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Georeactor: Advanced Geothermal Energy Utilization for Material Processing and Hydrogen Generation

N. Tsuchiya¹, Y. Suto¹ and K. Nakatsuka¹

¹Graduate School of Environmental Studies, Tohoku University, Sendai 980-8579, Japan

Keywords
Georeactor, material processing, steam generator, hydrogen generator, direct use

ABSTRACT

The chemical processes and design of a georeactor in the geothermal environment is proposed for direct utilization of geothermal energy resources. Material processing apparatus, comprising high aspect ratio, double and/or multiple tube reactors, were used for chemical reactions installed in a drill hole, with a steam generator supplying hot water and steam for a surface chemical reactor. Chemical processes in the georeactor require mild reaction conditions, accommodating a range of operating conditions, since the georeactor utilizes natural resources that are sometimes difficult to control.

A hydrogen generating system, produced from hydrogen sulfide and a high performance photocatalysis, was examined as a case study for use of the georeactor. Hydrogen generation by solar energy from hydrogen sulfide, and recycling of waste sulfur and its compounds using geothermal energy is a potential, environmentally friendly energy supply system.

Introduction

Geothermal resources in Japan have chiefly been developed for electric power generation, with additional utilization of geothermal energy providing hot water to green houses, district heating, drying and other facilities. In other words, geothermal energy is considered as a heat resource because geothermal energy has great efficiency for heat supply. It is also possible to utilize the geosphere environment for material processing, due to its high temperature-pressure conditions, which is an alternative direct use of geothermal energy.

The concept of the georeactor, as a geochemical reactor, was proposed by Takahashi et al. (1987), with a plant system for utilizing subsurface geothermal energy and use of geothermal drill holes for material processing. Facilities, installations and operation systems are not complicated. The most important point for realizing their practical models are what processes are suitable and efficient for the georeactor, but despite the concept of the georeactor being proposed more than fifteen years ago, no pilot plants have yet been developed. It is necessary to develop appropriate processes and a design for the georeactor for advanced utilization and direct use of geothermal energy.

Recently, a photocatalysis chemical process for hydrogen generation has been developed for aquatic solutions, using advanced nano-technology (Arai et al., 2001). Chemical processes for hydrogen generation by solar energy have been investigated using photocatalysis and pure water, however process efficiency and conversion rate of hydrogen from water is not high, and the practical design of the system has difficulties due to low hydrogen generation efficiency and cost performance issues. An advanced system for hydrogen production has been developed using electrolyte solutions that incorporate sulfur compounds.
hydrogen conversion compared to systems using pure water, and secondly is that it offers effective utilization and recycling of waste sulfur. In the advanced hydrogen generation process, the starting solution contains HS⁻, for effective reaction of the photocatalysis, with S²⁻ reacted as waste ions after production of hydrogen, as described by the following chemical reaction:

\[ 2 \text{HS}^- \rightarrow \text{H}_2 + 2 \text{S}^{2-} \quad (1) \]

Solar energy is a direct energy source for hydrogen generation, by high efficiency photocatalysis action, and we have to convert waste sulfur ionic species (ex. S²⁻) to HS⁻ to develop the complete sulfur recycling system.

The hydrogen generation system described in this paper utilizes solar and geothermal energy systems, which are representative of sustainable and reusable green energy. A key technology loop in the system is the re-conversion of waste sulfur to usable sulfur species in the georeactor, by utilizing geothermal energy. This study describes chemical processes in the georeactor, for hydrogen production, and future direct utilization of geothermal energy.

**Conceptual Model of Georeactor**

Takahashi et al. (1987) proposed two (ideal) geochemical reactor models, shown in Figure 2. One was the “so-called” single well system, which was composed of a tube-type reactor. In this system, raw materials undergo chemical reaction in the geothermal environment, with later recovery of reacted materials from the georeactor. Depending on the chemical processes, the tube-type reactor may comprise a double, triple or multiple tube system, with geothermal fluids also utilized as a raw material. The other idea was a more advanced system similar to the Hot Dry Rock (HDR) concept, in which two drill holes (i.e. tube reactors) are connected by artificial fractures. The starting material (i.e. solution) was supplied from an injection well, and reacted material (i.e. solution) was obtained from the production well via artificial fractures. This is an open system, with the geothermal environment providing not only energy but also subsurface reaction setting at high pressure-temperature conditions. Geological materials, including rocks and geofluids are utilized as raw materials.

An advantage of using the artificially fractured/connected environment is that it offers effective utilization of an entire natural geothermal energy resource, even though it is difficult to design and operate the system, due to uncertain subsurface physicochemical conditions.

Here, we propose two types of georeactor (Figure 3). Firstly, a tube type chemical reactor, which comprises either double and/or multiple tubes with extremely high aspect ratio, which is similar to the single well type reactor of Takahashi et al., (1987). Secondly, a steam (and hot water) generator that circulates cold water through an inner (or outer) tube. In the case of material processing type system, starting materials are supplied through the tube, which interact at pre-determined temperature-pressure conditions. Reacted materials (e.g. slurry of useful materials and/or gaseous components) can be recovered from the tube reactor. If the chemical process requires several raw materials, then multiple tubes may be utilized. In this paper, we describe chemical processes in the georeactor, which can be used to promote sulfur reduction for hydrogen generation.

