

## Influence of HTR core inlet and outlet temperatures on hydrogen generation efficiency using the sulphur-iodine water-splitting cycle

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### Abstract

Hydrogen generation is considered a promising application for VHTR. Simple thermodynamics show that the high temperature heat they can provide can lead to significant increase in efficiency when compared to low temperature processes, such as alkaline electrolysis coupled to a pressurised or boiling water reactor.

Sulphur-based cycles, such as the sulphur-iodine cycle, take full advantage of the range of temperatures at which the VHTR provides heat. In particular, the oxygen generation step (sulphur trioxide decomposition) requires very high temperature heat (typically  $T > 800^{\circ}\text{C}$ ), which can only be provided by a VHTR.

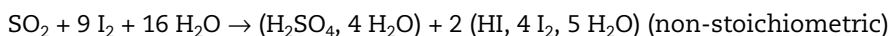
Discussions on how to increase the hydrogen generation efficiency therefore often focus on how to maximise the temperature that can be used by the process, whether by maximising the HTR outlet helium temperature or by reducing pinches in heat exchangers. On the lower end of the secondary helium temperature spectrum, the importance of the helium return temperature is often overlooked. However, as a component of the average heat source temperature, it must, according to the Carnot principle, have an influence on the efficiency.

General Atomics (GA) and the Commissariat à l'Énergie Atomique (CEA) have been working on sulphur-iodine cycle flow-sheeting for several years, leading to sometimes differing efficiency estimates. They have undertaken to understand and reconcile these differences, and have come to consider in more detail the effect of the VHTR characteristics on the optimisation of the sulphur-iodine flow sheet. This paper will present the outcome of these studies, and stress the interplay between nuclear reactor and chemical process.

## Introduction

Hydrogen is a promising energy carrier, which potentially could replace the fossil fuels used in the transportation sector of our economy. Fossil fuels are polluting and carbon dioxide emissions from their combustion are thought to be responsible for global warming. However, no large scale, cost-effective, environmentally attractive hydrogen production process is currently available for commercialisation. Thermochemical water-splitting cycles powered by nuclear or solar means are seen as possible candidates to supply hydrogen on a massive scale without the burden of greenhouse gas emissions. One of the most studied cycles is the sulphur-iodine (S-I) cycle, invented at General Atomics (GA) in the 1970s. It consists of three coupled chemical reactions as shown below:

- Bunsen reaction:  $\text{SO}_2 + \text{I}_2 + 2 \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2 \text{HI}$  (stoichiometric)



- Sulphur section:  $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_3 + \text{H}_2\text{O}$



- Iodine (or HIx) section:  $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$

Iodine and sulphur dioxide are combined with water in the Bunsen reaction to create two immiscible acid phases. The separation of these phases is facilitated by the presence of excess iodine. The lighter, sulphuric acid phase is decomposed first to  $\text{SO}_3$ , and then to  $\text{SO}_2$ .  $\text{SO}_2$  formation typically occurs in the presence of a catalyst at temperatures above  $800^\circ\text{C}$ . The  $\text{SO}_2$  and water are recycled back to the Bunsen reaction for reuse.

The heavy phase, consisting of water, iodine and hydriodic acid (the mixture is also known as  $\text{HI}_x$ ), is treated to result in the decomposition of HI to produce the product hydrogen and iodine. The iodine and water are also recycled back to the Bunsen reaction for reuse.

Water in excess of the stoichiometric requirement is necessary to hydrate the acids and shift the equilibrium toward the desired products. However, the separation of water from other components in the acid decomposition sections is a large contribution to the total energy required for the cycle. Thus, thermodynamically efficient means for carrying out the decomposition steps are essential for economic production of hydrogen.

This paper discusses in particular the elements of coupling an S-I process to a VHTR, and how the parameters that describe this coupling can affect the energy consumption of the cycle.

## Process flow sheet alternatives

In general, there are two alternatives for coupling the S-I process to a VHTR. In the first, secondary helium is initially used to supply heat to the MT/HT<sup>1</sup> sulphuric acid decomposition steps. LT helium heat is then consumed by the HI decomposition section before the helium return to the intermediate heat exchanger. In the second alternative, heat integration between the chemical process steps allows for helium heat supply solely to the MT/HT sulphuric acid decomposition steps. Residual process LT heat recovered there is utilised in the HI decomposition section.

