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Capture of Geothermal Heat as Chemical Energy

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Fluids that undergo endothermic reactions were evaluated as potential chemical energy carriers of heat from geothermal reservoirs for power generation. Their performance was compared with that of H_2O and CO_2. The results show that (a) chemical energy carriers can produce more power from geothermal reservoirs than water and CO_2 and (b) working fluids should not be selected solely on the basis of their specific thermo-physical properties but rather on the basis of the rate of exergy (ideal power) they can deliver. This article discusses the results of the evaluation of two chemical energy carrier systems: ammonia and methanol/water mixtures.

Keywords: chemical reactions, fluids, geothermal energy, power generation, thermodynamic analysis

1. INTRODUCTION

Geothermal energy in general—and enhanced geothermal systems (EGS) in particular—is a huge domestic energy resource (MIT, 2006). Capturing EGS heat requires pumping water through a fractured reservoir. Supercritical water is a good solvent for rock minerals (Reed and Spycher, 1984). Dissolved minerals could precipitate as the temperature (T) and pressure (P) fluctuate, thereby reducing the permeability of the EGS (Xu and Pruess, 2003). This article presents the results of an evaluation of the potential use of chemical energy carriers (CECs) for the transport of EGS heat for power generation. Ammonia (NH_3) and methanol/water mixtures (CH_3OH/H_2O) are discussed as examples, and their performance is compared with that of water (H_2O) and carbon dioxide (CO_2).

To illustrate the potential energy benefits of using CEC fluids, consider the decomposition of CH_3OH to carbon monoxide (CO) and hydrogen (H_2). Its standard heat of reaction is 129,173 kJ/kmol of CH_3OH, and the reaction is reversible by using commercial catalysts. If CH_3OH in one case and H_2O in another case are injected into the EGS at 27°C and 1 bar and exit at 527°C and 50 MPa, the CH_3OH would have gained 5,400 kJ/kg of methanol that decomposes, of which about 74% is captured as chemical energy, compared to only 2,770 kJ/kg for water.

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2. CEC PROCESS DESCRIPTION

The reactants can be pumped into the injection pipe of the EGS to be heated, which causes the endothermic reaction to occur. The products will also be heated and will rise to the surface in the production pipe. At the surface, the products are cooled in order to reverse the reaction. The recovered heat, including the heat released by the exothermic regeneration reaction, is used for power generation. The regenerated reactants are then re-injected into the EGS reservoir. When the EGS heat is targeted for power generation, the selection of a fluid on the basis of the heat it captures per unit mass can be subject to error because the differences in the mobility of the fluids lead to different practical mass flow rates. In addition, an equal amount of heat captured by two different fluids can have different exergy values (Lee, 2001) and, therefore, give different power outputs.

2.1. CH_3OH and CH_3OH/H_2O

CH_3OH can capture EGS heat by thermal decomposition or steam reforming. The standard heat of the reforming reaction ($CH_3OH + H_2O + Heat \longleftrightarrow CO_2 + 3H_2$) is 130,331 kJ/kmol of CH_3OH. At $T > 350°C$, near complete reforming of the methanol is achieved at equilibrium. CH_3OH can also be regenerated by using commercial catalysts. Methanol is also miscible with water and could extract H_2O from the EGS and increase its permeability.

2.2. NH_3

The thermal decomposition of NH_3 ($2NH_3 + Heat \longleftrightarrow N_2 + 3H_2$) is an efficient energy absorber. Its standard heat of reaction is 45,951 kJ/kmol of NH_3, or about 2,703 kJ/kg. It also has high heat of vaporization (~60% that of water) and boils at lower T than water. NH_3 and NH_3/H_2O mixtures can also be used as the working fluid in power cycles. The reverse reaction takes place at 400–550°C and between 150 and 250 bars. Therefore, it will deliver high-quality thermal energy for power generation. Both ammonia and methanol are, however, expensive and flammable, and so special designs are required to minimize their loss and avoid surface and underground contamination.

