Publishable Executive Summary

This document summarizes the HYTHEC (HYdrogen THErmo-chemical Cycles) project: objectives, partners involved, major developments and results, plan for using and disseminating the knowledge. This project has been conducted for 3 years and 9 months (initially 3.5 years, plus a 3 months prolongation), in the period 2004 – 04 – 01 to 2007 – 12 – 31.

1 – SCOPE

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. These processes have the potential for a better efficiency than electrolysis since they use heat directly, avoiding the energy losses associated with making electricity. As massive scale production will be required, this will lead to a need for substantial primary energy sources such as nuclear reactors and/or high capacity solar heat sources.

2 – OBJECTIVES

The project focuses on the two major thermochemical cycles, Sulfur-Iodine (S_I) cycle and Hybrid-Sulfur (HyS) cycle, aloso known as Westinghouse cycle, addressing both fundamental and industrial scale aspects. The approach is multi-faceted, involving modelling, chemical analysis, process flow-sheeting, experimental investigations on the critical high temperature and hydrogen production steps, capabilities of industrial scale-up (50 to 600 MWth) including the coupling to a high temperature heat source and the related safety aspects, and economic evaluation. The experimental work is focussed on the high temperature H_2SO_4 decomposition reaction step common to both cycles, which is performed with a solar primary energy source, and on the S_I cycle hydrogen production step, both to increase the knowledge of the chemical system and to improve the efficiency by the use of alternative, low energy separation techniques such as membranes.

The HYTHEC project aims to evaluate those two processes by the mean of two major quantitative values: thermal efficiency, cost of H2 production. The main expected achievements of the project are:

- Assessment and improvement of the S_I thermo-chemical cycle, including technical and industrial viability :
  - Flow-sheet evaluations, possible improvements using modelling;
  - $HI/I_2/H_2O$ system (H_2 production section of the cycle):
    - measurements of the vapour composition, to improve the vapour liquid equilibrium model;
    - relevance of membrane separation techniques;
  - Feasibility of solar thermal splitting of sulphuric acid for the H_2SO_4 decomposition section of the cycle (section similar to the Hybrid-Sulphur cycle one);

- Feasibility of coupling to a nuclear reactor, Safety assessments, feasibility of the main components at industrial scale and production costs.

- Assessment of the HyS thermo-chemical cycle, for a solar and/or nuclear driven process (in comparison with the S_I cycle) :
  - Flow-sheet evaluations;
  - Feasibility of solar thermal splitting of sulphuric acid for the H_2SO_4 decomposition section of the cycle (section similar to the S_I cycle one);
  - Safety assessments, feasibility of the main components at industrial scale and production costs.

3 – PARTNERS INVOLVED AND PROJECT ORGANIZATION

HYTHEC involves six partners in an international consortium, that consists of major players from a range of energy, scientific, research and engineering institutions together with an SME. By seeking directly to contribute to the overall goals and timelines of the European Hydrogen and Fuel Cell Technology Platform, it has achieved high levels of international visibility, recognition and acceptance.

CEA (partner 1) is a major French fundamental and applied R&D organization; the Department of Physico-Chemistry involved in this project is in charge of R&D programs on basic physico-chemistry for nuclear applications: corrosion, chemical analysis, modelling of elementary mechanisms, of physico-chemical processes. USFD (partner 2) is one of the top teaching and research universities in the United Kingdom, the Research Group involved works within the Department of Chemical & Process Engineering and is the leading University research group in this field. The university research group DIMI-RM3 (partner 3) is actively involved in the field of hydrogen production from renewables as well as from Nuclear, its research activities are related to process simulations, component design including cost accounting and optimum sizing and lab-scale experiments. Moreover DIMI-RM3 can perform part load analysis of components and lab-scale experiments including tests in the field of chemistry. DLR (partner 4) has an experience of more than 20 years in both national and international co-operative RTD projects concerning the application of solar radiation for power production, solar chemistry, solar materials research, techno-economic system analyses. EA (partner 5) is a leading engineering organisation providing a complete range of consulting, project management, engineering and design, procurement, construction management, plant testing, safety assessment to the electric utility industry. ProSim SA (partner 6) is a French SME with strong expertise in modelling of complex thermodynamic systems that has gained a leading position in Europe in the field of process simulation.

To reach the overall HYTHEC objectives, he work has been broken down in seven sub-projects:

- **SP1 Project management** (partners involved: 1, 2, 4, 6) - Organisation of the work (Management Committees, progress reviews and communications), relations with the European Community, dissemination and contacts with other European projects, progress reports and regular progress meetings.

- **SP2 The optimisation of the whole Sulfur-Iodine cycle (S_I)** (partners involved: 1, 3, 5, 6) – S_I cycle flow-sheets issued at various times of the project, to give theoretical descriptions of the process, that will be used for the industrial scale-up activities (coupling to reactor, component sizing and cost analysis), taking into account the theoretical and experimental improvements found during the project.

- **SP3 Vapour Liquid Equilibrium (VLE) analysis** (partners involved: 1, 2, 6) - Improvement of the vapour liquid equilibrium model of the HIx ($HI/I_2/H_2O$) system, for a better knowledge and improvement of the H2 production part of the S_I cycle production rate of hydrogen (partial pressure measurements of gases needed, mainly by the mean of mass or optical spectrometry methods).

- **SP4 Review of membrane Separation Techniques** (partner involved: 2) - Exploratory research into alternative, low energy separation techniques relevant to the S_I process, to be used in the HI_x separation steps ; membrane distillation and pervaporation, already used to separate azeotropes successfully, will be assessed as a technique to concentrate the HI solution.

- **SP5 Experimental study of membrane distillation and pervaporation of HIx** (partners involved: 1, 2) - Experiments at a laboratory scale, evaluation of the separation performances of selected membranes (partial pressures in the vapour will be measured by optical means, measurements similar to those of SP3).

- **SP6 Sulphuric Acid Decomposition** (partners involved: 1, 3, 4, 5) - Direct decomposition of H_2SO_4 in a solar furnace located in Cologne (up to 25 kW), at temperatures up to 1100 - 1200 °C; indirect heating in tube type reactor using a catalyst will also be performed, applying VHTR nuclear reactor temperature (850-900°C). Process simulations and assessment of the feasibility of scale-up at a commercial scale (including safety and costs evaluations).

- **SP7 Assessment of the Hybrid-Sulphur (Westinghouse) cycle (WH)** (partners involved: 1, 4, 5) - Study of the technical feasibility of a solar and hybrid (solar and nuclear) operation of the WH process (thermo-chemical and electrolysis steps), including industrial scale-up, safety aspects during normal and transient operation and economic potential, in comparison with the S_I process.

The main technical roles of the partners were the following ones:

- CEA : coordination (SP1), S_I and WH reference basic flow-sheets (SP2, SP7), evaluation of vapour liquid equilibrium experiments of the HIx system and modelling (SP3); participation to the economic analysis (SP2, SP7);
- USFD : review of membrane separation techniques (SP4), membrane distillation and pervaporation of HIx and modelling (SP5);
- DIMI : process chemical calculations, components sizing and costs evaluations of S_I (SP2) and solar H_2SO_4 decomposition (SP6), CFD modelling of H_2SO_4 decomposition (SP6);
- DLR : H_2SO_4 decomposition in a solar furnace (SP6), WH coupled to a solar and / or nuclear heat source, assessments to industrial scale-up (SP7);
- EA : coupling to reactor and safety evaluations of S_I and WH, and process modelling solar H_2SO_4 decomposition (SP2, SP7 and SP6), industrial scale-up and costs evaluations of S_I and WH (SP2, SP7), thermo-structural analysis of the solar test reactor (SP6);
- PROSIM : implementations of the S_I models in the code (SP2, SP3).

