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Hydrogen Production from Geothermal Sources in Turkey

Mehmet Haklidir[1], Fusun Servin Tut Haklidir[2]

[1]TUBITAK Marmara Research Center, Information Technologies Institute, 41470, Gebze-Kocaeli, TURKEY

[2]Zorlu Energy Group Avcılar - Istanbul, TURKEY

mehmet.haklidir@bte.mam.gov.tr, fusun.tut@zorlu.com

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ABSTRACT

Nowadays finding a sustainable energy source for the future is one of the more urgent priority for human being. Hydrogen is an energy carrier and may be produced from another substance. Hydrogen is not widely used today but it has great potential as an energy carrier for future.

Hydrogen can be produced from different resources (water, fossil fuels, biomass, geothermal) and it products of chemical processes. Among the use of non fossil energy sources for hydrogen production, geothermal energy seems an important alternative.

Geothermal energy is a form of renewable energy derived from heat deep in the earth's crust. This heat is brought to the near-surface by thermal conduction and by intrusion into the earth's crust of molten magma originating from great depth. As groundwater is heated, geothermal energy is produced in the form of hot water and steam. Geothermal fluids at depth are complex mixtures of dissolved gases and solids. The major gases in the non - condensing gas phase consist of carbon dioxide, hydrogen sulfide, ammonia, nitrogen and hydrogen. Concentrations of these major gases will change among wells in the same geothermal area. One of the major component of gas composition, hydrogen sulphide, is especially found in high- temperature geothermal fluids (>150 ºC). The reaction of sulfur is probably formed by a few following mechanism such as, present in reservoir rocks with hot water, magmatic functions and metamorphism of sedimentary rocks. Concentration of this gas sampled from geothermal fluids in USA range from 0.18 to over 50 mg/l. Turkey is also has rich geothermal areas that have high enthalpy in Western Anatolia. Depends on tectonic regime, the area has so many geothermal locations and some of them have over than 190 ºC geothermal fluids. In Kızıldere / Denizli region dry ice (solid CO_2) has been produced by geothermal fumerols.

In this paper, applicability of geothermal energy to the production of hydrogen has been discussed and the available techniques of hydrogen production from hydrogen sulfide, especially thermo-chemical and electrolysis, have been investigated.

1. INTRODUCTION

Geothermal energy is one of the renewable energy like solar, biomass, wind and hydrogen. Although the energy has some advantages for using, it contains some pollutant for nature. Geothermal fluids usually contain gases such as carbon dioxide (CO_2), hydrogen sulphide (H_2S), ammonia (NH_3), methane (CH_4), and trace amounts of other gases, as well as dissolved chemicals whose concentrations usually increase with temperature. For example, boron (B), arsenic (As) and mercury (Hg) are a source of pollution if discharged into the environment (Arnorsson, 2000).

Hydrogen sulphide is found in most - especially in high enthalpy systems- geothermal areas (Layton et al., 1981) and in some oil and natural gas that is highly toxic gas which is heavier than air. Meanwhile hydrogen sulphide is used to production of hydrogen in hydrogen energy systems.

Hydrogen can be produced from different sources. One alternative might be geothermal resources for hydrogen production in countries which has rich geothermal sources.

2. GEOTHERMAL SYSTEMS

A geothermal system is made up of three main elements: a heat source, a reservoir and a fluid, which is the carrier that transfers the heat. Fluids carry their heats from the upper crust of the earth to surface by fault zones (Fig.1).

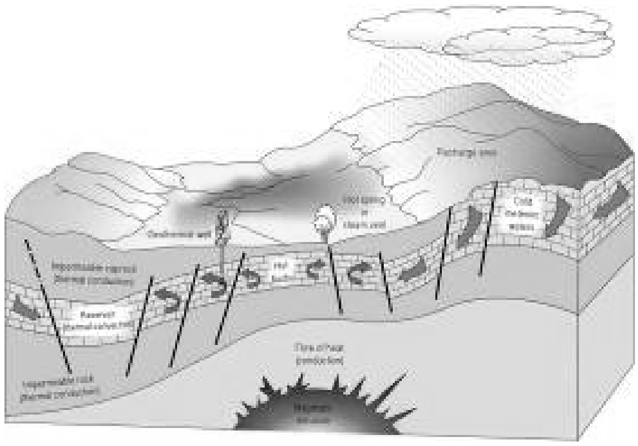

Figure 1: Geothermal Systems Elements: Heat source, reservoir and fluids (Hochstein, 1990)

