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LABORATORY SCALE DEMONSTRATION OF THE Mg-S-I CYCLE FOR THERMOCHEMICAL HYDROGEN PRODUCTION

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The Mg-S-I water splitting cycle was demonstrated on a laboratory scale by constructing an apparatus for repeated operations of chemical reactions of the whole cycle and by the circulation of reactants through purely thermochemical processes below 1000°C. Electric furnaces and quartz glass reactors were used. Sixteen times of cycle operations were performed in 16 h with production rates of 0.3 liter H_2/h and 0.15 liter O_2/h.

The thermochemical hydrogen production has been widely studied since the days of 1970's. The S-I cycle$^{1)}$ and the Ca-Fe-Br cycle$^{2)}$ have been elaborately developed for a bench-scale operation, however, the detailed informations on the rate of hydrogen production, the amount of circulating reactants and the number of times of repeated operations have not been shown in their studies. So far as the present authors surveyed, demonstrations of the purely thermochemical cycles with more than 10 times of repeated operations of the whole cycle have never been reported.

The authors have been studying on the Mg-S-I thermochemical water splitting cycle, since they presented an addition of magnesium ions for the separation of the H_2SO_4-HI solution together with the new cycle proposal$^{3)4)}$ in 1978. Equilibrium and kinetic studies$^{5)6)7)}$ were continued on each of the constituent reactions. The object of this work was focused on the construction of an apparatus on a laboratory scale and demonstration of repeated operations of the whole cycle.

The Mg-S-I cycle is expressed as follows:

$$I_2(c) + SO_2(aq) + 2H_2O(l) \longrightarrow H_2SO_4(aq) + 2HI(aq) \qquad \text{...R(1-1)}$$

$$2MgO(c) + H_2SO_4(aq) + 2HI(aq) \longrightarrow MgSO_4(aq) + MgI_2(aq) \qquad \text{...R(1-2)}$$

$$MgI_2(aq) \longrightarrow MgO(c) + 2HI(g) + nH_2O(g) \qquad \text{...R(2)}$$

$$MgSO_4(c) \longrightarrow MgO(c) + SO_3(g) \qquad \text{...R(3-1)}$$

$$SO_3(g) \longrightarrow SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \text{...R(3-2)}$$

$$2HI(g) \longrightarrow H_2(g) + I_2(g) \qquad \text{...R(4)}$$

As summarized in Table 1, sufficiently high conversions and rates of each constituent reaction have been confirmed in the previous studies.$^{6)7)8)9)10)}$ Detailed descriptions for reaction characteristics are omitted in this report. Since this work was aimed at the demonstration of whole Mg-S-I cycle, the design of the cycle apparatus and the operations were performed with particular emphasis on the verification of H_2 and O_2 productions with repeated runs of chemical reactions and reactant circulations. Problems of thermal efficiency, transportation of solid phase reactants and selection of apparatus materials were neglected in this study, although they are generally supposed to be critical factors of the feasibility of thermochemical cycles.

To simplify the total system and minimize the chemical engineering problems, the design of the cycle apparatus and the operations were made on following principles.

(i) Transportation of solid reactants is avoided. Only fluids are circulated within the cycle. Reactions involving solid reactants are made by heating or cooling reactants within a reactor.

(ii) As a reactor material, quartz is used for its high resistance to corrosion and thermal shocks.

(iii) The mixed (H_2,I_2,HI and H_2O) gas produced in R(4) is quenched to obtain H_2. The resultant $HI-I_2-H_2O$ condensate is reused for separation of the mixed SO_2-O_2 gas evolved in R(3-2), where only SO_2 is absorbed by I_2 through R(1-1) and O_2 is obtained.

Table 1 Running Conditions for Mg-S-I Cycle

Reaction	Previous Studies			Present Operation	
	Temp.(℃)	Conversion(%)	Ref.	Temp. (℃)	Conversion(%)
1 − 1	25	100	8	0 ~25	~100
1 − 2	70	100	7	70	~100
2	400	95	6	400~500	95
3 − 1	900 1000 1100	2.9[a)] 4.7[a)] 93.7[a)]	9	995	30[b)]
3 − 2	800 900 1000	70 85 92	10	995	99[b)]
4	600 800 1000	24.8 28.3 31.0	10	995	31
Total				0 ~995	29.5[c)]

a) in air, b) in N_2 (0.01atm SO_3), c) 0.95×0.31=0.30×0.99=0.295

<u>CYCLE APPARATUS</u> The apparatus is designed for production of 1 liter H_2 and 0.5 liter O_2 at one cycle operation. It consists of three main parts; Reactor A (related to solid phases), Reactor B (gas decomposer) and Reactor C (gas separating condenser) as shown in Fig. 1. The round-bottomed reactor A, made of quartz, (80mmD x 170mmH) is heated or cooled between 70 and 995°C by raising or lowering an electric furnace. The quartz reactor B (28mmD x 500mmL) is always maintained at 995°C by an electric furnace. The Pyrex glass reactor C consists of a Liebig-type condenser with a tapered inner tube and of a gas scrubber which is cooled by water with ice. Pumping system is used for recycling the H_2SO_4-HI solution from Reactor C to Reactor A. Evolutions of H_2 and O_2 are continuously measured by a thermal conductivity detector and a ZrO_2 sensor, respectively.