As showed by the lines above, an intensive interaction between the partners has been required all along the duration of the project: as a matter of fact, both modelling and experiments had to lead to a better knowledge, technical and economic evaluation of the two processes, and this can be summarized by the figure below. 24 deliverables have been given (22 initially planned, plus 2 decided during the project), associated with a reciprocal partners' reviewing to ensure a better scientific acceptance of the different issues.

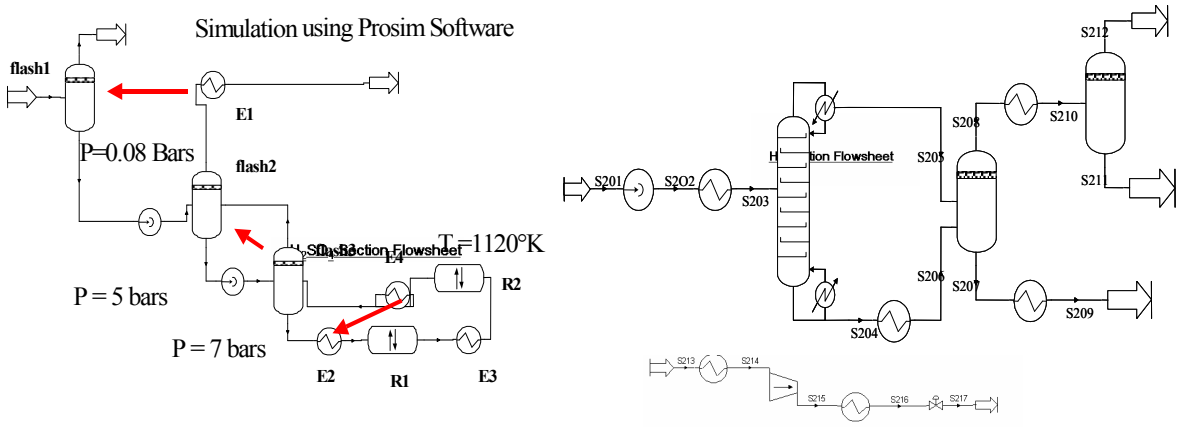
In addition to a detailed planning carried out before the start of the project, planning that indicates both the activities and the relationships inside the sub-projects and between them, the project global time schedule has been mainly divided into 3 parts:

- first year, month 12 : acquisition of the input data and flow-sheets, definition / construction of the devices and measurement techniques, and first steps in the modelling (membranes, coupling and safety, component sizing);
- second year (until the mid-term assessment meeting : April 2006), month 24 : first S_I and Westinghouse evaluations from theoretical, experimental, industrial scale-up and economic studies; a first set of results and data must be given at that date;
- until the end of the project (December 2007), month 45 : detailed S_I and Westinghouse evaluations from theoretical, experimental, second round for industrial scale-up and economic studies.

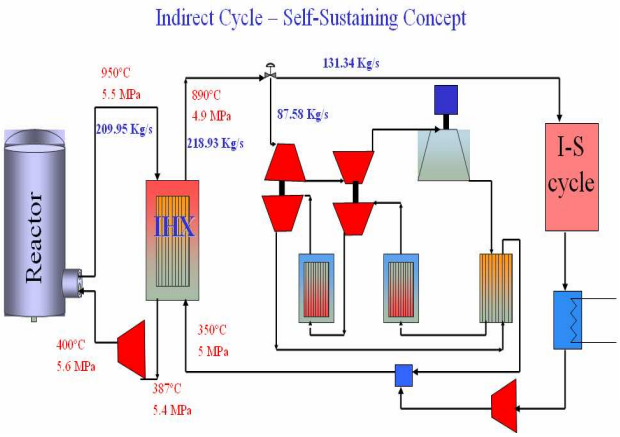
4 – ASSESSMENT AND IMPROVEMENT OF THE S_I THERMO-CHEMICAL CYCLE

This document will not describe the fundamental S_I cycle chemical reactions, description and history, it is deeply developed in the related HYTHEC publications, especially in http://dx.doi.org/10.1016/j.ijhydene.2006.10.047.

A reliable assessment of the S_I cycle is one of the major aims of the HYTHEC project. For this purpose, a series of steps have to be followed: flow-sheeting, feasibility of the coupling between the energy source (in our case a VHTR) and the Hydrogen generation process, chemical components sizing and costs, and economic evaluation. These steps have been already developed in a first cycle evaluation that finally lead to a global cost evaluation, as well as the calculation of an optimal cost for the overall system VHTR/H2 production plant. In a second step, sensitivity calculations have been developed. A first reference flow-sheet of the S_I cycle has been proposed and described, based on a critical review of the available S_I thermo-dynamical data. As a matter of fact, a large amount of data were available, but there were important lacks of informations on different steps of the process (vapour liquid equilibrium of the HIx section, enthalpy of mixing and immiscibility gaps, kinetics). The first contribution was then to give an appropriate classification for this (what is known, to be clarified or developed, needed, new, …). A general review of the different available flow-sheets have been done for the two acid decomposition sections. Possible calculation errors have been analyzed too. The design we chose used a distillative - reactive column with a heat pump and a flash to maximize efficiency of the HIx section. For the H2SO4 section, we designed a flow-sheet that shows a succession of three flashs at different temperature and pressure and a high pressure at the exit of the section. A first overall optimization lead to the S_I "reference" flow-sheet, on which the following activities had been based on (coupling to the VHTR, component sizing and economic evaluation).



Different possibilities have been carried out to update the flow-sheet given, the major aim was the possible impact on the efficiency: use of membranes (about + 3% efficiency, see later), adding a new flash in section II (efficiency increase), heat exchange re-arrangements in section III (efficiency increase), H2SO4 section Pressure and maximum Temperature variations due to the connection (distances) to the heat source (risk of efficiency decrease). But the fundamentals (mainly related to the section III) have not changed yet: low T and P experiments had an impact on H2 purity – specification [(I2+HI)/H2 < 10-5] reached - , but for high (process) T and P experiments, complementary data are still needed (large incertitude remaining on effective heat exchanges) to carry out a reliable model, then an really updated flow-sheet based upon new fundamentals (only trends for the flow-sheet could have been given).



On the basis of this first S_I reference flow-sheet, the coupling between the cycle and the VHTR nuclear reactor has been performed. It has proved that the nuclear reactor is able to provide with thermal energy for the chemical processes requirements, while at the same time is able to produce, via a Brayton cycle, as much electricity as the whole coupling scheme requires (specific cycle requests, as well as coupling fluid (helium): circulation: it is what we named the "self-sustaining concept".

The amount of hydrogen produced, 110ton/day (633 moles/s), represents a high value for a 600MW nuclear reactor taking into account the electricity production demanded, 110MWe, and the fact that a 60 MWth steam generator/cooler is used to decrease the helium temperature at the S_I cycle outlet, to adapt it to that at the turbine outlet. The corresponding overall efficiency (including NR coupling) is then about 30% (37% for the S_I cycle itself). It has to be noticed that the reactor characteristics, as well as IHX data, have been provided by FP6 EU-funded RAPHAEL-IP project, which meant a close collaboration between the two projects.

