APPLICATION OF GEOTHERMAL ENERGY TO HYDROGEN PRODUCTION AND STORAGE

Thorsteinn Sigfusson
Innovation Centre of Iceland

Preprint

APPLICATION OF GEOTHERMAL ENERGY TO HYDROGEN PRODUCTION AND STORAGE

Bragi Arnason and Thorsteinn I. Sigfusson
Science Institute, University of Iceland
Dunhaga 3, 107 Reykjavik, Iceland
arnason@raunvis.hi.is and this@simnet.is

Abstract

In Iceland there has been an official governmental aim to head towards a hydrogen society. In fact Iceland has been producing hydrogen for half a century by using alkaline electrolysis. The paper discusses the applicability of geothermal energy to the production, storage and use of hydrogen. After reviewing the vast geothermal resources of Earth a short description is given of the geothermal situation in Iceland, where geothermal energy accounts for 50% percent of the national energy scene. In Iceland this energy source has served as a great contributor to the reduction of CO_2 emissions from the overall energy system. Geothermal energy can be used to assist electrolysis of hydrogen by the use of steam turbine electricity generation and high temperature electrolysis or by solid state methods capable of using much lower temperature resources. For the use of metal hydrides geothermal energy can be used to assist the storage management. Also by using hydrides, heat energy can be transported considerable distances as hydrogen gas for heating and cooling purposes. Many communities in the world could benefit from linking their geothermal resources to the development of hydrogen energy economy.

Introduction.

Geothermal energy is a substantial indigenous energy resource on Earth which is believed to originate in geonuclear activity. The utilisable geothermal energy of Earth has been estimated to be about 18 exajoule per annum compared to 88 exajoules for the utilisable fraction of the solar irradiation. (Table I).

When considering the use of non fossil sources for hydrogen production, geothermal energy seems an important option. In Iceland where there has been an official governmental aim to head towards a hydrogen society, geothermal energy serves as a major energy source for space heating and accounts for about a fifth of the electricity production.

In this paper we wish to shed more light upon current work in the area of utilising geothermal sources for hydrogen production and some new ideas and concepts related to geothermal hydrogen with the emphasis on the experience in Iceland.

Direct hydrogen source.

Geothermal gas vent field sampling in Iceland and other plate tectonic spreading zones and volcanic regions of the Earth, see figure 1, indicates that directly above some of these zones, hydrogen gas makes its way to the surface and is released to the atmosphere in technically recoverable concentrations and quantities. The origins of this direct geothermal hydrogen is believed to be in a steam-iron like process where magma and groundwater are in contact at different depths in the crust.

Geothermal vents along the terrestrial section of the Mid-Atlantic Ridge are for example to be found at the Bjarnarflag Geothermal Field, near the Krafla Volcano, Northern Iceland (fig. 2) .

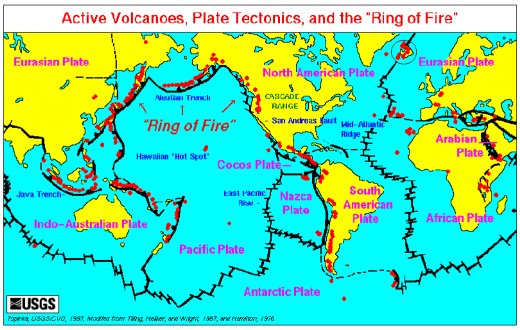

Figure 1. The ring of fire showing the edges of the tectonic plates and the active volcanic regions of the Earth.

Figure 2. The Krafla geothermal area in Northern Iceland has shown very large emissions of pure hydrogen together with other gasses. Some of the experimental boreholes are able to provide around 50 tonnes of H_2 annually. Hydrogen from the hydrogen sulfide could almost double the output for a given borehole.

The chemical composition of a representative bore hole in the Bjarnarflag area is shown in table II for two boreholes. A single borehole in this area is known to be able to produce up to about 50 tonnes of hydrogen annually. This figure is unusually high and represents the maximum capacity of hydrogen in the geothermal system.

The utilisation of this hydrogen directly requires cleaning of the gas, in particular ingredients like H_2S,CO_2,CH_4 and N_2. Cleaning of the hydrogen gas is of the utmost importance for any further utilisation of the hydrogen in fuel cells. It remains to be seen if this proves a possible task given the existing gas cleaning technologies.

