
Potential of hybridisation of the thermochemical hybrid-sulphur cycle for the production of hydrogen by using nuclear and solar energy in the same plant

Nathalie Monnerie, Mark Schmitz,
Martin Roeb*, Dominik Quantius,
Daniela Graf and Christian Sattler

German Aerospace Centre – DLR,
Institute of Technical Thermodynamics – Solar Research,
51147 Cologne, Germany
E-mail: monnerie@dlr.de
E-mail: mark.schmitz@dlr.de
E-mail: martin.roeb@dlr.de
E-mail: dominik.quantius@dlr.de
E-mail: daniela.graf@dlr.de
E-mail: christian.sattler@dlr.de
*Corresponding author

Daniel de Lorenzo

Empresarios Agrupados Internacional,
S.A., EA – Madrid, Spain
E-mail: ddm@empre.es

Abstract: The search for a sustainable, CO₂-free massive hydrogen production route is a strong need, if one takes into account the world-wide increasing energy demand, the deterioration of fossil fuel reserves and in particular the increasing CO₂ concentration leading to global warming.

Thermo-chemical cycles for water splitting are considered as a promising alternative of emission-free routes of massive hydrogen production – with potentially higher efficiencies and lower costs compared to alkaline electrolysis of water.

The hybrid-sulphur cycle was chosen as one of the most promising cycles from the ‘sulphur family’ of processes. Different process schemes using concentrated sunlight or nuclear generated heat or a combination of both have been elaborated and analysed by a comparative techno-economic study with regard to their potential of a large-scale hydrogen production. Options for a hybridisation of the energy supply between solar and nuclear have been also investigated, particular focused on the coupling of concentrated solar radiation into a round-the-clock operated process.

Process design and simulation, industrial scale-up assessments including safety analysis and cost evaluations were performed to analyse reliability and potential of those process concepts.

Keywords: thermochemical cycle; sulphur; hybrid sulphur cycle; solar; economics; sulphur-iodine cycle; sulphuric acid; process modelling.

Reference to this paper should be made as follows: Monnerie, N., Schmitz, M., Roeb, M., Quantius, D., Graf, D., de Lorenzo, D. and Sattler, C. (2011) 'Potential of hybridisation of the thermochemical hybrid-sulphur cycle for the production of hydrogen by using nuclear and solar energy in the same plant', *Int. J. Nuclear Hydrogen Production and Applications*, Vol. 2, No. 3, pp.178–201.

Biographical notes: Nathalie Monnerie received her Diploma in Chemical Engineering in Strasbourg in 1998. Since 1999, she has been active at the Solar Research Division in the Institute of Technical Thermodynamics at the German Aerospace Centre (DLR). She has been working within various projects on solar chemistry, in particular on the solar production of hydrogen. Her main tasks are process simulation, design and costs studies, literature and patent search, carrying out and evaluation of the experimental tests.

Mark Schmitz graduated as a Civil Engineer in 1999. He received his Doctoral degree (Mechanical Engineering) for his analyses of different solar collector systems at the DLR in 2005. After that, he worked on thermochemical cycles and solar desalination. Since the beginning of 2009, he has been the Head of Regenerative Systems at the Solar-Institut Juelich. His main research focus is now solar-thermal central receiver systems.

Martin Roeb holds a degree in Chemistry and received his Doctoral degree in Physical Chemistry at the University of Cologne 1997. Since 1998, he has been working as a Scientist at the DLR. He has been a Work Package Leader and responsible for several EU projects and a Project Coordinator of domestic research projects concerning high temperature solar processes. Since January 2008, he has been a Project Coordinator of the European Project Hycycles.

Dominik Quantius received his Diploma in Mechanical Engineering from the Technical University of Aachen in 2007. His thesis concerned solar-thermal hydrogen production and process design for the hybrid sulphur cycle. Now, he is a member of the Systems Analysis Department of the DLR Institute of Space Systems in Bremen. He is the Head of the Systems Analysis Group of Orbital Systems with focus on concept design, concurrent engineering and mission analysis.

Daniela Graf received her Diploma in Energy Engineering Management at the University of Applied and Science, Leipzig. Since 2005, she has been working at the DLR in the field of solar material conversion. More precisely, she is concerned with the technical and economic evaluation of solar-driven hydrogen production processes using thermochemical cycles.

Daniel de Lorenzo graduated as an Industrial Engineer in the Universidad Politécnica de Madrid. From 2002–2008, he worked in *Empresarios Agrupados* in the Mechanical Department for the management of detail-engineering of international nuclear projects under construction. He was also in charge of the project management of R&D projects for the 6th and 7th Framework Programme of the European Commission. Currently, he works for AREVA in Madrid as a Marketing Engineer, focused on the business development and nuclear market studies in Spain.

Christian Sattler graduated in Chemistry at the University of Bonn, Germany in 1993. In 1997, he received his Doctoral degree in the field of heterocyclic chemistry from the Faculty of Mathematics and Natural Sciences of the University of Bonn. Since 1997, he has worked with the DLR. Since 2002, he has been responsible for the solar materials conversion research area. Solar hydrogen production and solar chemistry are his main scientific interests.

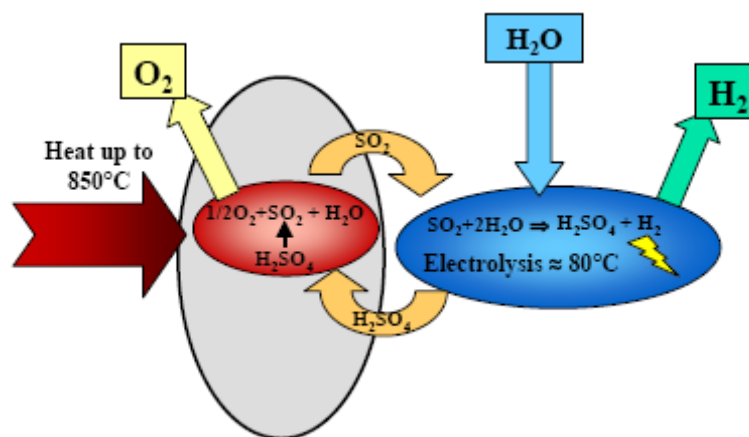
1 Introduction

Hydrogen is an environmentally attractive energy carrier with a long-term potential to replace fossil fuels in many applications. In particular this is true if the production of hydrogen is carried out with reduced, or even better completely without CO₂ emissions. However, currently more than 95% of the world hydrogen production is based on fossil fuels.

Only water and biomass are viable long term candidate raw materials for regenerative hydrogen production. Thermo-chemical cycles and electrolysis have the greatest likelihood of successful massive hydrogen production from water. In those processes, water is decomposed into hydrogen and oxygen via chemical reactions using intermediate reactions and elements which are recycled. Thus the sum of all the reactions is equivalent to the dissociation of the water molecule. These cycles have the potential of a better efficiency than the electrolysis because the heat can be used directly. Hence they have the potential to reduce the production costs of hydrogen from water significantly. The required energy can be either provided by a high temperature nuclear reactor (HTR) or by concentrated solar radiation, as well as by a hybrid system composed of solar and nuclear energy input.

Many thermo-chemical cycles have been studied in the 1970–1980s for massive hydrogen production. Two of them clearly emerged in the last comparative studies: the iodine-sulphur cycle (Schuster, 1977) and the hybrid-sulphur cycle (HyS), also called Westinghouse cycle (Brecher et al., 1976). Both include as a key step the thermal decomposition of sulphuric acid.

Figure 1 The HyS (Westinghouse) cycle (see online version for colours)



The HyS cycle is a process which combines a thermo-chemical and an electro-chemical reaction step to split water (Figure 1). The hybrid operation of the process offers the possibility to keep the cycle simple and to run low-temperature reactions on electricity. Sulphuric acid is thermally decomposed at 800 to 1,200°C. Catalysts are available for accelerating the rate of SO₃ reduction. The kinetic of this step is much faster if higher temperatures are available. The resulting sulphur dioxide is solved in water and then electrolysed, producing hydrogen and sulphuric acid, thus closing the cycle. Electrical power is required in the electrolyser, but the voltage and

therefore also power needed for the oxidation of SO_2 is significantly less than for the conventional electrolytic splitting of water. The HyS cycle has the potential for achieving high thermal efficiencies while using common and inexpensive chemicals.

Solar energy has demonstrated in many experiments its capability of reaching temperatures beyond the range necessary for the decomposition of sulphuric acid, i.e., up to $1,200^\circ\text{C}$, providing the potential advantage to improve the efficiency. Furthermore, Lüpfer and Funken (1996) showed that under the influence of concentrated solar radiation the reaction rate of SO_3 splitting increases compared to pure thermal reaction. Theoretically, water and electricity generated by concentrated solar radiation or by a nuclear reactor are the only consumables, and hydrogen and oxygen the only products.