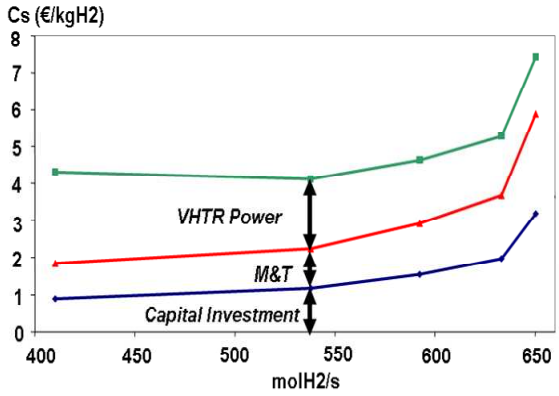
A safety assessment has been performed too, quite complete for the current conceptual stage of the project. Until there are remarkable changes on the flow sheet, the assessment is valid and should be the basis for the future component design, layout planning, auxiliary and safety systems design, etc. The safety distances (between the hydrogen storage and the nuclear reactor) evaluations have been addressed too, on the basis of a general formula approved during a HYTHEC / Hysafe workshop; depending on the capacity and type (gas, liquid) of the storage, as well as the risk taken into account, safety distances may vary noticeably, from some hundred meters to a few kilometres. To strengthen this activity, two workshops have been held with the FP6 EU-funded project Hysafe, on the basis of a request document written by HYTHEC. The only remarks that should be updated when there are more accurate values are: the evaluation of the safety distance of the Hydrogen storage and the nuclear reactor, the reactor tritium generation calculation and hazard evaluation (first steps already performed) and for example the inspection frequency of each of the components. In addition, on the basis of a specific HYTHEC request document too, a technical exchange has been held with the FP6 EU-funded EXTREMAT project.

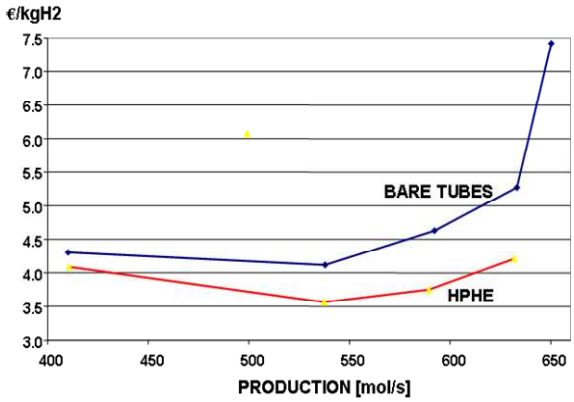
An ECOSIMPRO coupling model has been carried out. From this model, and using major components' sizing, transient simulations verified the behaviour of the IS cycle – VHTR coupling under accidental conditions of malfunctioning of any part of it, with the aim to protect the nuclear reactor from unpredicted shutdowns (reactor scram). In the case of a leak of Helium in one of heat exchangers, the He from the IS cycle is derived to the auxiliary safety loop branch in order to minimise the effect on the nuclear reactor, and the control system shall be very precise and robust to provide a quick and effective response. The case of a leak of the SO2/SO3 stream is more complicated, and the coordination between the control systems of the He and the mixture is very important. As a pump failure in the H2SO4 section is detected, the system starts diverting a part of the He to the auxiliary safety loop in order to accommodate the heat exchange to the demanded condition; the transient takes more time to reach to a new equilibrium.

On the experimental point of view, the description of the HIx section vapour/liquid equilibrium experiments, as well as the possible use of membranes, are given hereafter (§ 5), and the possible impacts on the S_I cycle modelling cost described below.

To perform the component sizing and cost accounting activities, first H_2SO_4 and HI_x section flow-sheets and VHTR data have been taken as reference. With these assumptions, only one design degree of freedom (DOF) has to be specified to completely define the VHTR-S_I cycle matching. The hydrogen production level has been assumed as DOF. A H_2 production level of 633 mol/s with an overall plant efficiency of some 35% has been taken as reference. Plant components have been sized and costs evaluated by using standard chemical engineering methods and by means of "ad hoc" developed databases. The SO_3 catalytic decomposition reactor has been sized as a tubular one. The H_2SO_4 concentration endothermical flashes have been sized as kettle boiler units. The HI_x section heat recovery devices have been assumed and sized as shell and tube heat exchangers. Suitable acid resistant materials have been selected, taking ceramic materials into particular consideration. Costs of installed equipment have been evaluated by adopting a factored method. The investment cost of the HI_x section has been found approximately eight times greater than that of the H_2SO_4 section, and roughly 80% of HI_x section overall cost is constituted by heat recovery devices. A hydrogen production cost of approximately 5.2 €/kgH_2 was estimated. The influence of investment costs on overall production costs is of some 40%.

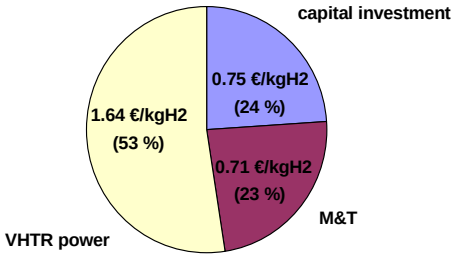
In order to find the best compromise between investment and operating costs a parametric analysis has been carried out by varying the hydrogen production level keeping the overall available thermal power from the nuclear reactor at the reference value (600 MW). For different H_2 productions detailed plant sizing and cost accounting have been performed. Results are reported in Figures below. The reduction of H_2 production level have led to a decrease of investment costs mainly due to the reduction of sizes of HI_x section recovery heat exchangers. The minimum cost (4.2 €/kgH2) is achieved at 540 mol/s and does not correspond to the maximum achievable efficiency. In order to obtain further reduction of costs, technology improvements concerning the HIx section recovery heat exchangers have been introduced. To enhance heat transfer coefficients bare tubes have been replaced by corrugated ones. In the figure below, results achieved by adopting HPHE (High Performance Heat Exchangers) are reported and compared with those already given in the other one (Bare Tubes).





A reduction of costs is observed all along the production range taken into consideration and the minimum is still achieved at 540 mol/s. A value of some 3.6 €/kgH_2 is found, which represents a noticeable 40% cost reduction if compared to the reference case. Finally the optimisation of HI_x section heat recovery network at 540 mol/s by adopting the pinch technique has led to a production cost of some 3.4 €/kgH_2. To achieve further hydrogen production costs reductions, a new matching scheme with the VHTR has also been set up, with removal of helium cooler (which in the previous arrangement absorbed a thermal power of some 60 MW) placed at the exit of the SI chemical plant. Data, unknown quantities and degrees of freedom of the whole system have been individuated in line with the old scheme evaluations. In this way only one DOF remains and, on the basis of previous results and experience a production of 620molH2/s has been assumed.

Eventually a specific H2 cost of approximately 3€/kg has been achieved. Influence of capital investment, nuclear thermal power (VHTR power) as well as maintenance and taxes (M&T) are shown in the figure below.



