

## Reaction of Sulfur with Water under Hydrothermal Conditions

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The interaction of sulfur with water or aqueous has been investigated at 40-250 °C with pressure less than 15 MPa. The reaction behavior of sulfur with water under hydrothermal conditions was studied by ion chromatography and UV spectro-photography. The results suggest that the disproportionation reaction of sulfur, yield of HS<sup>-</sup>, and other resultant sulfur species are dependent on reaction temperature and pH of aqueous. The main disproportionation mechanism includes the following reactions:  $(2n+1) S + 2NaOH + H_2O \rightarrow Na_2SO_3 + 2H_2S_n$  and  $(n-1) Na_2SO_3 + H_2S_n \rightarrow (n-1) Na_2S_2O_3 + H_2S$ . Under alkaline conditions, reaction of sulfur with aqueous can take place even at a lower temperature than 119.6 °C of sulfur melting point. The yield of HS<sup>-</sup> is higher than 57% at temperatures above 170 °C.

### 1. Introduction

Many researchers have examined the reaction of sulfur with water at elevated temperatures and pressures in solving geothermal problems or for technological purposes such as the hydrometallurgical processing of sulfur ores [1-5]. Most of the experiments were done in acid or neutral hydrothermal conditions at 200-350 °C for concerning the chemical equilibrium, and very few data involves the kinetics and intermediates in the

process of reaction of sulfur with water. For the complexity of sulfur species in solution and lack of accurately measurable quantitative methods, almost all the data about reaction of sulfur with water are not able to being given satisfactory agreement each other [5].

On the other hand, recently a new and promising hydrogen gas generation system has been proposed, as shown in Fig. 1. In this system, H<sub>2</sub>S gas dissolving in alkaline solution as raw material is efficiently split into hydrogen gas and

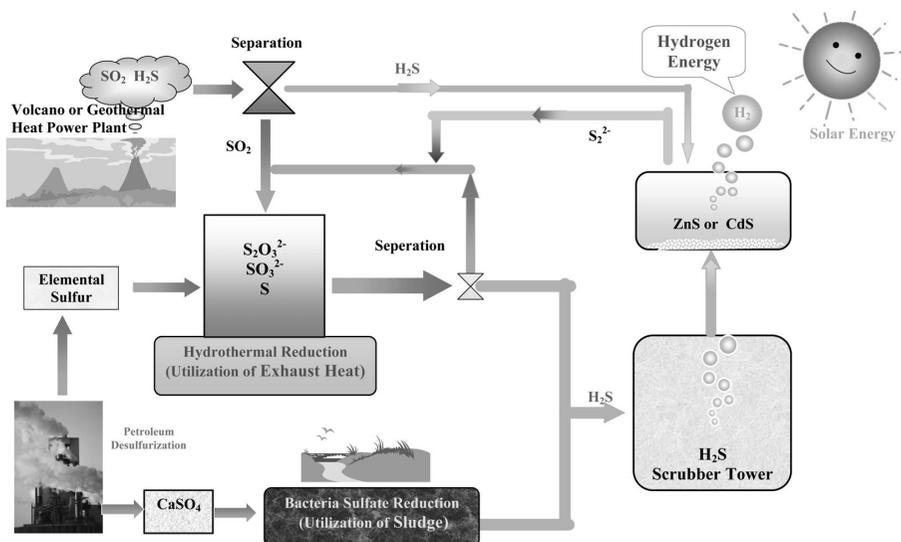


Fig. 1. The conceptual graph of sulfur recycling process for production of hydrogen.

commensurate disulfide ions  $\text{HS}_2^-$  based on photochemical reactions with nanosized ZnS or CdS photocatalyst by use of sunlight [6, 7]. It has also reported that it should be an alive and commercial potential method for production of hydrogen – the next generation energy source. In order to realize the system, there are two important key problems left to solve: (1) How to produce the raw material  $\text{H}_2\text{S}$  gas? (2) How to reutilize the disulfide ion  $\text{S}_2^{2-}$  comes from the photolysis of  $\text{H}_2\text{S}$  dissolving in alkaline solution?

