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Hydrothermal Reaction of Sulfur in Seawater for Georeactor

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Abstract. The concept of a georeactor in geothermal environment has been proposed for direct utilization of geothermal energy in the ground. Chemical processes in the georeactor must accommodate a range of operating conditions, because the georeactor utilizes natural resources that are sometimes difficult to control. Combination of hydrogen generation by solar energy from hydrogen sulfide, and reduction of waste sulfur and its compounds using geothermal energy is environmental energy supply system. The self-oxidation and reduction of sulfur is considered to be suitable for the thermal condition around 200 oC. In previous studies, the self-oxidation and reduction of sulfur proceeded in neutral or alkaline solution. The amount of formed hydrogen sulfide in strong alkaline solution was larger than neutral solution. But it was difficult to use the strong alkaline solution for self-oxidation and reduction of sulfur to georeactor. Therefore we applied the seawater for sulfur reduction because the seawater is alkaline solution and it can be available at a low cost. In order to study a self-oxidation and reduction of sulfur in seawater, we conducted the reaction between sulfur and seawater in hydrothermal conditions using a batch-type autoclave. The maximum conversion rate of elemental sulfur to hydrogen sulfide with the reactions in seawater is almost 50 % and the highest concentration of formed hydrogen sulfide is 0.026 mol/l in the experiments.

Keywords: Georeactor, self-oxidation and reduction of sulfur with seawater, sulfur recycle, hydrogen generator, direct use

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INTRODUCTION

Georeactor

The concept of georeactor was suggested as a large-scale reactor of high temperature and pressure installed in the ground (Takahashi *et al.*, 1987). Fig. 1

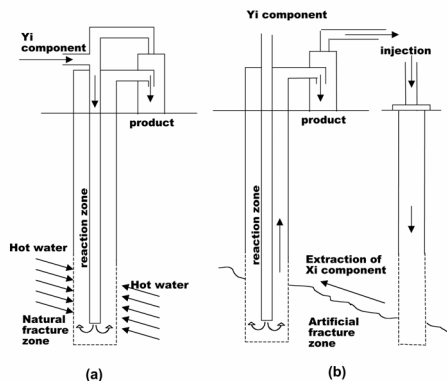


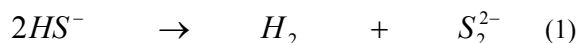
FIGURE 1. Concept of geochemical reactor, after Takahashi *et al.* (1987).

indicates a conceptual illustration of the georeactor. The georeactor is characterized by direct use of geothermal energy in the ground so that the costs of conversion geothermal energy is minimized and geothermal heat can be utilized for chemical reaction.

Installing and operating of the georeactor's facilities are not complicate. So the most important point for realizing the practical models of the georeactor is to discover which processes are suitable and efficient for the georeactor.

Hydrogen generation

Splitting of bisulfide(HS^-) using sunlight and stratified CdS photocatalyst is useful reaction for hydrogen generation. The photocatalyst causes dissociation of bisulfide (HS^-) to hydrogen and polysulfide (e.g. S_2^{2-}) in alkaline solutions (Arai *et al.*, 1987). The overall chemical reaction is considered as follows.



If waste polysulfide (S_2^{2-}) and elemental sulfur can be reduced to bisulfide by the georeactor, the

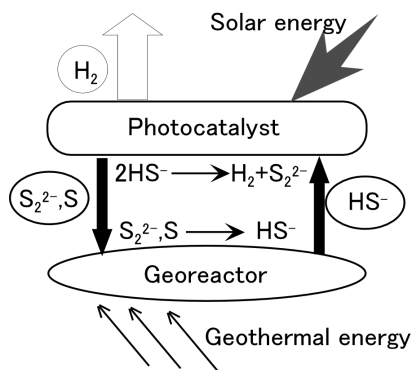


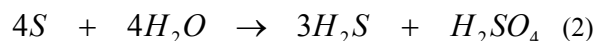
FIGURE 2. Concept of hydrogen generation cycle using solar energy and geothermal energy

polysulfide becomes available as starting solution for hydrogen generation. This sulfur cycle is shown in Fig. 2. If it is possible to construct the cycle of sulfur, the hydrogen generator utilizing geothermal energy and solar energy could be developed (Tsuchiya *et al.*, 2003).