When using heat produced by nuclear fission, the achievable temperatures will remain below 900°C in the years relevant to the scope of this paper. Catalysts will be necessary for achieving sufficient reaction rates for the reduction of SO_3 . The heat is coupled into the HyS cycle by means of heat exchangers, which typically serve simultaneously as splitting reactor.

The idea of hybridising the energy input from a nuclear and a solar heat source is to combine the advantages of both systems:

- solar splitting of sulphuric acid enables the use of less active catalysts, which may have a substantial influence on the hydrogen production cost – depending on its material and its deterioration. Thus, a hybrid system may reduce the catalyst costs down to zero
- nuclear energy has a high availability, as it does not exhibit fluctuations as solar energy does. This leads to less strain and better usage of plant components
- as electrolyzers suffer from being frequently turned on and off, a round-the-clock operation saves investment and replacement cost.

To evaluate and to improve the effective potential for massive hydrogen production of the hybrid sulphur thermo-chemical cycle within the European project HYTHEC (LeDuigou et al., 2007), different process schemes have been analysed using concentrated sunlight or nuclear generated heat or a combination of both by a comparative techno-economic study with regard to their potential of a large-scale hydrogen production. The calculation of heat balances and the component sizing are made for plants with an average annual thermal power of 50 MW and 300 MW at a suitable site.

2 State of the art

Some concepts of coupling solar energy to the HyS cycle have been introduced and discussed in the past. Knoche and Funk (1977) analysed efficiency and economics based on the flow-sheet from Farbman (1976). The H_2SO_4 decomposition was identified as the prevalent source of heat penalties. Later on Knoche also studied the solar decomposition of SO_3 (Knoche, 1989): concepts for decomposers and flow sheets adapted to the decomposer design were proposed.

Westinghouse itself carried out a study on a pre-design of a plant for a solar powered hydrogen production process (Lin and Flaherty, 1983). Solar dishes and parabolic troughs were proposed to produce the necessary heat input for sulphuric acid decomposition and

the electricity needed for the electrolysis of sulphurous acid. The SO_3 decomposer was based on a tube-and-shell design of a heat exchanger using SiC tubes on the chemical process side. As heat transfer fluid helium was proposed.

Bilgen et al. introduced a concept, flow-sheet and cost calculation for combining the so called Cristina process (Mertel et al., 1986) with a solar heat source giving the solar Cristina process (Bilgen and Bilgen, 1984; Bilgen et al., 1986; Bilgen, 1988). The principle is to heat a fluid in a solar receiver, either air or oxygen and to use it as a 'thermovector' meaning to transfer the heat to the reactants sulphuric acid or SO_3 by direct mixing. Challenge is the separation of huge amounts of oxygen or inert gas and the energy effort necessary to do this.

A screening analysis was performed to identify concentrating solar power (CSP) concepts that produce hydrogen with the highest efficiency. Several CSP concepts were identified that have the potential to be much more efficient than today's low-temperature electrolysis technology. They combine a central-receiver or dish with either a thermo-chemical cycle or high-temperature electrolyser that operates at temperature superior to 600°C . The solar to hydrogen efficiencies of the best central receiver concept exceed 20%, significantly better than the 14% value predicted for low temperature electrolysis (Kolb and Diver, 2008).

Kolb et al. (2007) have presented a study and process flow-sheets where the core part of the process is the usage of a particle receiver. This approach offers the chance to use particles like sand to absorb solar radiation and being at the same time the medium for thermal storage of solar energy, thus enabling a round-the-clock operation of the hydrogen production process. The development of receiver technology and of the necessary gas-solid heat exchanger is in an early stage.

Recently Schmitz et al. (2008) presented flow sheet, component sizing and techno-economic evaluations for the solar driven HyS with an annual average thermal power of $50 \text{ MW}_{\text{th}}$ located in the region close to Lake Nasser in Egypt. The analysis of one case applying a receiver-reactor for the H_2SO_4 splitting operated at $1,200^\circ\text{C}$ was shown.

The present analysis will pick up the assumption of this paper and will use this to compare different technologies, to analyse in particular the potential of a hybrid nuclear-solar operation of a HyS process and to evaluate potential production costs.

3 Methodology

Several tools are used for simulation, component sizing and cost evaluation. For the heliostat field layout, the simulation tool HFLCAL is used (Kiera, 1986). The calculations of the chemical part of the process were performed with Aspen Plus (2004).

For the component sizing, shell and tube heat exchangers have been sized by using the log mean temperature difference (LMTD) method.

Specific excel tools have been created as an interface between solar field simulation and process simulation. Another excel spreadsheet links the process simulation and the economic calculation.

The methodology used for cost accounting is described in Section 6.

4 Analysis of a solar plant as a reference

4.1 Basic considerations

The only sizeable solar technologies capable of providing process heat at temperatures above 800°C are solar central receiver systems or better known as solar tower systems. This part of the hydrogen production plant is responsible for the collection and concentration of solar radiation.

Thus solar powered HyS plants consist of a collector field, a tower supporting the receiver reactor and the chemical engineering part meaning the components necessary to operate the hybrid sulphur cycle itself. Two plant capacities have been sized and economically evaluated. They deliver an annual average 50 MW and 300 MW of thermal power into the receiver reactor. Due to the daily and seasonal cycle of the irradiation, the peak power is much higher.

The performance of solar energy plants strongly depends on the site where they are constructed and the corresponding insolation conditions. A good location offers a high average direct normal irradiation (DNI), sufficient access to fresh water (the sole consumable good of such a plant) and an infrastructure that allows efficient transport of the produced hydrogen. The region close to Lake Nasser in Egypt fulfils all of the criteria above. Not only solar conditions but also the energy policy of Egypt makes it a preferable site for such a solar application since the country supports the objective of the concentrated solar power (CSP) global market initiative (GMI) to facilitate and expedite the building of 5,000 MWe of CSP worldwide over the next ten years. In addition, a (global environment facility) GEF-funded CSP project with investments of about US\$160–200 million, is currently in the bidding phase.

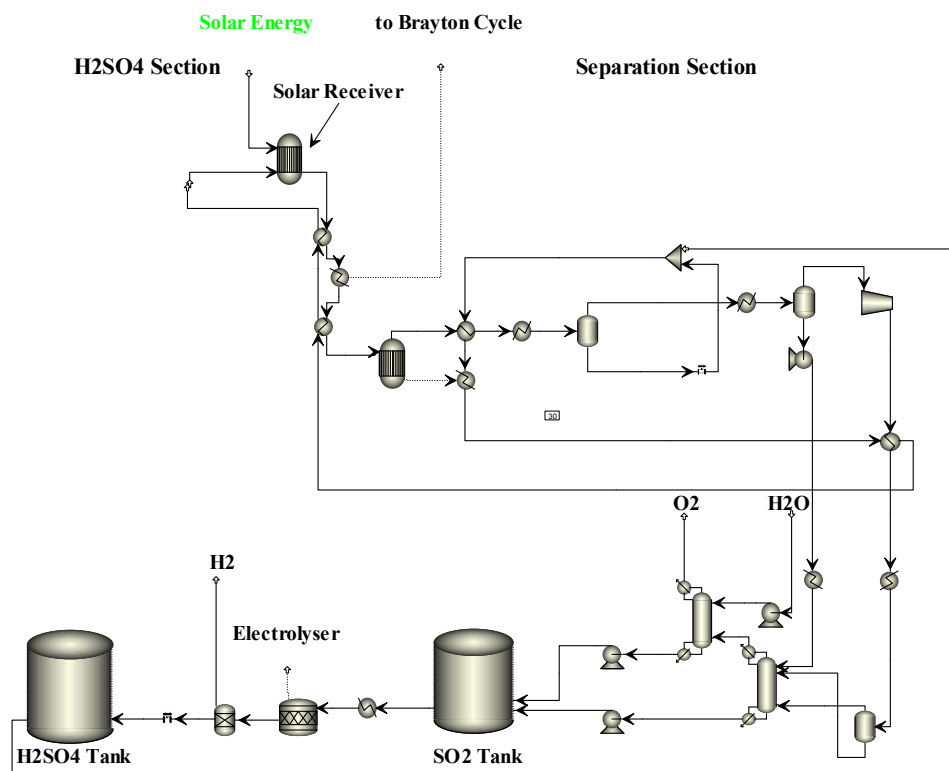
A power generation system is necessary to deliver the energy for the heliostat field, the pumps and compressors and the electrolysis, thus achieving an advantageous self-sustainability of the plant. Two possibilities of generating electricity within the plant were compared. The so-called integrated power concept used the off-heat of the product gas stream to drive the thermo-electric conversion system. A low concentration of sulphuric acid had to be chosen, so that the heat capacity of the additional water could be used as well. The second, the so-called separate power concept featured a receiver distinct from the receiver reactor. This system showed a superior efficiency and led to significantly lower hydrogen production costs (HPC).