Influence of cost items on the overall H2 production cost for a new matching 620mol/s SI plant

Comparison attempts have been made between the HYTHEC and the CEA S_I techno-economic analyses. As concerns the investment costs, the breakdown is detailed in different ways in the CEA and the DIMI studies. Since the amount of the investment versus the production capacity of the plant is very similar for the CEA and the DIMI 633 mol/s plant, for the HYTHEC 540 mol/s (economical best production rate described above), it is about twice as small, and the comparison pointed out the importance of the number of years of investment, but it must be compared to the accuracy of the capital cost assessment (about ± 30%). Interest amounts are similar, about 5% of the investment. The energy consumption costs are very similar too. The maintenance costs are much more expensive in the DIMI case, leading to a more precise and realistic evaluation; it is an important factor (for instance, considering 5% instead of 3% leads to a difference of 0.6 €/kg); let us mention that Peters recommends much higher values for what he calls "complex systems", which involve for instance important corrosion: 7 to 11%. Concerning the economic assumptions, the availability of the plant only influences the investment and maintenance shares (90% availability instead of 80% would lead to decrease the investment and maintenance costs by about 12%).

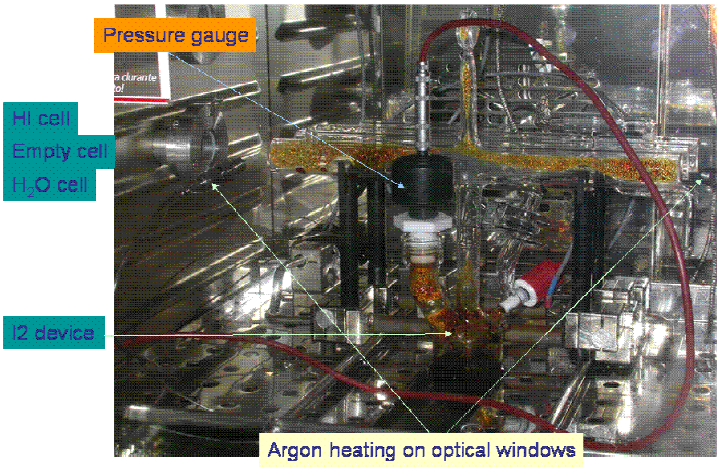
5 – S_I CYCLE EXPERIMENTAL STEP / HIX SECTION AND MEMBRANES

To design and optimize the reactive distillation column, a good knowledge of the total and partial pressures of the liquid vapour HI_x mixtures is required up to 320°C and 100 bar. We have developed a progressive methodology around three experimental devices which contain these corrosive and concentrated mixtures. I1 is devoted to the measurement of the total pressure up to 130 bar and 315°C.

I1 is composed of a microautoclave made of tantalum placed in a thermoregulated oven, a pressure gauge equipped with a tantalum membrane enables the pressure measurements for different HI_x compositions. After twelve experiments on pure water necessary to have I1 reactor operational, and important experimental difficulties, four HI-H2O binary media close to azeotropic compositions have been tested, up to 30 bar and 240°C, which showed hydrogen formation after HI decomposition in the vapour phase, leading to a quaternary (HI, H_2O, I_2, H_2) mixture.

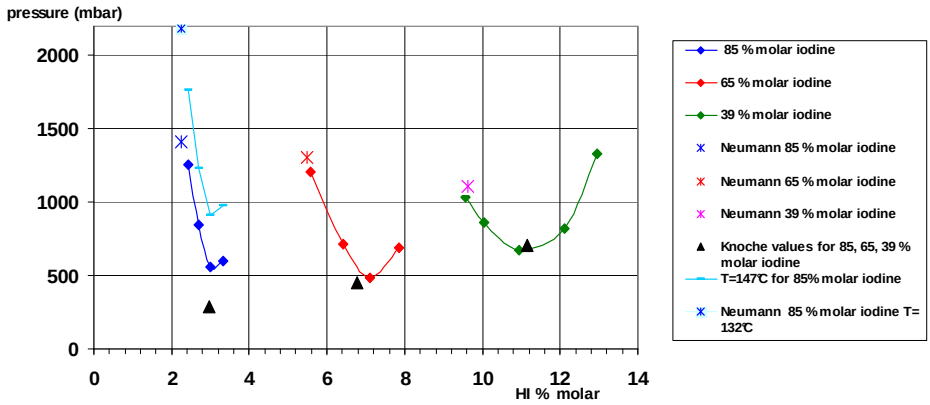
A HI-I2-H2O ternary system close to the composition of the ternary mixture of the Bunsen reaction defined by General Atomics, has been studied too, which showed a good agreement between the total pressure measurements versus temperature and the calculated bubble pressure values using Prosim code (discrepancy below 4%, negligible H2 formation – azeotropic area).

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 below).



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_2O concentration measurements.

Total and partial pressure measurements have been conducted in the experimental device I2. Pure samples, binary HI-H2O and ternary HI-H2O-I2 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 (then the present model underestimates the HI content). 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. Ternary mixtures HI-I_2-H_2O have been deeper analysed for various iodine and hydriodic acid compositions, in particular for various iodine concentrations (4%, 12%, 24%, 39%, 65%, 85%), the total and partial pressure have been measured around 100°C and 130°C for different HI concentrations. The general tendencies already observed have been confirmed.



For three different iodine concentrations (39%, 65%, 85%), the total pressure has been measured around 130°C for different HI concentrations.

I3 is an experimental device devoted to the partial pressure measurements of the HI_x mixtures in the process domain. It is composed of the I1 device equipped with a vapour chamber. HI, H_2O and I_2 concentrations are measured in the vapour phase using the optical diagnostics validated on I2 device: FTIR spectrometry for HI and H2O concentrations, UV-Visible absorption for I_2 concentrations.

First experiments have been conducted with pure water. Good concentrations results versus temperature have been obtained up to 280°C using FTIR measurements. Total and partial pressure measurements have been done in the process domain. HI, H_2O and I_2 concentrations were measured in the vapour phase using the optical diagnostics validated on I2 device: FTIR spectrometry for HI and H_2O concentrations, UV-Visible absorption for I_2 concentrations. UV-Visible spectrometry and pressure measurements on pure iodine have been given between 100 and 230°C. The results showed a very good agreement with the theoretical values calculated using ThermoCalc software. Concerning the ternary system, the concentrations of the two species HI and H_2O using two spectral regions (IRTF diagnosis) for different temperatures between 127 and 263°C, have been calculated. As expected, as we are on the left side of the total pressure minimum, very low HI content is expected in the vapour

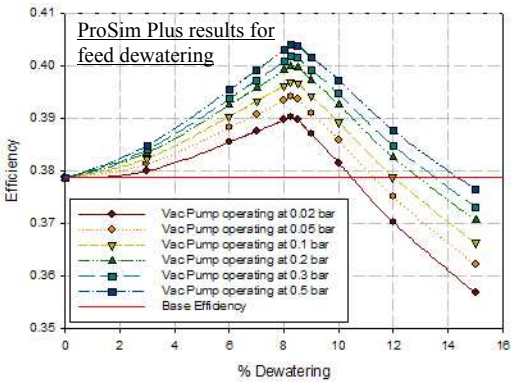
phase. Two measurements on different ternary HI-H_2O-I_2 mixtures have been conducted up to 270°C: a mixture with a composition close to the Bunsen exit defined by General Atomics, ie 39% I_2, 10% HI and 51% H_2O, and a mixture composed of 39% I_2, 13.5% HI and 47.5% H_2O. Due to concentration measurement uncertainties estimated around 20% in the vapour phase, a good agreement between molar fractions measured in the vapour phase with molar fractions calculated using Prosim code has been obtained for both cases. In any case, there is an overestimation of water and an underestimation of I_2 by the model.