Hydrogen sulfide an additional hydrogen source

Geothermal gas frequently contains considerable amount of hydrogen sulfide. Table II shows that H_2S emitted from two boreholes in the Bjarnarflag Geothermal Field, if split into its elements, could be used to produce about 40 tonnes of hydrogen annually in addition to about 50 tonnes of molecular hydrogen emitted.

The hydrogen in hydrogen sulfide is quite loosely bound compared to many other simple compounds that contain hydrogen. For instance the standard enthalpy of formation of H_2O is ΔH_f =

-286 kJ/mol but the standard enthalpy of formation of H_2S is only ΔH_f = -21 kJ/mol, which means that the energy needed to split water molecule is more than an order of magnitude larger than the energy needed to split hydrogen sulfide molecule.

Many processes are possible to make hydrogen from hydrogen sulfide. Considering possible processes that can become economically feasible we have focussed our attention to the fact that if ferric chloride is dissolved in hydrochloric acid solution the ferric ion can easily, when reduced to ferrous ion, oxidize the sulfide ion of dissolved hydrogen sulfide into elemental solid sulfur that can be separated from the solution. When the remaining ferrous and hydrochloric acid solution is subjected to electrolysis the ferrous ions are oxidized back to ferric ions in the anode chamber and the hydrogen ions reduced to hydrogen gas in the cathode chamber.

Therefore our attention is focussed on a possible two step hybrid process that can be described by the following chemical equations:

(1) $H_2S + 2Fe^{3+} \rightarrow S + 2Fe^{2+} + 2H^+$
(2) $2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2$ (electrolysis)

The equilibriun constant for step (1), K~ 10^{20}, is quite favourable. The standard reduction potential in acid solution for ferric ions into ferrous ions, 0.77 volt, and the standard reduction potentials for oxygen into oxygen ions and for chlorine into chloride ions, 1,23 volt and 1,36 volt respectively, show that keeping the voltage in the electrolysis cell below 1.23 volt neither oxygen or chlorine will be produced at the anode.

Geothermal heat and electricity.

Heat and electricity production from geothermal sources accounts for about 60% of the total energy consumption in Iceland and the amount of electricity or space heating produced from fossil resources is negligible. The ratio of hydroelectric to geothermal *electricity* in Iceland is roughly 4:1.

Typically, geothermal power is converted into electricity through turbines operating on the flash steam or the binary Rankine cycle. Geothermal heat is a huge energy resource. It has been estimated that the total worldwide harnessable power using turbines (steam >150°C) is about 1,300 GW_e and that lower temperature geothermal resources may provide about twice that using binary systems [Stefansson, 1998]. For comparison, the total installed power of all electricity generators in the world is about 3,300 GW_e

Hydrogen can be produced by numerous ways. Within the scope of this paper only a few major methods will be considered: electrolysis, themochemical methods and a mixture of both.

Figure 3 shows the use of primary energy in Iceland from 1940 to 2002. The amount of energy is denoted in PJ and theinserted figure shows how geothermal energy has gradually tended to dominate carbon sources and currently, together with hydroelectricity, account for about 2/3 of the primary energy sources.

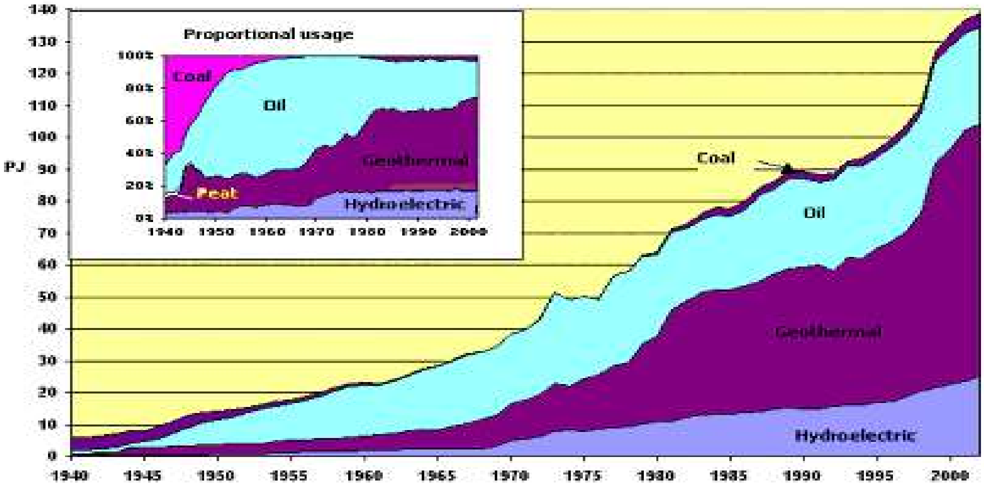

Figure 3. The use of primary energy in Iceland from 1940 to 2002. The amount of energy is denoted in PJ. The inserted figure shows how geothermal energy has gradually tended to dominate carbon sources and currently, together with hydroelectricity, account for about 2/3 of the prime energy sources.

