section of HI<sub>x</sub> in order to get the maximum HI concentration in the vapor phase, and therefore to improve the overall thermal efficiency of the process: a complete literature review must be performed, and test rigs will be built to investigate membrane distillation.

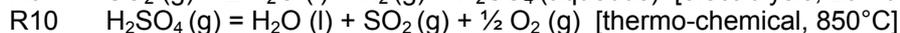
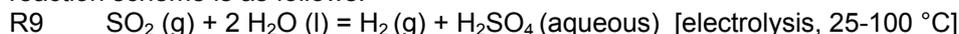
The present flow-sheets exhibit a reaction R3 split into the following steps, the SO<sub>3</sub> decomposition taking place at about 850°C. The efficiency is sensitive to the temperature of this latter reaction, and only high temperature heat sources, such as nuclear VHTR or solar energy devices, may be relevant for this process step.



A solar furnace gives the opportunity to study the chemical reaction in an original manner, both at nuclear VHTR reactor temperatures (HTR: 850 – 900°C) and at higher ones (1100 – 1200°C). The kinetics could thus be improved, and the possibility exists to directly split a concentrated H<sub>2</sub>SO<sub>4</sub> mixture into SO<sub>2</sub> + ½ O<sub>2</sub>, even without the use of a catalyst as needed at temperatures of about 850°C.

#### The Hybrid-Sulphur (WH) Cycle :

This cycle is a two-step thermo-chemical cycle for decomposing water into hydrogen and oxygen. The reaction scheme is as follows:



The cycle has the potential for achieving high thermal efficiencies, while using common and inexpensive chemicals.

Due to the fact that the Westinghouse cycle has the decomposition of the sulphuric acid in common with the S\_I cycle, it is worthwhile studying this cycle in the same project, even if the study is limited to literature review and engineering calculations to minimize cost.

For both S\_I and WH cycles, industrial scale-up studies are of great importance, for the assessments of the safety aspects of the process, the feasibility of the main components at industrial scale, and H<sub>2</sub> production costs. Specific R&D needs may arise. For this purpose, the possible cycle coupling schemes will be modeled, and will also allow for optimization of the cycle energy balances and efficiencies. Moreover, the cycle safety aspects during normal and transient operation will be studied using this model. The plant concepts will be analyzed regarding their comparative economic potential in comparison with the existing processes. Beyond that, the combination of electrolysis and thermo-chemical process steps in the Westinghouse process offers the opportunity for a combined use of solar and nuclear heat and this will be considered as well.

The partners involved in the Project are : Commissariat à l'Energie Atomique (CEA – F) (Coordination, S\_I and WH reference basic flow-sheets, S\_I cycle HI<sub>x</sub> section vapour liquid equilibrium experiments), University of Sheffield (USFD - UK) (Membrane Distillation of HI<sub>x</sub> and modelling), Università degli studi – Roma tre (DIMI – I) (components sizing and techno-economical evaluations, solar H<sub>2</sub>SO<sub>4</sub> decomposition flow modelling), Deutsches Zentrum für Luft und Raumfahrt (DLR – D) (H<sub>2</sub>SO<sub>4</sub> decomposition in a solar furnace, WH coupling to a solar and / or nuclear heat source), Empresarios Agrupados (EA – SP) (coupling to reactor and safety evaluations, thermo-structural analysis of the solar test reactor), PROSIM-SA (F) (implementations of the S\_I models in the code).

## 4 – THE HYTHEC PROJECT

### 4.1. Assessment of the S\_I thermo-chemical cycle; technical and industrial viability

A critical analysis of previous flowsheets published in the literature has been undertaken with optimization of heat transfer using the ProSim code. The H<sub>2</sub>SO<sub>4</sub> section is handled with a multiple flash distillation, followed by H<sub>2</sub>SO<sub>4</sub> evaporation and SO<sub>3</sub> decomposition. SO<sub>3</sub> is recombined in the late stages of the distillation process to optimize the global efficiency. The HI<sub>x</sub> section is handled by a reactive distillation process as proposed in [4]. The flash at the exit of the column is needed to recover some of the latent heat of water for efficiency optimization. The whole flow-sheet is given in Figure 3.

