COUPLING A HYDROGEN PRODUCTION PROCESS TO A NUCLEAR REACTOR

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Abstract

Work is currently underway to define a pre-conceptual design of a Hydrogen Production Plant. As a reference case, a VHTR is dedicated to Hydrogen production using the Sulphur-Iodine process. The chemical part of the plant is based on a reference very detailed flow-sheet where all components are listed. Considering the volume and flow-rates of the circulating products, a detailed image of the chemical plant is drawn with several shops in parallel. A coupling circuit in gas was also studied with two intermediate heat exchangers at very high temperature. A specific heat transfer circuit is added inside the chemical part to distribute heat at the good temperature level. Optimisation of this circuit should lead to raise the overall efficiency of the process. Finally a methodology is proposed for the safety of the HYPP.

Introduction

To evaluate the viability and the cost of a future process that produces hydrogen, it is necessary to design an industrial plant. Such a design will help looking at the key points and will overcome the efficiency calculation as the best criteria to choose a future technology. We describe here some studies that are relevant to the design of a hydrogen production plant coupled to a high temperature nuclear reactor.

Basic options

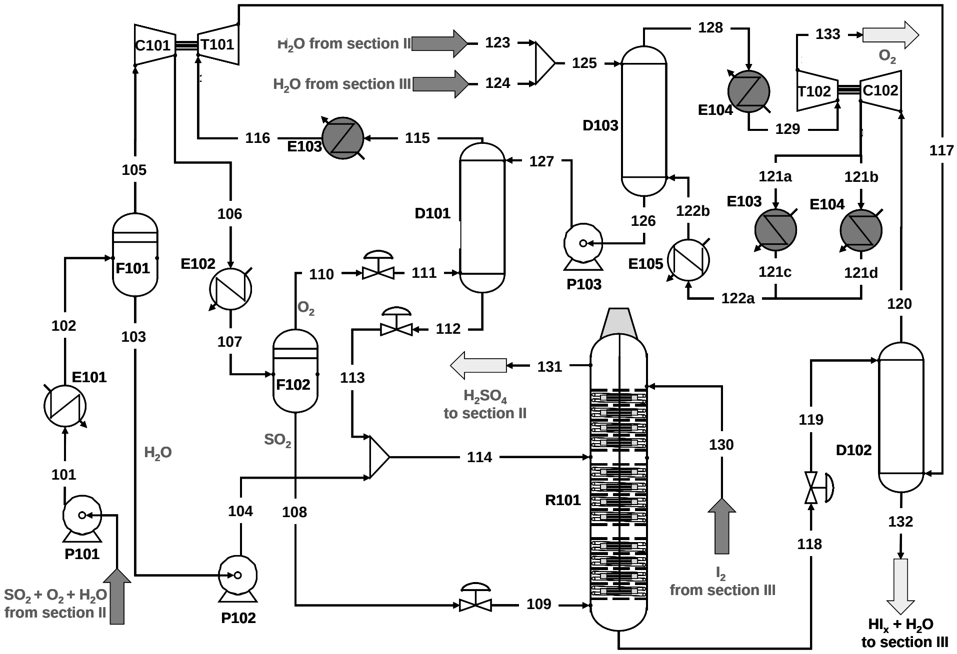
They are numerous possible arrangements to produce hydrogen using a very high temperature nuclear reactor (VHTR). In most of the cases related in the literature, people are dealing with co-generation when electricity and Hydrogen are both produced. In order to reduce the number of open parameters and to find a first set of operating conditions we will here study a dedicated plant. A 600 MWth VHTR will deliver heat to a hydrogen production plant (HYPP) based on a Sulphur-Iodine process. When electricity is needed to operate the process, it comes from the grid. The VHTR produces heat at the temperature needed by the process. The S-I process needs at least a temperature in the range of 840 to 870°C to operate with a sufficient efficiency.

The temperature level of the VHTR has to be established considering the heat delivering system. If one considers three intermediate heat exchangers (IHX), using a dedicated intermediate close loop, and takes a usual temperature pinch of 50°C for a gas-gas heat exchanger, the relevant VHTR temperature is above 990°C. But if optimisation only leads for instance to two IHXs and 30°C for the temperature pinch, the needed VHTR temperature decreases to 900°C. So it is important to optimise the coupling scheme and to validate the results with calculations. This is depending on the one hand of the knowledge we have on the HYPP and the other hand on the design we choose for the coupling. Both of them are presented in the following chapters.