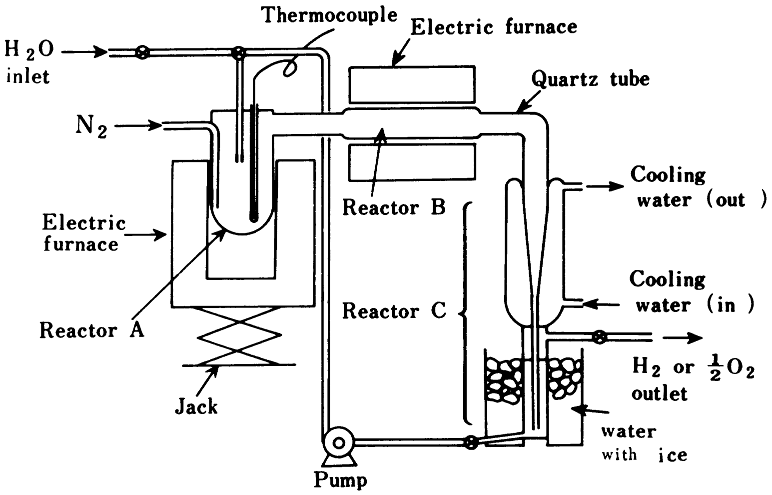

Fig. 1 Experimental Apparatus for Mg-S-I Cycle

CYCLE OPERATION The operating conditions for this demonstration were set as shown in Table 1. Since the conversions of R(1-1) and R(1-2) are 1.0, total yield of the whole cycle (0.295) is determined by the product of the conversions for R(2) and R(4) (0.31 x 0.95). To match the evolution of (H_2, I_2) with that of ($\frac{1}{2}O_2$,SO_2), total yield of R(3-1) and R(3-2) was set at 0.295. Thus, almost three times as much of reactants as theoretical were put into the cycle as follows: MgO: 0.304 mol, I_2: 0.152 mol, SO_2: 0.152 mol, H_2O: 9.73 mol. As illustrated in Figs. 2 and 3, the operations are carried out in three stages, where H_2 and $\frac{1}{2}O_2$ are alternately produced.

Stage 1: In the beginning of this stage the products of R(3-1), i.e., MgO and unreacted $MgSO_4$ are left in Reactor A and the H_2SO_4-HI solution has been accumulated in Reactor C through R(1-1). During this stage the crucible furnace was lowered to keep the temperature of Reactor A at about 70°C. As the mixed acid solution is pumped into Reactor A, dissolution of MgO into the solution (R(1-2)) takes place. Stirring of the suspension is made by bubbling the carrier gas (N_2) and $MgSO_4$-MgI_2 solution is obtained.

Stage 2: By raising the furnace, Reactor A is heated from 70 to 400°C. As the $MgSO_4$-MgI_2 solution is concentrated, an HI-H_2O gas mixture is formed by the hydrolysis of MgI_2, R(2). In Reactor B, HI decomposes to H_2 and I_2 reaching equilibrium of R(4) at 995°C.