4.2 Operation

The study includes as a first and central step the elaboration and optimisation of flow-sheets of the plants, resulting in the one presented in Figure 2. The calculations of mass and heat balances have been carried out by using this optimised flow sheet and are the basis for the component sizing and the cost estimation.

The chemical process can be divided into three major sections: the electrolyser, the acid decomposition, and the separation system. The power required for the electrolyser section is provided by a thermo-electrical cycle. For that purpose, a heat transfer fluid is used, which is heated in a solar receiver in another section of the solar tower coupled to a closed Brayton-cycle.

Figure 2 Flow sheet for the case of a 50 MW solar-only powered plant (see online version for colours)

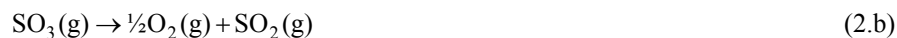


The first reactor is the electrolyser in which water and SO_2 react to produce H_2SO_4 and hydrogen. At the anode SO_2 is oxidised to H_2SO_4 , while H_2 is evolved at the cathode. The maximal concentration of H_2SO_4 at the exit of the electrolyser equals 50% (weight-%). A part of the produced H_2SO_4 is recycled to have a minimum concentration of H_2SO_4 equal to 35% at the entrance of the electrolyser. This is necessary to minimise the gradients of concentration of H_2SO_4 in the electrolyser between the input and the output. The electrolysis takes place at 5.7 bars and 90°C requiring 120 kWe for the production of 1 mol H_2 per second.

After exiting the electrolytic part the H_2SO_4 is heated up, vaporised and decomposed into H_2O and SO_3 in the receiver-reactor operating at ambient pressure. It is heated by concentrated solar radiation. The splitting reaction almost achieves equilibrium conversion. SO_3 is reduced into SO_2 and O_2 . The latter is available as a process by-product. The produced H_2O is reused in the electrolyser.

Reaction equation:





The last section is the separation of SO_2 and O_2 . First of all the gaseous flux coming from the reactor receiver is cooled down to 200°C at one bar in order to recombine the small amount of unconverted SO_3 in H_2SO_4 . Then O_2 is separated by a series of compression and cooling steps up to 25 bars and 25°C and SO_2 can be fed as aqueous solution into the electrolyser again.

4.3 Component sizing

4.3.1 Solar collector

The decomposition of H_2SO_4 is powered by concentrated solar energy of a central receiver system (CRS). The CRS consists of sun-tracking mirrors (so-called heliostats), which concentrate the solar radiation onto a target area at the top of a tower, where it is absorbed by a receiver-reactor. Time design point is June, 21st, noon. Moreover the solar power plant provides the electricity required for the electrolysis through a thermo-electrical cycle. The efficiency of transforming solar heat into electricity is assumed to equal 41% according to Pitz-Paal et al. (2005).

For the 50 MW plant the heliostat field is dimensioned in a way that the nominal receiver power of $140 \text{ MW}_{\text{th}}$ is reached at least 10% of all hours in a year. This gives a theoretical maximum power of 170 MW. The annual production of SO_2 is 70,542 t. This yields 2,200 t of hydrogen per year. The resulting annual efficiency (solar energy to higher heating value of hydrogen) is 19.8%.

The resulting heliostat field has 2,627 heliostats each with a reflective surface of 121.34 m^2 . The plant covers a roughly circular area of 1.2 km diameter, which equals about 1.1 km^2 . The annual average solar efficiency η_s is defined as the net thermal power P_{th} (i.e., including its thermal and optical losses) that can be used for heating the fluids in the receiver and for the chemical reaction divided by the theoretical maximum of solar radiation impinging on the mirror surfaces (A_{mirror}):

$$\eta_s = \frac{\int_{t=0}^{\text{TMY}} P_{\text{th}}(t) \cdot dt}{A_{\text{mirrors}} \cdot \int_{t=0}^{\text{TMY}} \text{DNI}(t) \cdot dt}.$$

The resulting value is calculated to be 42.6%.

For the '300 MW' plant the design led to an annual average thermal power of $300 \text{ MW}_{\text{th}}$, equivalent to a peak power of $840 \text{ MW}_{\text{th}}$. Due to non-advantageous part-load efficiencies in the power cycle it was decided to oversize the heliostat field in this scenario to reach the nominal peak power more frequently. The resulting heliostat field comprises 15,760 heliostats with a reflective surface of 121.34 m^2 each and covers a ground area of 5 km^2 . The free area around the tower base is sufficiently large for the installation of the HyS cycle components. The annual production of SO_2 is 386,000 t. This yields 12,000 t of hydrogen per year. The resulting solar efficiency η_s is 42.4% and the annual efficiency (solar energy to HHV of hydrogen) is 18.5%.

The solar tower is assumed to consist of a reinforced concrete tube, which could also serve as housing for certain components of the chemical part of the plant, especially those

operating at high temperatures, where the transport of the corresponding fluids would lead to substantial thermal losses.

For this study we assume that only the high temperature parts of the plant are installed on the tower top, i.e., the receiver reactor, the following heat exchanger, and the gas turbine. The temperatures in the other parts are low enough to assume low thermal losses even for a transport all the way to ground level. Chemical reactors on top of solar towers have already been demonstrated, e.g., a methane reformer at the Weizmann Institute of Science in Israel developed and test operated in the Solasys project (Solasys, 2002), where a solar driven gas turbine is used (Sugarmen et al., 2002).

The receiver reactor has primarily the purpose of converting the solar radiation into heat used for the generation of SO_2 at $1,200^\circ\text{C}$. The materials that can withstand such temperatures and the corrosive attacks were found in experiments in DLR's solar furnace (Roeb et al., 2008). Silicon infiltrated silicon carbide (SiSiC) performed well. A scaled-up receiver will use the same materials.

The receiver aperture is cylindrical, i.e., it is set into the circular wall of the tower top. The diameters were assumed to be 11.6 m (50 MW case) and 28 m (300 MW case), the corresponding heights are 12 m and 30 m, respectively.

4.3.2 *Chemical section of the plant*

Preliminary sizing of the main components has been done. For the high temperature heat exchangers, tubes are made of Incoloy, whilst for the other components, tubes are made of SiC. For the shell of heat exchangers, carbon steel material with internal cover of acid brick liner is adopted.

The flow sheets have been subject to constant change driven by the aim to improve the cycle efficiency. In Figure 2 an Aspen flow sheet is shown that was used for the component sizing of the $1,200^\circ\text{C}$ solar case.

For the high temperature heat exchangers (HX1) tubes are made of Incoloy, whilst, for the other components tubes are made of SiC. Following the approach adopted for the S-I plant, for the shell of heat exchangers carbon steel material with internal cover of acid brick liner (ABL) is adopted.

The 'cold utility' to remove the needed heat amount in C1, C2 and C3 heat exchangers is assumed to be water.

The distillation columns for the separation of O_2 from SO_2 and H_2O in the product gas stream have been sized by the Fair relationship (Stichlmair and Fair, 1998) for the flooding velocity factor.

The product tank is used to store the SO_2 that is produced but not directly electrolysed. It is also planned to use the tank to compensate for seasonal differences of available solar irradiation and allowing an optimised operation of the electrolyser over the year. In the 50 MW case the tank has to have a capacity 3,420 t. The solubility is about 50 g/l (at about 50°C , according to the flow sheet calculations). This gives a maximum tank volume of $68,000 \text{ m}^3$. For 300 MW the corresponding values are: 12,200 t SO_2 and $240,000 \text{ m}^3$ of solution.

The purpose of the H_2SO_4 tank is to have a reservoir of educts for the intermittently operating receiver reactor. Its filling corresponds inversely to that of the product tank, i.e., it is full, when the product tank is empty and vice versa. The maximum capacities for this H_2SO_4 tank are for the 50 MW case 5,200 t ($7,800 \text{ m}^3$) and ca. 18,800 t ($28,000 \text{ m}^3$)

for the 300 MW case. The peak productions of the 50 and 300 MW plant correspond to 612 and 8,100 kgH₂/h respectively.

5 Analysis of solar-nuclear hybrid cases

5.1 General design consideration

The hybrid operation of the HyS cycle in the sense of using at the same time solar and nuclear energy sources is very interesting from the point of view of finding the best way to incorporate synergies between both energy sources.

Solar energy systems are a reliable, mature technology, able to reach very high temperatures by applying a field of solar-tracking heliostats and central tower receiver. Unfortunately, it presents some disadvantages like inherent discontinuities (night time periods and adverse climate conditions), large fields are necessary to reach high power levels.

