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CO_2 EGS AND THE UTILIZATION OF HIGHLY PRESSURIZED CO_2 FOR PURPOSES OTHER THAN POWER GENERATION

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ABSTRACT

CO_2-EGS for power generation has been extensively modeled over the last few years, most notably by Karsten Preuss et al at Lawrence Berkeley National Laboratory. CO_2 has several drawbacks and advantages compared to water as a geothermal fluid. Overall, however, it is anticipated to be a better geothermal fluid than water with a heat extraction rate as much as 50% greater than that of water. Despite its operational advantages as a geothermal fluid, there are potential problems with the use of CO_2 in stand-alone power generation projects. In particular, the profitability of projects is sensitive to the cost of CO_2, the cost of compressing and transporting it, the loss rate (unknown) during rapid cycling of CO_2 through the system, and the conversion efficiency of heat to power. In the absence of a significant carbon tax, power projects may be restricted to areas with very low-cost CO_2 (e.g., natural deposits, natural gas processing plants) associated with geothermal resources instead of more costly CO_2 from power plants.

The highly pressurized CO_2 derived from CO_2-EGS offers one distinct advantage relative to hot water from water-based geothermal projects: it has great utility as an industrial chemical for a wide range of projects other than power generation. Under certain circumstances, the pressurized CO_2 in such projects may have significantly greater economic utility than for power generation.

One project utilizing CO_2 for a purpose other than power generation may be possible at the St. Johns Dome on the border between Arizona and New Mexico. The energy company that owns 90% of the CO_2 leases at the dome is building a pipeline to transport 10 million tons per year of CO_2 to the Permian Basin for enhanced oil recovery. Using CO_2-EGS to assist in pressurizing the CO_2 to the pipeline standard may cost significantly less than using conventional technology. Moreover, it would be possible to use the same geothermal resource to both produce power and compress CO_2.

Several other uses of hot pressurized CO_2 may be feasible and profitable. For example: 1) Supercritical fluid extraction, including hydrocarbon extraction from oil sands and oil shales; 2) desalination of seawater using chemical partitioning; 3) recovery of rare earth elements from ore or scrap.

Thus CO_2-EGS offers the potential to use geothermal energy in a wide range of large-scale, profitable industrial processes in addition to power generation.

INTRODUCTION

This paper will start with a quick review of why CO_2-based geothermal energy, more particularly, CO_2-based EGS, has drawn a fair amount of attention. Conventional geothermal and conventional Enhanced Geothermal Systems (EGS) have always been about water. The Geysers, the US' best-known hydro-thermal field, for example, uses naturally-heated water for its power generation facilities. Heat gradients in that field range up to over 250°C/km of depth. (Thomas 1986) EGS is sometimes known by its alternative name, "Hot Dry Rocks;" those rocks presumably need only water to turn into conventional geothermal systems.

ADVANTAGES AND DISADVANTAGES OF CO_2 IN EGS

In geothermal applications, CO_2 will essentially always be in the supercritical state. The critical point of CO_2 is only 31.1°C (88°F) and 73.77 atm (1070 psi), so the supercritical state is easily achievable. By comparison, water's critical temperature and pressure are 369.1°C and 218.3 atm, conditions much harder to attain. Supercritical fluids have density much like that of liquids, but many other properties like those of gases. However, for CO_2, the solubility properties

change immensely with the change in state, in that supercritical CO_2 tends to behave like an organic solvent, much like pentane or hexane. And of course, CO_2 has quite different chemical reactivity than water.

When considering geothermal applications, the heat capacity of the fluid is of primary concern. Figure 1 compares the heat capacities of water and CO_2 at 150°C.

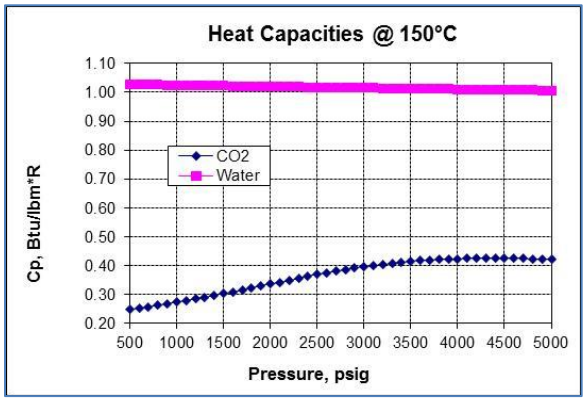

Figure 1: Heat capacities for water and CO_2

Clearly, water has greater heat capacity by factors of 2½ to 5, but other properties of CO_2 give it an advantage in geothermal energy production. To begin with, CO_2 is in general considerably more mobile in formations than water. Consider Figure 2, which plots the relative mobilities (density divided by kinematic viscosity) for water and CO_2 at a range of temperatures and pressures. For low to moderate temperatures, CO_2 is nearly twice as mobile as water.