Towards a Hydrogen Production Plant

From the basic studies for the S-I cycle we have derived a very detailed operating flow-sheet. It is based on a reactive distillation scheme. This flow-sheet has been designed taking into account present thermodynamics data and chemical engineering techniques. Expert judgements from people working in various areas related to the system were also used to assess each part of the flow-sheet and to validate its efficiency. Figure 1 shows the flow-sheet obtained for the Bunsen section.

Figure 1. Detailed reference flow-sheet of the Bunsen section.



The complete flow-sheet gives a global efficiency of the process equal to 35% with an estimated range of variation of ± 5%. For each section, the efficiency of each basic reaction has been studied and discussed and a set of components were designed that are able to operate.

For the Bunsen section I, an excess of Iodine and of water is introduce to make the reaction not reversible. The dissolved Sulphur dioxide must be eliminated from the hydriodic acid at the outlet.

For the sulphuric acid decomposition section II, conversion factors and kinetic were studied for the two main reactions:

$H_2SO_4 \rightarrow H_2O + SO_3$ (1)

$SO_3 \rightarrow SO_2 + 1/2\ O2$ (2)

For (1), the dissociation factor is high above 530°C. There is no kinetic data. One or more simple heat exchanger is convenient with an outlet temperature that reaches the one needed for (2). (2) needs a catalyst. A vanadium oxide catalyst was assumed, made of granulate. The temperature must be at least 827°C and a value between 840 and 870°C is considered that gives a conversion factor from 0,7 to 0,8.

For the hydriodic acid decomposition section III, a first step is the iodine separation, due to contact with phosphoric acid in a counter current contactor. Then a reaction with catalyst in a reactive distillation column separates the Hydrogen from Iodine. This reaction is very slow and a residence time of some 3s is estimated in the column. The mixture that contains Iodine is adjusted and recycled to the main reactor of the Bunsen section, while the unreacted hydriodic acid is re-circulated.

In a first step, the energy is assumed to be mainly recovered. This is not the case for section I were the temperature is too low, less than 120°C. Section II is most well known and it is possible to perfectly adjust the heat demand to the use. Section II is the one that really needs to be optimised. Also the reaction is almost athermic, the great quantity of re-circulated products, especially water that has to be vaporised, is energy consumer.

The detailed flow-sheet is derived from the expertise of each section. The needs for re-circulating compounds and for compounds separation gives a set of subsections that are composed of several apparatus. Pumps, pressure reducing valves and heat exchangers are part of these sub-sections.

For section I, one unique counter-current flow reactor is set up. At the inlet, Oxygen must be separated from SO2 and hydriodic acid must be concentrated.

For section II, optimisation leads to concentrate the sulphuric acid up to 80% before it is converted. Finally a temperature of 850°C at the outlet of the converter is required. For section III, a specific column is required. It is composed of 25 theoretical plates, including re-boiler and condenser. Inlet is done at plate n° 22 at a temperature of 316°C. An intermediate partial draught at plate n° 15 is a good compromise from an energetic point of view. The total length of the catalyst bed is adjustable.

In a second step each component is designed separately for a 1 mol/s unit, representative of a laboratory scale experiment. For instance, a heat exchanger is described in detail and mass flow rates, temperatures and compounds composition are calculated. This gives a first idea of the component that should be built.

In a third step, an extrapolation to a HYPP is made, assuming a 1 kmol/s plant, that is more or less a plant that needs some 600 MWth of energy. Hypothesis is the following:

- No heat losses from the heat exchangers.
- Isentropic efficiency of the rotating machines (turbines and compressors) set to 0,75.
- Mechanical efficiency of pumps set to 1.
- Average logarithmic pinch of exchangers are above 10°C.
- Heat to electricity conversion efficiency is set to 0,5.

Energy balance for each section gives values from Table 1.