3. CHARACTERIZATION OF THE ENHANCED GEOTHERMAL SYSTEMS (EGS)

Table 1 lists the conditions under which the fluids were injected and the property models used with the Aspen Plus® software in the analyses. The EGS system that was used in the analysis is characterized in Table 2. Because of the very high P encountered in deep EGS reservoirs, large differences resulted when different equations of state or activity coefficient models were used for

TABLE 1
Injection Conditions of the Different Working Fluids

Working Fluid	*Injection Temperature, °C*	*Injection Pressure, bar*	*ASPEN Plus® Properties Model Used*
H_2O/CH_3O	15	1	Schwartzentruber-Renon (SR)–POLAR
NH_3	20	10	Peng-Robinson
H_2O	15	1	STEAMNBS
CO_2[a]	27	136	Peng-Robinson Boston Mathias (PR-BM)

[a]Assumed available from a pipeline used for transporting CO_2 at these conditions for sequestration.

TABLE 2
Characteristics of the EGS Considered in the Analysis

Parameter	*Value*	*Units*
EGS type	Dry hole (no source fluids)	
Reservoir depth	3,000–15,000	m
Reservoir temperature	= 15 + (0.053*depth[m])	°C
Injection pipe inner diameter	0.25	m
Number of injection/production pipes	1/(1 or 4)	
Production pipe inner diameter[a]	0.25	m
Pipe roughness	0.004971	cm
(Permeability * thickness) of the EGS (k * h)	3.05 and 100	darcy.m
Distance between injection and production pipes	610	m
Well bore diameter	0.73	m
Temperature gradient along the injection pipe	0.015	°C/m

[a]Adiabatic flow was assumed in the production pipe.

analyzing the identical system. The lack of experimental data for some of these materials at such high P limits the ability to check the modeling results. Therefore, the quantitative results should be considered preliminary at this stage. Radial Darcy flow was reached in the EGS, and steady state and thermal and chemical equilibrium are assumed to have been reached in the EGS.

4. RESULTS

4.1. Flow Rates

Knowledge of the EGS structure is necessary in order to conduct rigorous heat, mass, and momentum transport analysis as the fluids undergo phase change and chemical reaction. The P drop in the EGS reservoir was calculated by assuming that the temperature of the working fluid in the EGS stays at the same temperature it attains at the bottom of the injection pipe until it reaches just before the end of the EGS reservoir (inlet of the production pipe) and then it attains thermal equilibrium with the EGS where the reaction takes place. The drop in the EGS reservoir is small (<10%) compared to the pressure drop in the production pipe. Therefore, the impact of the assumption on the overall P drop calculations is small. The flow rates that resulted in optimum power generation are presented in Figure 1. CO_2 and NH_3 have higher flow rates at shallower depths, but water has higher flow rates in deeper wells.

4.2. Specific Enthalpy and Specific Exergy Gains

The specific enthalpy and specific exergy gains are shown in Figures 2 and 3, respectively. CECs capture more heat per unit mass when the EGS T is high enough for the chemical reaction to occur. The enthalpy gain by a given fluid at a given depth is essentially constant because it was assumed that all fluids reach thermal equilibrium with the EGS. The exergy gain depends on the P drops, which depend on the flow rate. At a depth of 3,000 m (T = 175°C), ammonia captures the most exergy, followed by water and then by methanol/water. In deeper reservoirs, ammonia and methanol/water capture the most exergy.