The heat source can be very high temperature (over than 600 ºC) magmatic intrusion that has reached relatively shallow depths (5-10 km) or certain low-temperature systems, the Earth's normal temperature increases with depth. The reservoir is a volume of hot permeable rocks from which the circulating fluids extract heat. The reservoir is overlain by a cover of impermeable rocks and the meteoric waters can replace or partly replace the fluids that escape from the reservoir through springs or are extracted by boreholes (Dickson & Fanelli 2004). The geothermal fluid is water, in the majority of cases meteoric water, in the liquid or vapor phase, depending on its temperature and pressure. This fluid carries with chemicals and gases such as CO_2, H_2S, H_2 and CH_4.

2.1 Composition of Geothermal Fluids

Hot springs with major water outflows, the general chemical nature of the spring and well water has been found to be similar character, except for elements that are controlled by rapidly reversible temperature-dependent equilibria. Most common analysis of geothermal well discharges includes Si, B, Na, K, Ca, Mg, SO_4 and Cl and carbonate ions. The ratio of chloride, lithium, cesium, fluoride, bromide, iodide, arsenic, boron in waters from deep wells often differs from that in major surface springs (Ellis, 1967).

The steam phase contains most of the gases originally dissolved in the hot water. The gas content of steam from wells in different areas varies widely. In the geothermal areas carbon dioxide (CO_2) frequently is making up over 80% of the total gases (Table.1). In most volcanic hydrothermal areas, hydrogen sulfide (H_2S) is usually the next abundant gas (Fig.2). Sedimentary and metamorphic rocks areas may be exceeded by methane (CH_4). A geothermal system also includes other gases such as H_2, N_2, NH_3 and inert gases He, Ar. (Table.2).

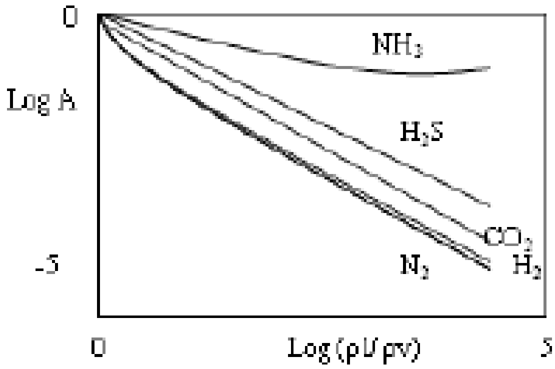

Figure 2: The Solubility of Various Gases (A: coefficient, ρ: densities of liquid and steam phases (Jones, 1963; Pray et. al, 1952)).

In some drilled main gases present; CO_2, H_2S, N_2, H_2 in Hveragerdi (Iceland, 1200 m., 232 ºC- Table.2) CO_2, H_2S, in Yellowstone Park (USA, 330 m., 240 ºC) (Sigvaldason,1973), in Kizildere (Denizli, 1600 m., 240 ºC).

Table 1: Composition of Steam in Geothermal Discharges (Ellis, 1967)

Source	Depth (m)	CO_2	H_2S	H_2	HC	N_2+Ar	NH_3
Well G3	400	73.7	7.3	5.7	0.4	12.9	-
Reykjavik wells	500	-	-	0.01	0.04	99.2	-
Average well Wairakei	650	91.7	4.4	0.8	0.9	1.5	0.6
Well E205 Matsao	1500	92	5	0.8	0.7	1.5	-
Well MR2	1080	81.8	14.1				

Table 2: Geothermal Gas Compositions in Bjamarflag Wells 11 -12 Iceland

Gas in Steam from well BJ-11

	CO_2	H_2S	H_2	CH_4	N_2	Total
Gas /kg	1587	1465	**110**	6	24	3192
Weight-%	49.7	45.9	**3.4**	0.2	0.8	100
Volume-%	26.8	31.9	**40.4**	0.3	0.6	100
Tons/year	681	629	**47.2**	2.6	10.3	1370