It is necessary to design sulfur reduction process for the georeactor in order to develop the hydrogen generator mentioned above.

Self-Oxidation and Reduction of Sulfur

Self-oxidation and reduction of sulfur under hydrothermal condition include sulfur reduction process. Self-oxidation and reduction is the reaction in which starting material is reduced and oxidized at once. In case of sulfur, elemental sulfur is reduced to hydrogen sulfide (H_2S). Hydrogen sulfide dissociates to bisulfide (HS^- and S^{2-}) in alkaline solution. On the other hand, elemental sulfur is oxidized to sulfate (Ellis *et al.*, 1971). This reaction is considered as follows.



Around neutral pH, hydrogen sulfide and sulfate are formed. In case of higher pH, thiosulfate and other species are formed. These species react with elemental sulfur or dissociate to hydrogen sulfide and sulfate (Ellis *et al.*, 1971; Giggenbach, 1974).

The authors focus on the amount of hydrogen sulfide formed by this reaction. Previous study has shown that much hydrogen sulfide is generated at high temperature and strong alkaline conditions (Fig. 3). However it is difficult to apply the reaction at strong alkaline conditions to the georeactor because it is expensive to keep high alkalinity. Therefore we investigate the use of seawater (around pH8) as a starting solution for self-oxidation and reduction of sulfur. Because seawater can be utilized at a low cost and larger generation of hydrogen sulfide can be expected because of the pH.

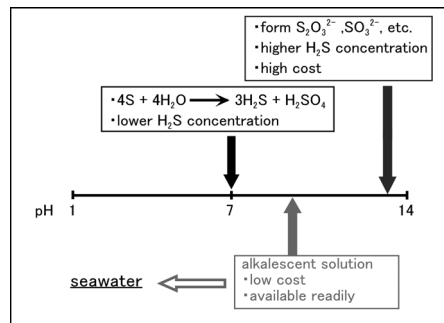


FIGURE 3. pH dependency of Self-oxidation and reduction reactions of sulfur

In this paper sulfur hydrothermal reactions in seawater are studied, in order to examine possibility of application of self-oxidation and reduction of sulfur with seawater to the georeactor. Particularly temperature and time dependency of the reaction is studied regarding to conversion rate of hydrogen sulfide. In addition the influence of the elemental sulfur quantities added to the seawater is studied in order to investigate optimal condition of hydrogen sulfide generation. This study can be used for estimating the interaction of sulfur and seawater in hydrothermal vent at ocean floor.

EXPERIMENTS

Experiments were performed to investigate temperature and time dependency of the amount of formed hydrogen sulfide, thiosulfate and sulfite, and seawater/elemental sulfur ratio dependency of hydrogen sulfide formed by the reactions. Before experiments, dissolved oxygen in seawater is removed by bubbling of nitrogen gas. Batch-type autoclaves with Teflon liner are used for experiments. A high temperature oven with a rotation shaft for stirring was used to heat autoclaves. After set duration, autoclaves were cooled in the air, and sulfuric species were identified and determined its quantity by high-performance liquid chromatography.

In the series of experiment to investigate temperature dependency and time dependency of the reaction, 5 mg of elemental sulfur and 20 ml of seawater was used as starting materials. Reaction temperatures are ranged from $150^{\circ}C$ to $250^{\circ}C$. Reaction times are ranged from 2 hours to 22 hours.