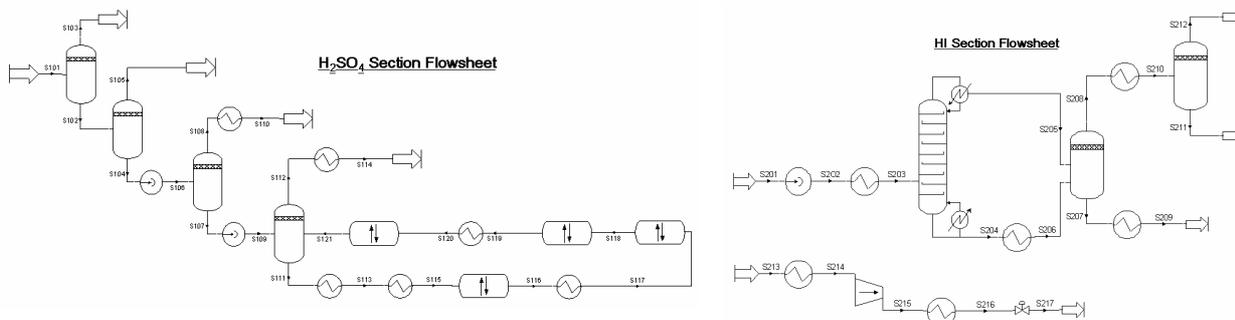


Figure 3 – S\_I flow-sheet

The coupling of the S\_I cycle to a Nuclear Reactor has been studied. Due to the high temperatures needed for the H<sub>2</sub>SO<sub>4</sub> decomposition, the best connection option is with a VHTR (Very High Temperature Reactor). Figure 4 shows a connection scheme as an example, between HYTHEC and the European Project RAPHAEL. This scheme represents a self-sustainable plant concept, in which, in addition to the heat supply to the S\_I cycle, the electrical demand of the internal consumers is provided by the nuclear reactor. Then, the high temperature flow coming out of the reactor is derived to an Intermediate Heat eXchanger (IHX). This IHX provides heat to a secondary loop that interacts with the S\_I cycle components, improving heat recovery. The flow goes partially to the IS Cycle and another part goes to a Brayton cycle for an electricity production that equals the S\_I cycle consumption.

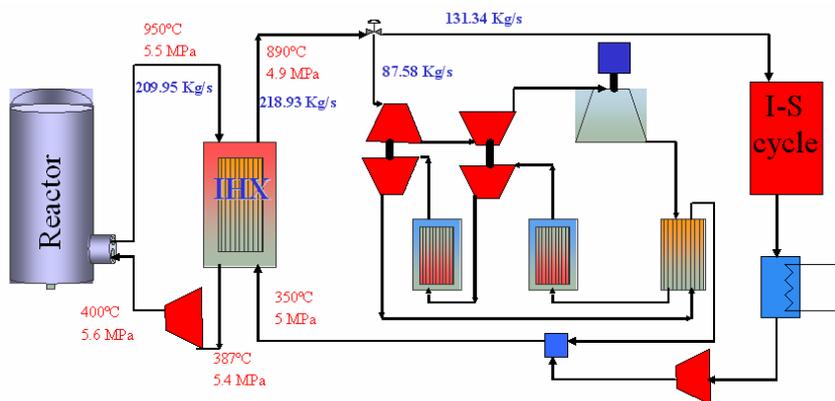


Figure 4: S\_I Cycle coupling to a Nuclear Reactor

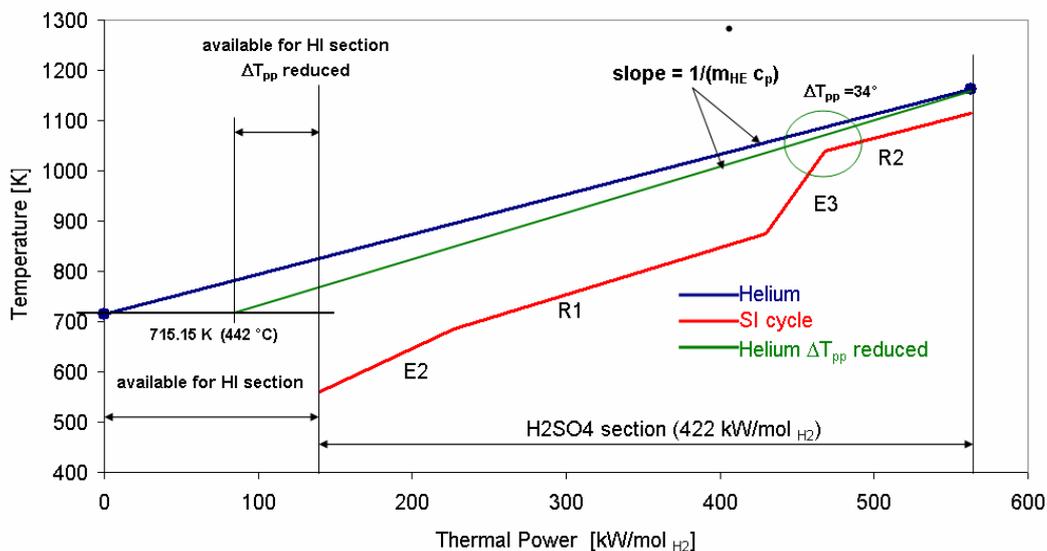
A preliminary sizing and economic feasibility of the plant has been performed. The proposed H<sub>2</sub>SO<sub>4</sub> and HI<sub>x</sub> section flow-sheets have been taken as reference. VHTR data reported in Table 1 have been assumed.