In this study, a quantitative investigation was made on the reaction mechanism of sulfur with water under hydrothermal conditions, and the possibility of recycling  $\text{S}_2^{2-}$  which comes from the photocatalytic hydrogen generation system to hydrogen sulfide was discussed.

## 2. Experimental Methods

Thermochemical reactions of sulfur with water or aqueous were done at 40-250 °C for 5 min up to 24 h under saturated vapor pressure less than 15 MPa. An autoclave using Teflon container with capability of 28 ml as a reactor was employed, 3.12 mmol elemental sulfur powder was selected as a source of starting sulfur, addition amount of reactant solution or water was 10 ml, the pH of which was adjusted by NaOH solution. All the reagents are chemical pure.

After being rapidly cooled, the resultant solutions and gas were absorbed by KOH solution in an inclosed box with protection of  $\text{N}_2$  gas from being oxidized by oxygen in air. And then the samples were diluted to the desired concentration and analyzed by ion chromatographs (TOSOH Corporation, Japan) and UV spectro-photograph (U-3300 spectrophotometer, HITACHI Corporation, Japan) [8].

## 3. Results and Discussion

**3.1. Effect of reaction temperature and time** When reaction temperature is higher than 119.6 °C which is the melting point of elemental sulfur, the melting sulfur forms an independent liquid phase surrounded by aqueous. Therefore, the solubility of sulfur into aqueous phase may be controlled by diffusion of reactants between liquid sulfur phase and aqueous phase or surface reactions. In Fig. 2, it shows the linear relation between  $W^{1/3}-W_0^{1/3}$  and reaction time  $t$  at different temperature, where  $W$  and  $W_0$  are the weight of the starting sulfur and

weight of sulfur, respectively. The result suggests that the external diffusion is the rate-determining step in the dissolution reaction of sulfur phase.

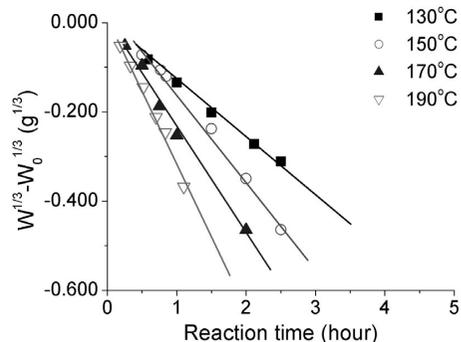


Fig. 2. The linear relation between  $W^{1/3}-W_0^{1/3}$  and reaction time at different temperature (Reactants: 3.12 mmol sulfur powder, 10 ml 0.5 M NaOH solution).

On heating a 0.5M NaOH solution containing elemental sulfur in a Teflon autoclave from 90 to 250 °C, the color of resultant solution is changed. At temperature less than 150 °C, all the resultant solution samples are yellow which suggests that polysulfides  $\text{HS}_n^-$  exist in the solutions (where  $n = 1, 2, 3, 4$ , etc.). With increasing temperature and time, the sample solutions become colorless and imply the degradation of polysulfides, that is to say, polysulfides  $\text{HS}_n^-$  are thermally unstable. In Fig. 3,

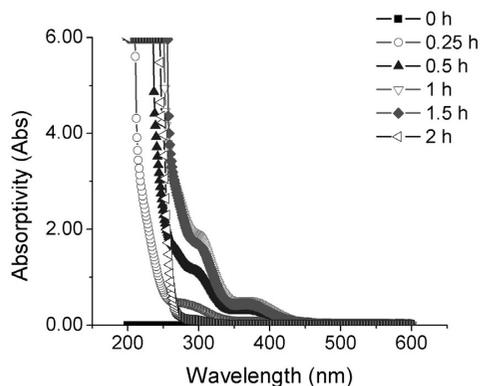


Fig. 3. Spectrophotometric of sample solution after sulfur reaction with solution diluted by 50 times (Reactants: 3.12 mmol sulfur powder, 10 ml 0.5 M NaOH solution; reaction temperature: 170 °C).

after sulfur reacting with 10 ml of 0.5 M NaOH solutions at 170 °C, polysulfides  $\text{HS}_n^-$  are produced which show eigen absorption of UV lights near 295 and 369 nm [9]. The absorption increase in the initial reaction stage, and then decrease, even disappear after reaction for 2 h.