Available data have been considered to upgrade the thermodynamic model. First impacts of new experiment data on Hix modeling and HIx section were evaluated; as already observed during the second period, it seems that the NRTL model is not adapted for concentrations over the azeotropic point, and that a new solvation equation for iodine with HI complex describes more accurately the system. After first promising trends toward a new model, difficulties appeared (mainly absence of polyiodide formation in the model), and we found that there was probably a large error in the measurement of the pressure done by RWTH Aachen at high temperature. By now, it is just possible to say that HI vapour pressure was probably overrated and iodine vapour pressure was probably underrated; an indirect consequence is that the heat exchanges in the HIx section were probably overrated. This is rather a good new, but in the absence of any relevant data in the right temperature range, it is not impossible to know the magnitude of this impact.

6 – S_I CYCLE EXPERIMENTAL STEP / MEMBRANES

The application of membrane separations to the HI_x processing section of the SI cycle has been investigated in depth by the University of Sheffield for the HYTHEC project. The work has been multi-stranded, encompassing the development of a database of candidate membranes, process modelling to investigate the impact of applying a membrane separation, stability testing of promising membranes identified, both batch and flow testing of membranes to investigate the fluxes and separations possible, modelling of a membrane process and spectroscopic studies on HI-H_2O-I_2 solutions to investigate speciation and equilibria. The work has been published at several international conferences, including The World Congress of Chemical Engineering in 2005, the AIChE annual meeting in 2005 and 2007 and IMSTEC 2007. One journal paper has been published, one submitted and four are in preparation. The research has yielded many interesting results and 'World firsts' and will have a significant impact on future research into the SI cycle.

Process simulations using ProSim Plus indicate that the efficiency of the SI cycle can be significantly increased, from 0.379 to 0.400 using a membrane separation unit on the feed to the reactive distillation column and a permeate side pressure of 0.2 bar. These efficiencies occur at a dewatering of 8.25%, above which the efficiency decreases again, due mainly to an increased energy requirement of the water heat pump. A trade off exists between the efficiency achieved and the permeate pressure used as with a higher pressure the flux will be lower and so the required membrane area greater.



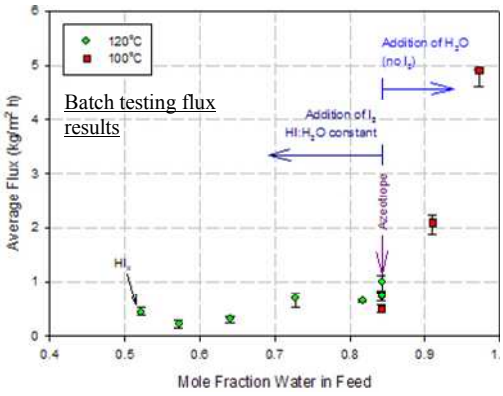
The membrane database was originally intended to provide a resource to assist the process of identifying potential membranes capable of working well in a range of locations within the SI process. It thus focussed on the very difficult area of high temperature membranes, many incorporating ceramic elements, and provides a comprehensive listing of such membranes and a great deal of information about their properties. However, early in the project, it became apparent that the best location for the membrane is at the feed to the distillation column. The conditions at this point are such that relatively common, commercially available

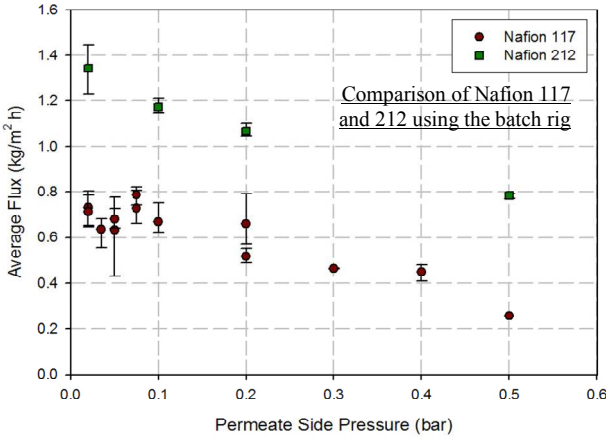
membranes are, at least notionally, capable of effecting the separation. The focus of the project thus shifted, away from exploration of novel, high temperature, membrane materials and geometries and towards demonstration of the performance of PTFE membranes in the, nonetheless, harsh process environments necessitated by their use for feed dewatering. A significant success resulting from the early concentration on high temperature ceramic membranes is the work programme recently begun at USFD studying high temperature ceramic membranes for separating oxygen from the sulphuric acid decomposition products at temperatures up to 1000 °C. The materials under consideration were identified as a result of the preparation of the database and that work is now being funded, under FP 7 as part of the HycycleS project.

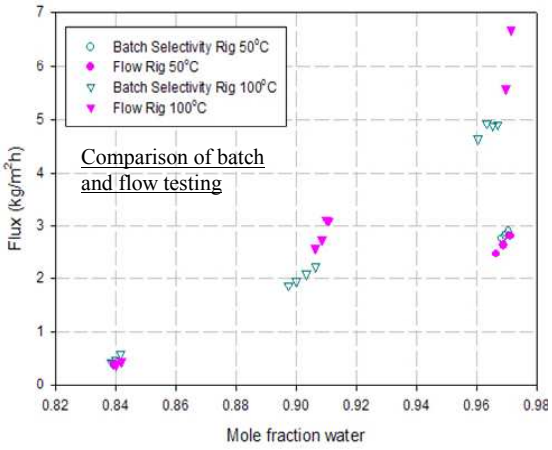
Nafion membranes were identified as having great potential in a pervaporation set up for the dewatering of HIx solutions, whereas using a membrane distillation process, porous PTFE membranes were identified as potential candidates. Stability testing of both Nafion membranes with varying thicknesses and porous PTFE membranes showed them all to be stable in HI solutions at 120°C for the maximum period tested of one day. Testing with Nafion 90209, a bilayer membrane, was inconclusive and the results not reproducible.

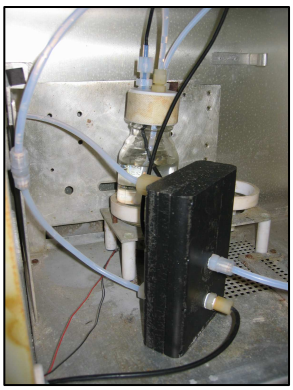
Batch flux and selectivity testing has shown that Nafion membranes can break the azeotrope and dewater HI_x solutions. Almost pure water permeates through the membrane. At 120°C and using an azeotropic feed, a flux of 0.7 kg/m^{2}h is observed using a Nafion 117 membrane, whereas with a HI_x feed the flux falls to 0.45 kg/m^{2}h. Using a Nafion 212 membrane the flux using an azeotropic feed is substantially higher at 1.35 kg/m^{2}h.

The membranes tested have shown that achieving 8.25% dewatering, and so maximum efficiency, is very possible. Employing a thinner Nafion membrane gives a significant increase in flux. Current predictions indicate large required membrane areas, and the challenge now is to investigate ways to increase the flux through the membrane whilst retaining the high separation factors so that the required membrane area decreases.









Flow testing using HI feed concentrations at the azeotrope and under show excellent correlation with results obtained using the batch selectivity rig. This suggests that the batch selectivity rig is a good emulation of an industrial, continuous flow, membrane process, thus validating the results obtained with that rig

Initial AGMD experiments have shown that 0.22□m PVDF membranes can be used to dewater HI-H_2O solutions. For dilute feed streams the permeate is almost pure water, whereas for more concentrated feed streams, up to the azeotropic concentration, the permeate has approximately half the HI concentration of the feed. Further work is needed to verify the results obtained and to investigate other feed temperatures and concentrations.