The first alternative simplifies the heat integration of the chemical process, and the second simplifies the interface between the chemical process and the secondary loop. CEA (Leybros, 2009) has designed their S-I process for the first alternative, as the requirements for the reactor expected to be used are most suitable for it. GA has developed flow sheets for both alternatives. Sandia National Laboratories (SNL) is a partner of both CEA and GA in the operation of a demonstration loop for the S-I cycle. SNL is charged with design and operation of the sulphuric acid decomposition section. They have developed a bayonet-heater design for the decomposer which incorporates internal heat recovery. As a result, the outlet temperature of the bayonet heat modules is too low to use in the HI decomposition section. Thus, helium is utilised in the HI decomposition section, as in the CEA flow sheets.

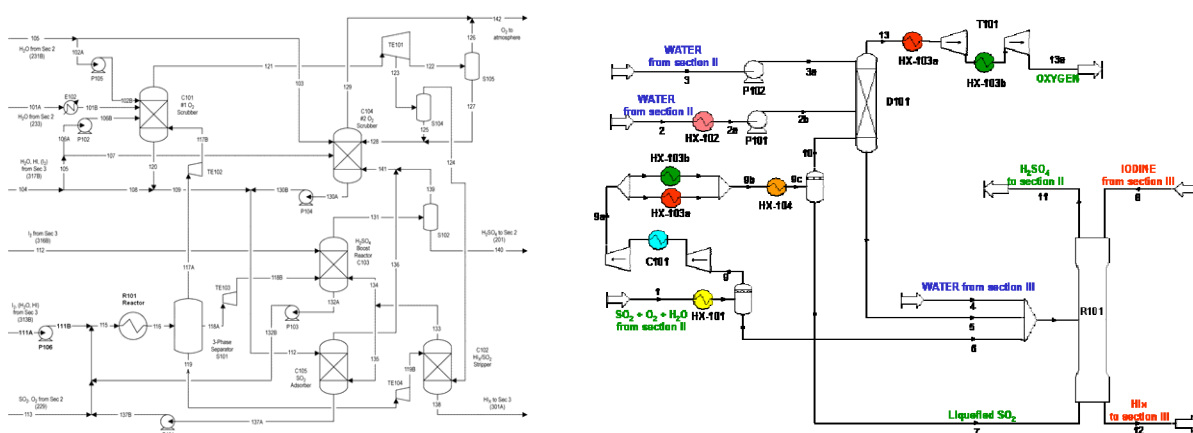
1. Abbreviations used in the text: HT, MT, LT are respectively high ( $> 600^\circ\text{C}$ ), medium ( $400\text{--}600^\circ\text{C}$ ), low temperature ( $<400^\circ\text{C}$ ); He(I), He(II) are primary and secondary helium; S-I is the sulfur-iodine cycle

In 2006, GA participated in a study conducted by the Savannah River National Laboratory (Summers, 2006). The S-I process was coupled to a VHTR with a required helium return temperature near 600°C. To efficiently match temperature requirements with available heat, a design was developed to supply HI decomposition section energy with recovered heat from the sulphuric acid decomposition section. For the purposes of comparison and analysis in this paper, the “GA” flow sheets will refer to this design, and “CEA” flow sheets will refer to a design in which helium supplies heat to both acid decomposition sections. CEA uses ProSimPlus™ for flow sheet analysis, and GA uses Aspen Plus™. A previous study (Buckingham, 2008) showed that the two process simulators give similar calculated results when the same unit operations and stream compositions are modelled, although different thermodynamic models are used for the calculations.

### The Bunsen reaction section

Figure 1 depicts the GA and CEA flow sheets of the Bunsen section.

**Figure 1: Bunsen section flow sheets: GA (left), and CEA (right)**



The Bunsen reaction proceeds at 120–130°C, under a pressure of 3 to 6 bars. For flow sheet calculations, product flows were supposed pure (i.e. no iodine trace in sulphuric acid, no sulphur trace in hydroiodic acid). Thermal balance of this section is summarised in Table 1, with values in kJ/mol H<sub>2</sub>.