Nuclear reactor power [MW]	600
H <sub>2</sub> production	100%
IHX Inlet / Outlet Helium temperature [°C]	350 / 890
IHX Inlet / Outlet S_I temperature [°C]	890 / 442
Helium mass flow rate [kg/s]	218.93
Helium pressure [MPa]	5

TABLE 1: HTR DATA

Regarding the chemical plant hazards, an identification and description of the different chemical hazards related to the species that take part in the IS cycle have been identified:  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_3$ ,  $\text{SO}_2$ ,  $\text{HI}_x$ ,  $\text{O}_2$ ,  $\text{H}_2$ . Safety considerations regarding the chemical plant have been stated. Extensive preliminary Failure Mode Effects and Criticality Analysis (FMECA) has been developed for the entire IS cycle plant. Chemical plant – Nuclear power plant interaction safety features have been appointed. Thus, events from the NPP affecting the  $\text{H}_2$  production plant and vice versa have been addressed. It includes a preliminary calculation of Tritium production in the reactor core and its transmission to the  $\text{H}_2$  storage devices as a consequence of a series of leaks (taking as a reference a MICHELANGELO NETWORK report). Also an estimation of the safety distance between both plants in order to prevent the nuclear reactor facilities from an eventual fire or explosion of  $\text{H}_2$  have been performed (based on US and German Guides).

With the above coupling assumptions defined, only one design degree of freedom (DOF) has to be specified to completely define the HTR-SI cycle matching: the temperature difference  $\Delta T_{pp}$  between Helium and reactants at  $\text{SO}_3$  decomposition reactor. Figure 5 shows  $\text{H}_2\text{SO}_4$  section temperatures profile versus thermal power, referring to one  $\text{H}_2$  mol/s production (i.e.  $422 \text{ kW/molH}_2$  required by  $\text{H}_2\text{SO}_4$  section), vs. the Helium line slope. For a given helium mass flow ( $131.3 \text{ kg/s}$ ) the assumption of reduced values of  $\Delta T_{pp}$  leads to an increased hydrogen production. Concomitantly, heat transfer surfaces (and costs) increase and for a given helium temperature at I-S outlet ( $442^\circ\text{C}$ ) a decreasing thermal power is available to feed the HI section (Figure 5); the temperature approaches for sizing heat recovery devices are reduced and, as a consequence, heat transfer surfaces noticeably increase. After preliminary evaluations, a  $\Delta T_{pp}$  equal to  $34^\circ$  seems to be a good compromise between hydrogen production (some  $633.19 \text{ mol/s}$ ) and plant component sizes. Finally components have been sized and costed by using standard chemical engineering methods. Technical proposals have been given for the most challenging equipment: the high temperature  $\text{SO}_3$  catalytic decomposition reactor and the  $\text{HI}_x$  section components, which require large heat exchange surfaces and process vessel volumes because of the relevant internal heat recovery and flow rates. Suitable acid resistant materials have been selected. The cost of the  $\text{HI}_x$  section is almost ten times greater than that of the  $\text{H}_2\text{SO}_4$  section, and roughly 80% of  $\text{HI}_x$  section overall cost is constituted by heat recovery devices. Thus, noticeable plant cost savings are achievable by assuming higher temperature approaches and by using different heat transfer devices. The best balance between cycle efficiency and plant cost must be obtained.



**Fig. 5: Helium -  $\text{H}_2\text{SO}_4$  section temperatures vs. thermal power (per  $\text{H}_2$  mol/s).**

The  $\text{HI}_x$  section is the most important section for the efficiency of the sulphur-iodine cycle. To design and optimize the reactive distillation column we have chosen, knowledge of the total and partial pressures of the liquid vapour  $\text{HI}_x$  mixtures is required up to  $320^\circ\text{C}$  and 100 bar. We have developed a progressive methodology around three experimental devices which contain these corrosive and concentrated mixtures:

- I1 is an experimental device devoted to the measurement of the total pressure up to 130 bar and  $315^\circ\text{C}$ . It is composed of a microautoclave made of tantalum and placed in a thermoregulated oven. A pressure gauge equipped with a tantalum membrane enables the pressure measurements for different  $\text{HI}_x$  compositions. First experiments have been completed with water up to 30 bar and  $240^\circ\text{C}$ . The solution introduction procedure has been validated.