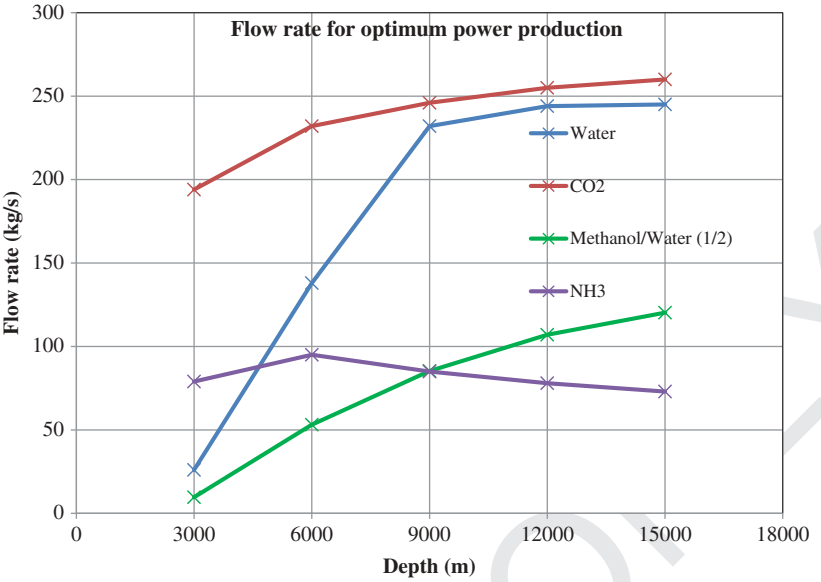

FIGURE 1 Flow rates of different fluids that resulted in optimum power generation using EGS heat. (1/2 represents the mole ratio of water to methanol.)

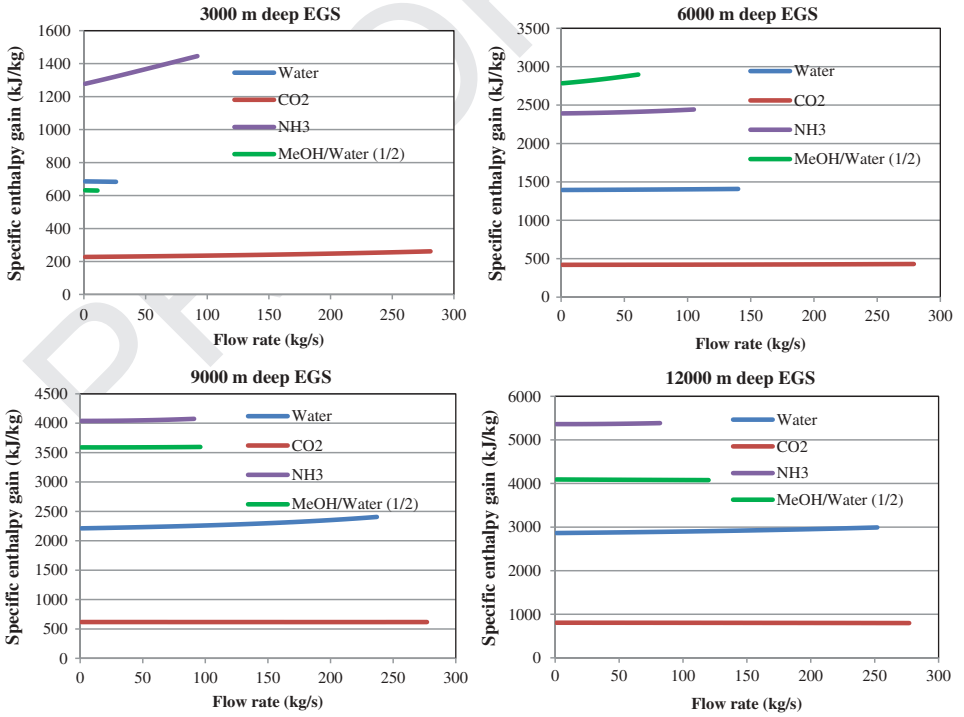

FIGURE 2 Specific enthalpy gain (kJ/kg) by the fluids at different flow rates and EGS depths. The X axis is the flow rate in kg/sec and the Y axis the specific enthalpy gain (kJ/kg).