On the nuclear field, although low-temperature nuclear technology is very much developed, high-temperature nuclear technology is still in an early stage of development and a limited number of plants have been operated in the last decades. Although important experiences have been obtained, the future reactors are still in an early stage of development which is likely to reach to commercial deployment in the medium term. The advantages of this technology are that it reaches high power levels (from 400 MW_{th} on), and the safety systems applied to a nuclear installation always surpass the safety levels of any other facilities because of more restraining design codes, which assures a very high reliable performance of the plant. This last fact leads to availability factors above 90% per year, operating most of this time at 100% of power capacity. A highly efficient electricity generation is available with high temperature reactors (>40%). Disadvantages are also present in this kind of facility, first of all the radioactive waste materials, the management and final disposition (or transmutation) of which are currently already assessed, but continue to be developed for a more secure handling and storage, avoiding the proliferation of radioactive material and enhancing the plant security. Another disadvantage is the difficulty to reach the levels of temperature necessary to run the HyS cycle: the current nuclear plant designs are foreseen to be in the range of 850°-950°C at the outlet of the nuclear reactor, which is at the borderline, but just suitable for catalytic operation of the SO₃ into SO₂ step.

Taking into account the above, it is clear that a link between both solar and nuclear technologies would be beneficial in order to try to compensate the areas where each technology faces challenges.

Hybrid solutions have been analysed with regard to their technical and economical feasibility. There are numerous possibilities to combine the two types of energy to form a hybrid powered design case of the hybrid sulphur process. Different operation and plant concepts have been generated including the solar and nuclear supply of heat for the thermo-chemical step and of solar and nuclear power for the electrolysis step. To select the most promising cases, a catalogue of criteria was defined. The studied flow-sheets were selected regarding the technical feasibility, the feasibility of a constructive interaction of nuclear and solar energy supply, the connection between the solar and the nuclear heat circuit, the operation time and temperature, safety aspects, and finally the expected plant efficiency and economics.

The characteristics, composition, temperature, pressure, energy balance, of each stream and unit operation of the flow sheet have been calculated. The hybrid powered process presented here is running with two H_2SO_4 splitting units: one is powered by solar energy and the other by nuclear energy. The required absolutely constant and undisturbed operation on the nuclear side of the process can only be ensured by widely separating process units depending on intermittent solar supply from the part powered by nuclear heat. There is only one electrolyser unit which is powered constantly with nuclear electricity. The solar thermal splitting process is carried out at 850°C to allow the hybridisation with nuclear heat. SO_2 and H_2SO_4 storages are applied to ensure a constant supply to the electrolyser unit and thereby to ensure a constant production of hydrogen. The calculations are made for an average annual thermal power of 50 MW.

5.1.1 System integration

The system integration is made by having two different areas, one solar-heated and another nuclear-heated, in which the steps of H_2SO_4 concentration and decomposition, and SO_3 splitting into SO_2 are performed. Then the mass-flows of both areas are mixed and reach the temporary storage of SO_2 . Afterwards, this SO_2 mixed with water passes through the electrolyser resulting in a H_2 yield and H_2SO_4 formation. Both species are separated and stored, the H_2 to be transported to a massive storage or to the H_2 distribution network (pipeline pumping station for example), and the H_2SO_4 to enter the cycle again.

These two last steps are made using both flows, coming from nuclear and solar sources, because of several reasons: the low temperature level, the independence from the heat sources, the possible modularisation of the electrolyser and the high storage capacity of the intermediate tanks that would allow performances even in the event of one or both energy sources being inoperative.

5.1.2 Energetic and electric requirements

The thermal and electric requirements are dependant on the mixtures' mass flows running in each of the system areas. The installation is dimensioned for a predetermined level of power, in this case $140 \text{ MW}_{\text{th}}$ for the solar part and $50 \text{ MW}_{\text{th}}$ for the nuclear part. The electricity demand of the electrolyser and the pumps and compressors shall be provided by a nuclear powered energy conversion system such as a helium cooled Brayton cycle. In case of its failure, the electricity must be taken from the electric grid.

The internal heat demands have been optimised so that the higher internal energy can be recovered and used in other parts of the system. Although this seems to be a clear advantage, and in fact it is beneficial in terms of efficiency, it is delicate to operate a cycle using regeneration of thermal losses into the system again. This last statement is supported by the fact that a problem in one component of the system might modify the conditions and equilibriums of the mixture flow, having unpredicted consequences on the characteristics of the flow in other parts of the system in a 'domino effect'. An example of a chain of subsequent failures might be: the malfunctioning of a heat exchanger in charge of heating the flow might lead to different equilibriums in flash tanks, which in turn could be followed by a different separation ratio of vapour and liquid phases, thus the flow through pumps and compressors could be different damaging them or corroding other components such as pipes or valves due to changes in the mixture composition.

After this sequence of unpredicted malfunctioning the outcome could be from several component damaged to a massive plant failure with possible releases of toxic products into the environment.

The size of the plant and its distance to the energy sources must be taken into account. The small size of the nuclear plant might not be the optimum because there would be a remarkable heat and temperature loss in the pipe that provides the energy from the nuclear reactor. It is not to be forgotten that the separation between each of the plants – solar heliostat field, nuclear facilities and chemical plant – might present difficulties in transferring the fluids from one to another.

5.1.3 Nuclear energy input

The nuclear reactor chosen for the coupling is a VHTR type. It belongs to the new GEN IV type of innovative nuclear reactors. Among these reactors, VHTR is the only one that can achieve coolant temperatures as high as the HyS cycle demands for the SO_3 decomposition ($>850^\circ\text{C}$).

VHTR is a gas-cooled reactor, using helium as coolant. Helium presents very favourable thermodynamic properties that enable it to be used in this kind of plants, especially its thermal capacity, which is 2.7 times higher than that of water. Unfortunately, it involves some disadvantages too: low specific volume which leads to big turbines, problems to control inventory due to its diffusivity and ease of gas leaks by the small molecule size.

The reactor operates between a temperature of 400°C at the inlet nozzle and the outlet temperature of 950°C while the pressure is 5.5 MPa. The reactor power is $600 \text{ MW}_{\text{th}}$ and the helium mass flow is 209.95 kg/s . The rest of the helium primary loop is composed of the intermediate heat exchanger (IHX) that exchanges heat with the secondary circuit and the primary compressor that compensates the pressure losses in the inlet nozzle of the reactor. The IHX transfers $614 \text{ MW}_{\text{th}}$, and therefore the consumption of the primary compressor is 14 MWe.

In the IHX the helium of the primary circuit transfers the heat to the helium from the secondary circuit making it rise its temperature from 350°C to 890°C at a pressure of 5 MPa. This secondary circuit helium then enters the HyS heat exchangers producing the chemical reactions necessary for H_2SO_4 evaporation, splitting into SO_3 and subsequent conversion of SO_3 into SO_2 .

The temperature of the secondary circuit helium at the outlet of the HyS cycle is high enough to be used for the power conversion unit. This way, the HyS cycle and the power plant are operated in series. The secondary circuit is composed of the IHX through which the circulating helium is heated up to 890°C . Then the helium flows through the HyS cycle heat exchangers (similar to those of the H_2SO_4 section in the SI cycle), coming out at a temperature of 677°C . In this case and due to the relatively high temperature of the helium, the power plant is connected in series to the chemical plant, thus avoiding the use of the cooler and achieving a higher efficiency. At the outlet of the recuperator the helium has a temperature of 350°C and returns to the IHX.

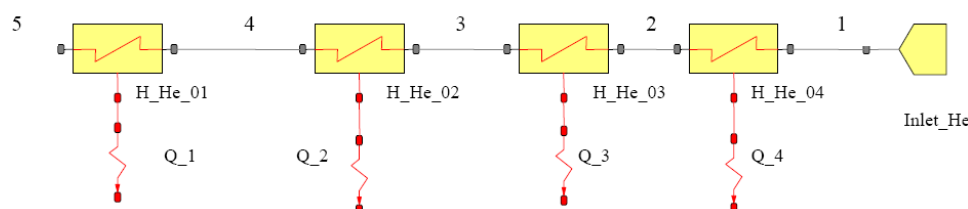
The power plant scheme selected for the coupling is a Brayton power cycle. The circulating fluid is the helium that comes from the HyS plant at high temperature and high pressure. The power train is composed of two turbo-compressors, an electricity generating turbine, a precooler, an intercooler and a recuperator. It is in charge of allowing a self-sustaining concept by delivering as much electricity as the HyS cycle

requires. In this case, the primary compressor is considered inside the self-sustaining concept, as it belongs to the nuclear plant and, as it is a safety related component, the energy should be delivered directly from the network. In case of accident or blackout; the compressor shall be equipped with emergency diesel engines in order to ensure the energy supply.