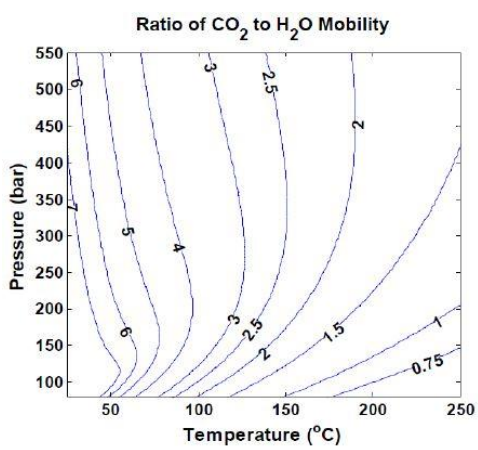

Figure 2: Ratios of CO_2 to water mobility

Moreover, since CO_2 in geothermal applications will be a supercritical fluid – and supercritical fluids do not exhibit surface tension – CO_2 will flow much more easily through formations than water. In fact, Pruess' calculations suggest that overall, CO_2 will be 50% more efficient at removing heat from rock than water!

CO_2 has two other significant advantages over water. First, CO_2 is not generally as reactive to rock formations as water. Secondly, the changes in density with temperature and pressure of supercritical CO_2 suggest that the use of pumps for moving CO_2 could be partially or completely eliminated by formation of a thermosiphon. Figure 3 shows the ratios of supercritical CO_2 density at several different temperatures over some pressure ranges typical of geothermal projects.

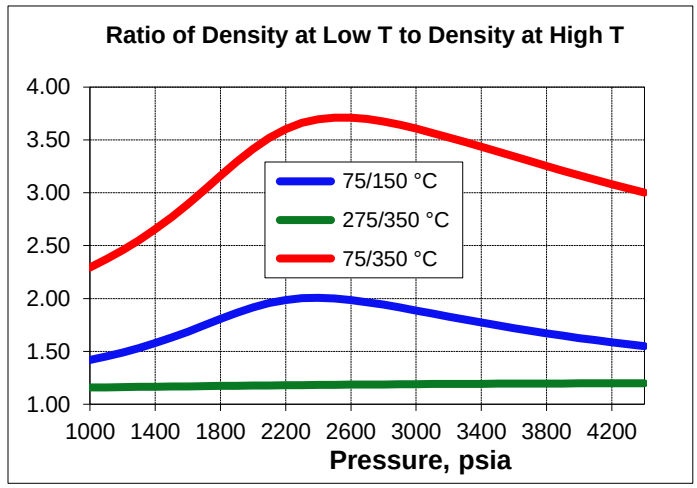

Figure 3: Density ratios of hot CO_2/cool CO_2

Note that CO_2 at 2600 psi is nearly four times as dense at 75°C as at 350°C. At 2400 psi, it is twice as dense at 75°C as at 150°C. Exploitation of this difference in density by setting up a siphon, called a thermosiphon, may allow supercritical CO_2 to flow through the entire system without any external pumping. Though this sounds unlikely, an analogous density siphon has been used in the HF alkylation process in petroleum refineries for more than sixty years on a routine basis.

THE PROBLEMS OF POWER PRODUCTION

Despite those operational advantages of CO_2 in geothermal heat recovery, there are also some potential problems connected with CO_2-EGS for power production. These can be best summarized as 1) the cost of the CO_2 itself, 2) the cost of CO_2 pressurization and transportation, 3) inefficiencies in converting heat to power, and, perhaps most importantly, 4) loss rates into the formation during CO_2 cycling.

The cost per ton of water in the Western US is on the order of \$0.10 to \$0.20. This is one to three orders of

magnitude less than the cost per ton of CO_2, which can rise to $100/ton or more for CO_2 captured from a coal-fired power plant, pressurized to pipeline standards and transported via pipeline to a point of use. Thus, the cost to fill a CO_2-EGS project at the start of operations and to replenish losses to the system during operation is a major expense.

