POTENTIAL FOR RECOVERY OF BY-PRODUCTS FROM SPENT GEOTHERMAL FLUIDS

Michael S. Wei

Engineering and Economics Research, Inc.
1951 Kidwell Drive
Vienna, Virginia 22180

ABSTRACT

This paper presents the results of a preliminary evaluation of the potential for recovering by-products from geothermal fluids. Over 30 chemical species found in geothermal fluids were systemmatically evaluated. A hypothetical 50 MWe power plant, using high salinity fluids, was used as a base for our estimate of mineral values. Our study indicates that Li, B, CO_2, NH_3, Br_2, I_2, Sr and heavy metals appear to be the most promising minerals to be recovered from geothermal fluids. However, improvement in process technology are still required in order to make the minerals competitive with conventional methods of production.

INTRODUCTION

Geothermal fluids are chemically complex with total dissolved solid (TDS) levels ranging from a few hundred to a few hundred thousand parts per million. With the high flow rates needed for power production, a substantial amount of chemicals inevitability passes through the geothermal power plant. While these chemicals may cause operational problems such as scaling and corrosion, there is a potential to recover some of these chemicals as by-products. This paper investigates the feasibility of recovering chemicals from spent geothermal fluids taking into consideration the mineral values, market demand, technology readiness, resource uncertainties and competition from other supply sources.

MINERAL VALUE

A first consideration for recovering minerals from geothermal fluid is to determine the amount of minerals that can be recovered from geothermal fluid and their monetary values so that decisions can be made regarding the worthiness of such an investment. Obviously, fluids of high salinity will potentially yield more recoverable products than low salinity fluids. In order to establish a baseline for comparison, a hypothetical "best-case" 50 MWe geothermal power plant was established. The assumptions used for this 50 MWe plant are:

- Brine flow rate = 100,000 lbs per hour per well
- 14 production wells
- Plant operates 7,000 hours per year (0.8 capacity factor)
- High salinity fluids with dissolved solids contents comparable to those of Salton Sea

Based on these assumptions, the total amounts of minerals recoverable and their mineral values are shown in Table 1. These figures were arrived at assuming that the minerals present in the fluid can be totally recovered and are saleable at current market prices. Because of the differences in mineral values, chemical species present in the highest concentrations do not necessarily yield the highest monetary return. Looking at the most likely recoverable forms of the listed brine species, 14 products exceed $1,000,000 in value. They are RbCl, Au, Li_2CO_3, CsCl, KCl, $Na_2B_4O_7$, MoO, $Mg(OH)_2$, $ZnSO_4$, NaCl, $SrCO_3$, $CaSO_4$, I_2, and Ag.

Table 1. Annual Amounts and Values of Recoverable Materials in a Best-Case 50 MWe Plant.

Chemical Species	Brine Concentration* (ppm)	Recoverable Materials	Amount of Recoverable Materials (tons)	Mineral Values**
Na	74,000	NaCl	919,000	$4,135,000
Ca	40,000	$CaSO_4$	666,000	$3,430,000
K	25,000	KCl	233,000	$10,600,000
Mg	3,000	$Mg(OH)_2$	24,400	$4,950,000
Fe	3,000	$Fe(OH)_3$	28,100	$793,000
CO_2	1,000	CO_2	20,200	$304,000
Si	1,000	$CaSiO_3$	4,900	$206,000
Sr	750	$SrCO_3$	6,210	$3,600,000
B	740	$Na_2B_4O_7$	32,000	$5,340,000
Zn	740	$ZnSO_4$	8,980	$4,850,000
Ba	570	$BaSO_4$	4,750	$264,000
Al	450	Al_2O_3	4,170	$792,000
Li	300	Li_2CO_3	7,770	$20,200,000
NH_3	300	NH_3	1,470	$176,000
Rb	169	RbCl	828	$129,000,000
Pb	155	Pb	760	$654,000
Br_2	146	Br_2	715	$315,000
Mo	110	MoO	730	$5,110,000
I_2	40	I_2	196	$2,665,000
Cs	20	CsCl	124	$16,400,000
Cu	16	Cu	78	$172,000
Ni	6	Ni	32	$162,000
Au	2	Au	9.8	$83,000,000
Ag	1.4	Ag	7	$1,175,000

* Reeber, 1980 ** Calculated from BOM, 1980

In addition, 10 products have values falling between \$100,000 and \$1,000,000 per year. They are: $Fe(OH)_3$, Al_2O_3, Pb, Br_2, CO_2, $BaSO_4$, $CaSiO_3$, NH_3, Cu, and Ni.