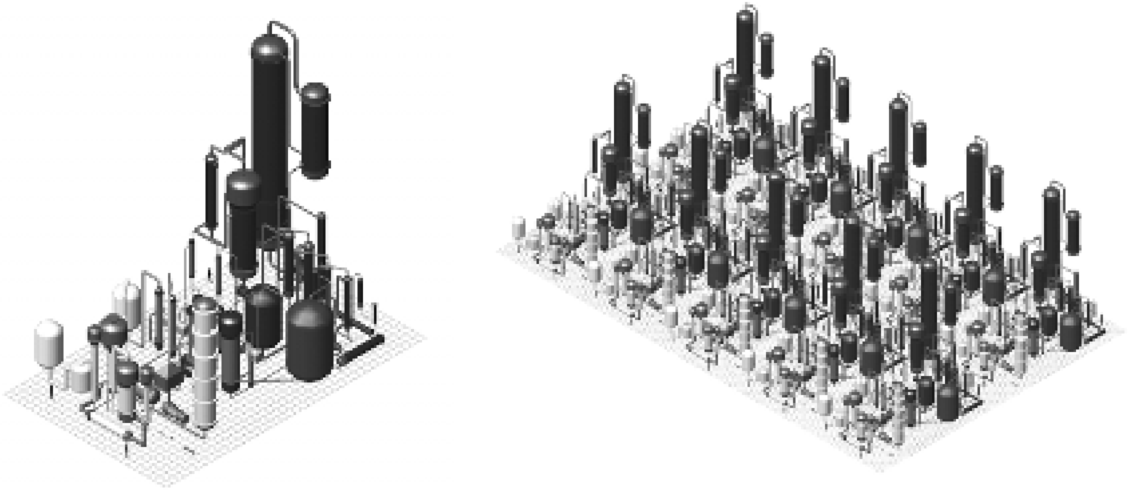
Table 1. Energy balance in each section of 1kmol/s HYPP

	Total Energy need	Heat fraction	Electricity fraction
Section I	34 MW	0	17 MWe
Section II	389 MW	385 MWth	2 MWe
Section III	376 MW	214 MWth	81 MWe
TOTAL	**799 MW**	**599 MWth**	**100 MWe**

This gives a global efficiency of 36%. The VHTR is totally dedicated to the heating of the HYPP. Additional 100 MWe are coming from the grid.

When dimensioning the components for the HYPP, measurements of the Bunsen reactor and the HI distiller are far from today technology. So it is proposed to split the factory into 10 shops. On this basis each component can be designed using available codes and standard. The pre-conceptual design of a shop and the factory are shown on Figure 2.

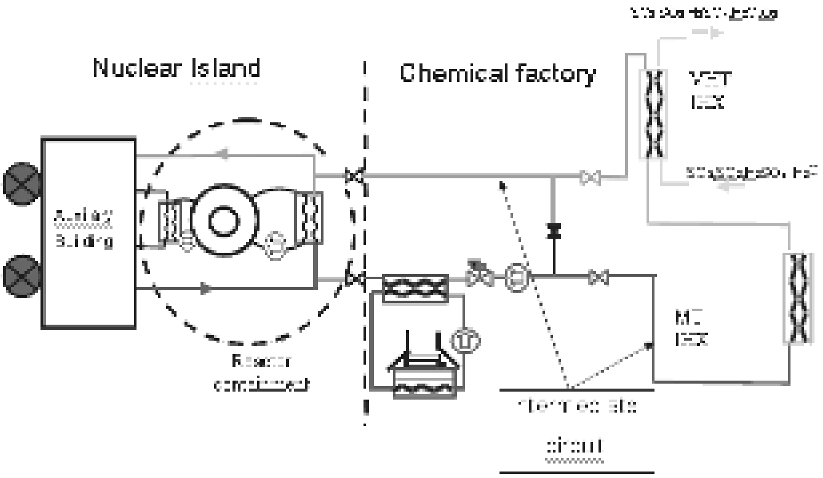
Figure 2. Pre-conceptual design of a shop delivering 100 mol/s H2 (left) and of the factory of 10 shops (right).



Coupling the HYPP with the VHTR

Coupling the VHTR to the HYPP consists in a first step in designing the system that is used to transfer the energy from the primary circuit of the nuclear reactor to the inlet of the chemical factory. It is necessary to take into account the minimum heat losses in this circuit by reducing the number of IHX and the length of the system. Figure 3 gives a sketch of this coupling circuit.

