APPLICATION OF A GEOREACTOR: SUSTAINABLE HYDROGEN GENERATION USING SOLAR AND GEOTHERMAL ENERGY SOURCES

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SUMMARY – An innovative method for hydrogen generation by photocatalysis has been developed at Tohoku University, from hydrogen sulphide ions in aqueous solution, using solar energy technology. Sulphide ions, however, remain in the reacted solution during the engineered hydrogen generation process. In an efficient closed-loop hydrogen production system, reacted sulphide ions should ideally be converted into photocatalysis-active hydrogen sulphide ions. Our research programme indicates that the application of a geothermal energy "georeactor" (i.e., a kind of chemical reactor), coupled with solar energy technologies, may prove to be effective in optimising hydrogen generation. We argue that an "Earth conscious", hydrogen (zero emission closed-loop) generation process, using sustainable natural systems (such as solar and/or geothermal resources) could prove to be an environmentally-friendly means of supplying hydrogen for future generations' energy requirements.

1. INTRODUCTION

Hydrogen! - it is regarded by some as the ultimate "clean energy", and potentially our main energy resource of the future. Hydrogen is a secondary energy resource, however, as no hydrogen deposit exists on (or in) the Earth. The current generation of hydrogen comes from the decomposition of fossil fuels (such as coal, oil and natural gas), with huge energy requirements required to convert the organic material into hydrogen. The most straight-forward means to produce hydrogen, however, is by the chemical decomposition of H_2O.

Methodologies for hydrogen generation by solar energy using photocatalysis and pure water have been investigated, yet the conversion/generation efficiency of hydrogen by existing (albeit new) technologies is low, and the design of the reaction system has cost performance issues. An advanced system for hydrogen production using electrolyte solutions that incorporate sulphur compounds is shown in Figure 1.

Recent experimental studies show photocatalysis is effective for hydrogen production, both in terms of energy efficiency and cost. However, sulphide ions remain as reacted waste ions after oxidation of the hydrogen sulphide ions. Ideally, the reacted sulphide ions (i.e. poly-sulphide ions in various chemical species) should be converted to "photocatalysis active hydrogen sulphide ions" in order to establish an efficient energy/chemical cycle (e.g. Figure 2).

Potential energy sources to facilitate sulphide conversion include biochemical reaction processes (e.g. use of sulphur reduction bacteria), combined

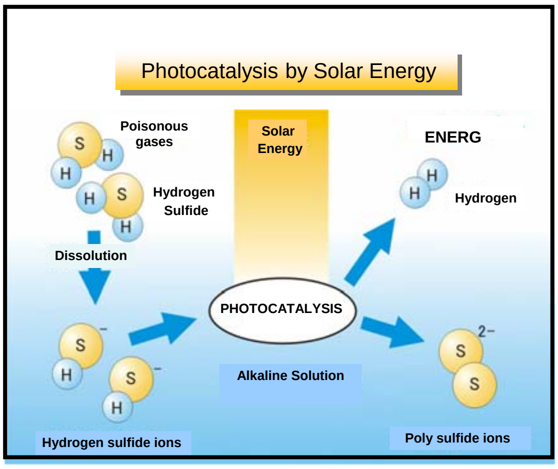

Figure 1. Conceptual model of photocatalysis for hydrogen generation using solar energy.

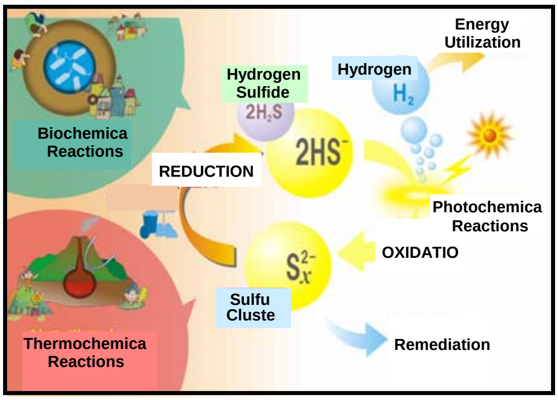

Figure 2. Sulphur circulation model for hydrogen generation.

with heat energy (e.g. from geothermal sources), although conversion efficiency and time required is long compared with other reaction processes. The initial concept of the “georeactor”, as a form of geochemical reactor system, was proposed by Takahashi *et al.* (1987), who envisaged a engineered system to utilise subsurface geothermal energy (and geothermal drill holes) for material processing and other applications (e.g. Figure 3).