Gas in Steam from well BJ-12

	CO_2	H_2S	H_2	CH_4	N_2	Total
Gas/kg	3675	1668	**157**	8	34	5542
Weight-%	66.3	30.1	**2.8**	0.2	0.8	100
Volume-%	39.4	23.1	**36.7**	0.2	0.6	100
Tons/year	1229	558	**52.5**	2.7	11.4	1854

2.2 Geothermal Energy in Turkey

The tectonically active areas are concentrated along high stress zones such as North Anatolian strike-slip fault, East Anatolian transform fault and Western Anatolia Grabens in Turkey. High entalphy geothermal sources discovered primarily in the extensional zone in Western Anatolia because of crust thinning in this region (Fig.3).

Geothermal energy exploration started in early 1960's in Turkey. First exploration studies such as Kızıldere-Denizli region. 240 ºC geothermal fluid was explored in this area. After that the geothermal exploration studies has became widespread especially Western Anatolia.

Turkey's geothermal potential was declared as 31.500 MWt by General Directorate of Mineral Research and Exploration (MTA). Installed capacity for direct application is 1229 MWt and the identified capacity is 3600 MWt in the country. Over than 415 geothermal wells have been drilled and their data were collected by MTA up to now in Turkey. There are four geothermal power plants in Western Anatolia and new power plants are under construction in Western Anatolia.

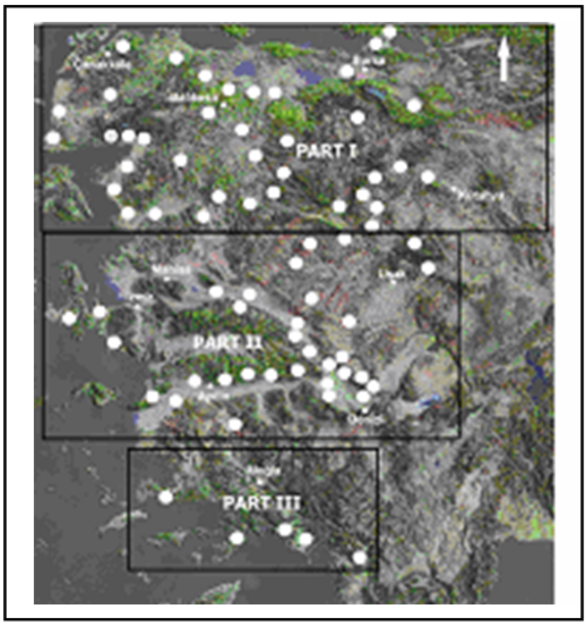

Figure.3 Distribution of Geothermal Resources in Western Anatolia

Although geothermal sources are environmentally friendly, there are some non condensable gases (such as CO_2, H_2S, N_2, H_2) from wells. CO_2 and H_2S are main gases for Western Anatolia and H_2S may use hydrogen production with electrochemical process.

3. PRODUCTION OF HYDROGEN FROM H_2S

Geothermal gas frequently contains considerable amount of hydrogen sulfide. The different process of hydrogen production from hydrogen sulphide can be grouped into five main categories, depending on the kind of process involved and the source of energy for the process (Haklidir et al. 2006):

1. Thermochemical Processes
    a. Steam Reforming Process
    b. Partial Oxidation
    c. Autothermal Reforming
2. Thermal Decomposition
3. Photochemical Processes
4. Electrochemical Processes
5. Plasma

3.1 Thermochemical Processes

3.1.1 Steam Reforming Process

Most of the hydrogen currently consumed is produced by Steam Methane Reforming (SMR), produces hydrogen with a high degree of purity and its operation is stable over a very large range of operating conditions. But it has the disadvantages that large quantities of natural gas, a valuable resource in itself, are required as both feed gas and combustion fuel and carbon dioxide is produced and discharged into the atmosphere thus contributing to the greenhouse effect (Cox, 1998). In this process, delivering three moles of hydrogen per mole of CH_4 reacted with production of greenhouse gases such as CO_2.