Figure 3. Sketch of the coupling circuit between the VHTR and the HYPP



The design of the circuit must answer to several problems:

1. Transfer the high temperature heat to section II with the best greatest efficiency.
2. Supply to and recuperate heat from medium and low temperature sections.
3. Respect operating and safety rules in each plant.
4. Maintain a barrel between the two plants.

Present studies are based on a circuit fill with helium. Pressure is set at the mid value between the one of the VHTR (around 5.0 MPa) and the one of the sulphuric acid decomposer (0.5 to 1.0 MPa) to minimise the pressure difference on both sides. So the pressure of the intermediate circuit is around 2.9 MPa. A reference is set to 2.7 MPa. To transport the 600 MW a flow-rate of 220 kg/s is necessary.

For point 1, a specific design of the pipes is necessary to reduce the heat losses and also the pressure drop to minimise the blowing energy. A minimum temperature of 850°C is needed at the inlet of the chemical reactor. When studying the different geometrical arrangement of the pipes, one can easily show that co-axial pipes are not convenient because they generate too high friction losses. So a special design of the thermal isolation of standard pipes has been studied. An optimisation of the isolating material, using an internal coat and an external one plus an outside thermal screen, gives as a result a heat loss of less than 0.001°C/m (1kW/m) and a pressure drop of 400 Pa/m. The temperature of the metallic pipe that withstands the pressure is no more 400°C. This allows to use several 100 m length of pipes.

For point 2, a specific tool was developed to calculate heat exchange coupled to a reactive flow. This tool, called SRDE, is based on the PROSIM chemical tool. It has been used to firstly design a SiC heat exchanger for the sulphuric acid decomposer. The heat exchanger is optimised with 5 heat exchangers of 441 pipes each, 13 m length. Helium circulates inside the 0.03 m diameter pipes. The chemical compounds circulate in an outside counter current flow with a 0.057 m equivalent diameter. The total energy exchange is 70 MW per exchanger. An iteration must be made with the description of the HYPP (see above) concerning the optimum number of shops. The same type of calculation was made for the medium temperature part of the circuit and for the IHX. It has been concluded, among others, that the minimum pinch temperature for the heat exchanger was around 30°C. This allows to calculate the minimum temperature required from the VHTR: 900°C, if everything works well!

For point 3, a boiler that stabilises the temperature of the helium coming back to the main IHX, has been added on the basis of the work done by JAERI for its Steam Methane Reforming project coupled to the HTTR. The design and the characteristics of this boiler are currently being studied.

Point 4 is achieved through the integration of the main IHX in the main confinement of the VHTR and the intermediate circuit that should prevent rapid interaction of one plant with the other.

Safety issue

The safety approach, guided by the regulation and based on safety analysis methodology, is a synthesis of the nuclear power plant and the conventional plants regulations. It gives a methodology for the safety approach of the VHTR coupled with the HYPP, consistent with both regulations. As a nuclear facility, the VHTR is submitted to safety rules. The strategy and the foreseen provisions are described in a safety report showing the compliance with these safety objectives. Physical barriers are interposed between the radioactive materials (fission product) and the environment, in order to prevent their release. Safety functions are defined to preserve the integrity of these barriers, for instance the control of the nuclear reactivity or the cooling of the fuel. Moreover, conception rules are adopted with respect to the principle of defense in depth (DID) including generally five levels.

For a conventional facility, the regulation consists in laws applicable to the facility "classified for environment" and eventually in the SEVESO II European directive, depending on the quantities of dangerous substances included in the facility. Of course, the conception rules of the art have to be applied. The deterministic approach is declined in a less rigorous way in the conventional industry, but it is more or less based on the DID principle and on studies of postulated major accidents.

According to the previous statements, three overall safety functions can be defined for the whole facility (VHTR/HYPP) in order to prevent and to limit the consequences of dangerous releases in case of accidents [1]:

- the control of the nuclear reactivity and of the chemical reactivity;
- the extraction of the nuclear power, of the thermal power (heat release by chemical reactions, phase changes) and of the mechanical power (compressors, pumps, pressure wave associated to phase changes or very rapid gas expansion due to heat release);
- the confinement of hazardous substances : fission product and chemical substances.

Obviously, the two first safety functions are required to avoid excessive solicitations of components constituting a barrier. The last safety function states the protection of the barriers in itself.