**Table 1: Bunsen section flow sheets – summary of energy exchanges (kJ/mol H<sub>2</sub>)**

	Thermal need	Thermal release	Thermal interchanges	Electrical need*
<b>GA</b>	0 (exothermal reaction)	128 (Bunsen reaction)	0 (inside Bunsen section)	2 (pumps,...)
<b>CEA</b>	0 (exothermal reaction)	93 (Bunsen reaction) + 46 (other heat losses)	3 (inside Bunsen section)	5 (pumps,...)

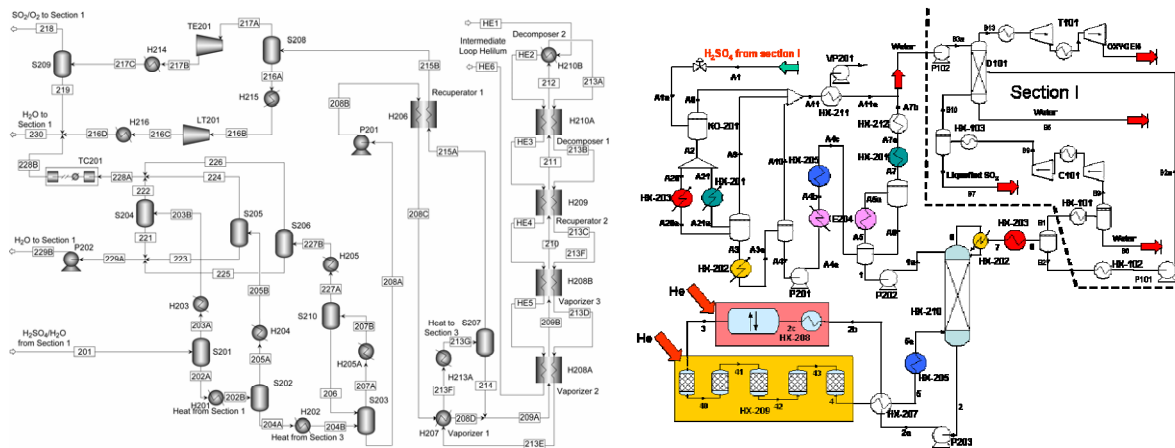
\* kJ<sub>el</sub>/mol H<sub>2</sub>, thermal-to-electrical conversion rate of 0.48 to be taken into account.

At present, no relevant thermodynamic model of the Bunsen section exists, although some research is in progress. Hence, the thermal values above have to be considered as orders of magnitude, not as accurate values. This section is not a net consumer of thermal energy, and electrical demand is relatively low. Thus, the Bunsen reaction section has minimal effect on overall process efficiency. The principal difference between the two flow sheets is that the CEA design uses a counter-current reactor, and the GA design is a co-current configuration. It is thought that the counter-current design may facilitate separation and enhance the purity of the acid phases, while the co-current design minimises contact time, and thus also minimises potential generation of hydrogen sulphide and elemental sulphur in undesirable side reactions.

### The sulphuric acid decomposition section

Figure 2 illustrates the GA and CEA flow sheets for the sulphuric acid decomposition section.

**Figure 2: Sulphur section flow sheets: GA (left) and CEA (right)**



The sulphuric acid decomposition section consists of three parts:

- a concentration section, in which sulphuric acid flowing from the Bunsen section is partially dehydrated;
- a decomposition loop, working at pressures from 5 to 70 bars;
- an SO<sub>2</sub> recovery section.

The thermal balance of this section is summarised in Table 2, with the values in kJ/mol H<sub>2</sub>. The acid concentration portions for the CEA and GA flow sheets are similar, but the decomposition loops are substantially different in several ways. The GA flow sheet shows significant process heat recovery at high temperatures, and the note “Heat to Section 3” indicates the use of process heat by the HI decomposition section.<sup>2</sup>

**Table 2: Sulphur section flow sheets – summary of energy exchanges (kJ/mol H<sub>2</sub>)**

	Thermal need	Thermal release	Thermal interchanges	Electrical need
<b>GA</b>	283.03	260.64	384.98	0.05
<b>CEA</b>	364.60	121.61	357.83	0.08

The CEA decomposition loop operates at low pressures, near 5 bar. This is because the decomposition reaction is favoured at lower pressures. However, the GA flow sheet is conducted at 70 bar, near the expected operating pressure of the secondary helium loop. This is to minimise mechanical and thermal stress induced by a large pressure gradient between the helium and the chemical process at high temperatures. The GA design of the decomposition loop allows for more heat recovery, but does so with a more complex configuration. In practice, trade-offs between complexity and cost will be necessary to develop the most cost-efficient design.