$$CH_4 + H_2O = CO + 3H_2 \ \Delta H_{298K} = +206.36 \text{ kJ/mol}$$

A process, capable of delivering at least four moles of hydrogen per mole of CH_4 reacted without production of greenhouse gases such as CO_2, could be conceived by using hydrogen sulfide reformation of natural gas. In a way, the reaction of H_2S with methane can be thought of as the sulfur analog of the SMR process (T-Raissi, 2001**)**. The overall reaction for the H_2S methane reforming process may be written as follows:

$$CH_4 + 2H_2S = CS_2 + 4H_2 \ \Delta H_{298K} = +232.4 \text{ kJ/mol}$$

The prospective process represented by the overall reaction above will produce carbon disulfide (CS_2). CS_2 can be used for the production of sulfuric acid (H_2SO_4) and carbon tetrachloride (CCl_4). H_2S-methane reformation is more suitable for utility type of operation with large-scale production rates.

3.1.2 Partial Oxidation

Marathon Oil has developed a thermochemical process based on the oxidizing ability of t-butylanthraquinone. The H_2S oxidation step takes place at 20 and 70 ºC and H_2S partial pressures of 5 to 507 kPa in a polar reaction solvent, whereas the regeneration step is performed over a dehydrogenation catalyst at 150 to 290 ºC (Plummer, 1987).

3.1.3 Autothermal Reforming

This is the combination of partial oxidation and stream reforming processes. In autothermal reforming, the process of partial oxidation and steam reforming are highly integrated, meaning both reactions take place in one reactor-thermos reactor. Autothermal reforming produces streams which are more concentrated in hydrogen than partial oxidation process but less than the steam reforming process. But large volumes of carbon dioxide are produced, which have to be separated to obtain a stream of greater hydrogen concentration (Ragwitz et al., 2003).

3.1.4 Thermal Decomposition

Thermal decomposition is the most direct process to dissociate H_2S into H_2 and S. In the temperature range of about 800-1500°C, the H_2S can be converted to H_2 and elemental sulfur. Thermolysis of hydrogen sulfide can be treated simply in terms of reaction:

$$H_2S = H_2 + 1/2S_2 \ \Delta H = 79.9 \text{ kJ/mol}$$

The equilibrium conversion is between 15-35%. The process needs no intermediary chemicals. Catalyst type has a significant effect on the amount of hydrogen produced and on the economics of the process. Catalysis could be useful to increase the conversion level (Raymond, 1975).

According to Cox (1998), using an efficient H_2/H_2S separation system, the thermal decomposition of H_2S is able to produce hydrogen at a cost approaching that of the conventional SMR process. Two processes for the thermal decomposition of H_2S were studied by Cox et al. First one involved the recycling H_2S through a modified steam methane reforming type furnace so that all of the possible hydrogen could be extracted. In the second one, H_2S was passed once-through a decomposition/heat exchanger type reactor then on to a conventional Claus sulphur recovery plant. In principal, first process can be integrated with a nonpolluting heat source (for example Solar) to eliminate emission of greenhouse gases from the combustion furnace. In a solar furnace, the thermolysis of H_2S and the recovery of H_2 and S were studied by Kappauf and Fletcher (1989) by using a simple, single pass reactor.

Since H_2S decomposition reactions run at relatively high temperatures, this process is a good candidate for interfacing to concentrated solar radiation.

3.2 Photochemical

Photochemical reactions use photocatalysts that absorb ultra-violet light from the solar spectrum to power chemical reaction. But this method is not effective since using UV light is very expensive to produce Hydrogen from H_2S. In addition, the conversion levels are quite low in present photochemical schemes, and they have not yet reached the stage of technology development (Plummer, 1987).

3.3 Electrochemical

In electrochemical methods, an electrolysis cell is used to produce hydrogen and sulfur from hydrogen sulphide by letting the direct electric current pass between the two electrodes of the cell like water electrolysis method. This method has three different techniques: Direct, indirect, high temperature.

Direct electrolysis can be performed in acids or alkaline media (Anani et al., 1990).

Indirect electrolysis methods use a chemical oxidant to oxidize H_2S in acidic or basic media (Kalina and Moas, 1985).

In high temperature electrolysis, hot H_2S flows past the cathode, where hydrogen is evolved. The sulphide ion moves through a molten salt electrolyte to the cathode (Alexander and Winnick, 1990).