Electrolysis at different temperatures.

In the work of Icelandic New Energy Ltd. And the EU supported Ecological City TranspOrt System project, ECTOS, three busses in the Reykjavik bus fleet are now powered by hydrogen produced at a Shell utility in Reykjavik by a Norsk Hydro alkaline electrolysis process fed by electricity from the municipal grid and water from the waterworks of Reykjavik Energy.

Three types of water electrolysis methods are in principle possible:

1) Alkaline electrolysis.
   Electrolyte: Aqueous KOH solution.
   Energy efficiency: 78%.

2) PEM electrolysis.
   Electrolyte: Hydrogen ion conducting proton exchange membrane.
   Energy efficiency: 90%.

3) High temperature steam electrolysis.
   Electrolyte: Oxygen conducting ceramics (ZrO$_2$ stabilized by Y$_2$O$_3$ and MgO).
   Energy efficiency: 94%.

Alkaline electrolysis is and has been the most common method for large scale production for a number of years. PEM electrolysis is reaching the stage of commercialisation, but high temperature electrolysis is still in early development state. In the Icelandic hydrogen project, the need in the ECTOS project was for clean hydrogen suitable for fuel cells and amounting to about 120 kg a day and the alkaline electrolysis technology is an all proven commercially proven process. Its uses in Iceland date back about half a century associated with fertilizer production. For the ECTOS project it was an obvious choice to select alkaline electrolysis. The electricity for the process comes from a hydroelectric/geothermal mix in the national grid.

Table I. Annual supply and potential of unlimited energy sources in exajoules/year. (Based on Nitsch, 1988).

Type of energy	Theoretical potential	Technical potential (secondary energy)	Possibly utilizable (secondary energy)	Relationship of technical potential to world secondary energy use
Solar radiation	791370	586	88	2.8
Wind energy	8793	94	32	0.45
Biomass	2931	191	158	0.95
Hydropower	158	70	47	0.35
Geothermal	1114	64	18	0.3
Others (OTEC, Wave energy, Tidal energy)	733	32	15	
Total		**1037**	**358**	**5**

Table II. Geothermal gas composition in Bjarnarflag, wells 11 and 12, in 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

The high- temperature steam electrolysis operates in the temperature range 800-1000 ^{0}C. It employs oxygen ion conducting ceramics. The most common material is zirconia, ZrO_2 stabilized by Y_2O_3, MgO or CaO. The steam to be dissociated enters on the cathode side. After the steam has been split into hydrogen gas and oxygen ions, the oxygen ions are transported through the ceramic material to the anode where they discharge and form oxygen gas. The interplay of temperature and required energy for high temperature electrolysis can best be seen through considerations related to the enthalpy of the water splitting process. The enthalpy is given as the sum of the minimum work needed and the temperature-entropy term:

$$\Delta H = \Delta G + T\Delta S$$

ΔH: The enthalpy change or total energy demand
ΔG: The Gibbs free energy or the minimum work
T: The absolute temperature
ΔS: The entropy change

The term $T\Delta S$ can be considered as the total amount of thermal energy needed to split water. The temperature dependence of the thermodynamic functions for splitting of the fluid is shown in Fig. 4. (Dönitz et al., 1990)