Circulating water, steam and hot water can be obtained from the steam generator shown in Figure 3. Whilst the total amount of steam is not enough for (electrical) power generation, it can be utilized for other purposes, such as drying, extraction of aromatic component from forest resources, etc.

**Sulfur Reduction Process**

**Self-Oxidation and Reduction Reactions of Sulfur**

Sulfur formation is complex, due to the behavior of many kinds of sulfide and sulfate compounds. In particular, the following
self-oxidation and reduction reaction is well known to represent chemical sulfur-water interaction:

\[ 4S + 4H_2O \rightarrow 3H_2S + H_2SO_4 \]  

(2)

One of the reacted products from elemental sulfur is sulfate ions (SO\(_4^{2-}\)), whilst the reduction of H\(_2\)S species dissociates to HS\(^-\) and S\(^2-\). Oxidation and reduction reactions may occur simultaneously in solution. Reduction products, H\(_2\)S\(^-\) or HS\(^-\) are useful for hydrogen production, and we examined the chemical behavior of sulfur, and corresponding self-oxidation/reduction reactions over a wide range of chemical conditions.

**Experiment**

Hydrothermal experiments related to sulfur – water interactions were carried out using a batch type autoclave (50 cc in volume), with an inside wall covered by Teflon liner. Reaction temperatures were 150°, 200° and 250°, with heating rate 3°/min, and initial pH in the range from 13 to neutral conditions. Autoclaves were set in a high temperature, drying oven with a rotated shaft for stirring. Reaction duration was 3, 5, 10 and 20 hours. After cooling in air, reacted species were identified by ion chromatography. Elemental sulfur as raw material is 0.005 g and pH of the solution was controlled by KOH. Total starting solution was 20 cc.

**Results and Discussion**

An indicator of reaction process is pH, which is related to the concentration of SO\(_4^{2-}\). Figure 4 is representative of our experimental results. Concentration of SO\(_4^{2-}\) is similar for initial pH 6 and 10 conditions, although final pH after reaction ranged from pH 8 to 7, and almost neutral (weak alkaline) conditions in the case of initial solution pH 12. Clearly, high alkaline conditions are the most suitable initial state to inhibit production of SO\(_4^{2-}\) and maintain neutral or weak alkaline pH conditions conducive for the formation of HS\(^-\).

Figure 5 shows the yield of HS\(^-\) and other species following the hydrothermal reaction of sulfur and alkaline solution. Ideal self-oxidation and reduction reactions of sulfur and water can be described by a single chemical reaction (2), but the true chemical behavior of sulfur and water interaction is more complicated. S\(_2\)O\(_5\)^2- and SO\(_3\)^2- is produced at the same time, and those ionic species are considered as intermediate products for production of final oxidation and reduction states of SO\(_4^{2-}\)and HS\(^-\). The following chemical reactions were considered, but these are only one possible mechanism, and other reactions may have occurred:

\[ 4S + 3H_2O \rightarrow 2H_2S + H_2SO_3 \]  

(3)

\[ (n-1)S + H_2S \rightarrow HS_n + H^+ \]  

(4)

According to the above reactions, the apparent amount of SO\(_4^{2-}\) decreased, but other complicated reaction occurred simultaneously. We have to reconsider the chemical reactions to describe realistic mechanisms of sulfur–water interaction at high temperatures (e.g. around 200°C) and saturated vapor pressure, in order to design a georeactor. Figure 5, however, shows promising results, because the conversion rate of elemental sulfur to HS\(^-\) is almost 40 %, which means that a conversion rate of 64% (40 % + (100-40) x 0.4) elemental sulfur to HS\(^-\) could be obtained after two times circulation of reacted solution through the georeactor.

**Conclusions**

The most important factor for designing a georeactor is not reactor hardware, but software related to chemical processes. The georeactor has several advantageous properties, such as a sustainable chemical reaction and it promotes an environmentally friendly system. However, the georeactor has some disadvantages, e.g. extremely high aspect ratio (long tube reactor) and the temperature - pressure conditions are not easily controlled, as the system is dependent on “natural” geothermal conditions. The chemical processes requires sensitive control of temperature, pressure and chemical reaction behavior, and is not ideally suited.
to the georeactor, as specific chemical processes may require a wide range of temperatures and pressures within the georeactor reaction system.

In this study, we focused on sulfur–water interaction, and particularly on the effective utilization of waste elemental sulfur, which can be converted to a useful sulfur resource for hydrogen production, using high performance photocatalysis.

Acknowledgements

We thank graduate students Y. Takano and T. Kabuta for experiment help during the course of this work. We are indebted to Prof. K. Tohji, Prof. N. Yamasaki and Dr. G. Bignall for helpful discussion. This study was financially supported by Grant-in-Aid Scientific Research A (No. 13305069).

References