For the most part, the facilities and operation systems envisaged by Takahashi *et al.* are not difficult to construct. However, although a variety of efficient direct use applications have been developed along ideas similar to the initial “georeactor”, no pilot plants, large-scale energy conversion or industrial (material processing) applications have yet been developed that take full advantage of the georeactor concept. Our goal, therefore, is to develop methodologies to promote new, direct geothermal energy utilization, through the use of advanced chemical georeactor and applied technologies.

The potential range of chemical reactions possible in a closed-loop geothermal reactor provides the possibility to design advanced technologies to better utilise geothermal energy resources, for a variety of direct use industrial applications.

Sustainable hydrogen generation, based on a system where hydrogen is produced from hydrogen sulphide by high performance photo-catalysis, is a case in point, and proposed here for future industrial-scale application of the georeactor system. Hydrogen generation by solar energy from hydrogen sulphide, and recycling of waste sulphur and its compounds using geothermal energy could prove to be an environmentally friendly energy supply system, with an enormous impact on future (geothermal) energy generation and utilisation (Tsuchiya *et al.*, 2002). This paper outlines the hypothetical utilisation of a “new application” georeactor, for the direct use of geothermal energy resources in future, industrial-scale hydrogen production.

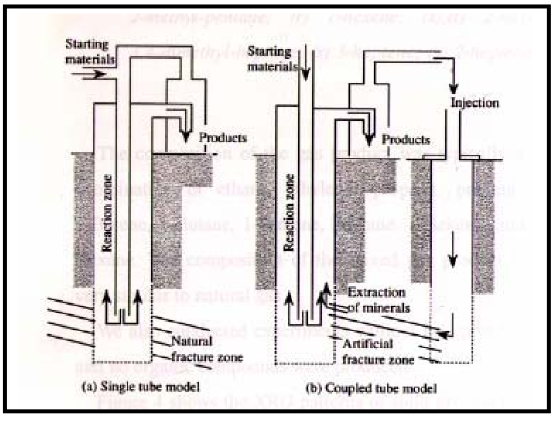

Figure 3. Georeactor of Takahashi *et al.* (1987).

2. HYDROGEN GENERATION

Sulphur is produced as a by-product of petroleum refining, and its disposal raises important issues related to environmental waste management. The development of processes for advanced hydrogen generation using sulphur electrolyte solutions has the potential to resolve this problem, plus the technique has a high hydrogen conversion efficiency rate (compared to systems using pure water) and can utilise waste sulphur from other industrial applications / sources.

Chemical processes for hydrogen generation have been developed for aquatic solutions, using advanced nano-technology (e.g. Arai *et al.*, 2001, Milczarek *et al.*, 2003). In hydrogen generation process, the initial reactive solution contains HS^- (for effective photocatalysis), with S^{2-} produced as waste ions, as described by the following reaction:

$$2\,HS^- \rightarrow H_2 + 2\,S^{2-} \qquad (1)$$

Solar energy is a direct energy source for the generation of hydrogen by photocatalysis, and other materials (e.g. production of photocatalysis CdS, as in Figure 4). For a hydrogen generation system to be most efficient, it requires waste sulphur ionic species (e.g. S^{2-} in Eqn 1), to be converted to HS^-, in order to develop the complete sulphur recycling. The hydrogen generation system utilises solar and geothermal energy (as sustainable green energy sources). A focal point of the hydrogen system is the development of technology to facilitate the conversion of waste sulphur to usable sulphur species, which may best be achieved by utilising the georeactor and geothermal energy resources.