3.4 Plasma

The plasma process uses microwave plasma chemistry to dissociate H_2S into H_2 and S. Back reaction of the products to H_2S is minimized by in situ cyclonic separation and a rapid quench of the products. Furthermore, experiments with water and carbon dioxide concentrations typical of acid-gas streams from refinery operations and natural gas production have demonstrated that these components are compatible with the proposed process. A preliminary economic evaluation indicates that the plasma-chemical process will be substantially cheaper to operate than the conventional sulfur recovery technology and that the sulfur emissions will also be lower (Balebanov et al., 1985).

4. CONCLUSION

Geothermal fluids at depth are complex mixtures of dissolved gases and solids. The major gases in the non - condensing gas phase consist of carbon dioxide, hydrogen sulfide, ammonia, nitrogen and hydrogen. Geothermal gas frequently contains considerable amount of hydrogen sulfide. In this study, the applicability of geothermal energy to the production of hydrogen has been discussed and the available techniques of hydrogen production from hydrogen sulphide, especially thermochemical and thermal process have been investigated. One of the geothermal system waste products is H_2S, the poisonous and pollutant gas, may be utilized to produce hydrogen, is a future secondary energy source.

REFERENCES

Alexander S, Winnick J, Electrochemical separation of hydrogen sulfide from natural gas, Sep. Sci. Techno.; 1990: 25, 2057.

Anani AA, Mao Z, White RE, Srinivason S, Appleby AJ. Electrochemical production of hydrogen and sulphur by low temperature decomposition of hydrogen sulphide in an aqueous alkaline solution. J Electrochem Soc.; 1990: 137, 2703.

Balebanov, A.V., Butylin, B A., Zhivotov, V.K., Krokvenko, V.l., Matolich, R.M., Macheret, S S., Novikov, G.I., Potapkin, B.V , Rusanov, V.D., Fridman, A.A. and Yavorskii, V. T., Dissociation of hydrogen sulphide in a plasma. Dklady Phys. Chem., 1985, 283(1-3), 709-712.

Cox, B.G., P.F. Clarke, B.B. Pruden. 1998. "Economics of Thermal Dissociation of H2S to Produce Hydrogen." Int. J. Hydrogen Energy, 23(7): 531-544.

Dickson and Fanelli, op. cit. note 54; Philippines share from World Bank, op. cit. note 53; California from Alyssa Kagel, Diana Bates and Karl Gawell, A Guide to Geothermal Energy and the Environment (Washington, DC: Geothermal Energy Association, 22 April 2005).

Ellis,A. J., 1967. The geochemistry of some explored geothermal systems in Geochemistry of Hydrothermal Ore Deposits. P.465-514.

Haklidir, M., Tut, F. S., Kapkin, S., “Possibilities of Production and Storage of Hydrogen in the Black Sea”, 16th World Hydrogen Energy Conference WHEC 2006, Lyon, France, 13-16 June 2006.

Kalina DW, Moas ET., Indirect hydrogen sulfide conversion-I. An acidic electrochemical process. Int. J. Hydrogen Energy ; 1985 : 10 (3), 157.

Kappauf, T., and Fletcher, E. A. (1989). Hydrogen and Sulfur from Hydrogen Sulfide VI. Solar Thermolysis. Energy 14, 443-449.

Plummer, M.A., Sulphur and hydrogen from H2S, Hydro-carbon Processing, 1987, April, 38-40.

Pray H.A, Schweickeret, C.E, Minnich, B.H. (1952). Solubility of hydrogen oxygen,nitrogen and helium in water: Ind. Eng. Chem. 44. 1146-1151.

Ragwitz, M., Wietschel, M., Hasenauer, U. and Fakolade, O. (2003) Introduction of Alternative Transport. Fuels in the European Energy Market. Techno-Economic

Barriers and Perspectives : Work Package D: Hydrogen. Afteem Esto Study, Technical Report.

Raymond, E.D., Make hydrogen from hydrogen sulfide. Hydrocarbon Processing, 1975, July, 139-142.

Sigvaldason, G.E. 1973. Geochemical Methods in Geothermal Exploration:in Geothermal Energy.P.49-60.

T-Raissi, A.,(2001) (USA) Technoeconomic Analysis of Area II Hydrogen Production - Part 1. Proceedings of the 2001 U.S. DOE Hydrogen Program Review (NREL/CP 570-30535).