- I2 is an experimental device devoted to the qualification of the analytical diagnostics for partial pressure measurements up to 130°C and 2 bar (Figure 6). It is composed of a glass cell equipped with a total pressure gauge and placed in a thermoregulated oven. This cell is equipped with two optical pathlengths because optical “online” diagnostics have been chosen for partial pressures measurements in order not to alter the vapour composition and prevent tedious manipulations. UV-Visible spectrometry has been chosen to measure iodine concentration and FTIR spectrometry for HI and H<sub>2</sub>O concentration measurements.



Figure 6: experimental I2 device

- I3 is an experimental device under construction devoted to the partial pressure measurements of the HI<sub>x</sub> mixtures in the process domain. It is composed of the I1 device equipped with a vapour chamber. The same “online optical techniques” are used. Raman spectroscopy is also under evaluation.

Total and partial pressure measurements have been conducted in the experimental device I2. Pure samples, binary HI-H<sub>2</sub>O and ternary HI-H<sub>2</sub>O-I<sub>2</sub> mixtures have been studied; the results have been compared with the literature and with Prophy code. Up to the azeotrope, a good agreement is observed, beyond the azeotrope, the total pressure measured is higher than the pressure calculated. Ternary systems with an iodine composition close to the Bunsen exit (39 % molar) have also been studied and exhibit the same behaviour beyond the azeotrope (Figure 7). An experimental design analysis exploring different iodine compositions is currently under way. The objective of the work is to collect unknown data, especially beyond the azeotrope, which will be included in Prophy code for the scaling of HI reactive distillation column.

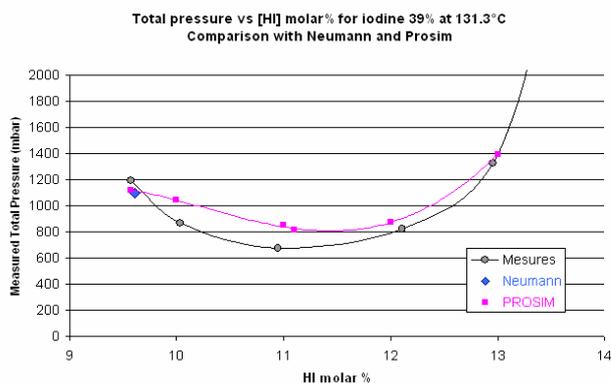


Figure 7: I1 device / total pressures for ternary systems

#### 4.2. The use of membranes to improve the S\_I cycle HI<sub>x</sub> section efficiency

Applying a liquid phase membrane separation unit to the HI<sub>x</sub> processing section has two potential advantages, an increase in efficiency and less extreme operating conditions. A membrane separation process could be used to separate the H<sub>2</sub>O and HI, thus having the effect of dehydrating the HI<sub>x</sub> by removing some water from the process stream. The membrane separation unit is considered in the following system positions: on the column feed, at the column reboiler and on a column sidestream.

Ideally the membrane would allow HI through and reject water and iodine as there is much less HI than water and iodine in the feed stream. In the majority of membranes, however, it is likely that H<sub>2</sub>O will have a higher flux than HI. The amount of water removed from the HI<sub>x</sub> stream depends on the fraction of the feed that is distilled and the flux ratio of the components. A distillation column can separate the distillate to give the azeotrope and pure water (Elder et al., 2005). As iodine is present there may be added complications due to membrane fouling and a high HI vapor pressure.

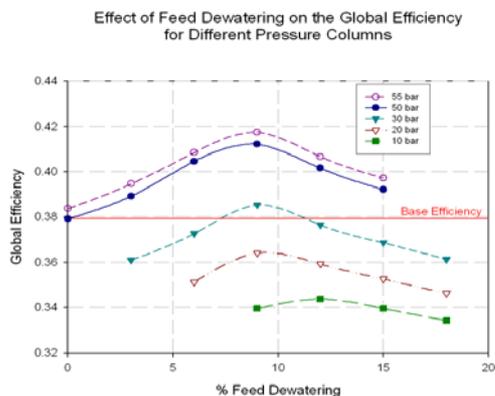
The three key factors that need to be considered when selecting the membrane unit are:

- The solution is a highly corrosive, strongly acidic, aqueous system
- The process temperature is 398K
- The membrane must be selective to either HI or H<sub>2</sub>O