Dependence of the conversion ratio of  $\text{HS}^-$  on reaction temperature and time is compared at 90–250 °C in Fig. 4, where the conversion ratio to  $\text{HS}^-$  of sulfur is equal to the yield of  $\text{HS}^-$  divided by the starting mole amount of elemental sulfur. With increasing temperature and time, the reaction rate and the yield amount of  $\text{HS}^-$  are increased sharply. Above 170 °C the reaction reaches equilibrium within about 2 h where all reactant sulfur is exhausted completely and the yield of  $\text{HS}^-$  approaches to a max of 58.4%. Below 170 °C, the reaction rate obviously slows down. But there is no visible evidence to show that the reaction of sulfur with aqueous is related to sulfur melting point (119.6 °C); since it is found that the reaction occurs even if reaction temperatures lower than 90 °C.

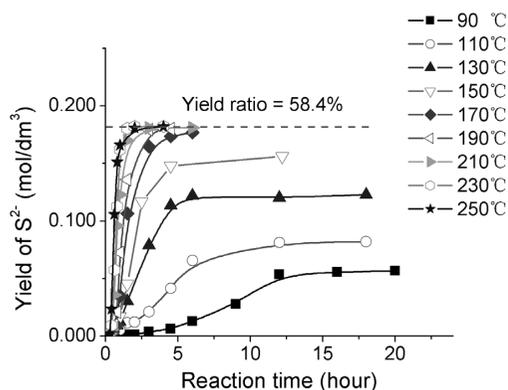


Fig. 4. Effect of reaction temperature and time on the yield amount of  $\text{HS}^-$  produced by sulfur reaction with aqueous solution (Reactants: 3.12 mmol sulfur powder, 10 ml 1 M NaOH solution).

**3.2. Effect of pH of aqueous** Dependence of  $\text{HS}^-$  formation on pH of aqueous at 170 °C, 210 °C, and 250 °C, is shown in Fig. 5. It is obvious that the reaction rate and the yield of  $\text{HS}^-$  exponentially increase with increasing pH. When pH is lower than 7, the redox or disproportionation of sulfur is very slow. Therefore scarcely any sulfur species formed, even if the reaction time is prolonged to 6 h at 170 °C.

On the other hand, with decreasing pH the main sulfur species change from  $\text{HS}^-$ ,  $\text{HS}_n^-$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{SO}_3^{2-}$  to  $\text{HS}^-$ ,  $\text{HS}_n^-$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and more. No  $\text{S}_3\text{O}_6^{2-}$  and  $\text{S}_4\text{O}_6^{2-}$  are detected during the whole reaction process. Commonly  $\text{SO}_4^{2-}$  forms in such a condition: reaction temperature higher than 210 °C or solution indicating acidity [8]. The difference of sulfur products under different pH conditions suggests the existence of several reaction mechanisms. It also shows that alkaline solution conditions should be in favor of the reduction of sulfur to  $\text{HS}^-$  in hydrothermal process, for the possibility of more  $\text{OH}^-$  being able to give more electrons to elemental sulfur during the reaction of sulfur with water.

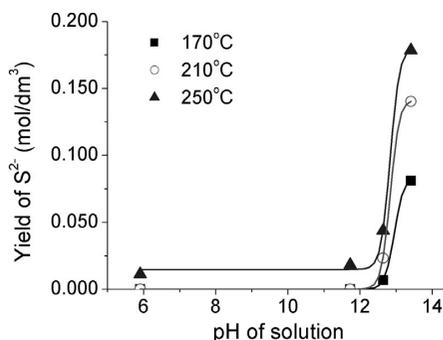


Fig. 5. The exponent relation between the yield amount of  $\text{HS}^-$  and initial pH value of aqueous solution when sulfur reaction to aqueous solution for 1.5 h (Reactants: 3.12 mmol sulfur powder, 10 ml solution).