MARKET DEMAND ASSESSMENT

Several factors were taken into consideration in order to identify a preliminary list of promising by-products recovered from geothermal power plant operations. These factors are:

- Quantity and form of materials producible from a "best-case" 50 MWe geothermal power plant
- Monetary values of by-products
- U.S. demand for commodity (ignoring regional demands)
- Import dependency
- Strategic consideration
- Existing sources of supply (competition)
- Technology readiness of recovery process
- Resource uncertainty

Table 2 lists in decreasing order the mineral monetary values obtained in the fluid of a "best-case" 50 MWe geothermal plant and some of the more readily quantifiable factors discussed above. Based on these considerations, the 24 minerals with values exceeding \$100,000 per year were classified as promising, marginally promising, speculative, and not promising. The rationale for this grouping is presented on a product-by-product basis in the following sections.

PROMISING MATERIALS

The following materials are considered to be promising for recovery from geothermal fluids:

- Lithium has a high mineral value and the process used to recover lithium, (aluminum oxide addition to produce lithium aluminate) appears to be promising. Lithium is currently produced from brine extraction and from the ore spodumene.

Table 2. Factors Considered in Determining the Marketability of Geothermal By-Products

Chemical Species	Brine Concentration (ppm)	Annual Mineral Value from 50MWe Plant	% of U.S. Demand from 50MWe Plant	% of U.S. Demand Met By Import*	Strategic Consideration*	Current Supply Sources*	Potential for Recovery from Geothermal Fluids**
Rb	169	\$129,000,000	72,000	0	-	Lepidolite	Not promising
Au	2	\$83,000,000	5	45	Stockpiled	Mines	Speculative
Li	300	\$20,200,000	46	0	-	Spodumene	Promising
Cs	20	\$16,400,000	700	100	-	Pollucite	Not promising
K	25,000	\$10,600,000	3.3	68	-	Seawater, Brine	Not promising
B	740	\$5,340,000	2.9	0	-	Brine	Promising
Mo	110	\$5,110,000	1.5	0	Strategic	Molybdenite	Promising
Mg	300	\$4,950,000	1.3	0	-	Dolomite, Brine	Marginal
Zn	740	\$4,850,000	0.4	51	-	Zinc Ore	Promising
Na	74,000	\$4,135,000	1.8	9.5	-	Seawater	Not promising
Sr	750	\$3,600,000	16.7	100	-	Celestite	Promising
Ca	40,000	\$3,430,000	1.2	2	-	Limestone	Not promising
I_2	40	\$2,665,000	4.5	72	Stockpiled	Brine	Promising
Ag	1.4	\$1,175,000	0.1	30	-	Ore	Speculative
Fe	3,000	\$793,000	0.008	33	-	Iron Ore	Promising
Al	450	\$792,000	0.003	93	Controlled	Bauxite	Marginal
Pb	155	\$654,000	0.05	15	Controlled	Ores with Zinc	Promising
Br_2	146	\$315,000	0.4	0	-	Brine	Promising
CO_2	1,000	\$304,000	0.01	0	-	Natural wells	Promising
Ba	570	\$264,000	0.16	33	-	Barite	Marginal
Si	1,000	\$206,000	0.7	13	Stockpiled	Sandstone	Not promising
NH_3	300	\$176,000	0.008	5	-	Natural gas	Promising
Cu	16	\$172,000	0.003	13	Strategic	Cu_2S Ore	Promising
Ni	6	\$162,000	0.015	65	Stockpiled	Sulfide Ore	Promising

