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PROGRESS REPORT ON THE DEVELOPMENT OF THE GENERAL ATOMIC THERMOCHEMICAL WATER-SPLITTING PROCESS

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MASTER

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GENERAL ATOMIC COMPANY

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PROGRESS REPORT ON THE DEVELOPMENT OF THE GENERAL ATOMIC THERMOCHEMICAL WATER-SPLITTING PROCESS

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Abstract

The major accomplishments of the DOE funded part of the GA thermochemical water-splitting program are reported. They include:

1. Completion of installation of all bench-scale equipment.
2. Operation and preliminary data acquisition for bench-scale subunits I and II.
3. Design, installation and operation of a system for iodine removal from the low phase.
4. Review and modification of section III of the engineering flowsheet resulting in an increase in process efficiency and decrease in capital cost.
5. Completion of the Funk panel review.

The results of the experimental work have demonstrated that flowsheet conditions can be achieved in all cases tested. Continued work on the flowsheet has increased our confidence in the economic viability of the sulfur-iodine process.

Introduction

Thermochemical water-splitting has been under investigation at GA since 1972. The U.S. Department of Energy (then ERDA) joined the program in 1976. At present, the total GA water-splitting project is cosponsored by the U.S. Department of Energy (Energy Storage Division and Solar Thermal Power Office), the Gas Research Institute, the Metal Properties Council, and General Atomic Company.

The process can be described by the following three chemical equations:

$$xI_2 + SO_2 + 2H_2O \rightarrow H_2SO_4 + 2HI_x \qquad 370\text{ K} \quad (1)$$

$$2HI_x \rightarrow H_2 + xI_2 \qquad 390\text{ K} \quad (2)$$

$$H_2SO_4 \rightarrow SO_2 + 1/2\,O_2 + H_2O \qquad 1144\text{ K} \quad (3)$$

The main advantages of the cycle are that it can be conducted as an all-liquid and gas-phase process and that its unit operations are simple, industry-developed processes like distillation, vaporization, and phase separation.

Bench Scale

A major part of the bench-scale effort was spent in the installation of bench-scale subunit III, (HI purification and decomposition). Figures 1 and 2 show photographs of the unit. The installation was completed on schedule and operational shakedown will be completed before the end of September.