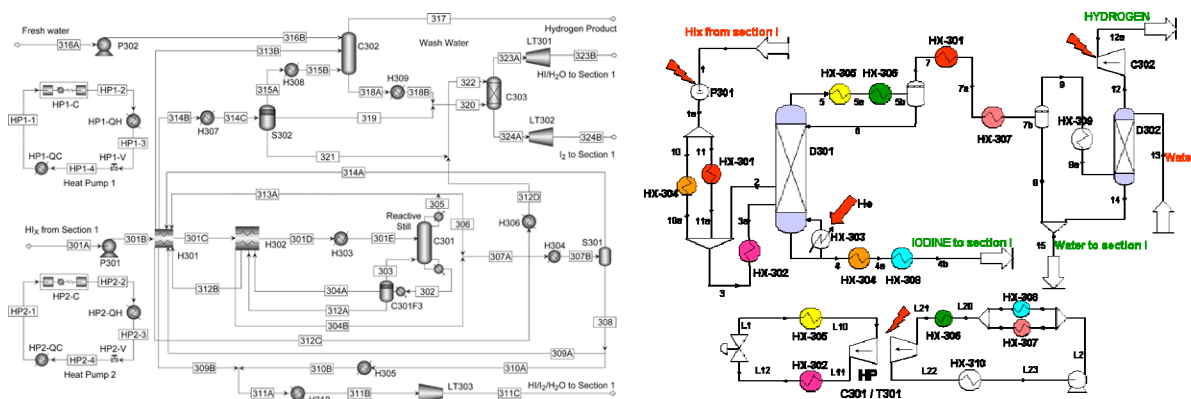
### The HI decomposition section

The HI decomposition section flow sheets for both CEA and GA are heavily focused on efficient heat recovery. The basic principle for decomposition is the same for each. Reactive distillation of the HI<sub>x</sub> feed results in the production of hydrogen. The operating pressures in the distillation columns typically

2. Common nomenclature is for the Bunsen reaction section to be called Section 1, for the sulphuric acid section to be known as Section 2, and for the HI decomposition section to be designated as Section 3.

fall in the range of 20 to 50 bar. This allows for column temperatures high enough (~300°C) to facilitate decomposition of HI, and allows for direct production of hydrogen at high pressure. This eliminates a hydrogen gas compression requirement. Figure 3 depicts the GA and CEA flow sheets of the HI decomposition section.

**Figure 3: Iodine section flow sheets: GA, using Aspen (left) and CEA, using ProSim (right)**



An important aspect of each flow sheet is the use of heat pump loops to recover heat and use it at higher temperatures. For a relatively small electrical input, substantial amounts of process heat can be recovered and reused within the section. Table 3 summarises the section energy requirements for both the CEA and GA flow sheets.

**Table 3: Iodine section flow sheets – summary of energy exchanges (kJ/mol H<sub>2</sub>)**

	Thermal need	Thermal release	Thermal interchanges	Electrical need
<b>GA</b>	104.85	14.11	2 273.33	122.07
<b>CEA</b>	235.40	247.39	1 949.76	59.87

The GA flow sheet consumes more electrical energy than the CEA configuration. This is largely due to the fact that the GA flow sheet uses a heat pump to recover the heat of mixing of distillation product streams. Earlier versions of the CEA flow sheet also utilised the heat of mixing, in fact CEA was the first to propose this configuration. However, the CEA uses a counter-current reactor in the Bunsen reactor section, and a pure iodine stream from the HI decomposition section is desired. Thus, the CEA flow sheet was altered to produce a pure iodine stream, though more energy is now required for the section. The GA Bunsen section, with a co-current reactor, is less sensitive to some iodine impurities (HI and water), so the recovery of this heat of mixing is retained. Also, some LT heat is recovered in the GA configuration, and used in the sulphuric acid section to concentrate the feed stream before entry into the decomposition loop. As in the sulphuric acid decomposition section, the GA flow sheet for HI decomposition is more energy-efficient, but the heat exchanger network design is simpler in the CEA configuration. Balance between efficiency and cost must be evaluated as designs mature.