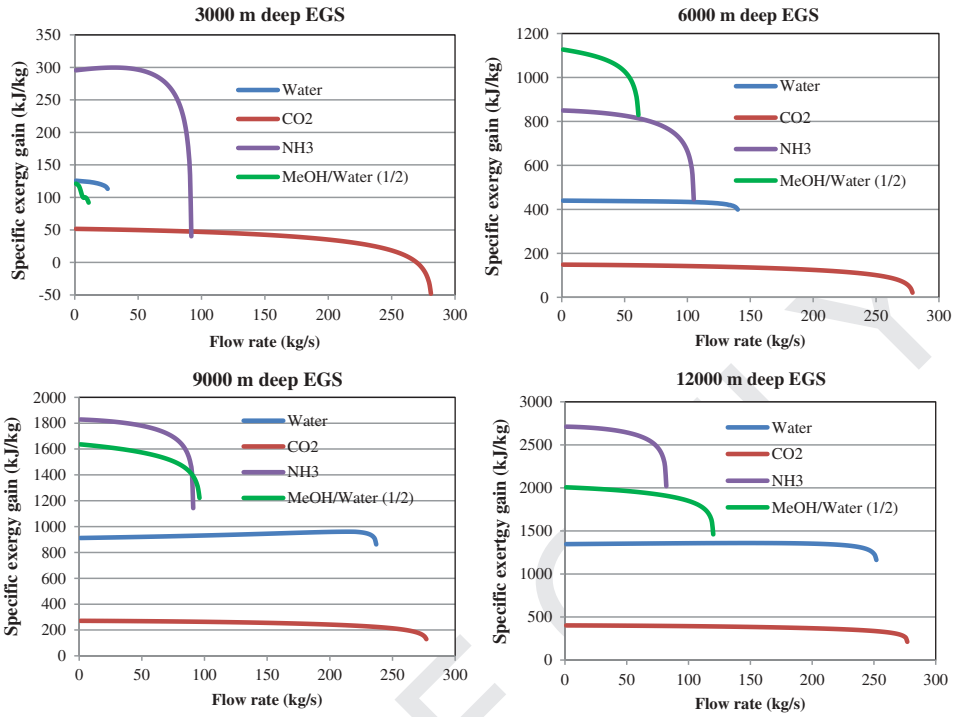

FIGURE 3 Specific exergy gain (kJ/kg) by the fluids at different flow rates and EGS depths. The X axis is the flow rate in kg/sec and the Y axis the specific exergy gain (kJ/kg).

4.3. Rates of Enthalpy and Exergy Gains

Because of differences in mass flow rates, the rates of enthalpy and exergy gains do not necessarily follow the same order as their specific counterparts. Figures 4 and 5 present the rates of enthalpy and exergy gains. The results show that at 3,000 and 6,000 m, ammonia leads in terms of enthalpy and exergy gains. At 6,000 m, the T is high enough to cause methanol reforming, and so its enthalpy gain increases sharply, but it lags behind water because water can attain a higher flow rate. At >9,000 m, water has the highest rate of enthalpy gain. At a depth of 3,000 m, ammonia has the highest rate of exergy gain, followed by CO_2. At 6,000 m, ammonia still has the highest rate of exergy gain, followed by water, and methanol/water is a close third. At depths of >9,000 m ($T \geq 500°C$), water has the highest rate of exergy gain.

4.4. Power Generation Potential by the Different Fluids

A key criterion is the potential power that the fluids can generate. Figure 6 illustrates the power the fluids can generate at the EGS initial T and after its T drops by 25%. Ammonia produces the most power at 3,000 and 6,000 m. At 9,000 and 12,000 m, where the T is higher so that near complete reforming of the methanol occurs, the CH_3OH/H_2O produces the most power. In yet deeper wells, water produces more power because water has the highest specific heat. In shallow wells, the reduction in power output is the highest for the CECs because no energy is captured as chemical energy at the lower T. However, in deeper wells, the drop is least for the CECs.