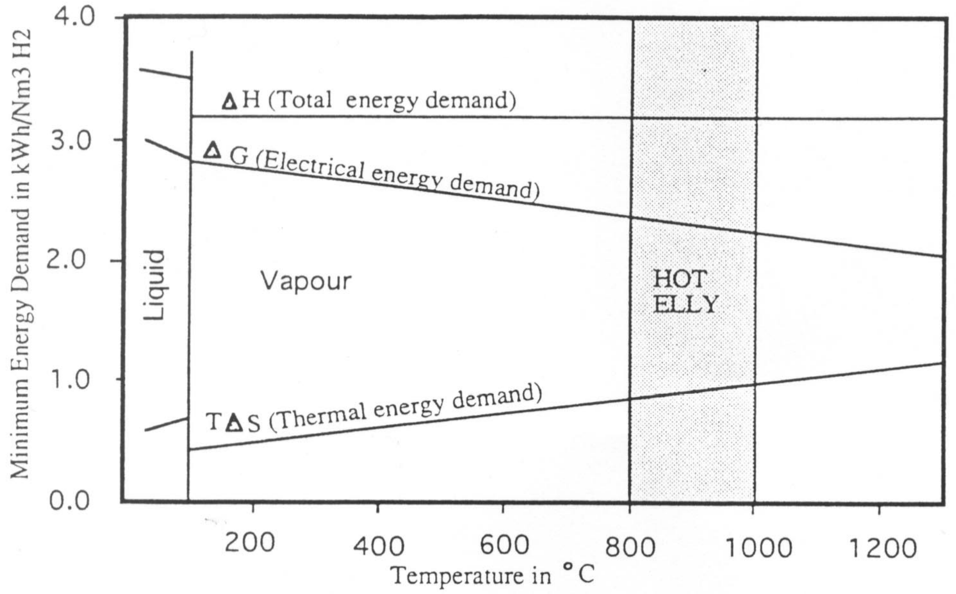

Figure 4. Minimum energy needed to split water liquid/vapour (From Dönitz et al. 1990)

Prefeasibility studies have shown that, if developed to a large scale, geothermal steam assisted high- temperature electrolysis in Iceland could possibly lower the hydrogen production cost by about 20% (Jonson et al. 1992)

The University of Iceland and Icelandic New Energy are currently preparing a campaign to work towards promoting high temperature electrolysis for hydrogen production.To this end, cooperation with CEA of France is under way in association with the University of Grenoble. The plan is to incorporate graduate projects and exchange of students and specialists between France and Iceland in order to realise this. Geothermal energy in Iceland and nuclear energy in France unite the partners in the search for high temperature electrolysis solutions. Various technologies available to the nuclear industry regarding utilisation of the thermonuclear energy are outside the scope of this paper.

Thermochemical and hybrid cycles for production of hydrogen.

When considering the use of geothermal energy for hydrogen production, it is important to note that the technically available geothermal heat presently does not always suffice to lead directly to for example thermochemical cycles or hybrid processes. However, available geothermal heat at temperatures up to about 300 Centigrades goes some way towards needed thermal conditions for some processes. Some well known of such hydrogen producing processes suitable in a geothermal situation are for example:

Thermochemical cycles (example Mark 9):

$6FeCl_2 + 8H_2O \Rightarrow 2Fe_3O_4 + 12HCl + 2H_2$ (650 ºC)
$2Fe_3O_4 + 3Cl_2 + 12HCl \Rightarrow 6FeCl_3 + 6H_2O + O_2$ (<200 ºC)
$6FeCl_3 \Rightarrow 6FeCl_2 + 3Cl_2$ (350 ºC)

$2H_2O \Rightarrow 2H_2 + O_2$

Hybrid processes (example Mark 13):

$SO_2 + Br_2 + 2H_2O \Rightarrow H_2SO_4 + 2HBr$ (50-100 ºC)
$2HBr \Rightarrow H_2 + Br_2$ (electrolysis)
$H_2SO_4 \Rightarrow H_2O + SO_2 + 1/2\ O_2$ (730-830 ºC)

$H_2O \Rightarrow H_2 + 1/2\ O_2$

Solid state electricity production from geothermal sources.

Finally we will comment the possibility of utilising lower temperature geothermal sources by the use of solid state technologies which have been developed in Iceland over the past years. The first such harnessing of geothermal energy based on Seebeck effect was performed by scientists of the Science Institute University of Iceland in a research station in the geothermal Grimsvötn area in Vatnajökull glacier about two decades ago. Here a small thermoelectric generator provides electric energy to power radio frequency communication system for data acquisition and on line analysis at the University in Reykjavik
.
A large proportion of the available geothermal heat sources in the world have temperatures below about 120 Centigrades and thus are not suitable for flash turbines. To meet this challenge a small University spin-off company in Iceland, Varmaraf Ltd., develops and manufactures heat exchangers designed to work with thermoelectric Seebeck cells of any kind. Inside the most common module, an array of p/n doped semiconducting crystals is connected in series and a voltage is induced in proportion to the temperature difference between the ends of the crystals.

