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Extracting Minerals From Geothermal Brines: A Literature Study

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EXTRACTING MINERALS FROM GEOTHERMAL BRINES: A LITERATURE STUDY

by

Rolland L. Blake[1]

ABSTRACT

The Bureau of Mines is concerned with extracting minerals from residual geothermal brines after their heat content and some demineralized water have been recovered. This literature study is based on a survey of the literature and discussions with individuals knowledgeable on various aspects of the subject. This report examines the potential of the domestic geothermal mineral resources, considers the technical problems involved, and outlines possible effects on the environment from reservoir fluid withdrawal and reinjection.

Geothermal resources in the Western United States were extensively explored during the 1960's. Limited development operations included exploratory drilling and operating wells producing hot brine, separating steam for experimental electric power generation, and recovering minerals in solar evaporation ponds or in extraction plants. Interest in the recovery of minerals and salts from geothermal fluids waned because of corrosion and scaling problems and low or no market value of the mineral products. Most of these problems can be controlled with existing technology and careful planning of processes and equipment. Extracting geothermal minerals is technically feasible, but the problems of low or no market value for major mineral products, and insufficient amounts of more valuable minor products, make mineral recovery uneconomical at present.

INTRODUCTION

Extraction of minerals from hot geothermal brines should be considered in planning the multipurpose development of geothermal resources. Reasons for considering extraction of minerals are (1) the hope that their market value will partly compensate exploration and development costs; (2) the need to produce potable water; and (3) the prevention of environmental damage upon disposal of the waste brine. Very little information is available on the technology and feasibility of extracting minerals from geothermal brines, although numerous articles mention such problems as corrosion and scaling to be expected. The objective of this study is to evaluate the feasibility and market potential for producing minerals from hot geothermal well brines. The

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[1] Supervisory geologist.

study considers mineral resources potential, technological processes and problems in mineral extraction, and possible effects on the environment caused by brine production and disposal. Information for this study was obtained mainly from the literature and was supplemented by discussions with persons knowledgeable on geothermal exploration as well as on mineral extraction from nongeothermal brines.

U.S. Government interest in domestic geothermal resources was considerably increased with passage of the Geothermal Steam Act of 1970[2] which had two effects as follows: (1) It made geothermal resources subject to provisions of the Mineral Leasing Act of 1920 and (2) it specified that the Secretary of the Interior would have the responsibility for administering such resources. No provision was made for research and development activities in this Act. Several areas of related government concern are electric power shortages, declining volume and quality of water in the Lower Colorado River Basin, environmental responsibility, and the continuing concern for wise conservation and use of resources. The Imperial Valley of California is the domestic area with most potential for multiple use of geothermal resources to help solve some of these concerns.

Four U.S. Interior Department agencies, the U.S. Geological Survey, the Bureau of Reclamation, the Office of Saline Water, and the Bureau of Mines, have been engaged in geothermal research and development investigations. The Geological Survey's geothermal program includes development of a reliable body of knowledge of the principles that control geothermal fields; development of more sophisticated exploration techniques; assessment of the resources potential; monitoring of environmental effects; and the classification and supervision of leases (35).[3] The Bureau of Reclamation, with assistance from the Office of Saline Water, is extracting geothermal steam and brine from the Imperial Valley sediments for the purpose of demonstrating the feasibility of producing demineralized water. The Bureau of Mines is developing methods for extracting potentially valuable minerals from the resulting concentrated brine effluent, and for disposing of waste brines in an environmentally acceptable manner.

Geothermal hot waters (brines) have been used for thousands of years for mineral baths and for many years to heat homes, greenhouses and furnish hot water to local communities in certain areas of the world. As early as 1913, geothermal steam flow at Lardarello, Italy, was developed to produce electric power, and over the years, a considerable production of chemicals has been extracted from the condensed steam (50). Although no other commercial mineral extraction from geothermal brines is known at present, geothermal electric power is being produced also at Bagnore, Italy; The Geysers, Calif.; Wairakei, New Zealand; and in Japan, The U.S.S.R., and Iceland.

In the two decades from 1950 to 1970, worldwide geothermal exploration was conducted in nearly 100 regions. In the United States, over 90 percent of the geothermal areas were found to be concentrated in 13 western States. This

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[2] U.S. Congress. Public Law 91-581, Dec. 24, 1970, 84 Stat. 1566.

