

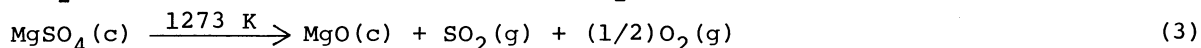
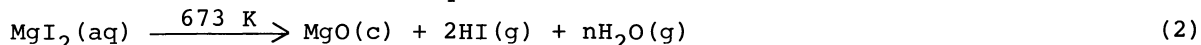
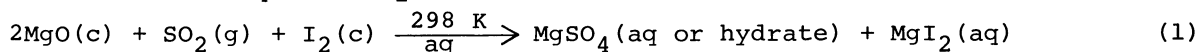
CONTINUOUS-FLOW DEMONSTRATION OF THE Mg-S-I CYCLE
FOR THERMOCHEMICAL HYDROGEN PRODUCTION

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The Mg-S-I water-splitting cycle was demonstrated on a laboratory scale by developing a continuous-flow system including solid-reactant transportation. The whole system was satisfactorily operated for 33 hours with roughly constant production of 0.5 dm³ of H₂ and 0.25 dm³ of O₂ per hour.

Since 1978 we have been studying on the Mg-S-I water-splitting cycle,¹⁾ where the separation of MgSO₄ and MgI₂ was avoided. The cycle is expressed as follows.



Recently many efforts²⁻⁴⁾ have been made on the improvement of the thermal efficiency by reducing the amount of H₂O used in reaction (1). Thus, the mixture of MgSO₄ and MgI₂ has been found to be separable by the common ion (Mg²⁺) effect under the highly concentrated conditions of the solution, as a result of the following experiment.

A mixed gas of SO₂ and O₂, evolved by reaction (3), was introduced into a mixture of MgO and I₂-H₂O solution containing HI which remained undecomposed in reaction (4) (MgO : HI : I₂ : H₂O = 4 : 4 : 1 : m, m = 15, 18, 25, 29 at 303 K; m = 15 at 373 K). Whereupon the SO₂ was absorbed by reaction (1), a slurry of MgSO₄·7H₂O (at 303 K) or MgSO₄·H₂O (at 373 K) with MgI₂ solution was obtained. The fraction of MgSO₄ precipitated or remained in the solution was determined by iodometry and chelatometry. The higher separability was found for the less amount of H₂O used; the results for the reaction at 303 K is shown in Fig. 1.

On the basis of the fundamental and engineering studies together with the above findings, we have developed a continuous-flow system with solid-reactant transportation to demonstrate the whole Mg-S-I cycle as depicted in Fig. 2; the reactors were made of quartz

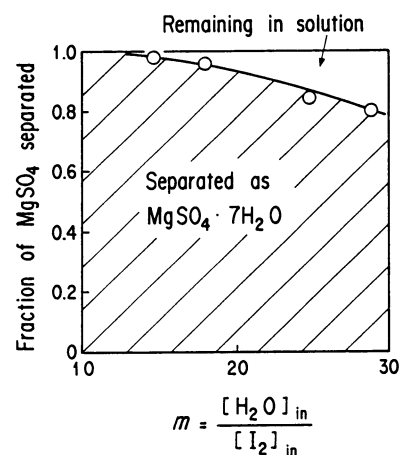


Fig. 1. Separability of MgSO₄ from MgI₂(aq) after SO₂ absorption with MgO + (HI-I₂-H₂O) slurry.

and Pyrex glass, and electric furnaces were used as heat source. The MgI_2 solution, dropped into Reactor 2, is immediately hydrolyzed at 673 K. The HI evolved is allowed to thermally dissociate at 1273 K in Reactor 4 and the product gas mixture (H_2 -HI- I_2 - H_2O) is condensed to separate the H_2 . Similarly the MgSO_4 solution, dropped into Reactor 3, is allowed to dehydrate and decompose at 1273 K. The SO_2 - O_2 mixed gas is bubbled in Reactor 1 where reaction (1) takes place to separate the O_2 . The solid products of reactions (2) and (3), i.e., MgO , are not sticky and are easily transported by quartz screw conveyers to fall down into Condenser and Reactor 1, respectively. The precipitated $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ powder is separated by filtration. The powder is dissolved again, into the H_2O produced by evaporation of the MgI_2 solution, to be recycled, because raking out and lifting up such small amounts of solid are so difficult on this laboratory scale.

The whole system was successfully operated for 33 hours, where all the chemical reactions smoothly proceeded and all the reactants including solids could be circulated. Roughly constant production of 0.5 dm^3 of H_2 and 0.25 dm^3 of O_2 per hour was achieved, where the initial amount of the reactants were 1.5 mol of MgSO_4 , 1.5 mol of MgI_2 and 45.0 mol of H_2O . The distinctive features of the present demonstration are conclusively summarized as follows.

- (i) Feasibility of the Mg-S-I cycle was confirmed by demonstrating the continuous-flow system with solid-reactant transportation.
- (ii) Thermal efficiency of the cycle was greatly improved since the heat of evaporation for the H_2O used in reaction (1) was markedly reduced.
- (iii) This system would readily be developed to a larger scale, as most operations involved are commonly used in chemical industries.

References

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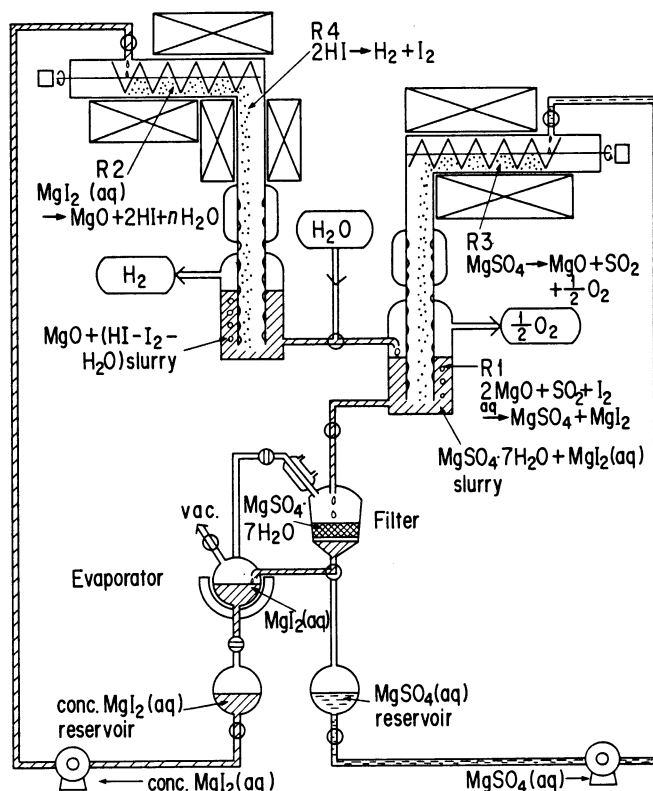


Fig. 1. Schematic diagram for continuous operation of Mg-S-I cycle via solid-phase transportation.

(Received November 8, 1985)