The efficiency of thermoelectric generation depends upon a number of factors. (Anatychuk, 1998, Sigfusson 2002). An important factor is the Seebeck coefficient, $\alpha = \delta V / \delta T$, denoting the gradient of the induced thermoelectric voltage V as the temperature T is changed. The efficiency η of a thermoelectric system depends upon the so called figure of merit and the temperatures of the hot and the cold ends respectively. *Z* is given by

$$Z = \alpha^2 \sigma / \lambda$$

σ denotes electrical conductivity and λ is thermal conductivity of the thermoelectric material. In this way the aim of the design is towards high Seebeck coefficient and electric conductivity whereas low thermal conductivity is desirable. In this way the maximum of the energy flow across a thermal gradient is converted from phonons into electrons.

The efficiency η of a thermoelectric generator depends upon the figure of merit and the temperatures of the hot T_h and cold T_c reservoir according to the equation

$$\eta = (1 - Tc/Th)*(M - 1/(M + Tc/Th))$$

where $M = (1 + Z(Tc + Th)/2)^{1/2}$

The development of Varmaraf in Iceland has been focused on what now is a state-of-the-art heat exchanger and generation system. (B. Hafsteinsson, 2002). By the patented technology of Varmaraf the efficiency of a fluid-fluid conversion from the hot fluid to the cold fluid through the electricity producing modules has been optimised. At temperatures as low as 90 Centigrades the Varmaraf technology is able to provide about 4% efficiency when the cold source is at 10 Centigrades. Steam based turbines are of course not possible at these relatively low temperatures.

When it comes to harnessing geothermal and waste heat, the most applicable device would be one that uses hot and cold water as the medium for transferring heat from the original heat source to the conversion device and transferring heat from the conversion device for disposal. This is because in many cases, such fluid loops are already available or they can be established at low cost using proven hardware. On the cooling side, air cooling is sometimes an option but often suffers from poor heat transfer that occurs on the metal/air interface in cooling fins or heat sinks even under forced convection. When heat must be dumped at only a few degrees higher temperature than the surrounding air, an extremely large heat transfer area is called for. Cold rivers, lakes and cooling towers may be the best way to dump heat for this application. The effectiveness of cooling towers is due to the evaporation that is involved and carries away the bulk of the heat. The design objectives for a heat exchanger that is suitable for thermal conversion are primarily the following two:

* Maintain the temperature at both the hot and cold work surface of the conversion device as close as possible to the hot and cold fluid temperatures, under heat conduction through the conversion device and adjacent material.
* Minimal total cost of the heat exchanger because with no moving parts and negligible maintenance required, it is the capital cost of the generator that determines the production cost of each kilowatthour.

Figure 5. Thermoelectric generator for geothermal water applications. Courtesy Varmaraf Ltd.

Solid state generator design issues.

What determines the success in achieving the first objective is the heat transfer coefficient at the interface between the fluid and the wall of the flow channel and the total thermal resistance from the inner surface of the flow channel to the work surface of the conversion device. The more heat conducted per unit area through the conversion device, the higher demands are placed on these external factors. While very high thermal conductivity through the conversion device is desirable in principle, as this also gives most electrical output, a difficulty arises in maintaining the temperature difference across the work surfaces of the conversion device. In plate heat exchangers, it is also important to maintain as high heat transfer at the channel wall as possible. The classical plate heat exchanger design addresses this by corrugating the plate separating the fluids, thus inducing turbulence that enhances the heat transfer. In a heat exchanger that accommodates flat thermal conversion devices, this is not possible without resorting to expensive machining on one side while keeping the other side flat. Furthermore a uniform surface pressure must be maintained across the heat exchanger plate layers, with the conversion devices arranged in between hot and cold channels, so as to achieve good thermal contact between the devices and the flow channels. The unit has four ports, two for hot water, in and out and another two correspondingly for cold water.

An important feature of this design is how it addresses the second design objective, namely low cost. Varmaraf's design calls for minimal machining and offers the possibility to use special metals, such as titanium, without unreasonable cost.

On the future scene of Varmaraf is the anticipated collaboration with Power Chips a company planning to introduce thermionic devices expected to increase efficiency of solid state electricity conversion considerably.

It is a basic characteristic of solid state generators that they can not benefit from economy of scale in the same way as, for example, turbine systems, where several components enjoy eightfold increase in useful volume while the enclosing material is only quadrupled with a doubling of a linear dimension. If a double size solid state generator is called for, twice the number of conversion devices must be applied and the heat exchange area doubled, hence also twice the investment. Consequently, the cost advantage of the solid state generator over steam or binary systems is greater at the lower end of the power scale. There are other important advantages:

- The solid state generator is perfectly modular and scalable and can be delivered in single watts or in megawatt installations.
- This modularity also provides redundancy since larger installations will be made of parallel units of identical design. This enhances the reliability and maintainability of the plant.
- It is perfectly suitable for harnessing water at temperatures where even binary systems are not applicable.