Level 1

The prevention of abnormal operation and failures can be divided into two folds: selection of design rules related to chemical substances specificity and to different operating conditions; provisions regarding parameter variations transmitted from one facility to the other through the coupling system. Items related with this level 1 of the DID are for example:

- Material resistant to the corrosion of acids.
- Hydrogen embrittlement of the walls of cryogenic storages.
- Hydrogen diffusion through metal.
- Control of the heat exchange between the two facilities.

Level 2

The control of abnormal operation forms the level 2 of the DID. This level deals mainly with surveillance, control and regulation systems. The security and limiting systems acting automatically in case of abnormal operation are designed to operate before the triggering of systems of third level of DID, especially, the automatic emergency shutdown of the facilities (for the VHTR and the HYPP) mainly the uncoupling and shutdown of the H2 units that are out of normal operation domain, but also the uncoupling needed when the temperature of the VHTR varies outside the operating range (see for instance the case of a slow starting-up).

Level 3

In the level 3 of the DID, one needs to control the progression of accidents and to limit their consequences. The accidents considered here should be controlled within the design basis conditions and, therefore, should not induce large leakages through the last physical barriers nor explosions/fires being likely to aggress significantly the HYPP or the VHTR. By the way, the safe states of the facilities correspond to an uncoupled state that allows to insure independently the safety functions of each facility. In this level we need provisions and systems devoted to the fulfillment of safety functions.

The control of the nuclear and chemical reactivity in case of accidents is insured by the emergency shutdown systems. The safety function devoted to the thermal power extraction from the HYPP is directly linked to the control of the chemical reactivity because the kinetics of chemical reactions increases with the temperature. The HYPP must be cooled by emergency systems, water streaming on equipments, spraying systems, and so on.

The extraction of the mechanical power has an influence on the chemical reactivity as well, by controlling the pressure in the HYPP components. Provisions like safety valves, expansion tanks, flarestacks, can be foreseen in order to release the pressure, thus avoiding the failure of equipments

The main accidents considered at this level are listed below:

- the loss of electric supply or other support systems (secondary products evacuation, pneumatic systems);
- coupling system failure or rupture as an accident initiator;
- design basis accident in the VHTR;
- equipment failure in the HYPP without external leakage;
- limited leakages without ignition in the HYPP;

- simultaneous rupture of IHX1 and IHX2, eventually initiated by a breach.

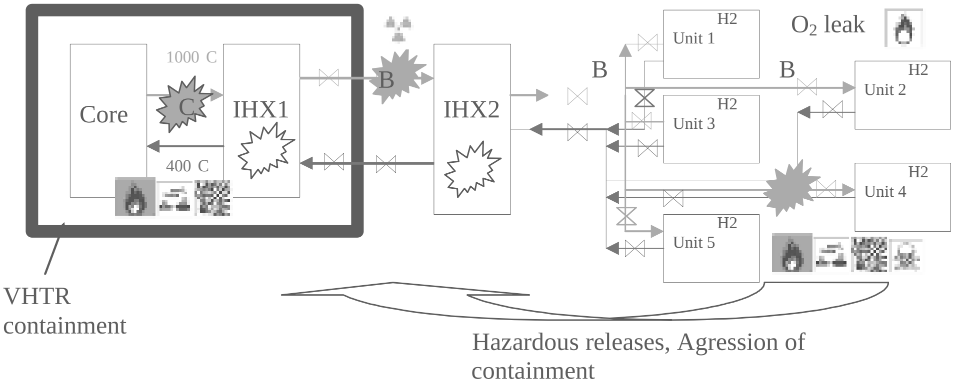
The prevention measures to control the accident consists in the triggering of emergency shutdown systems in VHTR and in HYPP associated to the overall decoupling of the facilities.

Level 4

Here are the control sever plant conditions and mitigation of severe accidents consequences. They results from low probability sequences including multiple failures. Complementary provisions aiming to limit the consequences of such accidents are provided, especially regarding the integrity of the last confinement barrier (containment for VHTR, last wall and safety distances for HYPP). At this level, provisions are also proposed in order to prevent and to mitigate possible “dominoes effects” due to the proximity of the two facilities and of the different units of HYPP.