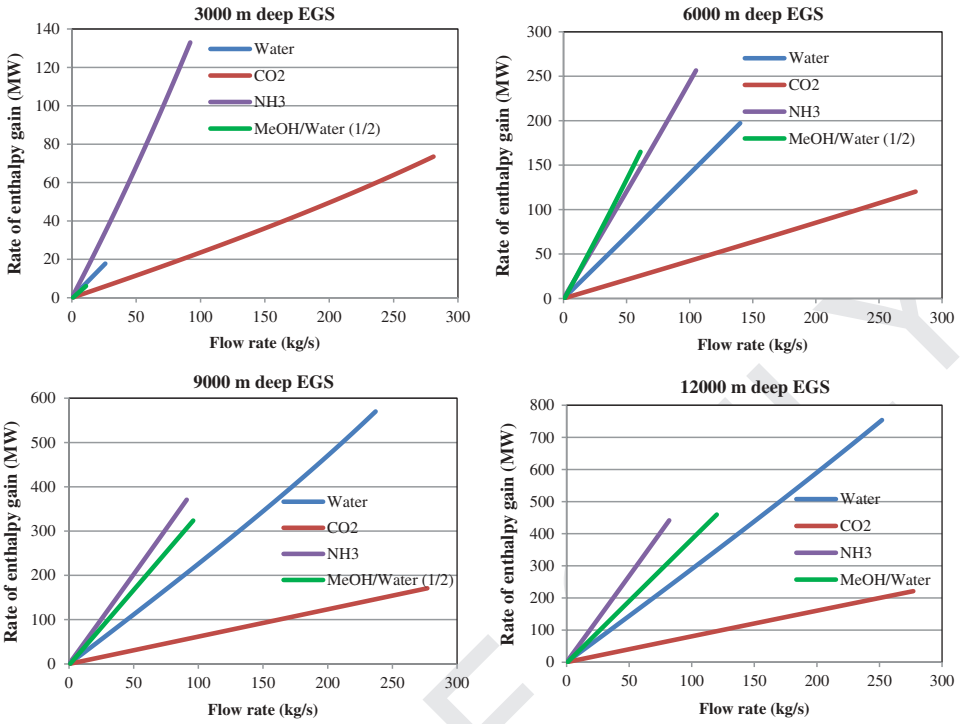

FIGURE 4 Rate of enthalpy gain (MW) by the fluids at different flow rates and EGS depths. The X axis is the flow rate in kg/sec and the Y axis the rate of enthalpy gain (MW).

5. SYSTEM DESIGNS FOR IMPLEMENTING CEC FLUIDS

Special designs are necessary to ensure that these fluids are not lost in the reservoir and do not contaminate surface or underground environments. These processes can be carried out by using a closed double-pipe system. The annulus can be fitted with catalysts in the reaction zone and/or with membranes to separate one of the products (H_2) and send it directly to the inner pipe to increase the reaction rate. The inner pipe will be insulated. The reactants (liquid NH_3 or liquid CH_3OH/H_2O) can be injected into the annulus. The products and any unreacted materials rise in the inner pipe and are cooled above ground with heat recovery for power generation. The regenerated materials-will be condensed and re-injected into the EGS. Pressurized water is injected through a separate single pipe to fill the fractures and keep them open. The water facilitates the conduction of the heat from the rocks to the reaction zone. The chemicals remain in the closed system and do not come in direct contact with the rocks or with the water.

6. COMMERCIALIZATION POTENTIAL OF THE TECHNOLOGY

This work has demonstrated the potential for increasing the power generated using EGS heat by using CEC fluids. Experimental work is needed to validate the results and to develop a design for testing. CECs offer the opportunity to enhance power production but add a level of risk. Implementation of CECs with surface heat sources (e.g., concentrated solar power) could be commercialized without the risk associated with deep-hole EGS systems.