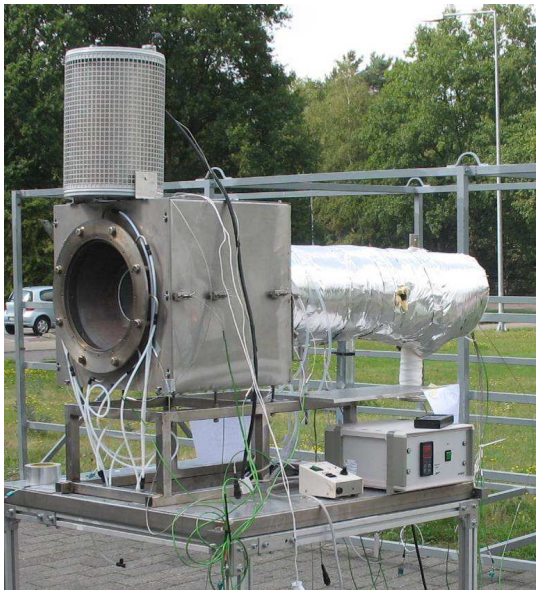
A membrane model has been created which is well behaved and predicts the flux trends seen in experiments. Further work is needed to improve the accuracy of the model.

A Raman scattering study has provided a self-consistent picture of the chemical nature of the HI_x phase of the sulphur iodine cycle, particularly in respect to the I_2-containing species present. The study combines new measurements on the two aqueous binary systems, I_2/H_2O and HI/H_2O, and on the ternary system, $HI/I_2/H_2O$, which are each closely related to HI_x, with an analysis of a wide range of previously published work on aqueous iodide-I_2 solutions and solid polyiodides. The local structure of concentrated HI solutions and HI_x is suggested to involve both neutral and charged HI-water clusters which interact with molecular I_2 to form I_3^- and iodide-I_2 species. The nature of the I_2-containing species present in these systems is revealed by the behaviour of 5 principal component bands. Separate measurements showed that saturation amounts of H_2SO_4 in the HI_x phase did not affect in any detectable manner the I_2-containing species and their local environment. Our studies of the condensed phase of HI_x are currently being extended to include neutron scattering measurements.

CARS has proven to be a powerful technique to provide *in situ* data of total pressure in this harsh system, even if there is no HI present in the vapour phase and even when the iodine vapour turns the system into a deep purple cloud at higher temperatures. CARS has also proven to be suitable for providing kinetic data for the hydrogen production step. Quantitative data is still to come and there are some pending measurements to be completed in order to support further arguments for a future publication.

7 – SOLAR DECOMPOSITION OF SULPHURIC ACID

A receiver-reactor for the solar decomposition of sulphuric acid has been developed and qualified. The reactor design was prepared with the support of experiments, testing of components, thermo-structural and fluid-dynamics simulations. The concept of a volumetric receiver-reactor has proven feasible in practise. High conversions almost up to the maximum achievable conversion determined by thermodynamic equilibrium can be achieved with a platinum catalyst. In addition investigations with a less expensive catalyst, iron oxide, provided evidence of the potential of such material. An operation with uncoated SiSiC absorbers applying mostly homogeneous decomposition requires much higher average temperatures to achieve the necessary yield.

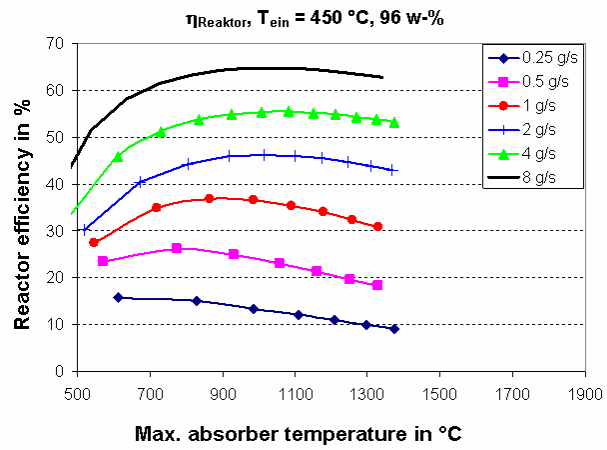


Test series for the quantification of the kinetics of the SO_3-decomposition have been carried out in a tube reactor. A suprising but promising finding was the significant catalytic activity of SiSiC. This activity depends very much on the characteristics of the material as its surface and pretreatment procedure. Further systematic investigation on the material characteristics crucially causing and influencing this activities are necessary.

The evaporation of sulfuric acid on ceramic foams is well suited for a direct application of solar energy. A modified design of the reactor with a separated chamber for the evaporation enables a larger vaporizer and therewith a higher flow rate and a separate control of the solar input to the vaporizer. Higher mass flows of the reactants improve the reactor efficiency because energy losses are almost independent of the mass flow.

The mass flow in the performed experiments was limited by the capacity of the foam vaporizer which could not be enlarged because of shadowing of the honeycomb absorber. After a modification of the reactor in a way that it was only applied forsolar SO_3-decomposition reactor efficiencies of more than 40 % were achieved. As the reradiation of the absorber is the main contribution to energy losses of the reactor a cavity design can also raise the efficiency.

A numerical model of the reactor has been developped. It allows for steady-state as well as transient simulation of the receiver-reactor operational behaviour. It was used to gain a detailed understanding of decomposition process, e.g. about thespatial distribution of SO3 conversion, to optimise the hardware (e.g. length of absorber) and process parameters, to simulate process conditions, which could not be realised in the solar furnace,and to evaluate the potential of the technology.



After validating the model with experimental data high reactor efficiencies are predicted - up to 70 % for the test reactor, for a scaled version even higher. A trade-off of efficiency and yield was detected, which means for several simulations the coincidence of the efficiency optimum at the fixed yield minimum of 50 %. The optimal operation temperature depends on various parameters, but is in most cases lower than 1000 °C. The presence of a homogeneous flux distribution like on a solar tower makes the difference: it lowers the optimum operation temperature, it provides higher yields, it reduces the requirements for catalyst performance and stability, and it reduces the impacts and stress on materials. Therefore a high potential of such technology is predicted if it is transferred to and operated at a solar tower platform.

Finally a performance and design study for a suitable set-up of a solar heated tubular receiver-reactor in commercial scale has been carried out. The results of the simulation propose that SO_3 decomposition might be possible if done with the described technology using a direct radiated solar tube receiver and applying pressures around 20 bars. For optimizing the receiver layout additional activities and future developments are necessary or at least recommendable as the Enhancements of kinetics, the detailed modeling the fluid and heat flow in the fixed bed, and an optimized receiver and heliostat layout. In summary it can be stated that a tube receiver-reactor might be a possible option

also for the decomposition of sulphuric acid. But serious obstacles have still to be overcome. The main questions are related to the temperature resistance, to thermal stress and to chemical stability of the metallic material foreseen for the tubes. For example the operational temperature is close to the upper limit of operability of the metallic materials, which is significantly lower than for ceramic absorbers present in a volumetric receiver-reactor.

8 – ASSESSMENT AND IMPROVEMENT OF THE HyS THERMO-CHEMICAL CYCLE

The work on the hybrid-sulphur cycle has led to a far better understanding of its components and their interplay. While previously there were rather common flow sheets for the nuclear and solar process, they now have been adapted to better accommodate the special requirements of the two energy sources.