The consequences of major accident scenarios postulated in the HYPP have to be assessed. The relevance of these scenarios regarding VHTR aggression has to be checked, because the “envelope” accidents are not necessarily the same for out-site consequences as for VHTR aggressions. As an illustration, the toxic consequences of a sulfur dioxide release could impose the larger safety distance regarding the environment, whereas a conservative scenario could be a hydrogen deflagration regarding the VHTR aggressions (Figure 4).

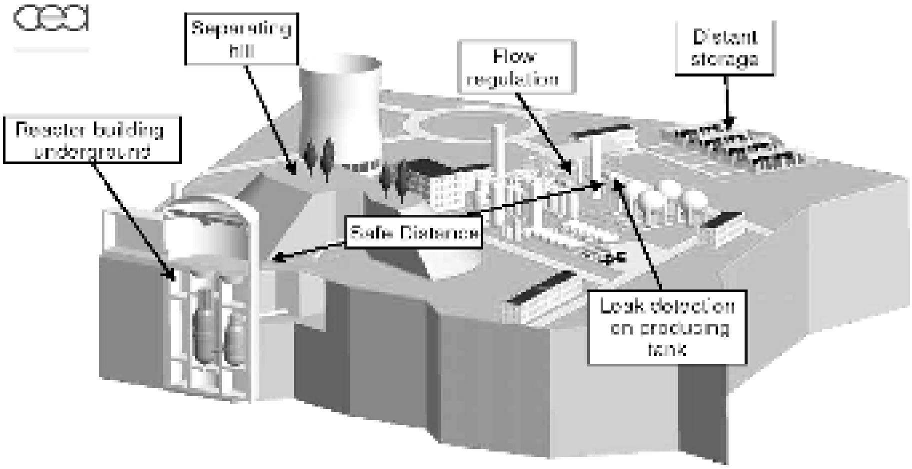
Figure 4. schematic of hypothetic severe accidents consequences



Especially, the containment resistance to an explosion wave must be evaluated in order to size it appropriately. One must limit its consequences by relevant provisions like (Figure 5) :

- reduction of energetic ignition sources (risk of fast combustion regime);
- absence of confinement and of obstacles (pipe agglomerate) to avoid flame acceleration and DDT;
- inerting or igniting systems in confinement;
- events systems, physical barriers between the VHTR and the HYPP, deflectors, reasonable safety distance;
- possible grounding of the coupling system and/or the VHTR;
- training of rescue teams and emergency means optimisation;

Figure 5. Possible provisions to mitigate pressure wave aggression on VHTR



Compounds issues

For the Sulphur-Iodine cycle, an obviously important challenge is related to Iodine itself, which is a not so abundant and rather expensive material. As said previously, a main characteristic of the process is the very important amount of chemicals involved in the process in relation with the quantity of hydrogen produced. This is due on the one hand to the balance of the molecular weight of hydrogen versus iodine (1 versus 127) and on the other hand to the fact that the Bunsen reaction is not stoichiometric and requires, for phase separation, 9 moles of I_2 to produce one mole of H2.

As a matter of fact, it is easily shown that, using an average cost of \$ 15 per kg of Iodine [11], the production of 1 kg of H_2 requires the handling of \$ 20 000 of iodine. As a direct consequence, Iodine molar losses of, for instance, 10^{-5}, would increase the hydrogen production cost of \$ 0.2 per kg H_2: clearly, the control of Iodine losses would be an important question in the operation of a Sulphur-Iodine plant.

Another question relates to the availability of large enough quantities of iodine in the world. First estimates of the Iodine hold-up in a 600 MW VHTR coupled hydrogen production plant, designed using a detailed flow-sheet of the cycle, are on the order of 3 000 t (corresponding to a \$ 45M capital cost, and consequently \$ 0.045 per kg H_2). This amount seems realistic when compared to the world yearly production of 20,000 t and the estimated world reserves of 15.10^6 t [2].

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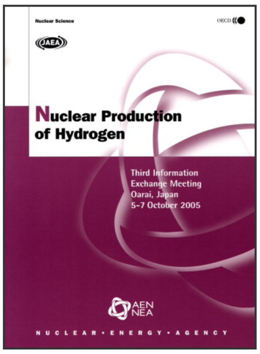

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