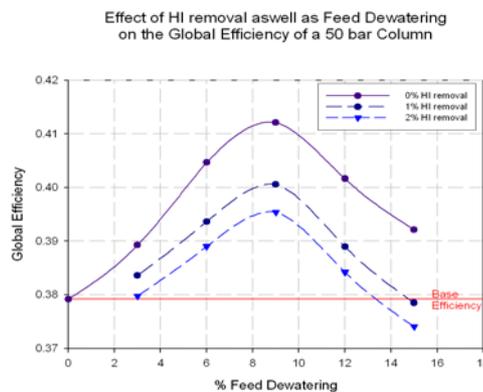
Both PTFE and ceramic membranes fulfill these criteria [5]. Recent work in America shows that Nafion-117 membranes can be used in a pervaporation process to remove water from aqueous HI [6]. The results are very promising for the application of liquid phase membrane separations to the SI process.

In order to investigate the effect of dewatering, simulations were carried out using the process flowsheeting code ProSimPlus, using a modified version of the process flowsheet which includes the membrane separation unit. The membrane is modeled as a splitter with zero enthalpy drop. This means that the retentate exits at a lower temperature than it would in practice. This is accounted for in the heat integration and so will not significantly affect the efficiencies calculated.

The base efficiency of using a 50 bar column with no membrane separation unit is 0.379. As shown in figure 8, with 9% feed dewatering this value is increased to 0.412, a significant increase. A maximum in efficiency occurs as the power required by the pump and that required surplus to heat integration decrease, whereas the additional power required by the heat pump increases. Using a 55 bar column the maximum efficiency obtained is 0.418, again at 9% feed dewatering. As the column pressure decreases the efficiencies obtainable also decrease. With approximately 7% feed dewatering a 30 bar column has the same efficiency as the 50 bar column with no membrane. A decision as to the best column pressure would depend on a detailed sizing and cost evaluation. With 1% HI removal along with 9% dewatering the maximum efficiency decreases to 0.401, as seen in figure 9. Although this is lower than with no HI removal it is still considerably better than the efficiency obtained with no membrane unit.



**Figure 8: The effect of feed dewatering**



**Figure 9: The effect of feed dewatering with HI removal**

Placing a membrane separation unit at the column reboiler or on a sidestream increases the efficiency slightly although it never exceeds 0.382. The simulations therefore suggest there is little benefit in applying a membrane unit in this way.

#### 4. 3. Assessment of the WH thermo-chemical cycle, for a solar and/or nuclear driven process

The co-application of electrolysis and the thermo-chemical step in the Westinghouse process offers the opportunity for a combined use of heat and power. The required thermal and electrical energy can be either provided by a nuclear reactor or by concentrated sunlight. This opens a wide variety of operational strategies. Hybrid solutions including solar and nuclear energy input are conceivable and are analysed with regards to their technical and economic feasibility. Different operation and plant concepts are generated, including the solar and nuclear supply of heat for the thermo-chemical step and of nuclear and solar power for the electrolysis step. For this purpose, the possible coupling schemes are modelled to enable optimisation of the cycle energy balances and efficiencies. The plant concepts are analysed with regards to their economic potential, particularly in comparison with the sulphur-iodine process. The overall flow-sheet of the Westinghouse process solar-only powered is given in Figure 10.