Experiment to investigate the conversion rate and the concentration of hydrogen sulfide with various elemental sulfur/seawater ratio, are carried out on two series. In first series of experiments reaction temperature was $250^{\circ}C$, reaction time was 5 hour and starting elemental sulfur quantities was ranged from 12 mg to 2 mg. In second series of experiments, reaction temperature was $250^{\circ}C$, reaction time was 3 hour and

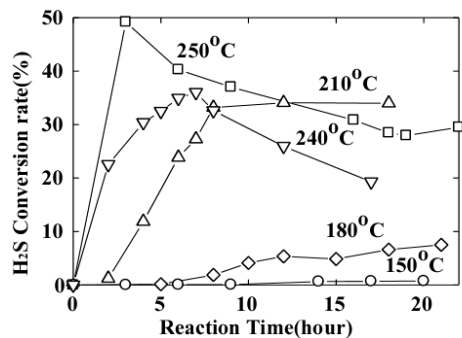


FIGURE 4. Time and temperature dependency of the generated hydrogen sulfide

elemental sulfur quantities was ranged from 10 mg to 100 mg. Total starting solution was 20 ml in both series of experiments.

RESULTS AND DISCUSSION

The temperature dependency and time dependency of formed hydrogen sulfide conversion rate with self-oxidation and reduction, is shown in Fig. 4. The conversion was maximized from 3 hours to 8 hours when reaction temperature was 250°C, 240°C and 210°C. At 150°C or 180°C, a few hydrogen sulfides is formed. As the reaction temperature increased, the reaction rate was faster and the maximal value of conversion rate was larger. The conversion rate of the hydrogen sulfide is maximized at 50 % when reaction

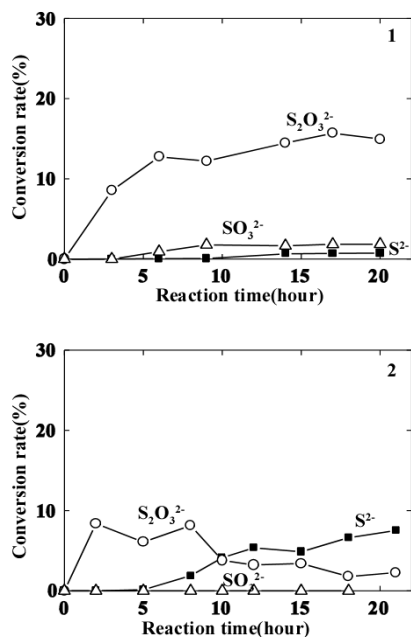


FIGURE 5. Yields of $S_2O_3^{2-}$ and SO_3^{2-} with self-Oxidation and reduction reaction of sulfur in seawater

1. reaction temperature 150°C
2. reaction temperature 180°C

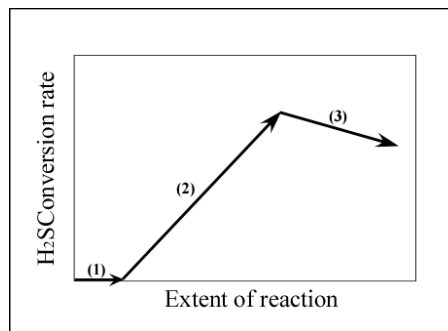


FIGURE 6. Concept of Self-oxidation and reduction of sulfur in seawater process

- Step1. form intermediate products
- Step2. dissociate intermediate products and form hydrogen sulfide
- Step3. react hydrogen sulfide with components in the solution

temperature was 250°C and duration time was 3 hours. Additionally the conversion rate decreases after the largest conversion rate at 250°C and 240°C.

Thiosulfate and sulfite were not formed when reaction temperature was 240°C and 250°C. At 210°C thiosulfate was found small quantity when duration time was around 3 hour. Fig. 5 shows conversion rate of thiosulfate and sulfite in the experiments at 150°C and 180°C. In the experiments at 180 °C, few amount of hydrogen sulfide were formed when thiosulfate had been formed. When thiosulfate decreased, conversion rate of generated hydrogen sulfide increased adversely.

