

ECONOMIC BENEFITS OF MINERAL EXTRACTION FROM GEOTHERMAL BRINES

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Abstract

The economic benefits of the co-production of minerals from geothermal brines far exceeds the potential revenue stream from the sale of marketable by-products such as silica, zinc, manganese, lithium and a number of rare earths. Extraction of silica can avoid scaling problems often associated with many geothermal power projects and may allow for additional power production through the use of bottoming cycles or the use of the brine in direct use applications now impractical due to scaling problems. An additional benefit of silica removal is the opportunity to use the geothermal brine as a source of water for enhanced evaporative cooling – a technique that can significantly improve the summer power output from binary power plants employing air cooling for condensing the working fluid.

Introduction

Geothermal fluids, heated as they percolate through hot rock bodies, interact with the host rock becoming increasingly saturated with various minerals. The chemical composition of the resulting fluids is determined by their origin, magmatic, meteoric etc., the lithology of the rocks with which the fluids have interacted, the temperature at which that interaction takes place, the chemistry of the fluids (e.g. pH) and impacts of such things as boiling. As a general rule the higher the temperature, the greater the chemical content of the brine, everything else being equal (Entingh and Vimmerstedt, 2005). Resulting geothermal fluids may have significantly different compositions in both pH and salinity and in fact some low-temperature geothermal fluids may have salinities below 1,000 parts per million (ppm) TDS, while some high temperature brines exceed 300,000 ppm.

Table 1 provides an example of fluid chemistries at a number of operating geothermal fields.

Table 1. Examples of Mineral Composition at Selected Geothermal Fields

Item	Salton Sea	Coso	Dixie Valley	Cerro Prieto	Wairakei	Milos	Mammoh Lakes
Temp., °C	296	274	246	340	260	300+	165
Silica, mg/kg	>461	>711	>599	>864	>670	>950	ca 250
Boron, mg/kg	257	119	9.9	9.4	<0.01	125	NA
Lithium, mg/kg	194-230	45	2-4	27	13.2	81	NA
Zinc, mg/kg	438	0.03	NA	NA	NA	NA	NA

Bourcier et al, 2003 and Gallup, 1998

The presence of high concentrations of minerals in most geothermal brines has often been considered a major nuisance creating major engineering challenges to deal with severe corrosion and/or scaling problems, which often results when these fluids are brought to the surface for purposes of power generation or direct-use applications. Some early power plants such as the one at Brawly, California, had redundant piping of all above-ground systems so that one piping system could be operated while the other one was down for the removal of scale. Such a configuration obviously significantly increases the capital cost of the facility as well as operation and maintenance costs.

Scale is however not only a problem within the plant itself, but also in injection wells where precipitated minerals can quickly lead to increased injection pressures and eventually the need to work over the wells or drill additional wells.

However, as is often the case, what is a problem for one may be a treasure for another.

Mining Geothermal Fluids

Many of the chemical constituents in geothermal fluids are a potential source of valuable minerals and metals. Recovery of minerals and metals from geothermal fluids can be viewed as "solution mining by nature" followed by application of established or new hydro-metallurgical techniques for isolation and purification (Bourcier et al., 2003). The first application of such "mining" techniques took place at Larderello, Italy, as early as the turn of the last century where boric acid was extracted from geothermal steam. Some geothermal fields such as those found in the Salton Sea, Brawly and Niland in the United States, the Milos field in Greece, the Assal field in Djibouti and the Cheleken geothermal field in Russia, to mention only a few, contain significantly rich mineral brines to make them potentially economically viable sources of some minerals. For example, a 50 MW_e geothermal power plant could have as much as 35,000 m³ of brine pass through the facility daily. At a concentration of only 1 mg/kg approximately 30 kg of metal passes through the facility each day (Gallup, 1998) making the amount of recoverable minerals large despite relatively low concentrations.

Minerals of primary interest include silica, zinc, lithium, manganese and a number of rare earths. Some brines may even contain significantly high concentrations of precious metals such as silver, gold, palladium and platinum to make recovery potentially attractive.