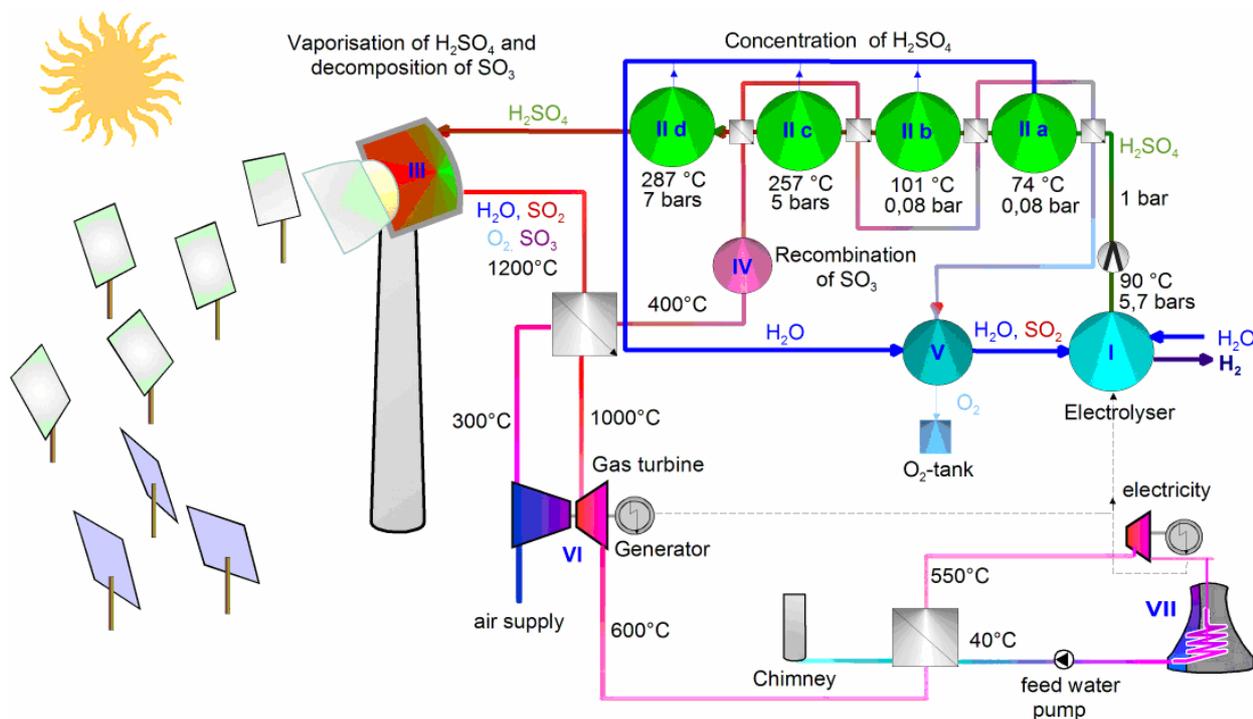


Figure 10: overall flow-sheet of the Westinghouse process (solar-only)

#### 4.4 Development of a dedicated solar receiver-reactor for the decomposition of sulphuric acid

The “solar” focus of the investigations addresses the development of a technology and a process to allow the coupling of concentrated solar radiation into the  $\text{H}_2\text{SO}_4$  splitting process, which is a highly heat consuming and at the same time technically challenging step in both thermochemical cycles. One important task in the framework of this project is the investigation of sulphuric acid decomposition by concentrated sunlight in the DLR solar furnace in Cologne.

One of the major findings of a former project was a significant enhancement of the splitting of  $\text{SO}_3$  when using concentrated solar radiation as the energy source for that reaction. This was due to a photolytic effect of concentrated solar radiation on the  $\text{SO}_3$  molecules [7]. Under solar irradiation and temperatures above 1100 K there is an irradiance-dependent photochemical increase of conversion, giving the chance to operate the process without a catalyst or to accelerate the reaction and thereby to increase the potential throughput. This effect is only advantageous if a receiver-reactor is used which allows for direct absorption of sunlight by the reactants itself.

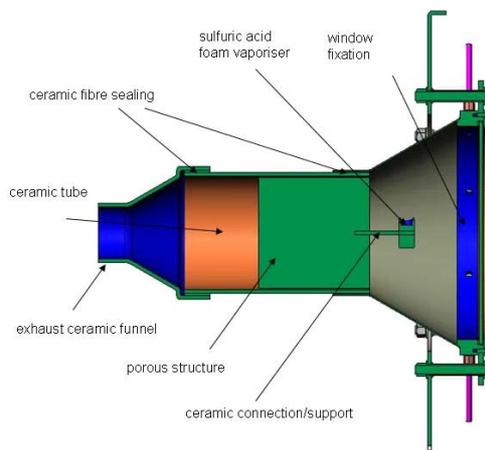
According to this, the goals of the current activity are the development of a direct absorbing receiver-reactor and of a corresponding process, the verification of their feasibility and viability with respect to the splitting of sulphuric acid, and their assessment in comparison to other reactor and process concepts.

The primary goal of the activity described was the development of the necessary hardware for the solar process, which includes as a key component a dedicated converter capable of directly absorbing concentrated solar radiation, which is a so-called receiver-reactor. It was decided to investigate and put into practice one particular concept of such a direct absorbing receiver-reactor, which was called the *porous absorber reactor*.

For that purpose concepts of volumetric receivers have been adapted to the requirements of the two-step splitting reaction of concentrated  $\text{H}_2\text{SO}_4$ . Those requirements are connected to the characteristics of corrosive liquid and gases, to the performance of a change of phase, to the kinetics of the reactions involved, and to the required temperature levels. The central innovation of the concept is the execution of an evaporation process, i.e. the evaporation of sulphuric acid, in a solar heated porous structure. The idea is to feed the liquid sulphuric acid onto or to directly inject it into a solar heated porous structure to initiate a rapid and homogenous evaporation of the acid at the inner surface of the porous structure. The necessary heat is supplied by concentrating the sun and transferred to the liquid by the porous structure. During and directly after the evaporation the sulphuric acid is dissociated. The resulting  $\text{SO}_3$  molecules have to be split into  $\text{SO}_2$  and  $\text{O}_2$  to provide the necessary feed for the ensuing step of the S\_I cycle and Westinghouse cycle respectively. For the execution of this splitting step another porous structure, a honeycomb, is foreseen.