For the solar option the focus was laid on a plant delivering annual average of 50 MW_{th} at 1200°C to the process. This is equivalent to a design power of 140 MW_{th}. The component sizing has shown no problems with the capability of scale-up. Even the solar system necessary for coupling up to 840 MW_{th} (300 MW case) is feasible, but economically less attractive and more challenging from a civil engineering point of view. The strong interaction between the optic lay-out and the process design led to a changed pressure level (from 5.7 to 1 bar) in the H_2SO_4 splitting section.

The best economic results were found for a plant featuring separate receivers for power generation and the splitting of H_2SO_4. In the former receiver, Helium is heated to drive a closed Brayton cycle, providing the electricity for electrolysis, pumps and compressors. The splitting reactor is fed with the sulphuric acid as delivered by the electrolysis section, thus saving the concentration section. The off-heat of the product gas stream is used for the (partial) evaporation of the feed steam. Separation of oxygen from the product gas is most economically achieved by a series of scrubbers.

The more detailed simulation of the chemical part of the plant has led to a realistic design, but the efficiency decreased compared to previous analyses due to the close-to-reality considerations and calculations (now around 30%). There is, however, potential for significant efficiency improvements:

- modified flow sheets, in particular cost-optimised by applying a better knowledge of component costs,
- definite source of improvement for solar-only: using the heat of the cooler and intercooler of the closed Brayton cycle,
- better usage of off-heat at different points in the process,
- new operational concepts for intermittent energy input,
- non-self-sustaining concepts, i.e. using external (solar) electricity,

The detailed calculation of hydrogen production costs revealed which components lead to critical contributions to costs. Cost efficiency and the energetic efficiency required in some cases different approaches in the flow sheet layout. So while the understanding of cost sensitivities has strongly increased, so has the need for further techno-economic optimization. The best hydrogen production cost (HPC) of 3 €/kg appears still above the optimum. Further improvements can be achieved through cheaper (solar) components and new materials –for the high-temperature section as well as for the electrolyser.

For the coupling to a nuclear energy source the first preliminary flow sheet of HyS cycle has been successfully done. In this case the nuclear reactor chosen is a Helium-cooled VHTR from the new and evolutionary GEN IV reactor type, because it is the only one that can achieve the required temperature for the cycle's effective performance. Due to the high temperature at which the helium comes out of the HyS cycle, a power plant can be coupled in series with the HyS. The HyS cycle has the H_2SO_4 decomposition stage in common with the IS Cycle its maximum temperature is 850ºC. The energy supplied to the HyS cycle comes from the Helium of the secondary loop and provides 241 MW_{th}, generating a total H_2 production amount of 567 mol_{H2}/s, equivalent to 98 t_{H2}/day. Mechanical equipment and other apparatuses consume 109 MW_e, the principal consumer of electricity is the electrolyser, which consumes 91.8% of the total electricity (100 MW_e), while the rest of the

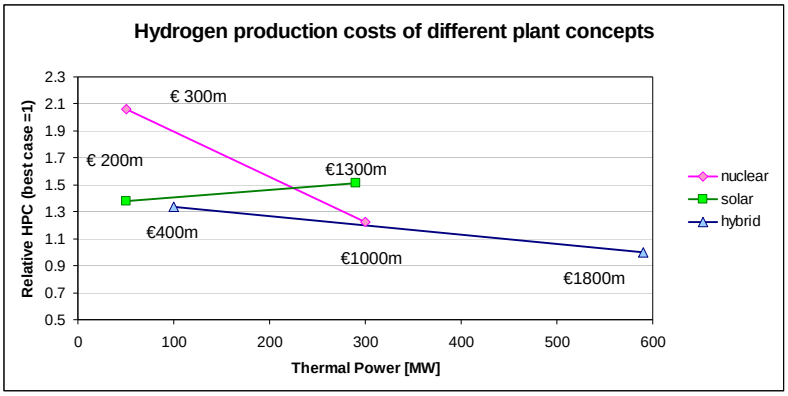
components (compressor and pumps) consumes only 8.2%. The power plant (Brayton cycle) takes up the rest of the energy from the Helium in the secondary loop and it is able to cover the HyS cycle's demand for electricity by producing 158 MW_e, of which 109 MW_e are to supply the electrical consumers in the HyS cycle and the remaining 48.9 MW_e are to be delivered to the electric grid.

The possible advantages of hybridizing the energy supply are obvious: The advantages of both systems can be combined:

- Solar splitting of sulphuric acid poses much less requirements to the activity of catalysts as the higher operational temperature can be achieved, which may have a substantial influence on the hydrogen production cost – depending on the material used and its deterioration. Thus, a hybrid system may reduce the catalyst costs significantly.
- Nuclear energy has a high availability, as it does not have constant fluctuations as solar energy does. This leads to less strain and better usage of plant components.
- As electrolysers suffer from being frequently turned on and off, its electric input can be delivered by nuclear power.

Two hybrid plant designs were analyzed:

- The first is the trivial case of hybridisation: The energy for all process steps using thermal energy, mainly the vaporization and splitting of sulphuric acid, is delivered by solar, whereas all electric consumers, mainly the electrolysis are driven by a nuclear power plant associated with the HyS plant. This way the electrolysis can be run continuously, while the sun provides the high-temperature heat for the splitting process
- In a second approach a high temperature nuclear reactor is assumed to produce SO_2 from H_2SO_4 in parallel to the solar reactor. The nuclear energy drives the electric power generation for the electrolysis of all SO_2 produced. We thus have a constantly running nuclear powered HyS cycle, which consumes additional solar produced SO_2. This way each technology is well used, but there is a high degree of redundancy regarding the plant components.



Other concepts were excluded from detailed analysis due to excessive redundancy of components associated with nuclear and solar power or due to safety concerns, as the reactor cooling was influenced by the fluctuating solar power.

A preliminary evaluation of the HPC based on solar, nuclear and hybrid operation lead to following results: Small plants are powered most favourably by solar energy, while nuclear plants are most economic at high power levels; hybrid systems have their niche in the mid-range (100 to 300 MW_{th}).

For neither energy source the analysis of safety indicated prohibitive obstacles. Points were careful attention must be paid were identified: The thermal interaction between the chemical apparatus and the nuclear power plant, and the directly irradiated solar receiver reactor.

9 – DISSEMINATION

The HYTHEC project lead to a very large dissemination. A public internet site was launched in October 2006, to enhance the dissemination of the project: www.hythec.org, which gives the description of the activities and major public results obtained, the partners activities, EC news, H2 production congresses and conferences, and the communications and publications accepted and presented. This site received more than 10 000 successful connections, from all over the world.

More than 20 communications, dedicated to part or all HYTHEC, have been given in international congresses: Hydrogen Energy Congress in Brussels (March 2005), IHEC (July 2005, July 2007), EHEC 2005), WHEC 2006, AIChE 2005 and 2007, 8th Cologne Solar Symposium (June 2006), 7th WCCE (Glasgow, July 2005), German Energy Congress (February 2006), Solar Paces (June 2006), 13th Symposium on Concentrating Solar Power and Chemical Engineering Technologies, IEA/HIA (2 meetings), Energy Sustainablilty (ES2007), WHTC 2007, IMSTEC2007 (Sydney), 2nd SOLLAB Doctoral-Colloquium on Solar Concentrating Technologies, HFP 2005, HFP 2007, and the HYTHEC final meeting in Brussels in November 2007.