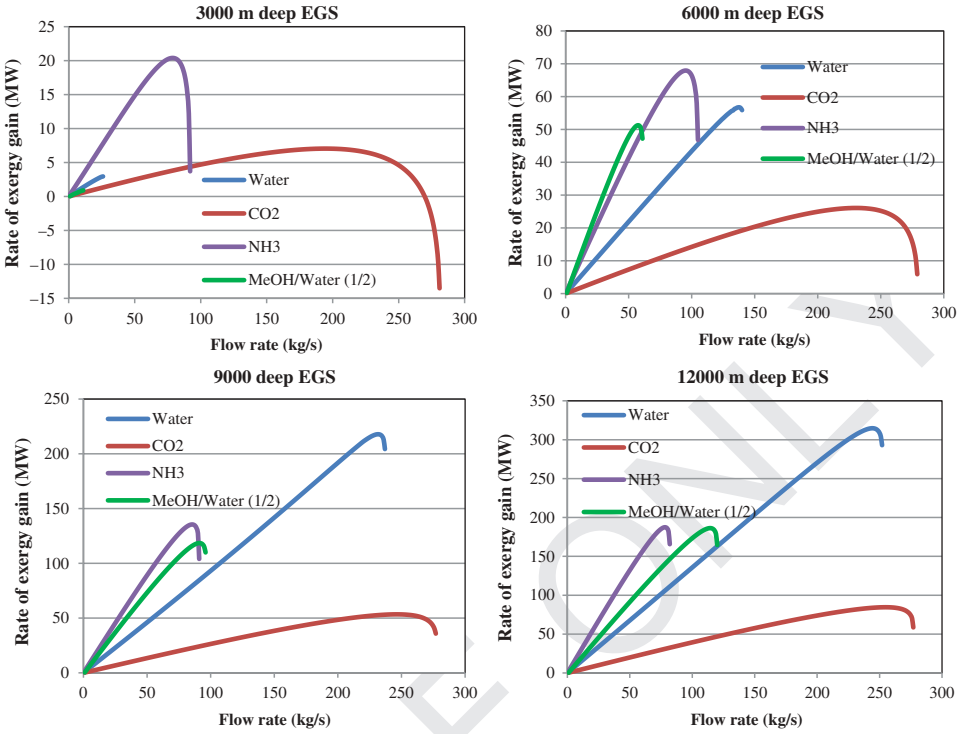

FIGURE 5 Rate of exergy gain (MW) by the fluids at different flow rates and EGS depths. The X axis is the flow rate in kg/sec and the Y axis the rate of exergy gain (MW).

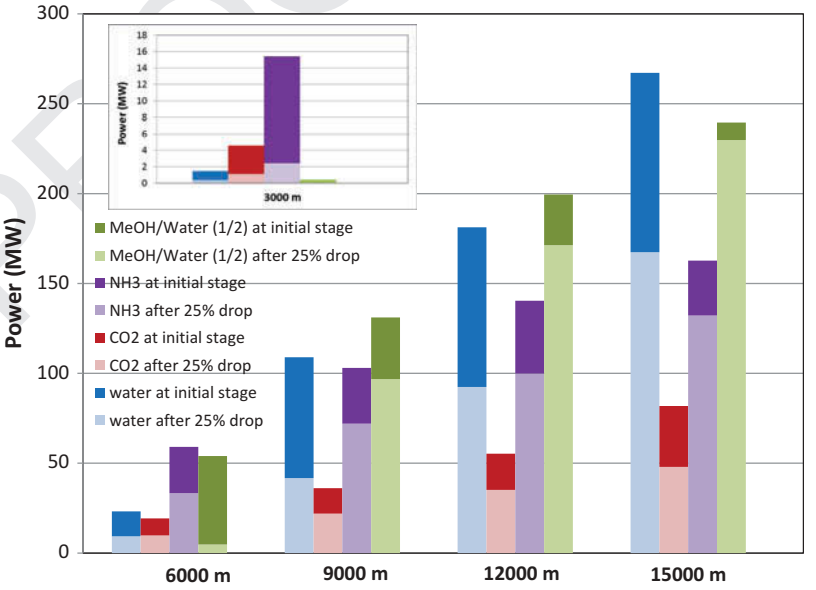

FIGURE 6 Optimum power generation (MW) at the initial state and after 25% drop in the temperature the EGS for different EGS depths.

7. CONCLUSIONS

The results lead to the following:

a. The selection criterion for a working fluid should include the rate at which the working fluid delivers exergy and produces power, not the exit T or enthalpy gain (of course, other considerations—including cost, safety, environmental impact—are important factors).
b. Working fluids that result in maximum heat capture may not necessarily result in maximum power production.
c. No one working fluid is best for all EGS projects.
d. Analysis should be done by using actual EGS parameters when selecting a fluid.

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