### Overall energy consumption

The overall thermal energy consumption of the CEA flow sheets is assessed in Table 4 for a coupling to a VHTR of 600 MWth.

**Table 4: CEA's flow sheet – summary of heat needs (kJ/mol H<sub>2</sub>)**

	LT iodine section	MT sulphur section	HT sulphur section
<b>Heat needed</b>	235.4	154.4	210.2
<b>Temperature range (°C)</b>	375	403-600	600-850

Total energy extracted from helium is 600 kJ/mole  $H_2$ . The GA flow sheets require 390 kJ/mole from helium, all of which is introduced into the sulphuric acid decomposition section. A summary of the differences between the two designs is shown in Table 5.

**Table 5: Main differences between the GA and CEA processes**

	GA	CEA
Couplings with He(II)	He(II) $\Rightarrow$ Sulphur section	He(II) $\Rightarrow$ Sulphur section He(II) $\Rightarrow$ Iodine section
Couplings between sections	Sulphur section $\Rightarrow$ Iodine section (HT) Iodine section $\Rightarrow$ Sulphur section (MT) Bunsen section $\Rightarrow$ Sulphur section (LT)	None
Maximal temperature	950°C (pinch: 25°C)	850°C (pinch: 40°C)
Pressure in sulphur loop	70.5 bars	5.0 bars
HTR outlet temperature	925°C	900°C
HTR inlet temperature	590°C	400°C
Molar ratio water/ $H_2SO_4$ *	4.00/0.53	4.00/1.30

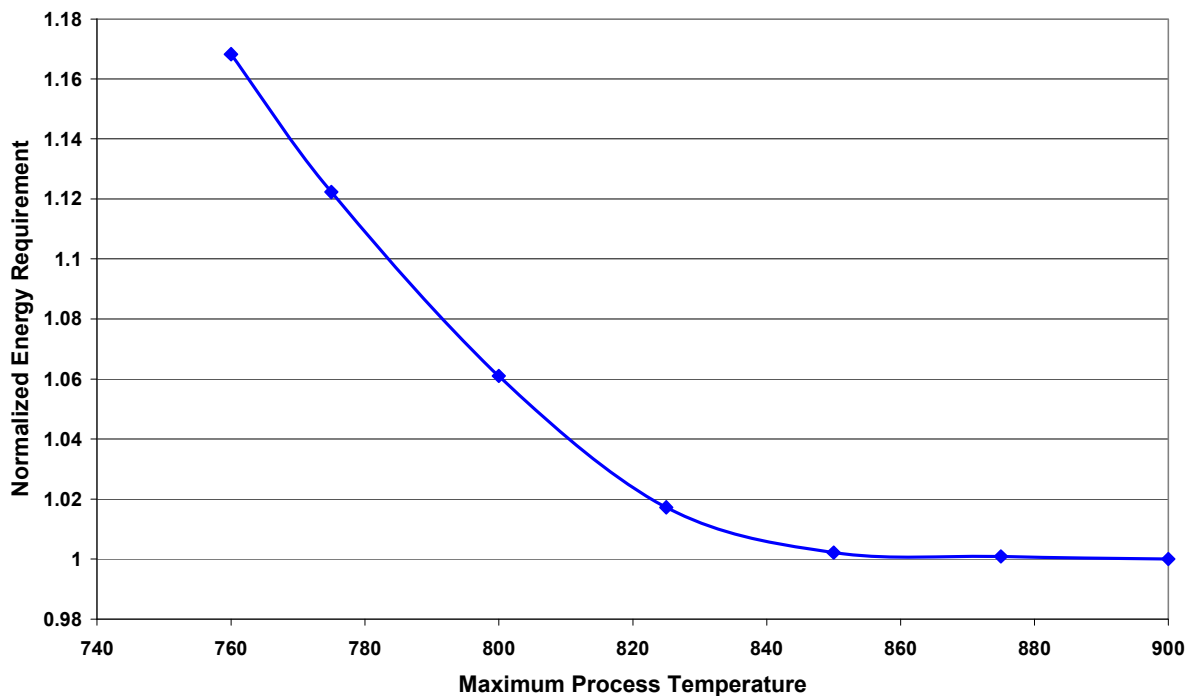
\* First value: input of sulphur section; second value: after initial dehydration of aqueous sulphuric acid.