3 CONCEPTUAL GEOREACTOR MODEL

Takahashi *et al.* (1987) proposed two geochemical reactor models, as shown in Figure 3. One was the “so-called” single well system (left), composed of a tube-type rector (a “flow-through reactor”) in

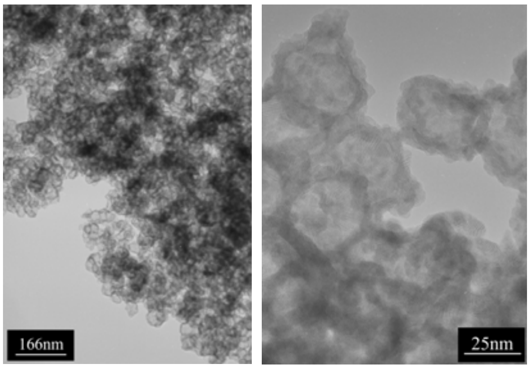

Figure 4 TEM image of photocatalysis CdS (Arai *et al.*, 2001). Monolayer CdS nano-particles (~5 nm diam.) form ~30 nm micro-capsules.

which initial raw materials undergo a chemical reaction at geothermal reservoir conditions, with later recovery of materials from the georeactor. In fact, the tube-type reactor may comprise a double, triple or multiple tube system, with geothermal or injected fluid(s) being utilised as a raw material.

An alternative suggestion by Takahashi *et al.* (1987) consisted of a system similar to the Hot Dry Rock (HDR) concept, in which two (or more) drill holes (i.e. tube rectors) are connected by an artificial fracture network. In this case, the starting material (i.e. solution) is supplied from an injection well, and reacted solution is recovered from the production well(s), via the artificial fracture network. This is an open system, with the geothermal environment providing energy, but also the high pressure-temperature, heat exchange reaction setting. In this type of reactor system geological materials, such as rocks and geofluids are utilized as raw materials. The advantage of utilising an interconnected, artificially fractured network is that it offers a more effective way of exploiting the natural geothermal energy resource, even though it is difficult to design, due to the uncertain nature of subsurface physicochemical conditions.

Here, three georeactor types are envisaged (Figure 5). Firstly, an open system (Figure 5, left), similar to the "HDR georeactor" of Takahashi *et al.* (1987). Secondly, a tube-type reactor (Figure 5, middle) comprising double and/or multiple tubes, with an extremely high aspect ratio for material processing applications (starting materials may be supplied via an injection tube, and interact at pre-determined temperature-pressure conditions). Thirdly, a flow-through-type reactor (Figure 5, right) in which injected solution (or steam) flows through the system, from an inlet towards an outlet.

Reacted materials (e.g. a slurry of (new) processed materials and/or gaseous components) can be recovered from the tube reactor. If the chemical process requires several starting (raw) materials, then these may be supplied via a multiple tube system. Here, we describe the chemical processes in the georeactor to facilitate sulphur reduction for hydrogen generation.

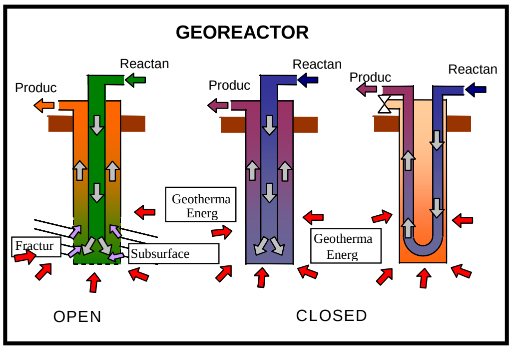

Figure 5. Georeactor-types (Suto *et al.*, 2002).

The most important factor for designing a georeactor is actually not the reactor hardware or drilling technology, but establishing the physico-chemical conditions that will the facilitate reaction processes. The georeactor is inferred to have several advantageous features, such as its potential to sustain a long duration, environmentally friendly, chemical reaction setting. The georeactor, however, does have some detrimental features that have to be overcome, e.g. a high aspect ratio (long tube reactor), whilst temperatures and pressures in the reactor may be difficult to control, as the system is dependent on "natural" geothermal conditions. Viable material processing on a sustainable industrial scale will require sensitive control of the temperature and pressure conditions, as they affect chemical reaction behaviour (Tsuchiya *et al.*, 2003, Suto *et al.*, 2003). This is a major challenge for the use of the georeactor as a means of developing advanced material-chemical reaction processes, as two or more reaction steps may be required, which necessitate a range of temperature and/or pressure conditions within the georeactor reaction system.