**3.3. Mechanism of sulfur disproportionation with water** From the foregoing discussion, it can be concluded that the sulfur reaction with aqueous is complex and multi-step depending on temperature and pH of solution. The nature of the reaction is that sulfur disproportionate to  $\text{HS}^-$  and sulfur oxides under hydrothermal conditions. In order to determine the mechanism the reaction process should be simplified, for example, in the case of less consideration of some minor sulfur resultants. Based on this consideration, the reaction process under reaction conditions corresponding to the temperature (< 210 °C) and high pH was discussed. In this case  $\text{HS}^-$  and  $\text{S}_2\text{O}_3^{2-}$  are main resultants with the least  $\text{SO}_3^{2-}$  when the reaction of sulfur with 0.5 M NaOH solution reaches equilibrium at 170 °C, as shown in Fig. 6. It shows that both the yield of both  $\text{SO}_3^{2-}$  and polysulfides  $\text{HS}_n^-$  increase and arrive at a

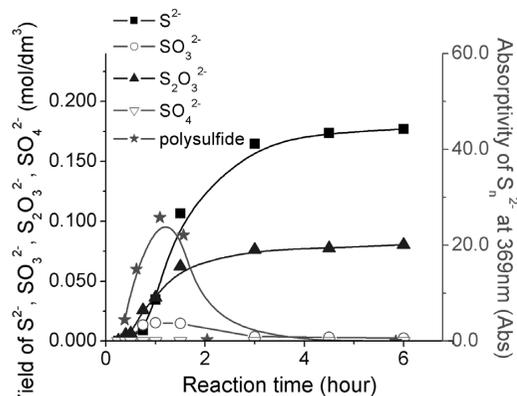
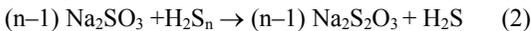
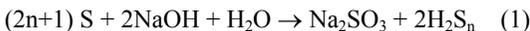


Fig. 6. The amount of sulfur species dependence of time (Reactants: 3.12 mmol sulfur, 10 ml 1 M NaOH solution; reaction temperature: 170 °C).

maximum during the initial 1 h, and then decrease to a low value, even disappear finally. This suggests that both  $\text{SO}_3^{2-}$  and polysulfides  $\text{HS}_n^-$  are important intermediates for the reaction of sulfur with aqueous under hydrothermal conditions. In the initial reaction stage, it firstly forms  $\text{SO}_3^{2-}$  and polysulfides  $\text{HS}_n^-$ , and then  $\text{HS}^-$  and  $\text{S}_2\text{O}_3^{2-}$  are produced with the degradation of polysulfides  $\text{HS}_n^-$ . In fact all the reactions go on simultaneously. The reaction process includes the following main reactions:



Thus, under such conditions: strong alkaline hydrothermal solution and lower temperature,  $\text{S}_2\text{O}_3^{2-}$  produced by reaction (2) is relatively stable and does not decompose further. So, it is believable that the processing of reaction (2) accelerates the reaction of sulfur with aqueous, and finally leads to the complete consumption of reactant sulfur powder.

The detail reaction behaviors about polysulfides  $\text{HS}_n^-$  and  $\text{S}_2\text{O}_3^{2-}$  under hydrothermal conditions should be discussed in another report.

#### 4. Conclusions

The disproportionation reaction of sulfur under hydrothermal conditions was studied by ion chromatography and UV spectro-photograph. Main sulfur species such as  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{HS}_n^-$ , and  $\text{HS}^-$  were successfully separated and determined.

The results suggest that the disproportionation of sulfur with aqueous, yield of  $\text{HS}^-$ , and yield of other

sulfur species depend on temperature and pH of aqueous. High temperature and pH have a great advantage to reduce sulfur to  $\text{HS}^-$ . Under alkaline conditions, the disproportionation can take place at temperatures lower than 119.6 °C of sulfur melting point. The yield of  $\text{HS}^-$  is higher than 57% while reaction does at temperatures above 170 °C within 2 h; it suggests that it is advisable for making an effective recycling process of sulfur species come from the photochemical hydrogen generation process.

The main disproportionation mechanism of sulfur under hydrothermal conditions includes two main reactions:  $(2n+1) \text{S} + 2\text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{S}_n$  and  $(n-1) \text{Na}_2\text{SO}_3 + \text{H}_2\text{S}_n \rightarrow (n-1) \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{S}$ .

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