### Effect of HTR outlet temperature

Figure 4 illustrates a common trend between the CEA and GA flow sheets in energy consumption as a function of maximum process temperature. The energy requirement as a function of maximum temperature is depicted as a ratio of the value to that at the highest process temperature examined.

In order to lighten the calculations, a simplified loop is taken into account, in which dehydration of  $H_2SO_4$  into  $SO_3 + H_2O$  is performed in a single isotherm reactor (without catalyst), whereas dissociation of  $SO_3$  into  $SO_2 + \frac{1}{2} O_2$  is performed in another single isotherm reactor (with catalyst), at a higher temperature called Tmax. Only this last temperature is varied in the sensitivity analysis.

**Figure 4: Influence of the maximal temperature (Tmax) in the decomposition loop on energy requirement of the sulphur section**



Following Le Châtelier's principle (or Carnot's principle), the global heat demand of the section decreases when the maximal loop temperature increases. However, no sensible decrease is pointed out above 840°C. Thus, increasing the maximal temperature in the cycle is not useful beyond ca. 840°C. Two antagonist phenomena can explain the levelling off:

- On the one hand, a decrease in recirculation flow rate, which decreases the energetic need of sulphuric acid dehydration at 760°C.
- On the other hand, increase of HT needs (heating from 760°C to T<sub>max</sub>), despite a slight decrease of reaction heat (endothermic reaction of decomposition).

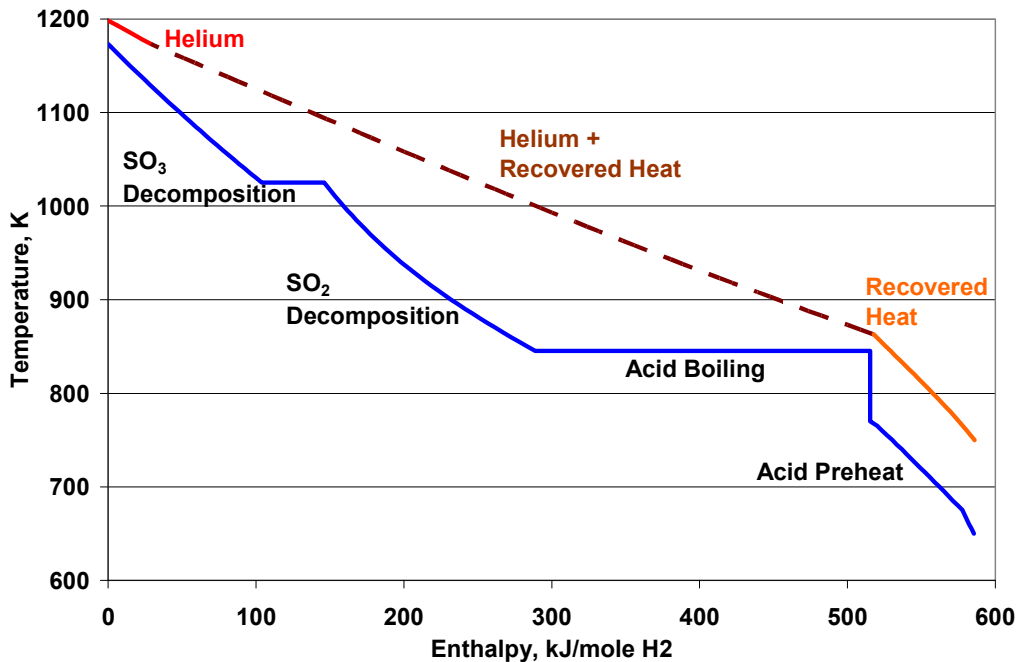
The only interest in increasing the maximal loop temperature is increasing the reaction kinetics.

### Effect of HTR inlet temperature

There exists an important difference between GA and CEA assumptions about the HTR inlet temperature. Can this temperature difference explain efficiency differences?

In the CEA process, heat exchange with the sulphur section takes place between 900 and ca. 600°C, whereas heat exchange with the iodine section takes place between around 600 and 400°C. In the GA process, no nuclear heat exchange with the iodine section exists, allowing thus a higher return temperature (590°C instead of 400°C). Figure 5 depicts Q-T curves for the GA Section II.