Pressurizing and transporting CO_2 to the geothermal power production site are critical factors in profitability, especially because geothermal heat is not available everywhere. In an ideal situation (such as at the St. Johns dome where GreenFire's initial project is located) or at the numerous sites where fossil-fuel fired power plants are located at or near geothermal heat, transportation costs are minimal. It is unlikely that, at least initially, pipelines will be built only to supply CO_2-EGS power plants.

Compressing CO_2 from the gaseous state to pipeline-pressure (~2200 psi) liquid or supercritical fluid is expensive. The best way accomplish the pressurization is to use a mechanical compressor to raise the pressure from atmospheric (0.1 MPa) through the gas/liquid phase change to near the critical point (7.38 MP), then use a pump to raise the pressure further. (McCollum 2006) Because the compression ratio is far greater for the compressor (73.8) than the pump (2-5), the cost of compression represents 95% of the total power demand for compression. The relative power requirements for the compressor and the pump are shown in Figure 4. Under these conditions, the cost of the power for compression is on the order of $10 per ton.

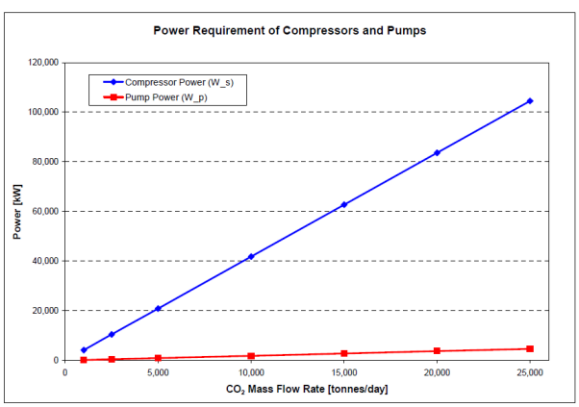

Figure 4: Power Requirements for Compression

Some of the cost of compression can be avoided if the CO_2 comes from natural deposits that produce CO_2 at high pressure, like the Jackson Dome in Mississippi, where production pressures can reach 1500 psi or greater. Similarly, though it represents only a minor part of the entire cost of compression, liquid CO_2 can be pressurized by the simple expedient of injection into geothermally-heated formations, where the CO_2 is pressurized by the heat and can then be re-produced at the higher pressure.

Naturally, there are important efficiency losses in the process of converting geothermal heat to power. Binary power plants have an efficiency of 10-13% (DiPippo 2007), lower than the typical flash steam water-based geothermal plants. New turbine technology developed at Sandia (Energy Daily 2011) may raise CO_2-EGS efficiency to 25% by using CO_2 directly to turn the turbine that runs the generators.

The most important parameter in estimating CO_2 cost during operation is the loss rate per cycle. By analogy with water-based EGS, CO_2 loss has been estimated at around 5% of the flow rate. CO_2 loss occurs in this scenario mostly through seams and permeable areas of the formation. (Pruess and Azaroual, 2006, and Pruess, 2007) Assuming 50 complete cycles per year per megawatt, this is 250% of the system capacity. Again, assuming 5000 tons of CO_2 per megawatt capacity, 12,500 tons of CO_2 per year per megawatt will be required. The cost of this CO_2 (plus the costs of compression and transportation) is high enough to reduce or completely eliminate any profitability for the project as a whole.

On the other hand, since GreenFire envisions creation of the EGS reservoir in deep impermeable geothermally-heated rock, the loss rate is likely to be far less than 5%. Two recent papers (Dunn 2010, Mobley 2011) In such a reservoir, since CO_2 escape through seams is unlikely, only four mechanisms to trap CO_2 in the formation (and thus remove it from circulation) are possible: hydrodynamic trapping in the pores of the rock; solubility trapping in water or other liquids in the reservoir; adsorption trapping on organic matter in the formation; and mineral trapping from reactions to form carbonates. (Nelson et al 2005) In a deep, impermeable, artificially-created EGS reservoir, only mineral trapping is possible, resulting in extremely low loss rates. (Dunn 2010) In one scenario, CO_2 consumption was only 0.1% of flow. In that case, power production using CO_2-EGS could be quite profitable; not only would not pipeline to supply CO_2 be required, but no external compression would be necessary, and pumping would be almost eliminated due to the thermosiphon effect. One paper (Mobley 2011) estimates that 75% of the power output of such a system would derive from geothermal energy.