* BOM, 1980

** See text for rationale of classification

- Boron has a relatively high mineral value and can be recovered as borax by the addition of sodium compounds. This process is similar to the current method of commercial production and thus, recovery technology is demonstrated. However, marketing boron from geothermal fluids will face stiff competition from alternate sources of production.
- Carbon dioxide can be recovered using technology similar to conventional commercial methods. Despite its marginal mineral value, CO_2 can penetrate local markets and can also be used on site in the drilling process to control the acidity of drilling muds,
- Ammonia can be recovered through the air stripping process. It has the potential of penetrating small local markets.
- Bromine can be recovered from geothermal using the same process as the commercial production process, i.e. chlorine addition. Br_2 from geothermal resources will face stiff competition from conventional sources.
- Iodine can be recovered in a similar method as bromine. However, the 40 ppm of iodine in brine is probably optimistic.
- Heavy metals (Ni, Cu, Pb, Fe, Zn, and Mo) can be collectively precipitated from geothermal fluids as hydroxides and/or sulfides. These metals are either strategic or imported to a large degree.
- Strontium can be recovered as $SrCO_3$ through the addition of carbonates. Its relatively high mineral value and the high import reliance make the recovery from geothermal fluids attractive.

MARGINALLY PROMISING MATERIALS

These minerals are considered as marginally promising for recovery from geothermal fluids:

- Magnesium is currently recovered from seawater which has a magnesium level of 1,350 ppm. Except for Salton Sea, most geothermal resources have Mg contents substantially less than seawater.
- Aluminum can be extracted as hydroxide through the addition of lime. Recovery of aluminum warrants consideration because of the large import dependencey of this critical material.
- Barium can be recovered as $BaSO_4$, which can be used as a weighting material in drilling mud. Thus some of the recovered products may be used on-site.

SPECULATIVE MATERIALS

Recovery of gold and silver from geothermal fluids is at best speculative primarily due to uncertainty in resource characteristics.

- Gold has a mineral content of $83,000,000 per year based on our best-case calculation. However, this value is derived from one data point. The uncertainty of Au content in geothermal fluids makes the recovery of this valuable mineral a highly speculative endeavor.
- Silver may appear to be a good compromise for gold. However, its mineral value is relatively small due to the low level of Ag in geothermal fluids.

NOT PROMISING MATERIALS

This group of minerals is considered to be not promising in terms of marketability in the U.S. market. Situations may be different in other countries to warrant their recovery.

- Rubidium from geothermal fluids would not be marketable because of the low domestic demand. One best-case 50 MWe geothermal power plant will produce enough Rb to supply 720 times the U.S. requirement.
- Cesium is not a good mineral to market because of its low market demand.
- Sodium, as NaCl (salt), is unattractive because the only viable technology for recovery is solar evaporation. In addition there are ample supplies of salt from seawater.
- Potassium is not an attractive mineral to recover because solar evaporation is the only viable technology. It will also face competition from other sources such as marine evaporates, brines, and seawater.
- Calcium will most likely be precipitated as $CaCO_3$ scales in the energy conversion plant. There is also ample supply of $CaCO_3$ as limestone.
- Silicon will most likely be precipitated as silica scales in the plant. It is also doubtful that high quality silicon compounds can be recovered from geothermal fluids.

CONCLUSIONS

Recovery of by-products from geothermal fluids appears to be an attractive option and may be feasible for certain chemical species. Li, B, CO_2, NH_3, Br_2, I_2, Sr and heavy metals are identified as most promising materials in this report. However, there are problems yet to be overcome even in this most promising category. There is a need to improve process efficiency so as to reduce cost for materials recovery. The uncertainty in resource characteristics is another major problem. This of course can only be resolved through extensive site specific monitoring.

REFERENCES

(1) Rebeer, K.R., 1980, "Coating in Geothermal Energy Production". Thin Solid Films, Vol. 72.

(2) Bureau of Mines, 1980, "Mineral Facts and Problems". United States Department of Interior, BOM Bulletin 671. U.S. Government Printing Office, Washington, D.C.