An article have been published in the 2007 January 29th Parliament Magazine issue, and 7 publications were published (3) or will be given (4) in international reviews, mainly IJHE (a publication summarizes all the project activities, referred by IJHE 32 (2007) 1516 – 1529 / doi:10.1016/j.ijhydene.2006.10.047).

HYTHEC has been formally recognized and endorsed by the Steering Committee of the International Partnership for the Hydrogen Economy (IPHE), in 2006.

A collaborative work with RAPHAEL (4 meetings) enabled an fruitful exchange of data, and the choice of a common coupling scheme (boundary temperatures, pressures, heat exchangers pinches, heat to electricity efficiency) between a VHTR and the H2 production plant. Two workshops with Hysafe, based upon a dedicated HYTHEC request document, reinforced the safety analyses engaged in HYTHEC, mainly the possible safety regulations and the evaluation of safety distances between a VHTR and the plant. HYTHEC carried out a materials request document as a basis of a workshop organized with Extremat. HYTHEC participated to some INNOHYP-CA meetings, mainly to present S_I and HyS cycles characteristics to allow comparisons with other cycles. A 2 days workshop was dedicated to the comparisons of HYTHEC and CEA activities on Materials, Components and Costs of the S_I cycle, and HYTHEC and ENEA activities related to the HIx section of the S_I cycle.

HYTHEC sent comments to the SRA and DS draft documents, description of the contributions to the overall goals and timelines of the European HFC Technology Platform.

10 – CONCLUSION

An overall analysis of the S_I cycle, based upon a reference flow-sheet used for the coupling to a VHTR, the major components' sizing and costs, and an overall cycle economic evaluation, has been carried out by the mean of a fruitful interplay between different activities and partners. Different possibilities to update the flow-sheet have been given, with the related impact on the efficiency: increase by the use of membranes (about + 3%), new flash in section II, heat exchange re-arrangements in section III; but unavoidable uncertainties and constraints due to the connection to the heat source (safety considerations) may have a negative effect. Anyway, the fundamentals (mainly section III modelling) could not change yet. The coupling and safety evaluations have been reinforced by connections with other European projects (RAPHAEL, HYSAFE). The first S_I reference cost evaluation was found higher than the usual target (5,3€/kg H2), but the strong impact of the interplay between the heat (and electricity) source coupling, and the component sizing has been shown, leading to the existence of an optimal value (5,3€/kg H2 → 4,2€/kg H2) that doesn't correspond to the best efficiency. Costs are strongly dependent on technical sensitivities (HPHE, plant rearrangement), and therefore may be lowered to 3,1€/kg. Economic hypothesis (maintenances, discount rates, availability, plant life) have a strong impact too.

A successful progressive methodology has been applied to study the liquid vapour equilibria of ternary HI-H2O-I2 mixtures. Optical analytical techniques (FTIR and UV visible) characterized the speciation of the vapour phase. Up to 2 bars and 130°C, an important set of liquid vapour equilibrium data gave [HI] contents in good agreement with literature on the left of the azeotrope (more on the right side), and enabled a more precise evaluation of the H2 produced purity: the specification [(I2+HI)/H2 < 10-5] is reached. Up to 50 bars and 270°C, the total and partial pressures measurements

conclusions were similar as low T and P experiments; but complementary data are still needed to carry out a reliable HIx new model, then an really updated flow-sheet based upon new fundamentals.

A membranes' database dedicated to HIx section enrichment in HI has been given. Flow-sheet modelling to identify the best process conditions showed that feed dewatering, then under low temperature and pressure conditions, is the most efficient: maximum 3% increase in efficiency obtained at a dewatering of 8.25%, the impact of the permeate side pressure has been given too. The stability of Nafion® 212 and 115 membranes in azeotropic HI solution has been shown. Flux and selectivity data have been obtained, in particular very high separation factors (Nafion®117, Nafion®212): between 0.5 and almost 1.35 Kg/h/m2. Flow testing using azeotropic and more dilute HI feed concentrations shows good correlation with results obtained using the batch selectivity rig. Initial experiments have shown that 0.22□m PVDF membranes can be used in an AGMD set up to dewater HI-H_2O solutions. For dilute feed streams the permeate is almost pure water, whereas for more concentrated feed streams, up to the azeotropic concentration, the permeate has approximately half the HI concentration of the feed. A membrane model has been created which is well behaved and predicts the flux trends seen in experiments.

A Raman scattering study has provided a self-consistent picture of the chemical nature of the HI_x phase of the sulphur iodine cycle, particularly in respect to the I_2-containing species present. Raman scattering measurements have been done on the two aqueous binary systems, I_2/H_2O and HI/H_2O, and on the ternary system, $HI/I_2/H_2O$, which are each closely related to HI_x, with an analysis of a wide range of previously published work on aqueous iodide-I_2 solutions and solid polyiodides. The nature of the I_2-containing species present in these systems is revealed by the behaviour of 5 principal component bands. CARS has proven to be a powerful technique to provide *in situ* data of total pressure in this harsh system, even if there is no HI present in the vapour phase and even when the iodine vapour turns the system into a deep purple cloud at higher temperatures.

Feasibility and successful test of solar H2SO4 splitting has been proved : conversion rates up to 90 %, at direct "solar" decomposition high temperatures (ca 1200°C maximum; 1000°C average), in a Pt coated SiSiC absorber. The reactor efficiency is up to 40%. Efficiencies dependent on several process parameters; trends show that the maximum values could rather been obtained at temperatures lower than 1000°C, due to re-radiation losses. Pure SiSiC is catalytic active, with a strong effect (up to the possible maximum achievable) even at 850°C, in a packed bed tube-type reactor (strongly dependent on pretreatment and surface characteristics). There is a fruitful interplay between experimental results and the CFD and FE thermostrucural simulations. The analysis of the potential for scale-up behavior and elaboration of safety concept have been given too. A FE tube-type reactor has been modeled (lower temperatures, 800 – 900°C); conversions up to 80% seem achievable, but there are important mechanical stresses and temperatures close to the upper limit acceptable. A Scale-up scenario based on a tower system with round field has been done (1200°C and 850 °C), performance and efficiency evaluated, based upon modeling results in combination with data from the SOLASYS project.

Similarly to what has been done on the S_I cycle, an overall analysis of the HyS cycle, based upon a reference flow-sheet used for the coupling to a solar source, and/or a VHTR, has been done. The major components' have been sized, and overall economics evaluated. The flow-sheets must be specifically adapted for each case (solar only, nuclear, hybrid); the total solar power installed are roughly 3 times the average value (Assouan / Egypt location). Operational strategies need to be defined (including calculation of time-dependent storages of SO2 and H2SO4), and it seems that a self-sustaining concept is not desirable for the pure nuclear coupling. For the solar only case, a 50 MWth (140 MWth installed) seems to be close to the optimal; tower heights of 230 m for 50 MW (470m for 300 MW) were found to be economically optimal. Solar components have been sized, and the costs evaluated; the major chemical cycle components have been sized similarly to the S_I cycle ones (except electrolyser), and the overall economics evaluations showed that the costs are in the range 3 - 6€/kg. For small plant sizes (50 MWth) solar only plants are advantageous, while for large scale production (more than 500 MWth) purely nuclear energy lead to the most economic results. In the range in between, hybrid plant have the lowest hydrogen production costs.