Figure 5: Q-T curves for GA Section II configuration

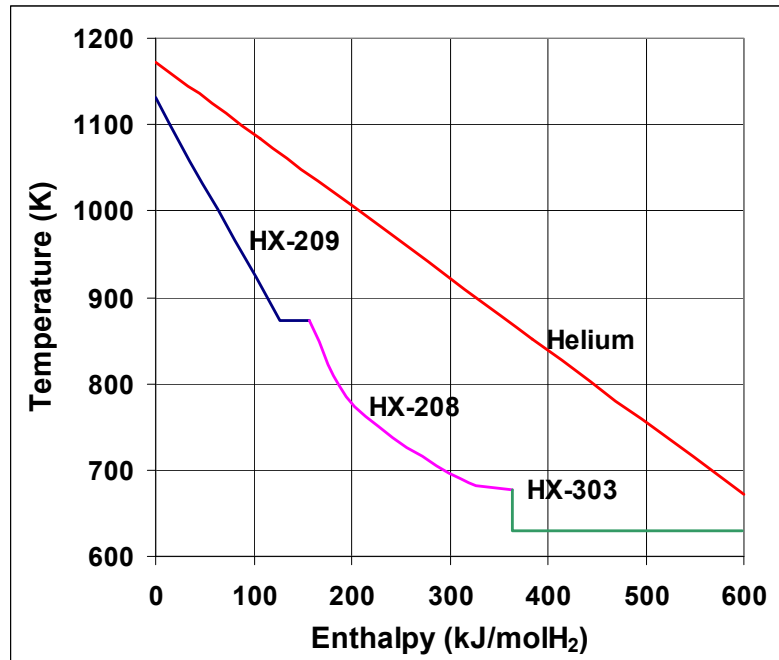


Process heat is recovered at high temperatures and is used in conjunction with helium to provide energy for much of the sulphuric acid decomposition process. In addition, recovered process heat at over 400°C is used by Section III. This design was optimised for these particular temperature parameters, but the concept of exchanging heat between process sections could be utilised with somewhat lower helium return temperatures.

Figure 6 represents for the CEA configuration the temperatures of secondary helium (red line) and of process temperature as a function of enthalpy released by He(II). Secondary helium flows from 900 to 400°C in the standard configuration.

The CEA process, as it is, would be compatible with GA's secondary helium, but an analysis with a helium inlet temperature near the GA value indicates that this coupling is probably not optimal. Indeed, whereas the helium flow rate would be increased by a factor of  $(900-400)/(900-565) \sim 1.50$  (i.e. +50%), the overall production of the HTR production plant would not increase, since the total heat demand of the process would not change. In other terms, CEA's process efficiency would not increase.

**Figure 6: Q-T curves in CEA configuration (Leybros, 2009) and corrections on helium inlet temperature**



Conversely, would the GA process be compatible with CEA secondary helium? The answer is yes, but the overall production of the HTR coupled plant would be lower. Indeed, one could say that the GA Q(T) curve, as it is, is compatible with the CEA's helium Q(T) curve: in both processes, secondary helium leaves Section II at a temperature around 600°C. However, this coupling implies the presence of a pinch point at the end of Section II which precludes increasing the helium flow rate, and hence the hydrogen production rate. Furthermore, setting the helium return temperature to 400°C implies that its heat content between 600°C and 400°C must be used in some way.

Thus, the only use for extra helium heat would be to convert it to work and provide this work to Section III. But the maximum temperature for this work generation is now only 600°C, implying a heat to work conversion coefficient probably not above 40%, and a maximum recoverable work of  $600 \text{ MW} * (600-400^\circ\text{C})/(900-400^\circ\text{C}) * 40\%$ , i.e. about 100 MW.

In conclusion, using the GA process with CEA secondary helium constraints would lead to:

- *In comparison to the GA reference solution:* A reduction of hydrogen production, but also a reduction of external electricity requirements.
- *In comparison to the CEA reference solution:* A decrease of external electrical demand, but no modification of hydrogen production.