The process to prove the feasibility is composed of HyS cycle flow sheeting and modelling of both nuclear and chemical plants using EcosimPro (2008).

The heat required for the HyS cycle is supplied by the circulating helium from the IHX via four heat exchangers shown in Figure 3: H_He_01, 02, 03 and 04, which supply heat to the H_2SO_4 evaporator, to the reactor for H_2SO_4 decomposition, to a pre-heater, and to the reactor for SO_3 decomposition.

Figure 3 HyS heat exchangers (see online version for colours)



5.2 Schematic layouts of hybridised HyS plants

The HyS cycle offers various possibilities of combining solar and nuclear energy input. The following diagrams depict two of the apparently most reliable of these combinations. After an initial comparative screening of the various different schemes only the reference case and the most promising hybridisation scheme were picked up for the subsequent thorough analysis.

The 'reference case' (Figure 4) is the trivial case of hybridisation: The energy for all process steps using thermal energy, mainly the vaporisation and splitting of sulphuric acid, is delivered by solar, whereas all consumers of electricity, mainly the electrolysis, are driven by a nuclear power plant associated with the HyS plant. Doing so the electrolysis can be run continuously, whilst the sun provides the high-temperature heat for the splitting process. The analysis of this reference case is rather straight-forward. By adopting the results from the solar-only powered cycle including solar part of the plant and the chemical part and by adding the necessary nuclear equipment for the power generation it is possible to size the components and calculate installation cost and hydrogen production costs (see Section 6).

In a second case (so-called Case 2a, Figure 5) 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' SO_2 . This way each technology is well used, but there is a considerable degree of redundancy regarding the plant components. This redundancy appears necessary to match the safety requirements of the nuclear reactor powering the cycle. This Case 2a is exemplarily analysed in detail in the following section.

Figure 4 Scheme of the ‘reference case’ of the hybridisation of the HyS cycle (see online version for colours)

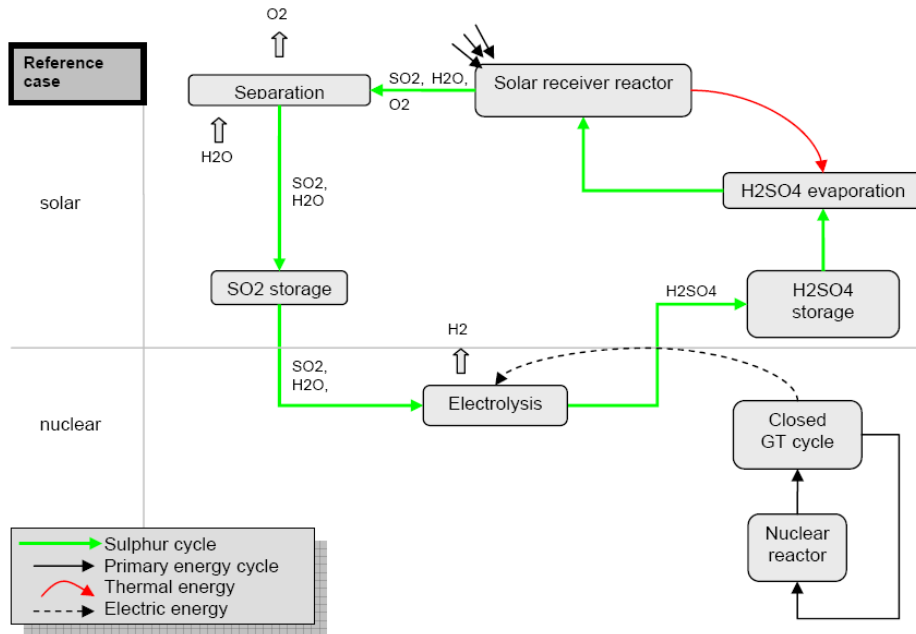
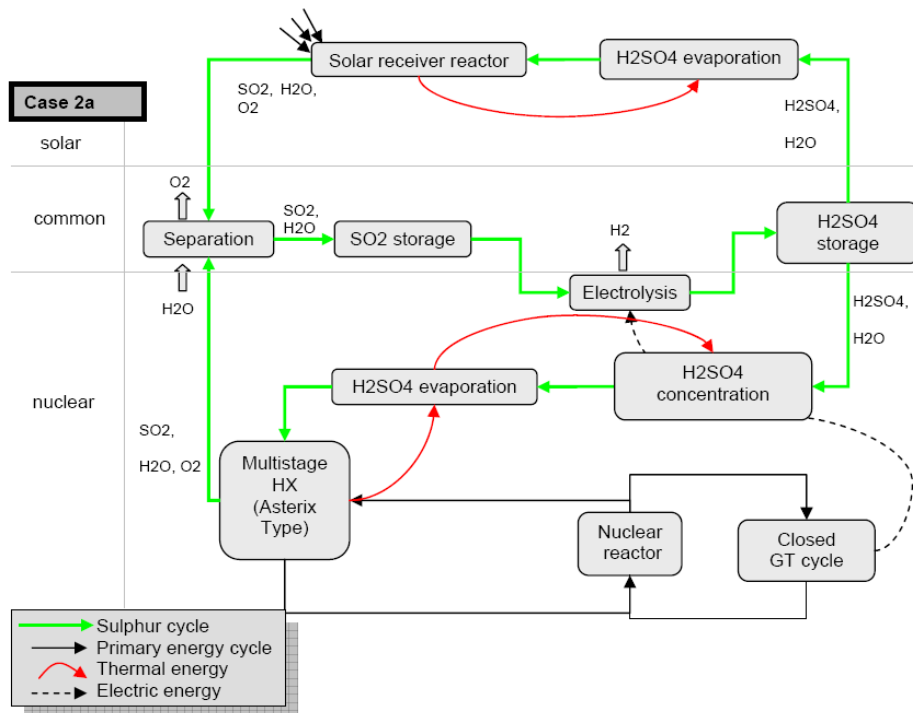


Figure 5 Scheme of ‘Case 2a’ of the hybridisation of the HyS cycle (see online version for colours)



5.3 Analysis of the Case 2a

For the solar part of Case 2a the flow sheet of the solar-only plant with separate receivers for splitting and power generation, is adopted. That means that the design power level is $140 \text{ MW}_{\text{th}}$, in order to reach an annual average of $50 \text{ MW}_{\text{th}}$.

The nuclear process flow sheet is also adapted from the solar flow sheet mentioned before. As the temperature that can be reached is only 850°C two parts of the plant have to be altered: the splitting reactor only achieves reasonable yields of SO_2 , when catalysts such as platinum are applied. This was modelled by assuming that the splitting reaction reaches the thermodynamic equilibrium. A concentration unit for the sulphuric acid seems advisable from literature, e.g., Farbman (1979). This is accomplished by a specific distillation scheme. For the integration of the concentration of sulphuric acid the flow sheet of the nuclear part was rearranged as to make the best use of the heat of the product gas stream, which has to be cooled.

5.3.1 Overall process flow sheet

In the process flow sheet of the hybrid plant all the equipment is brought together. For better readability it is represented in three figures (Figures 6, 7, 8). One part of the flow sheet is taken up by HyS components associated with the nuclear plant (Figure 7); another part by the solar associated equipment (Figure 6). The third part includes the units which are common to both energy sources, which are the O_2/SO_2 separation, the electrolysis and the tanks.

As only the nuclear part requires concentration of the sulphuric acid, also the subsequent evaporation takes place in separate components.

The product gas of the splitting is combined into one flow, and supplied to the SO_3 recombination (' $\text{SO}_3\text{-REAC}$ '). The available product stream is divided for heat transfer according to the two components into a nuclear and a solar flow. The sulphuric acid portion is separated from both flows with a part of water.

In order to make off-heat available for the solar part, the gas flow containing SO_2 , O_2 and steam is divided again into two flows. The liquid fraction is introduced to the gas scrubber for the separation of SO_2 and O_2 (' O_2SEP '). The gaseous fraction is compressed to a pressure of 3.1 bars. In a further compressor the two flows are brought to a pressure of 7.8 bars. Then the gas stream is introduced into the gas washer column. In addition the water from the H_2SO_4 concentration of the nuclear part the flow is used for the washing process. With additional water the SO_2 is completely solved and the O_2 is separated at the upper column end. The SO_2 in solution (H_2SO_4) withdrawing down will reduced to a pressure of one bar, in order to be stored in the tank ' SO_2TNK '. In the electrolyser hydrogen is produced at a temperature of 90°C . 90% of the output flow containing H_2SO_4 is re-circulated, while the remaining 10% is expanded to one bar and fed into the sulphuric acid tank. Hence 50 weight-% H_2SO_4 is taken again. From the closed gas turbine cycle a power of $47.82 \text{ MW}_{\text{th}}$ is transmitted from the nuclear reactor in the heat-exchanger ' REACTORB ' by means of a helium cycle.