NON-POWER PRODUCTION USES OF CO_2

Combined CO_2-EGS and CO_2 Sequestration

Though not strictly a "non-power" application of CO_2-EGS, in some locations it should be possible to use power generated by CO_2-EGS to partially offset the power demands of CO_2 capture in a fossil fuel-fired power plant. (e.g., Frank, et al, 2012) In this case, loss of CO_2 into the formation would be encouraged as a way to sequester the plant-produced CO_2. It has been estimated that a CO_2-EGS plant using a coal-fired plant's CO_2 emissions could supply enough power to almost exactly offset the energy required to remove that CO_2 from the plant's stack gas. Unfortunately, this application is somewhat limited because of the distributed nature of existing power plants and the requirement for proximity to geothermal resources.

Transporting CO2 via Pipelines

The US currently has a CO_2-pipeline network approximately 6,300 km long. The primary use is to transport CO_2 from sources, most of which are natural deposits, to oil fields for use in enhanced oil recovery. The first large-scale project to transport CO_2 via pipeline was the 30-inch Cortez Pipeline, which began operations in 1983 and supplies 30 MM tons of CO_2 annually. It extends approximately 800 km from the McElmo Dome in SW Colorado to Denver City, Texas, the pipeline hub for the oil fields of West Texas, where CO_2 is used for enhanced oil recovery. A second intended use for CO_2 pipelines is for carbon sequestration. To date, however, little of the intended pipeline network for sequestration has been built.

Figure x, US CO_2 Pipelines

CO_2 pipelines are driven by pressure gradients. Liquid or supercritical CO_2 at high pressure is injected into the pipeline. The injection pressure is typically on the order of 15.1 MPa, but may be as high as 19.3 MPa, as on the Weyburn Midale Project Pipeline. Recompression stations are located at intervals along pipelines with a spacing that averages about 150 km. Power demands for such stations are minimal.

The cost of compression is a significant driver in the economics of CO_2 pipelines. As noted earlier, these costs may represent as much as 40% of the total cost of the power demand for a carbon capture and sequestration project.

Again as noted earlier, when CO_2 is sourced from natural deposits, the initial pressure can range from near ambient, such as at the Bravo Dome, to in excess of the critical point, as at the Jackson Dome. If the initial pressure in these natural deposits is even 2 MPa, this can cut the cost of compression in half, as compared to a project in which the initial pressure is atmospheric.

The economics of CO_2-EGS can be particularly favorable for use with CO_2 pipelines. The most favorable scenario assumes that the company transporting the CO_2 provides the CO_2-EGS project with the necessary CO_2 feedstock at no cost and at a pressure sufficient for injection into the geothermal project, and that the compressor station and the CO_2-EGS project are co-located. The St. Johns Dome represents a variant on this. The most favorable geothermal conditions are several miles remote from the projected location of the compressor station. Thus, it may be most economical to install wells at the site of the CO_2-EGS project to supply the necessary CO_2 feedstock instead of piping it from the area of the compressor station. This local CO_2 supply will then need to be compressed to injection pressure at the site prior to injection into the geothermal reservoir. Finally, a transmission line will need to be installed connecting the generating station with the compressor station.

The economics of such a project are favorable for several reasons:

1. To the degree that the CO_2-EGS project is provided with pressurized CO_2 at no cost, it greatly reduces startup expenses and, to a lesser degree, ongoing operational expenses.
2. The levelized cost of energy from a CO_2-EGS project with inexpensive CO_2 and a loss rate of 1% of fluid injected can be fully competitive with that of power from a fossil-fuel-powered generating station.
3. Assuming that the CO_2-EGS project is dedicated to supplying power for the compressor station, it is not required to sell the power through the local utility. Under those conditions, it can provide power at a price higher than the local wholesale rate, but still lower than the local retail rate.

4. Additional economic advantages may accrue in jurisdictions with a carbon tax.

Supercritical Extraction Processes

Extraction processes using supercritical CO_2 are hardly new. However, the ability of pressurized CO_2 coupled with geothermal heat to furnish large volumes of hot supercritical CO_2 (HSC-CO_2) opens up a number of interesting and potentially profitable things besides power generation. The heating aspect is important because extraction rates normally increase with temperature, increasing efficiency.