There are a number of optimisation issues in determining the best system configuration. The optimal result is in most cases heavily dependent on performance parameters and costs. At this early stage of the systems development such results are not available yet but the questions are well defined. These relate to the minimal temperature difference for economic harnessing and influence of auxiliary components, such as pumps, on total system performance.

The most appropriate system configuration is also strongly dependent on local conditions. In some cases, the hot water may be sufficiently pure and void of dissolved minerals to allow it directly into the generator unit. Here, the tradeoff is between using the water directly and running the risk of some fouling and corrosion or set up a secondary loop with the associated losses. On the cooling side, the question is about the availability of a river or lake into which the heat could be dumped with due consideration of the environmental effects of the heating although no material contamination would be involved. Without a cold reservoir, a cooling tower is probably the best bet. Deposits could also be a factor on the cold side if a reservoir is used, depending on the water chemistry.

Hydrogen produced from "tap water"

Varmaraf is now marketing a thermoelectric generator specially designed for giving low DC voltages suitable for PEM electrolysis. Using such a device the Science Institute laboratory at the University of Iceland is producing hydrogen by the use of hot and cold tap water from the municipal utility in Reykjavik. By the use of this technology hydrogen can be produced from a relatively low temperature geothermal or waste heat source. This is believed to have many niche applications throughout the world.

Solid state generation and metal hydrides.

As soon as the Icelandic team had mastered the electricity and hydrogen generation aspect, focus was turned to applications within hydrogen storage. One of the areas being examined in Iceland currently is the merger of solid state heat generation, geothermal heat and the heat management of metal hydrides. The first such project was initiated by T.I. Sigfusson under the support of the Icelandic Energy Fund (Orkusjodur) in 2001.

Metal hydrides involve exothermic/endothermic energies as they release or bind hydrogen inside. The most common metal hydride storage devices up to now have been based on a passive function of a metal hydride container working at a the temperature (usually room temperature) available and at most capable of varying the gas pressure of the hydride.

In a geothermal/solid state heat management system being developed by the University of Iceland and Varmaraf currently, the active management of temperature of a hydride, together with the exchange of heat to and from a given reservoir of hydrogen inside a hydride, will be the focus of attention. First tests indicate that the capacity and release/absorption speeds of a given low temperature hydride can be increased significantly. This work is done in cooperation with Institute for Energy Technology in Norway and Japan Steel Works who are among the owners of Varmaraf and will be reported in due course.

In many ways the interplay of metal hydride bound hydrogen and thermal management in general has the potential to increase the applicability of metal hydrides as potential storage media for hydrogen. It is hoped that commercialisation of this technology is not far on the horizon.

Conclusion.

The hydrogen research in Iceland involves a number of factors which are special to Iceland. It is believed that the use of geothermal energy in Iceland will develop at a faster pace compared with hydroelectric harnessing in the future. The interplay of geothermal energy and hydrogen being examined currently will hopefully have its influence in other areas of the world and may lead to more attention given to the vast resources of waste heat of different origins available in the world

References.

Stefansson, V. (1998). Estimate of the World Geothermal Potential. Proceedings of the 20th Anniversary Workshop of the Geothermal Training Programme, October 1998. Orkustofnun 111-121.

J.Nitsch (1988). Energy Supply Structures and the Importance of Gaseous Energy Carriers, In Hydrogen as an Energy Carrier (Ed. Carl-Jochen Winter), Springer Verlag p.13-29.

Dönitz W., Erdle R. and Streicher R (1990). High Temperature Electrochemical Technology for Hydrogen Production and Power Generation. Electrochemical Hydrogen Technologies. Electrochemical Production and Combustion of Hydrogen, pp. 213-259, Ed. Hartmut Wendt, Elsevier.

Jonsson V.K., Gunnarsson R.L., Arnason B. and Sigfusson T.I. (1992), The Feasibility of Using Geothermal Energy in Hydrogen Production, Geothermics, Vol 21. No 5/6 pp. 673-681.

Anatychuk L.I., Physics of Thermoelectricity, Institute of Thermoelectricity, Ukraine, 1998.

Hafsteinsson B., Thesis, University of Iceland, 2002.

Sigfusson T.I., Eðlisfræði varmarafmagns, The Physics of Thermoelectricity, Eðlisfræði á Íslandi X, Proceedings of the Icelandic Physics Society Biennial Meeting, Ed. A. Ólafsson, June 2002, pp203-213.