Figure 6 Flow sheet of the solar part of the hybrid plant according to Case 2a (see online version for colours)

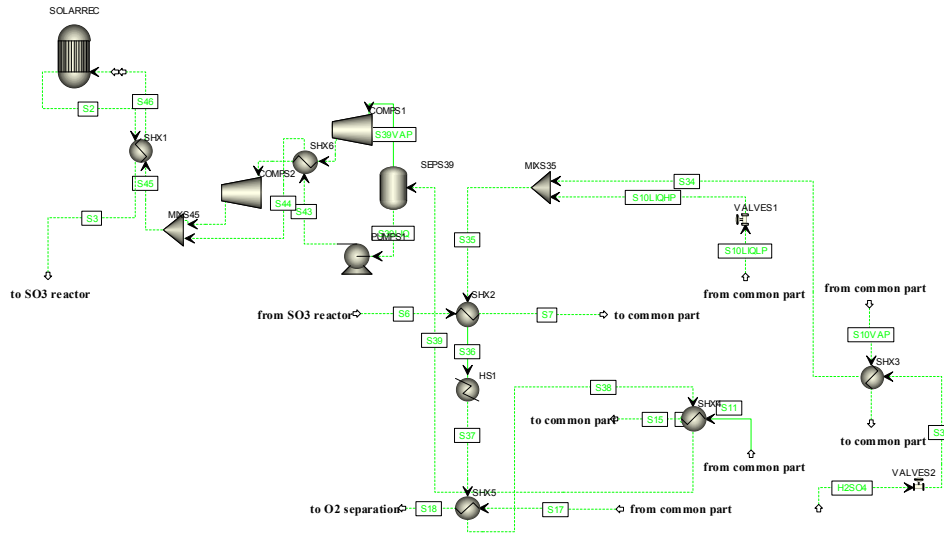


Figure 7 Flow sheet of the nuclear part of the hybrid plant according to Case 2a (see online version for colours)

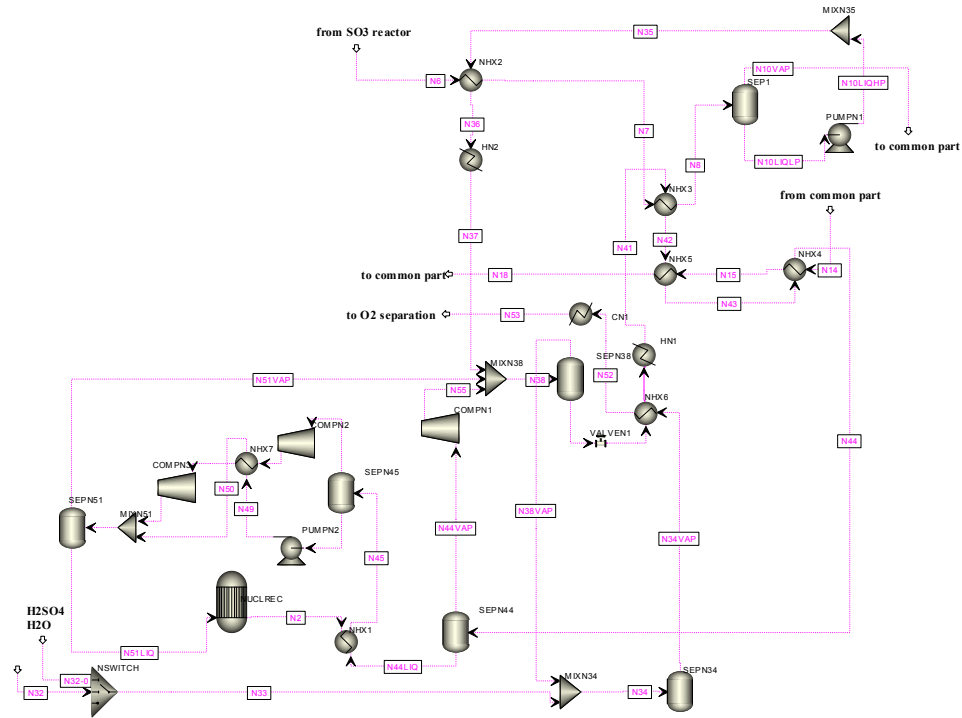
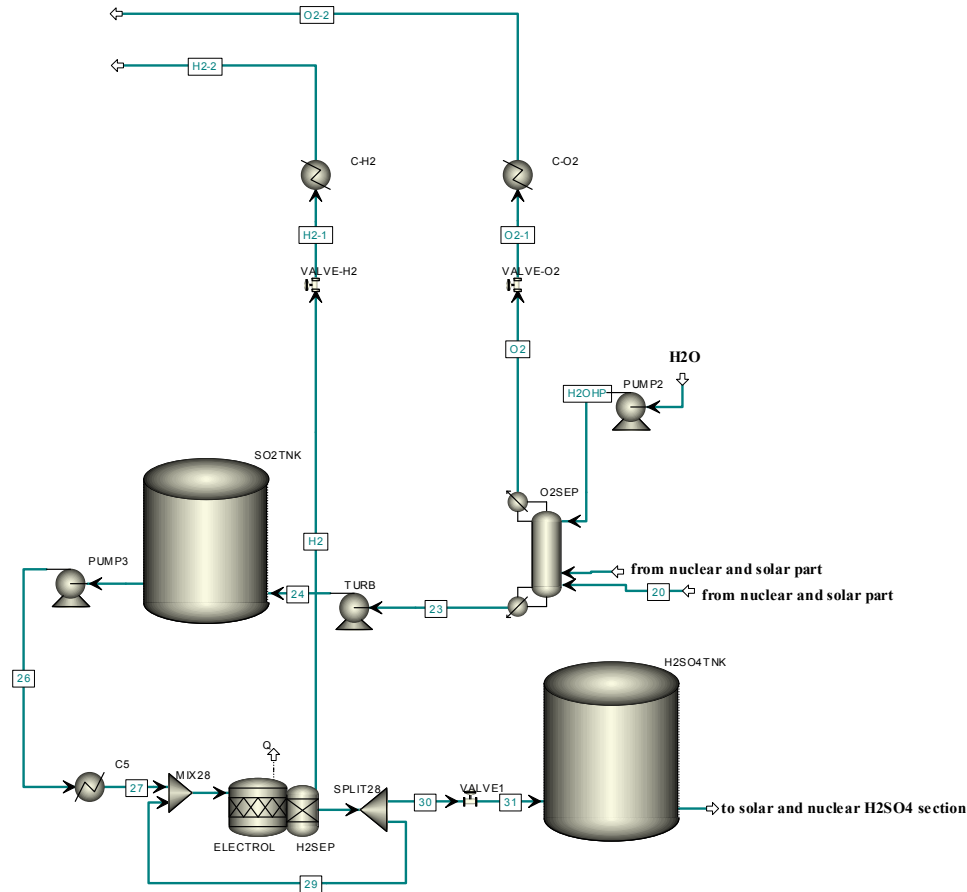


Figure 8 Flow sheet of the interfacing part of Case 2a (see online version for colours)

All mass flows associated with the nuclear heat source are kept constant by changing the mass fractions at stream splitters.

One of the challenges that this kind of hybrid plant faces is the sizing of the components, especially from the point of view of the discontinuity on the operation. This discontinuity means that there is a fluctuation/modification in the characteristics of the flow and/or in the amount of mass-flow. Either with a flow reduction when the solar part is not running, as well as due to modifications in the mixtures' composition due to transient events (start-up and shutdown for example), the size of the components must be such that it can accommodate this kind of modification.

For the above reasons, the sizing of the components is determined by the amount of flow and energy exchange they are submitted to. In this case it would be reasonable to separate as much as possible the solar-heated part from the nuclear-heated part because it would be easier for the control of components. Unfortunately this would lead to duplication in the number of components of the plant (pumps, compressors, heat exchangers, control devices, emergency actuators, etc... and their redundancies), and thus increasing the plant cost. If this separation is done as much as possible, the current calculations shall be revised so as to check whether both systems are able to sustain each

thermal exchange with the heat fluxes calculated so far, and, in case this condition is not fulfilled, a new configuration shall be arranged.