Due to the different temperature levels and requirements needed for the evaporation and dissociation of the acid (350-550°C) on the one hand and for the spitting of SO<sub>3</sub> without catalyst (1000 – 1200 °C) on the other hand two porous components had to be implemented to meet the requirements of each reaction step individually. For the evaporation step a foam with a large inner surface was chosen. The splitting step shall be carried out in a honeycomb structure stable and robust enough to stand the required temperature level and capable of being coated by catalyst materials if necessary.

The design of the receiver-reactor comprises as main elements the ceramic components (SiSiC) as heart of the reactor which contains the reactive zone, a window, a housing, a support for the central ceramic part of the reactor, a flange junction between reactor and off-gas line, a suitable inlet enabling the feed of liquid sulphuric acid into the reactor. Figure 11 shows the design principle of a porous absorber reactor to fulfil those requirements.



**Fig. 11: Draft design of porous absorber reactor.**

The reactor concept has been investigated with a finite element model using ANSYS as well as with computational fluid dynamics (CFD) to assist in enhancing and optimising the geometry and arrangement of components. The modular assembly and multi-step processing of the reactor promise a suitable thermal and structural behaviour of the reactor compared to the aerosol reactor design. Simulations and parametric analyses proved this hypothesis to be correct. The effect of the size (diameter) and position (distance from the honeycomb structure) of the foam vaporiser, the effect of the position of the focal plane in the axial direction of the reactor and the effect of the solar flux power have been studied. The temperatures of components are within the thermal-use range, the reactor thermal behaviour assures sufficient temperature distribution and heat transfer. Structural deformations and stresses are acceptable, the quartz window holder design is appropriate and no leak tightness hazards are foreseen.

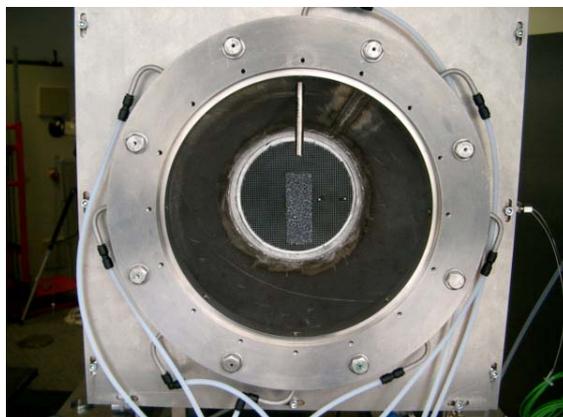
Also the modeling of the thermo-fluid dynamic aspects has shown a satisfactory behavior of the porous absorber reactor. The simulations predict that the use of porous structures turns out a good solution to achieve a uniform temperature field in the reactor body. Moreover they seem suitable to allow a homogeneous vaporization and an adequate residence time in order to achieve a sufficient dissociation rate.

Beyond the simulation the detailed design was further influenced by results of preliminary experiments in the lab and in the solar furnace addressing the vaporisation process of liquid and its operational limits, the suitability of materials with respect to the harsh conditions applied, the feeding of concentrated sulphuric acid, the shape and position of the foam, the potential shadowing of the honeycomb, the temperature distribution inside the honeycomb, and the performance of a start-up procedure.

The shadowing of the honeycomb by the foam vaporiser is a rather minor effect if the diameter of the foam is restricted to about 40 mm. The evaporation of a liquid in a solar heated porous structure was shown to be feasible. The vaporisation process proceeded satisfactorily and controllable within a reasonable range of mass flows. The temperature level achieved within the honeycomb was shown as sufficient high for the homogeneous decomposition of SO<sub>3</sub>. The major part of its volume exhibits a temperature level beyond 1273 K. In steady state the maximum temperature difference is lower than 225 K. The amount of volume flow of flushing gas has only a minor influence on the temperatures inside the honeycomb. In principle it is preferable to minimise this amount to prolong the residence time of the reactants in the reaction zone and to minimise losses due to the warming of that flushing gas. At a temperature level of up to 1473 K in the honeycomb the necessary solar input was about 10 kW when operating without quartz windows. The net power was about 2.5 kW. No significant impact of the evaporating liquid on the quartz was observed. A straightforward start-up procedure was possible by cooling the feeding tube by flushing gas and by

temporarily diminishing the solar power. By that means the partial evaporation of liquid in the feeding tube could be avoided and the foam vaporiser could be operated in the suitable temperature regime.