### **Discussion: How to explain the differences in energy consumption between the two alternatives?**

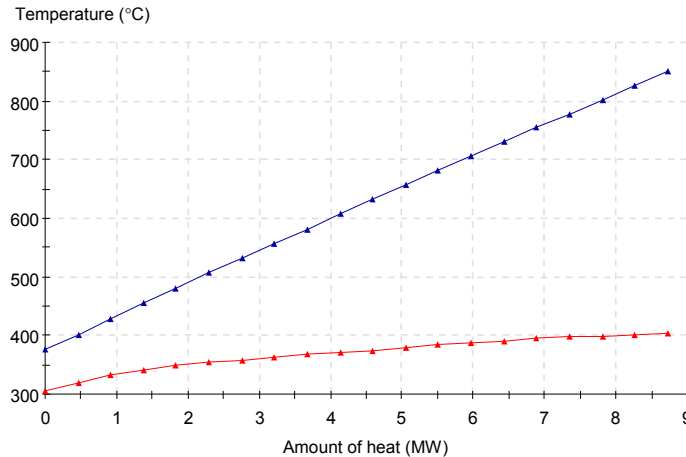
Two causes seem available to explain the efficiency differences between GA and CEA flow sheets: temperatures and couplings.



The effect of the maximal temperature of the cycle and/or of the HTR outlet temperature does not seem to be relevant (see Figure 4). The increase of HTR inlet temperature is closely related to coupling between sections (see for example Figure 5). What is the main role of coupling?

Let us comment on features of heat exchanger HX-207 in the CEA flow sheet. The temperature profile is given in Figure 7. The hot flow is cooled from 850 to 375°C, whereas the cold flow is heated from 305.4 to 403.3°C. The entrance pinch is ca. 450°C, which is thermodynamically not favourable (high loss of exergy). A better use of the available heat could be found inside the section, for example by optimising the internal heat exchanges with pinches of ca. 50°C.

**Figure 7: Temperature profiles in the main heat exchanger of the CEA sulphur section**



Another difference between schemes is the final temperature of the decomposition loop: about 400°C for GA and 230°C for CEA. In the CEA case, it is not possible to transfer heat from the end of the loop to the HI decomposition section, whereas it is possible in the GA process.

And the global heat released by the decomposition loop is not large enough to satisfy the energetic need of the HI decomposition section iodine section. In the GA case, the heat requirement is lower but the electrical need is higher. In order to increase the available heat in the sulphuric acid decomposition section, a solution could be to increase the working pressure in the loop. According to Le Châtelier's principle, a pressure increase leads to a lower efficiency, to larger flow rates in the loop and finally to an increase of the heat demand in the loop. GA compensates for the lower efficiency due to increasing pressure by increasing the peak process temperature.

Optimising the heat exchanges is now like a "sliding puzzle", including sulphur-to-iodine and iodine-to-sulphur couplings. At the colder end of the puzzle, the He(II)-to-iodine coupling heat has to be recovered, either by using waste heat from inside the sulphur section (solution not available, temperatures too low) or from heat from Bunsen reaction (provided the temperature range is correct).

In short, a coupled scheme based on the current CEA flow sheet would need:

- an increase of pressure in the decomposition loop;
- an increase of the maximal temperature of the loop;
- an increase of the end temperature of the loop;
- an increase of the electrical part of heating the iodine section;
- likely a coupling between Bunsen section and sulphur section.

Taking into account all these modifications, a coupled CEA-like flow sheet would be very similar to the GA flow sheet.

## Conclusion

Both GA and CEA have an optimised flow sheet, but the constraints taken into account are different.

Compared to GA, CEA:

- has a reactor with a lower outlet temperature, and much lower return temperature;
- avoided heat transfers between sections to make them relatively independent.

Both of these factors tend to lower the efficiency of the process.

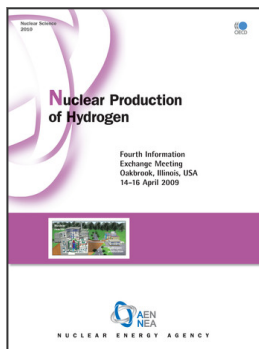
The lower CEA efficiency can therefore be, to a large extent, attributed to more conservative assumptions, whereas the GA scheme appears to be more innovative, though potentially more complex. As designs mature, it may be found that elements of both alternatives may be used to advantage.

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