5.3.2 Annual hydrogen production

- 50 MW_{th} plant: in the present configuration the hybrid operated cycle produces 7,434 t/a (848.6 kg/h) of hydrogen and 59,000 t/a (6,735.3 kg/h) oxygen with a total power of 100 MW_{th}. The energy (HHV) stored in hydrogen represents 33.7 MW (i.e., thermal-to-chemical efficiency is 33.7%). The SO₂ production is subject to daily and seasonal fluctuations in the solar part. Therefore the mass flows and the required electric power vary, depending on the power of the solar receiver. Missing electricity must come from the grid, while a surplus is fed into it. At the end of the year the balance of the energy transfer is equalised. The electrolysis unit is supplied constantly with 14.76 MWe of power.
- 300 MW_{th} plant: similarly a larger, hybrid operated plant for hydrogen production was designed. The nuclear reactor was assumed to deliver 300 MW_{th}. At the same time, the solar receiver was assumed to convert with a larger heliostat field an annual average of 290 MW. Under these conditions sulphuric acid can be split with a power of 18.3 MW_{th} in the nuclear heat-exchanger reactor, while the gas turbine cycle is operated to generate electricity with the remaining nuclear heat of 281.7 MW. Thus 45,314 t (5,173 kg/h) of hydrogen and 360,684 t (41,174 kg/h) of oxygen are produced with an annual average power of 590 MW_{th} from 405,921 t (46,338 kg/h) of water. The energy stored in hydrogen represents 205.4 MW (34.8% thermal-to-chemical efficiency).

6 Cost accounting

The hydrogen production costs (HPC) are calculated using the annuity method. They are composed of annual costs for the interest on the investment and of the continuous costs for operation and maintenance (O&M). We assume an interest rate of 6% and a plant life of 20 years, resulting into an annuity factor of 8.72%. The total capital investment (TCI) includes the investment for all installations, piping, and buildings plus the indirect investments, such as land, the sulphuric acid and a safety surcharge, which accounts for uncertainties connected with the investment cost assumptions (TCI).

Unit cost data are taken from Schmitz et al. (2006). The receiver size is based on an assumed average flux density of 0.800 MW/m² at design point. This yields a surface area of:

$$\text{Area (c)}_{50 \text{ MW}} = 140 / 0.800 = 175 \text{ m}^2$$

$$\text{Area (c)}_{300 \text{ MW}} = 840 / 0.800 = 1,050 \text{ m}^2.$$

The cost for the solar tower were calculated according to the empirical equation:

$$\text{Cost (Tower _ installed)} = 410 \text{ k€} \exp^{(0.011 \frac{\text{h}}{\text{T}})}$$

The investment costs used in the analysis are representative for a process heat (PH) HTGR providing heat to a central thermo-chemical process. Those are adapted from EPRI (2003) and normalised to the necessary power level by the following equations:

$$P_c = P_r \left(\frac{sz_c}{sz_r} \right)^{0.6}$$

To perform cost accounting of the HyS components, the factor method was adopted. Thus, in this section, two costs (for all the components) are reported: The FOB cost refers to the free on board cost of the component, getting the selling price, without all the installation, taxes, etc.

The installed cost refers to the 'bare' installed components, taking some adjunctive costs (such as piping, concrete, instrumentations, labours and so on) into account.

The investment costs take into account the demanding conditions, i.e., high temperatures and corrosivity. Costs for piping are defined with 1% of the component investment. All components are housed in a light metal construction or similar for the protection of sand, wind and sun, at a unit price of 1,000 €/m².

Due to the fact that H₂SO₄ has to be filled at the beginning of plant operation, this amount of acid has to be provided for start-up, the costs of 300 €/t are also considered as investment.

A safety surcharge of 10% of the total direct investment was added, in case of unexpected investments and contingencies in the construction. Sensors and other means for safe plant operation are also included.

The operation costs (OC) reflect fixed and variable costs per year, add for the whole period of consideration. Beside hydrogen, in all considered processes the by-product oxygen is produced whose revenue (RO2) is set off against the OC.

Further assumptions are the following:

- employers costs 48 k€/a
- the costs for insurance and maintenance are defined to be 2% and 4% of the TCI respectively
- water costs: 1.09 €/Nm³
- oxygen can be sold for 0.15 € per standard cubic metre.

Investment (TCI) and annual operational costs (O&M) as well as the revenue from the sale of oxygen (RO2) are considered within a present value (PV). O&M and RO2 are assumed to be constant over the entire time wherefore the PV reflects the cost which incurred during the whole plant lifetime (np).

$$PV = TCI + \sum_{n=1}^{n_p} \frac{(O \& M)_n - R_{o2_n}}{(1 + i_r)^n}$$

Then the PV is put on an evenly annual base by multiplication with the annuity factor (AF).

$$AF = (1 + i_r)^n \frac{i_r}{(1 + i_r)^n - 1}$$

Finally, the HPC is calculated by division of the annual amount of produced hydrogen (P_H):

$$HPC = \frac{PV * AF}{P_H}$$

Table 1 Investment cost of different design cases

	50 MW nuclear €/a	300 MW nuclear €/a	50 MW solar €/a	300 MW solar €/a	50 + 50 MW hybrid €/a	300 + 300 MW hybrid €/a
<i>Solar equipment</i>						
Heliostats	0	0	38,251,000	229,478,000	38,251,000	229,478,000
Tower	0	0	3,700,000	57,882,000	3,700,000	57,882,000
Receiver	0	0	7,420,000	44,520,000	7,420,000	44,520,000
Land	0	0	1,100,000	5,000,000	1,100,000	5,000,000
<i>Total</i>	0	0	50,471,000	336,880,000	50,471,000	336,880,000
<i>Nuclear plant</i>						
Nuclear reactor	147,283,874	539,455,920	0	0	147,283,874	539,455,920
Decomposition reactor (nuclear)	32,745,271	96,111,073	0	0	7,399,559	26,580,278
<i>Total</i>	180,029,145	635,566,993	0	0	154,683,434	566,036,197
<i>Chemical application</i>						
Heat exchanger	1,541,202	8,430,441	5,385,282	17,852,798	4,646,462	25,482,088
Cooling	6,304,000	18,471,704	6,304,000	18,134,724	9,555,077	27,997,867
Separation	2,527,645	7,207,071	4,196,310	15,994,071	5,460,252	31,760,893
Pumps	41,683	218,032	348,690	803,190	220,116	679,586
Compressor	5,716,119	31,606,587	14,642,756	110,242,302	23,390,959	138,211,286
<i>Total</i>	16,130,649	65,933,835	30,877,037	163,027,086	43,272,866	224,131,720
<i>Tanks</i>						
Sulfuric-acid	0	0	9,619,048	53,866,667	4,040,000	13,466,667
Sulfur dioxide	0	0	19,238,095	106,194,286	3,847,619	23,085,714
<i>Total</i>	0	0	28,857,143	160,060,952	7,887,619	36,552,381

Table 1 Investment cost of different design cases (continued)

	50 MW nuclear €/a	300 MW nuclear €/a	50 MW solar €/a	300 MW solar €/a	50 + 300 MW hybrid €/a	300 + 300 MW hybrid €/a
<i>Power cycle and electrolyser</i>						
Brayton	15,550,794	85,609,524	34,307,937	282,383,175	29,415,728	234,833,016
Electrolyser	12,745,803	59,000,782	13,315,161	60,628,395	31,182,305	107,197,000
<i>Total</i>	28,296,596	144,610,306	47,623,097	343,011,569	60,598,033	342,030,016
<i>Others</i>						
Piping	Included	Included	Included	Included	Included	Included
Buildings	15,539,289	58,576,925	10,926,573	92,759,511	21,940,127	104,235,945
<i>Total direct investment</i>	239,995,679	904,688,058	168,754,850	1,095,739,119	338,853,079	1,609,866,259
Safety surcharge	23,999,568	90,468,806	16,875,485	109,573,912	33,885,308	160,986,626
Sulfuric-acid	6000	36,000	9,561,390	53,853,586	2,142,000	12,282,770
Land	Included	Included	Included	Included	Included	Included
<i>Total indirect investment</i>	24,005,568	90,504,806	26,436,875	163,427,498	36,027,308	173,269,396
<i>Total capital investment</i>	264,001,247	995,192,864	195,191,725	1,259,166,617	374,880,387	1,783,135,655
	€/kgH2	€/kgH2	€/kgH2	€/kgH2	€/kgH2	€/kgH2
<i>Specific investment costs</i>	6.54	4.09	4.50	4.94	4.40	3.43
<i>Specific O&M costs</i>	2.02	1.00	1.24	1.33	1.15	0.72
<i>Hydrogen production cost</i>	8.56	5.08	5.73	6.27	5.55	4.15

Table 1 summarises the cost contributions and resulting investment and operational costs for differently operated plants. Two plants are powered by ‘virtual’ 50 MW or 300 MW VHTR. Two plants are heated by concentrated solar radiation with an average power level of 50 MW and 300 MW, respectively. The two hydride plants are designed according to the flow sheets of Case 2a and share an even contribution of thermal energy input from a nuclear reactor and a solar central receiver system.