1. Intermediate products such as thiosulfate are formed by sulfur hydrolysis. Then a little hydrogen sulfide is formed.

2. Intermediate products are dissociated and hydrogen sulfide is formed abundantly.

3. Hydrogen sulfide reacts to components in seawater and decreases gradually on this stage. This is caused by decrease of pH.

With the reaction temperature increasing, these reaction rates are faster. As a result, it can be considered that different trend of the conversion rate (Fig4) is occurred by difference of reaction rate.

Fig.7 shows the conversion rate and the concentration of hydrogen sulfide with quantity of sulfur added to 20 ml of seawater. When reaction temperature is 250°C, the maximum value of conversion rate is almost 50%. Maximum value of concentration is about 0.026mol/l in these experimental conditions.

These experiments indicate that there is suitable ratio to maximize conversion rate. In addition, by means of adjunction of enough sulfur to seawater, concentration of hydrogen sulfide is converged to maximum value.

Conversion rate of hydrogen sulfide is maximized when starting elemental sulfur is ranged from 40 mg to

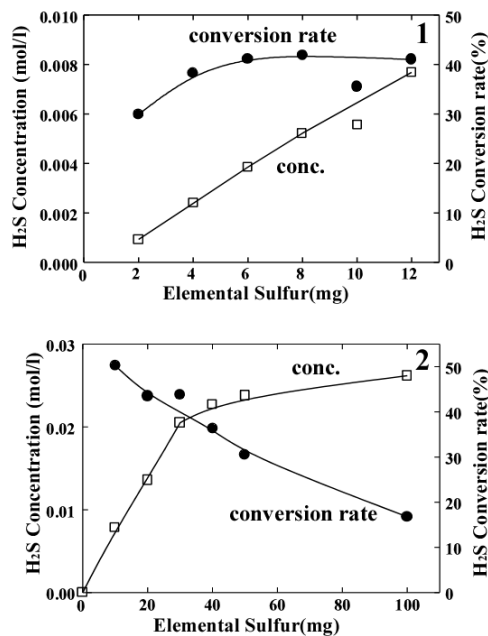


FIGURE 7. The elemental sulfur/seawater ratio dependency of H₂S concentration and conversion rate
 1. duration time 5hour, reaction temperature 250°C, added sulfur 0.002g to 0.012g
 2. duration time 3hour, reaction temperature 250°C, added sulfur 0.01g to 0.1g

20 mg per 20 ml of seawater. Then concentration of hydrogen sulfide is up to 0.01 mol/l. The concentration of hydrogen sulfide is too low to use reacted seawater for solvent of hydrogen generation by photocatalyst. Augmenting elemental sulfur added to seawater increases moral concentration of hydrogen sulfide and decreases conversion rate when amount of added elemental sulfur is large. Elemental sulfur/seawater ratio of high concentration and conversion rate is about 40 mg of the sulfur per 20 ml of seawater.

In addition the self-oxidation and reduction expend alkalinity of solution. The reacted seawater is low pH (around 2), hydrogen sulfide is easy to run off to air becoming vapor. Accordingly, we have to devise a method of picking up hydrogen sulfide from reacted seawater and providing hydrogen sulfide to photocatalyst.

CONCLUSIONS

In order to design the georeactor, it is important to determine the chemical processes that will be able to occur in the georeactor. We researched self-oxidation and reduction of sulfur with seawater in the hydrothermal condition. We experimentally found that the conditions that maximized the conversion rate of elemental sulfur to hydrogen sulfide and the concentration of hydrogen sulfide. In this study, the

maximum conversion rate of hydrogen sulfide is almost 50 % when reaction temperature is 250 °C and duration time is 3 hours. Either concentration and conversion rate are high when 40 mg of sulfur and 20 ml of seawater are used for starting material. Then hydrogen sulfide concentration is almost 0.02 mol/L and conversion rate of hydrogen sulfide is about 40 %. Although there are several difficulties in use of seawater, self-oxidation and reduction of sulfur with seawater is available for the georeactor.

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