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STATUS REPORT ON SULFUR IODINE THERMOCHEMICAL WATER-SPLITTING CYCLE

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ABSTRACT

Major process improvements which had been identified in an earlier phase of this program were investigated and their feasibility demonstrated. The engineering process flowsheet was revised to incorporate the newest process improvements. It is now being used for an estimate of hydrogen production cost from the General Atomic Company (GAC) cycle. An energy storage cycle for a solar adaptation of the sulfur-iodine cycle has been identified and is being evaluated along with features particularly concerning the availability and level of insolation and how it affects engineering design of the chemical plant. Efforts are also underway with Lawrence Livermore National Laboratory (LLNL) to design the sulfur-iodine cycle around the Tandem Mirror Fusion Reactor. Potential systems for HI purification are being investigated which could eliminate the need for the present phosphoric acid treatment completely and could result in significant savings in capital cost for this part of the process. Potential catalysts for the liquid HI decomposition step were evaluated. Noble metals appear to have highest activity; however, attrition of the catalyst occurs.

INTRODUCTION

The sulfur-iodine thermochemical water-splitting cycle is under investigation as a concept for the production of hydrogen. Its high thermal efficiency (47%) and a seasonally effective energy storage system make it particularly attractive for solar insolation energy. This could result in significantly lower overall plant cost for a process with higher insolation energy utilization.

The cycle has already been designed for nuclear process heat sources such as the High Temperature Gas Cooled Reactor (HTGR) (Ref. 1). In a joint effort with LLNL and GAC this cycle is being flowsheeted and costed as a process heat application of the Tandem Mirror Fusion Reactor. With accepted materials temperature and corrosion limitations, the cycle is well suited to this application.

GAC has been working on this cycle since 1974. The main goal for the development effort, both in laboratory and in design, has been to demonstrate the feasibility of the concept and to improve the system to the state where it can be competitive as a hydrogen production process in the future. The major effort over the last year has been to identify and develop concepts which would increase the efficiency and decrease the capital cost of this process. The testing and operation of a bench-scale system has been a valuable tool in this work.

Bench-Scale Engineering

The equipment of Hydrogen Iodide (HI) Purification and Decomposition (Section III, see Ref. 1), which had been previously installed, was operated successfully. A major part of the effort was expended in modifying the equipment to improve operability, increasing throughput, and gathering process data during operation.

The HI separation column and H_3PO_4 concentration columns were modified to increase boilup rate and thus throughput. High throughput rates of viscous H_3PO_4 resulted in flooding of the columns. The separation efficiency decreased when the flooding was eliminated through the use of large packing in the columns. Plate type columns have been ordered, which will eliminate this problem.

The HI decomposer was operated with no major problems from the beginning. A conversion ($2HI \rightarrow H_2 + I_2$) of 22% per pass has been routinely obtained. The predicted equilibrium conversion at the measured reactor outlet temperature is 16%. This discrepancy has not been fully explained yet. However, it is believed that there is temperature maldistribution at the reactor inlet which, if propagated, could give the observed result. Efficient iodine removal from the product stream was achieved by increasing the heat transfer area of the iodine trap and by lowering the temperature. Glass HI traps were replaced with stainless-steel pressure vessels allowing longer run times and better control of the recycle HI flow.

The iodine knock-out portion of Section III has been moved closer to the Section I prime reactor to allow short circuit return of the separated iodine. In the new location, the equipment is placed in a "hot box" for improved temperature control. In addition better use was made of fluid density differences to obtain self-automation of process flows.

Engineering Flowsheeting and Costing

The flowsheets for Sections I, III, and IV were revised. These revisions are the basis for a hydrogen production cost estimate which is now being carried out at GAC. Preliminary indications are that the cost of hydrogen from the GAC thermochemical water-splitting process using solar heat as the energy source is in the range of $12 to $20 per MBtu depending on the cost of solar heat. These numbers compare very well with an earlier cost estimate published by K. Ekman of Jet Propulsion Lab (JPL) (Ref. 2).

PRELIMINARY COST ESTIMATE FOR GAC PROCESS

[400 MW(th) Solar Plant]

	Section	Eckman (JPL)* $ ($X10^6$)	GAC $ ($X10^6$)
I.	Main Solution Reaction	54	28
II.	H_2SO_4 Decomposition	100	Not done yet
III.	HI Purification	167	162
IV.	HI Decomposition	14	16
V.	Power Generation and Heat Transfer	47	Not done yet

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*Reduced to 400 MW(th).