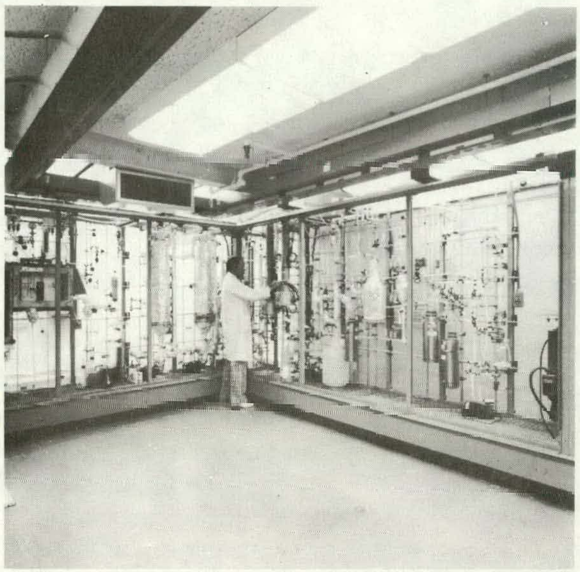

Fig. 1. Bench-scale subunit III: Overview

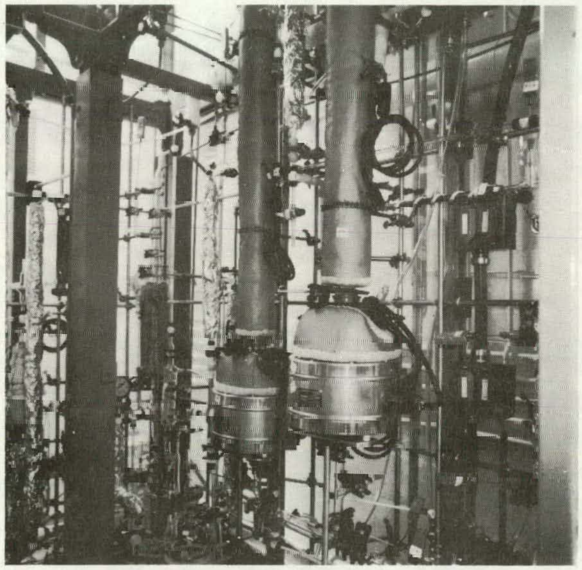

Fig. 2. Bench-scale subunit III: HI extractive distillation column

Data acquisition on bench-scale subunits I and II (main solution reaction and H_2SO_4 decomposition, respectively), was carried out and resulted in the verification of flowsheet conditions for all of the unit operations tested. Figures 3, 4, and 5 show photographs of subunits I and II. Early tests on subunit I resulted in H_2SO_4 concentrations in the upper phase of 42 -44 wt % while the design concentration is 50%. Recent tests have resulted in H_2SO_4 concentrations of 49 -52 wt %. This is well within the flowsheet design conditions. The experiments in subunit II were carried out to evaluate the performance of the iodine strippers and of the sulfuric acid decomposition system.

The iodine stripping column shown in Fig. 6 consists of a pyrex tube (60 cm long, 3 cm diam) filled with glass beads (3 mm diam). The column is externally heated and insulated. Sulfuric acid (~50 wt %) containing ~1.2% HI and 0.6% I_2 is fed to the top of the heated column. Iodine is removed from the liquid by steam stripping with the water evaporating from the liquid. This changes the HI/I_2 equilibrium, allowing the hydrogen iodide to react with the H_2SO_4 to form I_2, SO_2, and H_2O via Eq. 1. The I_2 and SO_2 so formed are further stripped from the liquid. The experiments were carried out at various temperatures and three different feed flow rates. The results plotted in Fig. 7 indicate that at flowrates of 10 and 17 cm^3 H_2SO_4/min very good stripping of the iodine can be achieved at relatively low temperatures. At a flowrate of 5 cm^3/min, bypass flow apparently occurs in the column, and the results are erratic.