Silica Recovery

Silica is one of the most common and ubiquitous components of geothermal fluids. It is also one of the biggest problems and potentially one of the most valuable minerals. Most hydrothermal systems equilibrate with quartz (SiO_2) causing the fluid to have silica concentrations that reflect the temperature of the reservoir. The hotter the reservoir, in general, the higher the silica concentration of the fluid. During energy production (power generation and/or direct-use applications) the geothermal fluid cools as heat is extracted. Water may also be extracted as steam as for example in a flash power cycle and pH may change as well (Bourcier et al., 2003). All these processes cause the silica to become increasingly supersaturated, eventually precipitating and forming scale on various plant components or in injection wells. Because the degree of precipitation increases with decreasing temperature of the brine, it often is the limiting factor in determining how much energy can actually be extracted. For example, in the Wairakei geothermal field in New Zealand, 130° Celsius is the lower limit for energy extraction because silica scaling becomes too difficult to control (Brown and Bacon, 2000). If the temperature of the re-injected fluids at Wairakei could be reduced from 130°C to 90°C, over 1 MW_e could be generated from approximately every 60 liters per second of brine flow.

Silica scale also interferes with the extraction of other minerals such as zinc, manganese, lithium, etc., and must be dealt with if such mineral extraction is to be technically feasible. Although dealing with silica scale is a major challenge that must be addressed, when dealt with successfully, it can allow for additional energy extraction while at the same time minimizing operational and maintenance costs associated with scaling in surface facilities and injection wells and facilitating the co-production of marketable minerals.

Thus the key to both additional power generation and mineral co-production is to minimize silica scaling. Silica removal can be forced by precipitating it as a high surface area porous material with properties similar to those of commercially produced precipitated silica (Bourcier et al., 2003).

There is an increasing worldwide interest in silica production from geothermal brines to meet the demand for over 6 million pounds of commercial grade silica per day. The value and price for silica varies widely and is very dependent upon purity and physical properties. Silica is used in applications in rubber, plastics, paint, paper, ceramics, pharmaceuticals, pesticides, chemical and odor absorbents, and adhesive industries.

Some specific uses include (USGS, 1999):

- Desiccants and anti-caking agents in human and animal food;
- Abrasives in sandpaper and for use in silicon wafer-polishing;
- Filler in plastics, paper, paint and rubber tires;
- Fiber optics and catalyst manufacture; and,
- Feed stock for making semiconductor silicon, fine chemicals, and chromatographic silica.

The current market is about 190,000 tons per year for precipitated silica and 68,000 ton/yr for colloidal silica with a 4 percent annual rate of increase in demand (Bourcier et al., 2003).

Price for silica varies widely and is very dependent upon the value to the particular application, while silica used in the production of rubber for tires, dental products and pesticides may bring

\$1/kg, silica used in paint can approach \$2 to \$4/kg (Smart 1998). Chromatographic grade silica may justify a price as high as \$6/kg to as high as \$7/gram when used in high-pressure liquid chromatographic applications (Entingh and Vimmerstedt, 2005).

The potential revenue stream, as calculated by Entingh and Vimmerstedt, 2005, based on a 50 MW_e power plant in the Salton Sea geothermal field could provide as much as \$10.2 million per year, while a similarly sized facility at the Coso, California, geothermal field could result in a revenue stream of up to \$12.9 million per year. These figures are based on a 60 percent silica recovery rate and a selling price of \$2,200 per metric ton and a plant capacity factor of 95 percent.

Other Metals

Once the silica has been removed to the point where precipitation no longer is a problem at the temperature required, other metals can begin to be removed from the brine. To date interest has been concentrated in the recovery of zinc, manganese and lithium. However, both cesium and rubidium are also often enriched in geothermal brines. Both are used in applications in thermionics, as oxygen getters in vacuum tubes, and alloys used in photocells. Both sell for a few dollars per gram and the total U. S. market is estimated at thousands of kilograms per year (Bourcier et al., 2003).

The current market for lithium is estimated at approximately \$350 million per year for use in the production of ceramics, glass, and aluminum and in rechargeable lithium batteries. Total U. S. consumption of lithium compounds is approximately 2,800 metric tons per year while the potential production of lithium from a single 50 MW_e geothermal plant in the Salton Sea geothermal area could potentially produce in excess of 3,400 metric tons per year thus flooding the United States and world markets and almost certainly driving the market price for lithium down.