Solar Adaptation of the GAC Sulfur-Iodine Water-Splitting Cycle

Central power tower receivers can be provided with sufficiently concentrated insolation energy to decompose H_2SO_4 to SO_2, O_2, and H_2O. Thus, solar energy can provide a heat source capable of powering thermochemical hydrogen cycles requiring H_2SO_4 decomposition as does the GAC sulfur-iodine cycle. Because of the high cost of delivering the energy in solar systems, it is important to manage the collected energy to result in a high fraction of the deliverable energy being "stored" in the conversion of H_2O to H_2.

A major problem with solar energy use is that it is periodic in character (both diurnal and seasonal) and somewhat undependable on a short-time basis. One possible response to this characteristic is to make H_2 while the sun shines and be idle when it does not. If this is the choice, the chemical plant size is totally dependent upon insolation level. Moreover. the chemical plant must be sized to accept at any time a major fraction of the insolation deliverable by the mirror system. This latter point impacts strongly on the economics of the receiver-chemical system since it means that, for a southern USA desert location, it needs to be built to accommodate about five times the average yearly insolation energy (corresponding to energy available at peak noon summer solstice).

Depending on the cycle, the importance of this factor of 5 causes different actions. The chemistry of the sulfur-iodine cycle is sufficiently extensive that immediate production from delivered insolation appears uneconomic. The way to get around this is to institute energy as well as chemical storage (chemical storage during the night is required in any case). One of the tasks performed under a contract with the USDOE was to identify a storage technique that would be appropriate for the sulfur-iodine cycle. In an earlier study (Ref. 3), molten salt storage and SO_2-H_2SO_4 chemical storage had been investigated. For a selected 64-h storage period the tankage costs for the chemical system were very high, and for this long a period the molten salt storage was marginal. A proprietary storage system has been uncovered that requires less tankage for seasonal storage (24 days) than either the salt or the SO_2 storage system does for 2-1/2 days. The storage medium is inexpensive, and energy-conversion equipment is relatively simple.

This storage system allows consideration of operating a three-function chemical plant:

1. A hydrogen plant wherein the H_2SO_4 and HI components are made by reacting SO_2, H_2O, and I_2; the H_2SO_4 is treated to recover iodine; and H_2 is made from the HI after employing the H_3PO_4 treatment of the HI_x solution--the H_3PO_4 being dehydrated as part of the hydrogen plant operation.

2. A day plant which operates during insolation periods, concentrating and decomposing H_2SO_4 and energizing the storage cycle as well as supplying energy to operate the hydrogen plant.

3. A night plant which supplies energy to power the hydrogen plant when the day plant cannot.

The GAC sulfur-iodine cycle has been reported to have a 47% thermal efficiency (Ref. 1). The storage cycle is expected to reduce the efficiency of the solar energy based cycle somewhat. It allows, however, a major section of the chemical plant to be levelized and, thus, minimized in cost. Moreover, seasonal storage allows this chemical plant to be levelized throughout the year at tolerable costs for tankage and inventory. This impacts greatly on the ability to utilize available insolation without overbuilding the solar mirror field.

A conceptual basis for maximizing economic return from a solar concentrator--water-splitting cycle couple has been established. An effort to evaluate this system is planned.

Fusion Adaptation of the Sulfur-Iodine Cycle

The University of Washington, LLNL, and GAC are cooperating on establishing the design of a Tandem Mirror Fusion Reactor process heat application. GAC is contributing its cycle experience to this cause with LLNL being the lead organization in this effort. This program is described in LLNL reports from last year (Ref. 4) and in a report soon to be issued covering this year's efforts (Ref. 5).

Process Chemistry

The processing of the lower-phase HI solution, high in iodine and containing significant amounts of H_2O, is a critical step in the GAC sulfur-iodine water-splitting cycle because of its potentially high cost. At present, the recovery of HI is accomplished by adding concentrated H_3PO_4 such that the final H_3PO_4-H_2O solution exceeds 85% H_3PO_4 (Ref. 6). In doing so, two things happen:

1. Much of the excess I_2 separates as a second liquid phase.

2. The HI is increased in chemical activity while the H_2O activity is decreased. and HI can be distilled out of this mixture at superazeotropic conditions such that the distilled HI can be recovered as a dry liquid.