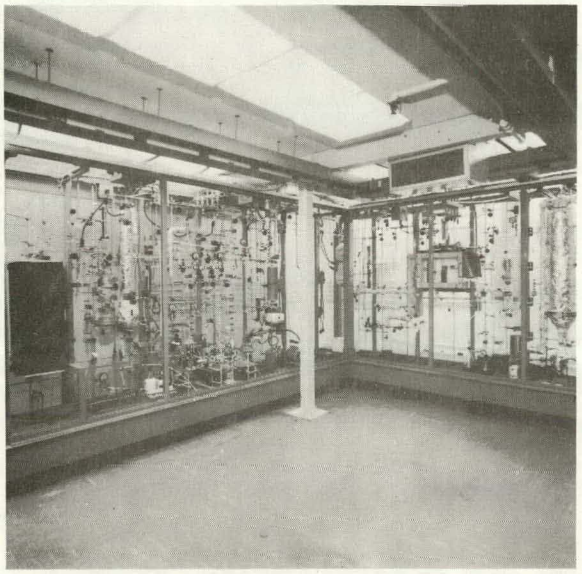

Fig. 3. Bench-scale subunit II: Overview

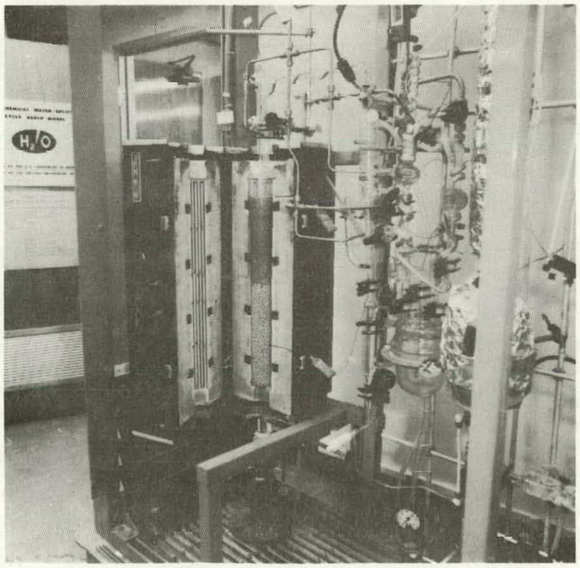

Fig. 4. Bench-scale subunit II: SO_3 decomposer with catalyst in place

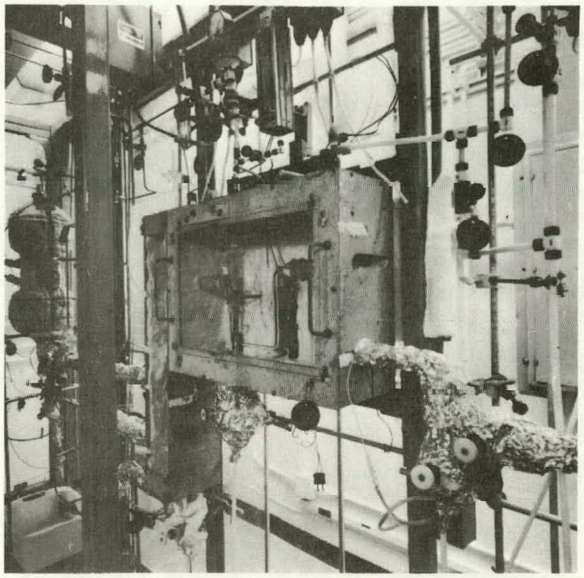

Fig. 5. Bench-scale subunit I: Main solution reactor and phase separator

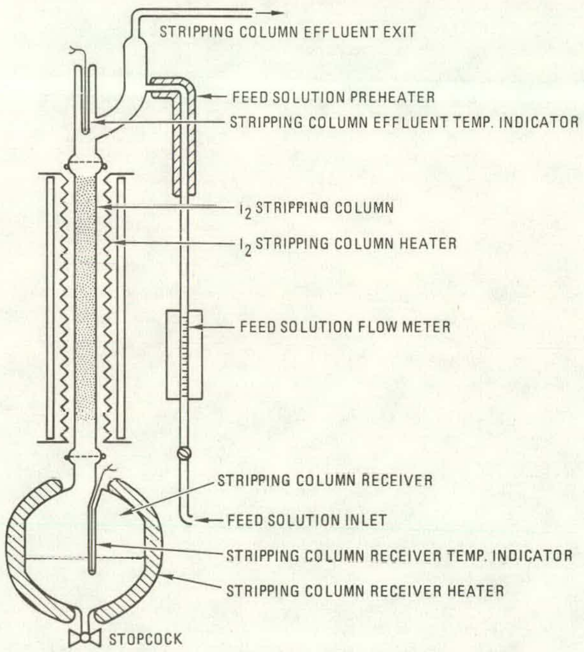

Fig. 6. Schematic of iodine stripping column in use in subunit II

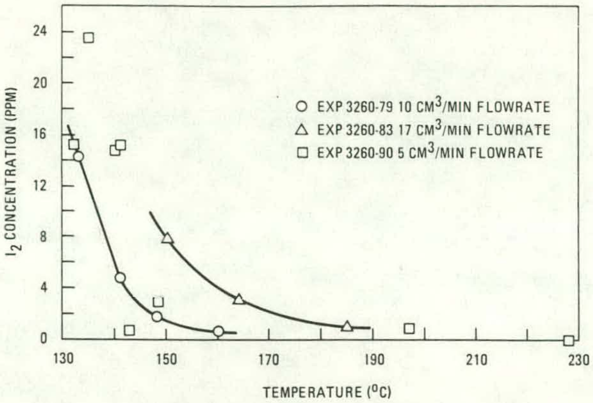

Fig. 7. I_2 concentration versus column temperature for subunit II for 5, 10, and 17 cm^3/min feed flowrates

It is believed that the I_2 concentration in the liquid effluent is controlled by the rate of reaction between HI, which is also present in the upper phase (~1%), and H_2SO_4 to generate free, volatile I_2. Also, probably, the average residence time of the fluid flowing through the column is an important parameter with respect to this reaction. Further experiments to test the foregoing hypothesis are planned.