4 THE SULPHUR REDUCTION PROCESS

4.1 Self-oxidation / reduction of sulphur

Sulphur formation is complex, due to the variable behaviour of sulphide and sulphate compounds (Lin *et al.*, 2003). Figure 6 shows a pH-Eh diagram of the S-H_2O binary system at 200^{o}C. The following self-oxidation and reduction reaction is regarded as having the most influence on sulphur-water interaction processes at these conditions:

$$4S + 4H_2O \rightarrow 3H_2S + H_2SO_4 \qquad (2)$$

In addition, the following self-oxidation and reduction reactions can be occur (3 - 5), due to the chemical condition of the solution:

$$3S + 2H_2O \rightarrow 2H_2S + SO_2 \qquad (3)$$

$$4S + 3H_2O \rightarrow 2H_2S + H_2S2O_3 \qquad (4)$$

$$4S + 4H_2O \rightarrow 3H_2S + H_2SO_4 \qquad (5)$$

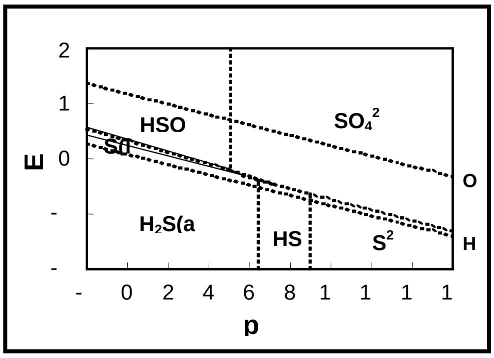

Figure 6 pH – Eh diagram for S – H_2O system at 200°C

One of the products from the reaction of elemental sulphur is sulphate ions ($SO_4{}^{2-}$), as shown in Eqn. 2, whilst H_2S species dissociate to HS^- and S^2. Oxidation - reduction may occur simultaneously. As the reaction products H_2S or HS^- are possible raw materials for hydrogen production, we examined their chemical behaviour and self-oxidation/reduction reaction potential over a range of chemical (and temperature) conditions.

4.2 Experiment

Hydrothermal experiments related to sulphur - water interaction were conducted using a batch type autoclave (volume 30 ml), shown schematically in Figure 7. The inside wall of the autoclave is covered by a Teflon liner. Reaction temperatures were 150°C, 200°C and 250°C, with a 3°C/min heating rate. The drying oven is fitted with a rotating shaft for stirring. Reaction duration was 3, 5, 10 and 20 hours, respectively.

Seawater (collected from Sendai Bay; pH ~8) and elemental sulphur (0.005 g) were used as raw materials. The pH of the solution was controlled by KOH, with an initial pH varying from 13 to neutral conditions. The total starting solution was 20 cm^3. Reacted species were identified by ion chromatography (after cooling in air).

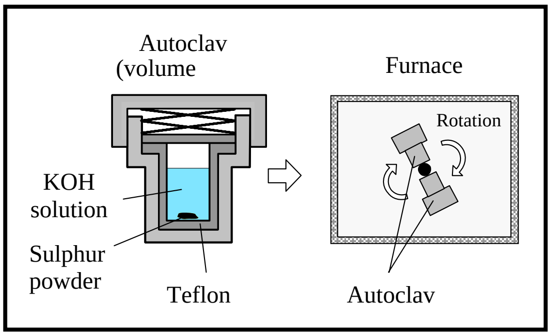

Figure 7. Hydrothermal experimental apparatus.

4.3 Results and Discussion

A useful indicator of reaction process is pH, which is affected by the concentration of $SO_4{}^{2-}$ and, to a lesser extent, by other sulphate species. Figure 8 shows representative experimental results from a series a batch autoclave sea water–sulphur experiments, over a range of temperatures (150°C, 200°C and 250°C), with initial fluid pH of 12. Preceding sulphur dissolution, pH decreases due to the formation of acid sulphate ions.

The experiments show that the dominant chemical species and formation ratio of sulphate - sulphide ions differs for each temperature condition. For example, $S_2O_3{}^{2-}$ is dominant at 150°C, but $SO_4{}^{2-}$ is the main ionic species at 250°C. The predominant ionic species in the reacted solution can not be clearly identified at 200°C, which suggest complex sulphate ions were formed.