While H_3PO_4 accomplishes the necessary steps, it requires a considerable H_3PO_4 recycle flow. Also, the energetics for removing the H_2O from the H_3PO_4 are demanding. At present this is designed to be done quite efficiently by the use of compressive work. but the equipment, in the form of heat exchangers and vapor recompression turbines, is quite expensive.

Research has been carried out to investigate other methods of processing the HI_x product solution. We were successful in identifying two potentially very attractive processes which can accomplish the necessary separations. The advantage of these concepts is in the fact that no phosphoric acid treatment is required. In one, the amount of water that needs to be evaporated is only a fraction of the old flowsheet value. In the other. the water still needs to be evaporated but not from as deep a thermodynamic sink as H_3PO_4 Patent protection is being sought for these new process improvements. However, there are still a number of process details that need to be investigated before the system can be adopted as an alternative for HI_x product solution purification.

LIQUID HYDROGEN IODIDE CATALYST STUDIES

During the past years, GAC has studied the advanced concept of decomposing HI in the liquid phase (Ref. 7). Theoretical calculations had indicated that high conversions were possible. Experiments conducted in glass pressure vessels under restricted pressure and temperature conditions and batch operation showed great promise for the use of the method in the sulfur-iodine cycle. Measured conversion values were comparable to the high values predicted theoretically; and reaction rate data, extrapolated to higher process temperatures. indicated that application of the system to the GAC cycle would result in a viable process. In order to evaluate this concept under anticipated process conditions, a system was designed. constructed. and operated in which the decomposition of liquid HI at temperatures and pressures and flow conditions leading to reasonable reactor residence times could be investigated. In addition, some batch studies were performed in parallel in an attempt to evaluate catalyst stability in the liquid HI environment.

Two major conclusions can be drawn from the work performed to date. First, noble metal catalysts provide the highest rates of decomposition and second, there is significant attrition of noble metal into the liquid HI environment. The cost involved in using noble metal catalysts for this process were not found to be excessive. Also, catalyst recovery is common in the chemical industry. Therefore, catalyst attrition is not expected to be an insurmountable problem in the process. We are also pursuing a new, very attractive scheme for catalyst recycle which does not involve total catalyst recovery and regeneration.

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REFERENCES

1. "Thermochemical Water-Splitting Cycle Bench-Scale Investigations and Process Engineering," Annual Report for the Period October 1, 1978, through September 30, 1979, General Atomic Report GA-A 15788, UC-94d, March 1980.

2. Ekman, K. R., "Cost of Hydrogen Production from Fossil and Nuclear Fuels," Jet Propulsion Laboratory Report 5030-461, July 15, 1980.

3. Besenbruch, G. E. and K. M. McCorkle, "Thermochemical Water Splitting with Solar Thermal Energy: Final Report," General Atomic Report GA-A 16022, February 1981.

4. Werner, R. W., et al., "Synfuels from Fusion-Producing Hydrogen with the Tandem Mirror Reactor and Thermochemical Cycles," Lawrence Livermore Laboratory Report UCID-18909, January 21. 1981.

5. Lawrence Livermore National Laboratory Report to be published.

6. Norman, J. H., et al., "Chemical Studies on the General Atomic Sulfur-Iodine Thermochemical Water-Splitting Cycle," in "Hydrogen Energy System," Proceedings of the 2nd World Hydrogen Energy Conference, August 21-24, 1978, Zurich, Switzerland, v. 2, T. N. Veziroglu and W. Seifritz (eds.), Pergamon Press, Oxford, 1978, p. 513.

7. O'Keefe, D. R. and J. H. Norman, "The Liquid Hydrogen Iodide Decomposition Process Step for Water-Splitting Applications," in "Hydrogen Energy Progress,"Proceedings of the 3rd World Hydrogen Energy Conference, Tokyo, Japan, 23-26 June 1980, Vol. 1, T. N. Veziroglu, K. Fueki, and T. Ohta (eds.) Pergamon Press, Oxford, 1980, p. 277.

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