Based on the results of experimental pre-tests and the described reactor modelling the design of the porous absorber reactor has been refined yielding the hardware, after manufacture, as shown in Figure 12. It has been installed and tested in the solar furnace in Cologne with the following results.



**Fig. 12: Front view of porous absorber reactor after mounting**

The receiver-reactor behaved well during the first experimental campaign in the solar furnace. About 75 hours of operation were performed. A flow of concentrated sulphuric acid was completely vaporised inside a porous absorber made of SiSiC. Other ceramic materials turned out or appear respectively not suitable for the solar vaporisation of sulphuric acid. Cooling of the feeding tube and an additional device (a temperature resistant “duct” for the liquid acid) ensured a vaporisation process without any splashing and impacts on the window. Sulphuric acid was homogeneously decomposed without the use of catalysts with conversions between 20 and 55 %. No visible corrosion occurred at the ceramic parts of the reactor. Some metallic parts of the reactor and off-gas line experienced corrosion at their surface if the temperatures at those positions were allowed to fall below the condensation point of H<sub>2</sub>SO<sub>4</sub>.

It can be stated that the concept of a porous absorber receiver-reactor has proven feasible in a first step to decompose concentrated H<sub>2</sub>SO<sub>4</sub> by solar radiation. Further steps aim now at the stepwise improvement of the conversion and of the operating procedure. The main focus of the upcoming experiments and the accompanying modelling of the reactor is the evaluation of the capability to scale up the concept to a commercial scale and to operate the solar process with satisfying conversion and efficiency.

## 5 – CONCLUSION

HYTHEC is a European collaboration involving a restricted number of partners (6, in 5 countries) to give a first evaluation, both on technical and economic points of view, of an interesting route for future H<sub>2</sub> production, via promising CO<sub>2</sub> free Thermo-chemical Cycles: mainly the Sulphur-Iodine cycle, and to a lower extent the Westinghouse cycle as an alternative “hybrid” solution. Acquisition of the input data and first modelling, flow-sheeting, construction of the devices and measurement techniques, as well as industrial scale-up and techno-economic evaluations have been performed up to now. The first, S\_I cycle HI<sub>x</sub> section experimental results have been obtained. A technology and process to allow the coupling of concentrated solar radiation into the H<sub>2</sub>SO<sub>4</sub> splitting process has been developed; it can be stated that the concept of a porous absorber receiver-reactor has proven feasible for this purpose.

We would like to acknowledge the European Community which is funding the HYTHEC project - Sixth Framework Program Priority [6.1] - Sustainable Energy Systems, Medium to Long Term –(contract number: 502704).

## REFERENCES

- [1] G.E.Besenbruch and coll – GA-A18257 (1982)
- [2] H. Nakajima, K. Ikenoya, K. Onuki et al. – “Closed-Cycle Continuous Hydrogen Production Test by Thermochemical S-I Process”, *Kagaku Kogaku Ronbunshu*, 24 (1998) 352 (in Japanese)
- [3] M.Roth, K.F. Knoche – Thermo-chemical water splitting through direct HI decomposition from H<sub>2</sub>O - HI- I<sub>2</sub> solutions - *Int. J. Hydrogen Energy*, 14, N°8, 545-549 (1989).
- [4] Stephen Goldstein, Jean-Marc Borgard and Xavier Vitart - Upper bound and best estimate of the efficiency of the iodine sulphur cycle - *International Journal of Hydrogen Energy*, Volume 30, Issue 6, May 2005, Pages 619-626
- [5] Elder, R. H., Priestman, G. H., Ewan, B. C. and Allen, R. W. K. (2005) The Separation of HI<sub>x</sub> in the Sulphur-Iodine Thermochemical Cycle for Sustainable Hydrogen Production, *Trans IChemE, Part B, Process Safety and Environmental Protection*, **83**, 343-350.
- [6] Orme, C. J., Jones, M. G. and Stewart, F. F. (2005) Pervaporation of water from Aqueous HI using Nafion-117 Membranes for the Sulfur-Iodine Thermochemical Water Splitting Process, *J Membrane Sci*, **252**, 245-252.
- [7] E. Lüpfer, K.-H. Funken, in: M. Becker, M. Böhmer (eds.): *Solar Thermal Concentrating Technologies*, Proc. of the 8<sup>th</sup> Int. Symposium, Oct. 6-11, 1996, Köln, Germany, Vol. 3, C.F. Müller-Verlag, Heidelberg.