These figures are derived from non-optimised flow sheets and have to be regarded as exemplary intermediate results, but give some trends concerning plant sizing. For the solar plant an increase of HPC can be observed – mainly due to the over-proportionally increasing costs for the tower and the over-proportionally increasing optical losses of the solar field.

The HPC of the nuclear plants decreases with a very great slope when the plant size is increased.

The HPC of hybrid plants decrease as well with the size of the plant, but the size dependency is much lower compared to purely nuclear powered plants.

Those trends hint at a possible scenario for the market introduction of the HyS cycle from an economic point of view:

- first small plants might make use of solar energy demonstrating the feasibility at an industrial scale
- mid-scale plants may introduce both high temperature nuclear and solar heat into the process, if the boundary conditions fit.

The cheapest bulk production of hydrogen is obviously possible using nuclear energy in large scale plants in the GW range.

7 Summary

Case studies including flow-sheeting, component sizing and techno-economic evaluations have been carried for hydrogen production plants applying the hybrid sulphur cycle with annual average thermal power of 50 MW and 300 MW located in the region close to Lake Nasser in Egypt.

The solar powered process was set up as base and reference case and analysed in detail. The component sizing enabled the calculation of the hydrogen production costs for both plant sizes. The larger plant is predicted to cause 25% higher hydrogen production costs than for the smaller version, which is due to significant lower optical efficiencies of the extremely large solar collector and due to the high investment of the high solar tower. This suggests setting up larger plants in a multi-tower arrangement.

Of the various possibilities of combining the usage of a solar and a nuclear heat source for a hybrid operation of the process, two have been selected and analysed in detail. They are based on the solar flow sheet in which the solar power generation system is left out. In one case nuclear energy only delivers the necessary electric energy for the process, in the other it also adds thermal energy for the SO₂ production.

Cost analysis indicates that solar systems are economically competitive at power ranges of up to 50 MW_{th}, in the mid-range hybrid plants appear to have their niche, while nuclear driven HyS plants in the gigawatt range seem to be most cost-effective. Those

trends are not very pronounced. However, slightly different assumptions (e.g., regarding fuel or land costs) may change this conclusion.

Even though hybridisation has advantages, it also incurs very specific problems: an extremely fluctuating process is combined with a system, very sensitive to changing conditions and a possibly catastrophic mode of failure. Therefore very strong safety measures have to be applied. Proactive maintenance and in-service inspections are a necessity. A multitude of small buffer tanks is proposed to ensure the design composition of all flows even despite the malfunctioning of a previous process step.

Acknowledgements

The authors would like to acknowledge the funding of the HYTHEC project by the European Commission (contract number: SES6-CT-25004-502704).

References

- Aspen Plus (2004) Aspen Technologies, Inc., Massachusetts.
- Bilgen, C., Broggi, A. and Bilgen, E. (1986) 'The solar cristina process for hydrogen production', *Solar Energy*, Vol. 36, pp.267–280.
- Bilgen, E. (1988) 'Solar hydrogen production by hybrid thermochemical processes', *Solar Energy*, Vol. 41, No. 2, pp.199–206.
- Bilgen, E. and Bilgen, C. (1984) 'An assessment on hydrogen production using central receiver solar systems', *Int. Journal of Hydrogen Energy*, Vol. 9. No. 3, pp.197–204.
- Brecher, L.E., Spewock, S. and Warde, C.J. (1976) 'The Westinghouse sulfur cycle for the thermochemical decomposition of water', *1st World Hydrogen Energy Conference, Conference Proceedings*, Vol. 1.
- EcosimPro (2008) *Empresarios Agrupados Internacional*, Madrid, 1992–2008.
- EPRI (2003) *High Temperature Gas-Cooled Reactors for the Production of Hydrogen: An Assessment in Support of the Hydrogen Economy*, EPRI-1007802, Palo Alto, California, USA.
- Farbman, G.H. (1976) 'The conceptual design of an integrated nuclear-hydrogen production plant using the sulfur cycle water decomposition system', Report NASA-CR-134976.
- Farbman, G.H. (1979) 'Hydrogen production by the Westinghouse sulfur cycle process: program status', *Int. J. Hydrogen Energy*, Vol. 4, pp.111–122.
- Kiera, M. (1986) 'Beschreibung und handhabung des programmsystems HFLCAL', Interatom Report.
- Knoche, K.F. and Funk, J.E. (1977) 'entropy production, efficiency, and economics in the thermochemical generation of synthetic fuels', *Int. Journal of Hydrogen Energy*, Vol. 2, pp.377–385.
- Knoche, K-F. (1989) *Thermochemische Wasserstoffzersetzungsprozesse*, VDI-Berichte 725, pp.235–248.
- Kolb, G. and Diver, R. (2008) 'Screening analysis of solar thermochemical hydrogen concepts', Sandia Report SAND2008-1900.
- Kolb, G.J., Diver, R.B. and Siegel, N.P. (2007) 'Central-station solar hydrogen power plant', *Journal of Solar Energy Engineering*, Vol. 129, pp.179–183.

- LeDuigou, A., Borgard, J-M., Larousse, B., Doizi, D., Allen, R., Ewan, B.C., Priestman, G.H., Elder, R., Devonshire, R., Ramos, V., Cerri, G., Salvini, C., Giovannelli, A., De Maria, G., Corgnale, C., Brutti, S., Roeb, M., Noglik, A., Rietbrock, P-M., Mohr, S., de Oliveira, L., Monnerie, N., Schmitz, M., Sattler, C., Martinez, A.O., de Lorenzo Manzano, D., Rojas, J.C., Dechelotte, S. and Baudouin, O. (2007) 'HYTHEC: an EC funded search for a long term massive hydrogen production route using solar and nuclear technologies', *Int. Journal of Hydrogen Energy*, Vol. 32, pp.1516–1529.
- Lin, S.S. and Flaherty, R. (1983) 'Design studies of the sulfur trioxide decomposition reactor for the sulfur cycle hydrogen production process', *International Journal of Hydrogen Energy*, Vol. 8, pp.589–596.
- Lüpfert, E. and Funken, K-H. (1996) 'The high temperature dissociation of waste sulphuric acid with concentrated solar radiation', *Solar Thermal Concentrating Technologies: 8th International Symposium*, Köln, Germany, C.F. Müller, Heidelberg.
- Mertel, G., Dworschak, H., Broggi, A. and Vasallo, G. (1986) 'The thermal decomposition of sulphuric acid by the Cristina process', *Proceeding of 6th World Hydrogen Energy Conference*, Vol. 2, pp.673–687, Vienna, Austria.
- Pitz-Paal, R., Dersch, J., Milow, B., Téllez, F., Ferriere, A., Langnickel, U., Steinfeld, A., Karni, J., Zarza, E. and Popel, O. (2005) 'Concentrating solar power plants – how to achieve competitiveness', *VGB Power Tech.*, Vol. 8, No. 85.
- Roeb, M., Noglik, A., Sattler, C. and Pitz-Paal, R. (2008) 'Experimental study on sulfur trioxide decomposition in a volumetric solar receiver-reactor', *ASME 2nd International Conference on Energy Sustainability*, Pinehurst Technologies, Jacksonville, Florida, USA.
- Schmitz, M., Monnerie, N., Graf, D., Quantius, D., Roeb, M., Sattler, C., Corgnale, C., Salvini, C., Cerri, G. and Mansilla, C. (2008) 'Process design for solar thermochemical hydrogen production and its economic evaluation', in Mancini, Thomas (Ed.): *14th SolarPACES Biannual Symposium*, 42709_5c_3, *14th Biannual SolarPACES Symposium*, Las Vegas, NV, USA.
- Schmitz, M., Schwarzbözl, P., Buck, R. and Pitz-Paal, R. (2006) 'Multiple-aperture receivers with secondary concentrators for solar gas turbine cycles', *Solar Energy*, Vol. 80, pp.111–120.
- Schuster, J.R. (1977) *Status of Thermochemical Water-splitting Development at General Atomics*, GA-A14666, General Atomics.
- Solasys (2002) 'Novel solar assisted fuel driven power system', Contract No, JOR3-CT98-0300, Publishable report July.
- Stichlmair, J.G. and Fair, J.R. (1998) *Distillation – Principles and Practice*, Wiley-VCH.
- Sugarmen, C., Ring, A., Buck, R., Uhlig, R., Beuter, M., Marcos, M.J. and Fernandez, V. (2002) 'Solar-hybrid gas turbine power system', *Proceedings 11th Int. Symp. IEA-SolarPACES*, pp.101–108.