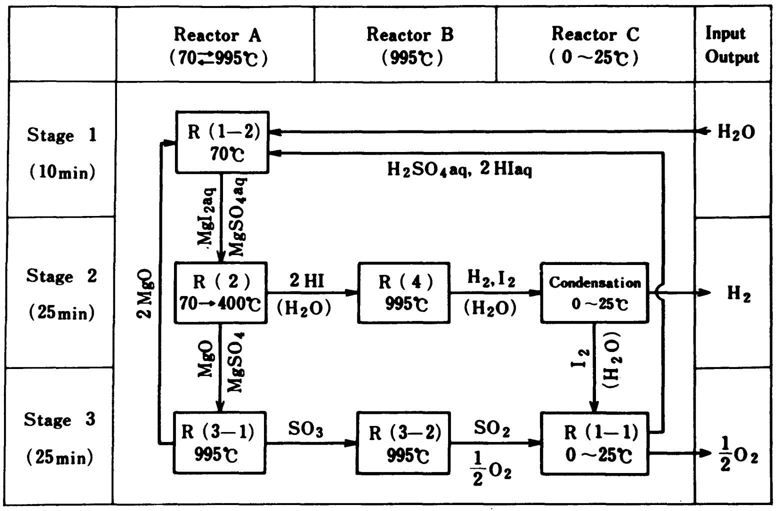

Fig. 2 Material Flow in Mg-S-I Cycle

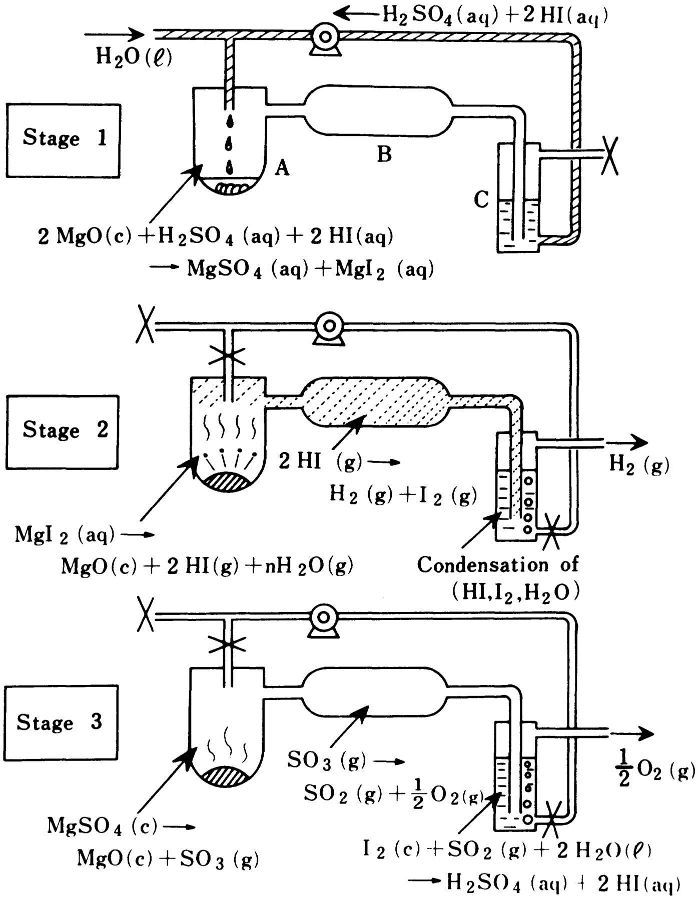

Fig. 3 Stages of Mg-S-I Cycle

The separation of the mixed gas (H_2,I_2,HI,H_2O) is made in Reactor C at 0-25°C, where I_2, H_2O and HI condense to form an HI-I_2-H_2O solution and the product hydrogen is obtained. The total amount of hydrogen evolved is calculated with the total gas flow rate and hydrogen concentration.

Stage 3: By raising the furnace, Reactor A is further heated to 995°C to decompose $MgSO_4$ in it (R(3-1)). In Reactor B, evolved SO_3 gas is converted to an SO_2-O_2 mixture at 995°C (R(3-2)), which is scrubbed with the HI-I_2-H_2O solution in Reactor C at 0-25°C where SO_2 gas reacts with I_2 to give an H_2SO_4-HI solution (R(1-1)). Thus, the product oxygen is separated from the SO_2-O_2 mixture. When the amount of oxygen evolved reaches a half amount of hydrogen, the furnace is lowered to cease $MgSO_4$ decomposition.

RESULTS As shown in Fig. 4, sixteen times of cycle operations with roughly constant production of 0.3 liter H_2 and 0.15 liter O_2 per cycle were successfully achieved. The time requirement for one cycle operation was one hour (10,25 and 25 min for the three stages shown in Fig. 2), where all the chemical reactions proceeded and all the reactants were circulated. Since the cycle apparatus and the operation mode have been designed for production of 1.0 liter H_2 and 0.5 liter O_2 per cycle, further studies on optimum operating conditions for 1.0 liter H_2 production are still in progress.

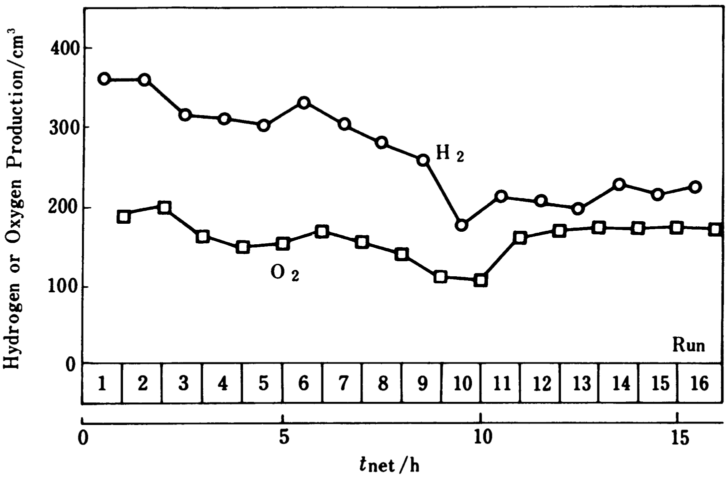

Fig. 4 Results of Hydrogen or Oxygen Production through Repeated Cycle Operations of Mg-S-I Cycle

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