For all these processes, it is necessary, of course, to be located near a geothermal heat source.

Extraction of hydrocarbons from tar sands, oil sands, and oil shales

Steam extraction of tar sands in northern Alberta has recently received extremely negative comments because of excessive water use and pollution of that water and the mining areas. Similarly, proposals to produce shale oil in Colorado and Utah have met strong opposition because of the presumption of high water usage and fears of pollution in environmentally sensitive areas of those states.

A recent study on extracting Alberta tar sands with SC CO_2 found extraction rates as high as 65% and low water utilization. (Hartzell, et al, 2012)

Though there is no geothermal resource close enough to the Athabasca tar sands area to permit geothermal heating, certain of the tar sand areas in Utah are relatively close to both geothermal heat and natural CO_2 deposits.

HSC-CO_2 extraction is not a particularly new idea. (see, for example, Deo, et al, 1991 and Das, 1989) However, the proximity of the Utah oil shale area to geothermal heat and natural CO_2 suggest that it is an idea whose time may have come.

Extractions of rare-earth compounds from ore and recycled materials

The idea that rare-earth oxides can be solubilized in supercritical CO_2, usually with some adjuvant like tri-n-butyl phosphate, has given rise to a very large literature. (see, for example, Erkey 2011) Because China possesses and produces 95-97% of the world's supply of rare earths, there has been increasing interest in this way to recover rare earths from other materials, even leading occasionally to articles in the popular media. For example, one method (Science Daily, 2009) utilizes TiO_2 waste as the raw material. Another (Gillentine, 2012) would use fly ash from power plants.

Of course, rare earths can also be extracted from ores as easily as from fly ash or discarded fluorescent lights. The US has only one rare earth mine, the Mountain Pass Mine in California, which has recently reopened.

Because of concerns over water pollution and low-level radioactive waste, HSC-CO_2 would be an ideal extractant for rare earth ore. Happily, the Mountain Pass Mine is near a geothermal reservoir, though not near any natural CO_2 deposits.

Extractions of radiochemicals from nuclear waste

Because of the need to separate radioactive heavy metals from stored waste streams generated by nuclear reactors, there have been numerous studies on how exactly to do that. HSC-CO_2 extraction is a method that has received considerable attention. (see, for example, Shadrin, et al, 2004) It may even be possible to remove radiochemicals from contaminated soil. (Fox, et al, 2003)

Use as a chemical solvent and/or feedstock

Over the years, a tremendous amount of research has gone into attempting to manufacture commodity industrial chemicals starting from CO_2. Though CO_2 is a ubiquitous and inexpensive feedstock, in general this work has not led to economic technologies. The fundamental problem is CO_2's thermodynamic stability: significant energy is required to make it reactive.

Combining CO_2-EGS with natural deposits of inexpensive CO_2 may offer a way to begin developing competitive technologies that can be competitive.

An example of the potential of this approach can be demonstrated with the manufacture of formic acid by hydrogenation of CO_2.

Formic acid is used in a range of industries, including leather products, as a substitute for antibiotics in agricultural feed and rubber production, as well as a mild substitute for inorganic acids in metal cleaning. Worldwide production is on the order of 700,000 tonnes/year.

BASF is building the US' first formic acid plant, with a capacity of 50,000 tonnes/year. The output will be mostly for new uses in the shale gas industry and cleaning processes.

Conventional technology typically involves hydrogenation of methanol produced by steam reforming of natural gas. However, formic acid can

also be produced by direct hydrogenation of CO_2 using an organometallic catalyst and with supercritical CO_2 as the solvent.

Production of formic acid at the St.Johns Dome offers several advantages, since the CO_2 is produced on site, is easily heated and is partially pressurized when produced.

Numerous other chemicals' production could be facilitated by easy access to HSC-CO_2.

CONCLUSIONS

Heated supercritical CO_2 HSC-CO_2 can be used as a substitute for water in geothermal power generation. However, HSC-CO_2 also presents opportunities for use in a variety of other profitable applications, including CO_2 pipelines, environmentally acceptable extraction of hydrocarbons from tar sands and oil shales, extraction of rare earths from ores and recycled materials, separation of radioactive metals from nuclear waste, and a variety of chemical synthesis and solvent uses. Though not available everywhere because both geothermal heat and a source of CO_2 are required, HSC-CO_2 may well provide a way for geothermal heat to make its way into the industrial mainstream.

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