Manganese is another element highly enriched in Salton Sea geothermal brines. One of the highest value uses of manganese is the production of electrolytic manganese dioxide (EMD) for use in dry cell batteries, and it is this market that would likely be targeted by production from geothermal brine (Entingh and Vimmerstedt, 2005).

Based on the assumption that a successful recovery method can be developed, Entingh and Vimmerstedt, 2005, have estimated that the potential revenues from EMD production based on a 50 MW_e plant at the Salton Sea, operating at 95 percent capacity, could equal \$48 million per year. Unfortunately as with lithium, manganese (EMD) production from the existing 290 MW_e at the Salton Sea could flood the United States and world markets driving down prices and minimizing economic viability.

Zinc is another metal found in highly concentrated amounts in Salton Sea brines. In the late 1990s, Cal Energy entered into a contract for the construction of a zinc recovery facility that was designed to produce 30,000 metric tons of 99.99 percent pure zinc per year to be sold to Cominco, Ltd. for a value of some \$40 million per year. The zinc plant went on line in 2002 and at that time Cal Energy anticipated that the 177 million dollar facility would generate as much revenue as they were then recovering from energy sales.

Unfortunately by mid 2003, it became common knowledge that the Cal Energy zinc plant was experiencing operational difficulties and on September 10, 2004, the operating company decided to cease operation and liquidate the assets.

Other Economic Benefits

Although additional energy extraction and recovery and marketing of metals and other by-products of generation such as elemental sulfur, sulfuric acid and even carbon dioxide have been the focus of most research and analysis, recent work at the Mammoth Pacific power plant in Mammoth Lakes, California, points to another potential viable economic benefit from mineral extraction.

In the early 2000s, the operators of the Mammoth Pacific facility, an air-cooled 30 MW_e binary plant, began testing the use of enhanced evaporative cooling as a way to improve summer power output. As with most all binary plants, air cooling was the norm as the geothermal fluid was kept under pressure throughout the process, from production to injection, and no water was thus available for cooling. A stand alone 10 MW_e facility, part of the 30 MW_e complex, was initially retrofitted by enclosing the sides of the air cooling tower with a corrugated paper material, and subsequently modified, with a fiberglass fill through which water was percolated. The modifications resulted in dropping the dew point and significantly increasing power output. When the test was first initiated, Mammoth Pacific was able to purchase treated effluent from the city of Mammoth Lakes, but after one year of operation the city decided there were other more attractive uses for the treated effluent and the power plant was forced to turn to the use of untreated geothermal brine for cooling. According to Bob Sullivan (Personal Communication, 2005) loss of output at the 10 MW_e power plant, prior to the use of enhanced evaporative cooling, could easily exceed 20 percent or 2+ MW_e during periods of warm weather. Enhanced evaporative cooling resulted in recovery of as much as 40 percent of that loss with an average recovery of 20 percent or 400+ kW_e. Considering that enhanced evaporative cooling is employed approximately 50 percent of the time during the period from June to September, and to a lesser extent during the shoulder periods in the spring and fall, up to an additional 4.8 MW hours can be produced and sold per day. Using a conservative rate of 10 cents per kWh during peak demand periods, that amounts to \$480 per day in added revenue. The use of the untreated brine does, however, cause a certain amount of added operational and maintenance cost and since 2003 Mammoth Pacific has been testing reverse osmosis as a way to concentrate the silica that is available in the brine and make silica recovery economically viable. According to Bob Sullivan, the value of clean water is so great that if the silica recovered were equal to the cost of operation of the reverse osmosis facility it would be an economically viable operation because of the increase in power production.

Conclusion

Mineral Extraction can provide a number of economic benefits to geothermal energy extraction whether it is for power or direct use applications. The ability to remove silica can allow for added energy extraction, reduce operation and maintenance cost and open the way for the recovery of such metals as zinc, lithium, manganese, cesium, rubidium and even precious metals such as gold, silver and platinum. The risk, however, is that the tremendous amounts of some metals such as lithium in geothermal brines, for example at the Salton Sea, could well exceed worldwide demand and result in driving the market price down to uneconomical levels.

The ability to use geothermal brine for enhanced evaporative cooling of binary plants could well provide an additional incentive to find viable methods for silica removal.

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