In the sulfuric acid cracking experiments the decomposition of H_2SO_4 into SO_2, H_2O, and O_2 was evaluated. A platinum on zirconia catalyst, 0.3175 cm (1/8 in. diam) right cylinder pellets containing ~0.2 wt % platinum was used at temperatures between 800° to 900°C. The gas slugflow residence time in the reactor was between 0.3 to 1 s. Figure 8 shows the gas decomposition results for the experiments. The data points were calculated both by measuring the amount of unreacted H_2SO_4 which condensed in the decomposer effluent and the oxygen output flowrate after caustic absorption of the SO_2. The two methods agree to within ±5%, with the condensed H_2SO_4 analysis being preferred as the more accurate; this latter method is the basis for Fig. 8. Catalyst bed temperature is taken to be the maximum reading of an axial temperature traverse of the bed taken during steady-state operation.

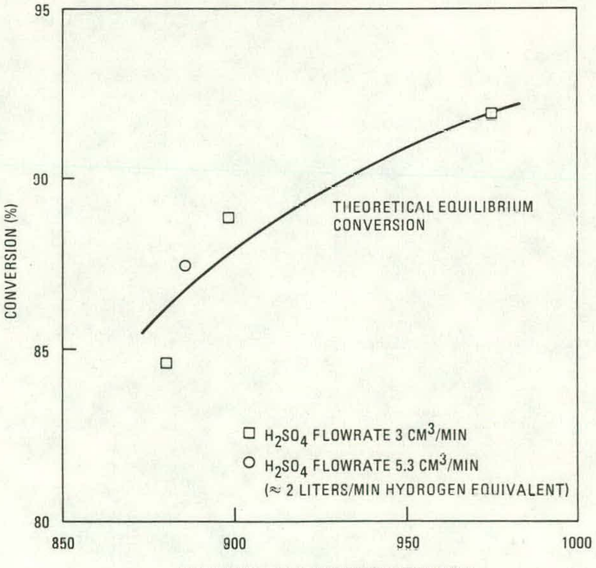

Fig. 8. Performance of bench-scale H_2SO_4 decomposition equipment

The experimental results are within ±2% of the theoretical prediction using the maximum catalyst temperature and the equilibrium composition calculated from the JANAF tables. The low point at ~875°C in Fig. 8 was obtained in a loading of the catalyst bed for which a significant portion of the bed was in the exit region where the temperature had substantially fallen off from the maximum near the axial center of the decomposer. This resulted in a significant back reaction of the decomposition products from the hotter region and thus a low conversion compared to theoretical. This problem was rectified by shortening the catalyst bed and using only the hottest region of the decomposer. The other data points in Fig. 8 were taken using such a configuration. The overall simultaneous operation of all subunit II components was demonstrated at a flowrate equivalent to 2 std liters/min H_2. All process steps functioned as designed.

Engineering

Redesign of section III of the engineering flowsheet was completed. The changes incorporated include the use of a medium pressure extractive distillation system for separation of HI from the HI/H_2O/HI phase. The redesign resulted in an increase in thermal efficiency equivalent to 1.5%. The equipment requirements were also significantly reduced through elimination of two turbine expanders, two turbine compressors, and several heat exchangers. A conceptual flowsheet of the revised section III is shown in Fig. 9.

Conclusions

Installation and operation of the bench-scale system have shown that design conditions assumed in the engineering flowsheet are being verified in each of the subsystems tested, demonstrating the validity of the GA water-splitting flowsheet. Additionally, the flowsheet design effort continues to improve the efficiency of the process while at the same time reducing the capital equipment requirements. The significant progress made in the last year further increased our confidence that thermochemical water-splitting utilyzing the GA sulfur-iodine cycle is a viable, economic alternative for hydrogen production.

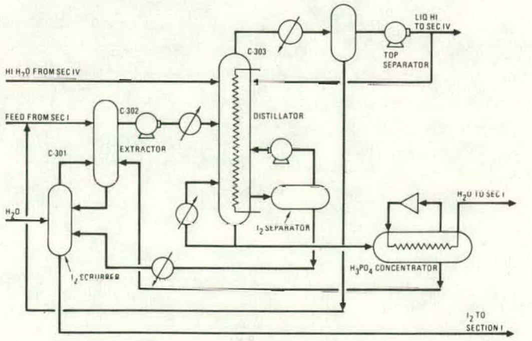

Fig. 9. Section III HI separation

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