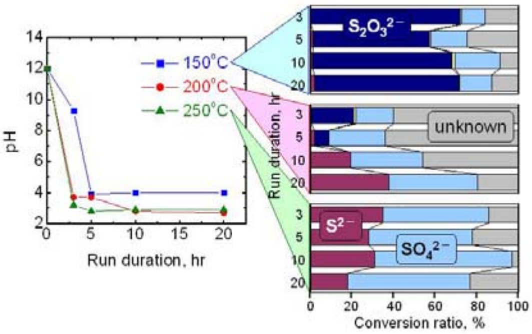

Figure 8 Relationship between pH, run duration for 150°C, 200°C and 250°C experiments, and conversion ratio, for initial fluid of pH 12.

Based on sulphate ion concentration, the main species instrumental for controlling pH change are likely to be $S_2O_3{}^{2-}$ and $SO_4{}^{2-}$ at 150°C, an unknown species at 200°C, and $SO_4{}^{2-}$ at 250°C.

The tendency for pH change at the various experimental temperatures is similar, although the concentration and formation ratio of sulphate and sulphide ions differs, due to complex self-oxidation and reduction reactions (described by Eqns. 2 to 5, and pH-Eh diagram in Figure. 6).

Figure 9 shows the experimental results of seawater -sulphur interaction at 150°C, 200°C and 250°C. The dominant hydrogen sulphide species is HS^- for the weak alkaline sea water conditions (pH ~8), which is adequate for photocatalysis.

The highest HS^- yield is >40% at 250°C after 5 hours, however the conversion ratio of HS^- decreases with the duration of the experiment. The same tendency was recognized at 200°C, where the peak yield time shifted to longer experiment times. It is likely that complex, parallel self-oxidation and reduction reactions occurred during the experiment.

Clearly, we have to carefully consider the inferred chemical reactions that occur, in order to describe the mechanisms of sulphur–water interaction at

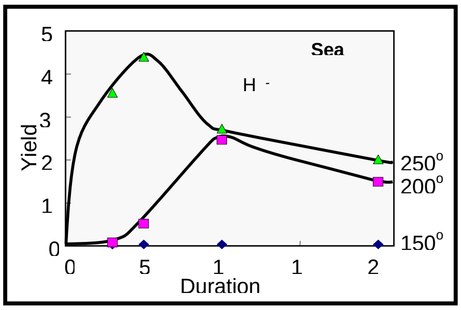

Figure 9. HS^- yield from native sulphur-seawater hydrothermal reaction experiments.

high temperature (e.g. at 200°C) and saturated vapour pressure, to facilitate the design an efficient georeactor. Figure 9, however, shows several promising results, not least that the conversion rate of elemental sulphur to HS^- is >40%, which means a conversion rate of *at least* 64% (i.e. 40% + (100-40) x 0.4) elemental sulphur to HS^- could be obtained after two circulations of reacted solution through the georeactor.

5 CONCLUSIONS

To date, geothermal resources in Japan have been developed for (electric) power generation, as well as providing hot water to green houses, district heating, drying and other facilities. Geothermal energy, however, can be considered to be a heat resource, as it has great efficiency for heat supply. It is demonstrated, even though the total amount of geothermal steam may be insufficient for power generation, that the resource can be utilised for other purposes, such as drying, extraction of aromatic component from wood products, etc.

It is possible to utilise the geosphere for material processing, due to the high temperature-pressure conditions prevalent in the Earth, as an alternative use of geothermal energy. In this study, we have focused on sulphur–water interaction, and the utilisation of waste elemental sulphur, as a potential resource for hydrogen production, using high performance photocatalysis. Hydrogen has been promoted as the future ultimate clean energy source, even though we have yet to design a viable, industrial-scale, hydrogen generation system!

We suggest that geothermal resources could prove to be a potential energy source for sustainable hydrogen production, but there is a long way to go to realise this possibility. We hope, via interdisciplinary international collaboration, to instigate a far-reaching research project to develop new methodologies for hydrogen generation. Future work will consider aspects of geothermal research (e.g. fluid-rock interactions), as well as nano-technology, high efficiency photocatalysis, and case studies in New Zealand and elsewhere that accommodate the environmentally-friendly utilisation of geothermal resources.

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