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this circular.

included over 1,000 warm and hot springs and fumarole localities (1, 2, 42, 12, 28, 33, 66). Test drilling was conducted in six western States, resulting in discovery of the following five potential geothermal fields: The Geysers, Imperial Valley and Casa Diablo, all three in California, and Beowawe and Brady's Hot Springs in Nevada. The Geysers produce "dry" steam while the Imperial Valley and other fields contain hot waters (29).

Except for The Geysers and some space heating systems, most private exploration and development of U.S. geothermal resources came to a halt in the late 1960's because the problems appeared too costly when compared with the benefits. Explorations carried out by two oil companies involved drilling deep wells, testing their hot brine and steam flow, and operating pilot plants to develop steam electric power and to extract minerals. The market price of their mineral product dropped 50 percent during this period, and their equipment was damaged by corrosion and deposits of mineral scale. These negative factors caused the companies to withdraw from any further geothermal exploration in the foreseeable future, although they have retained their leases for the future in anticipation that the problems will be resolved. With the Nation's energy supplies becoming more critical, renewed interest has been shown in finding and developing clean sources of energy including geothermal energy.

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GEOTHERMAL SYSTEMS

The recent worldwide exploration of geothermal areas has provided valuable new information which the U.S. Geological Survey continues to study and to interpret. Good progress is being made toward a better understanding of geothermal resources from the geological viewpoint, as summarized by Muffler (36). White and others (67) classify geothermal resources as either hot water systems or vapor dominated systems.

The hot water system is usually located in permeable sedimentary or volcanic rocks or in competent rocks such as granite which can maintain open channels. This type of system has large volumes of water (brine) and is usually sulfur deficient and chlorine rich, with the elements Na, K, and Ca the dominant species present, and with lesser amounts of SiO_2, Fe, Mn, base metals and other alkali metals as Li, Rb, Cs, and usually some ammonia and bicarbonate ions. The dissolved mineral constituents in the hot waters are believed to originate principally from leaching action of water migrating through rocks. The Imperial Valley is an example of a hot-water geothermal system.

Vapor-dominated (dry-steam) systems have smaller volumes of water, lower permeability, higher heat content, and are low in chlorides and high in sulfates in comparison with hot-water systems. The Geysers is an example of a vapor-dominated system. Both hot-water and vapor-dominated systems can occur in different areas of the same region and there may be gradational representatives of the two types.

Geothermal brines are believed to consist of about 95 percent or more ground water with possibly up to 5 percent magmatic water. Some of the water is connate (originally trapped in the sediments when buried), while some represents recharged ground water. The whole system has reached some degree of dynamic flow equilibrium while influenced by permeability channels, a heat source of hot rocks at depth, tectonic movements, topography and drainage basin characteristics, and climatic conditions of precipitation and evaporation.

MINERALS FROM GEOTHERMAL FLUIDS

Brines

Analyses

The amounts of each of the dissolved ions varies considerably from brine to brine. Table 1 lists analyses of three geothermal and three nongeothermal brines for comparison. The IID (Imperial Irrigation District) analysis represents geothermal well No. 1 brine, which is highly enriched and apparently unique (35). This brine is derived from sediments in the Imperial Valley and contains 25.9 percent dissolved solids. This is one of two analyses considered both complete and accurate according to Muffler (35), but it should be remembered that it represents the maximum of the highly enriched brines. It is not known how extensive they are or if their dissolved mineral content could be sustained by continuous flow from the reservoir.

The Cerro Prieto well M-8 brine (table 1) is from a high thermal anomaly area near Cerro Prieto, an ancient volacano in the Mexicali Valley (the Imperial Valley extension into Mexico). This brine (2.2 percent dissolved solids) is thought to be representative of average brines expected throughout the Imperial Valley reservoir. However, Rex (49) believes that taking one-half of well M-8 values for each ion would give a more representative brine. The third analysis in table 1 is from the New Zealand well headwater before some of it flashes to steam upon pressure reduction. These three analyses represent chlorine-rich sulfur-poor waters typical of hot-water system geothermal brines.

TABLE 1. Some geothermal and nongeothermal brine analyses, in ppm of dissolved ions

Constituent	Geothermal			Nongeothermal		
	Niland, Imperial Valley, Calif. IID No. 1[1]	Cerro Prieto, Mexico Well M-8[2]	Wairakei, New Zealand[3]	Ocean[4]	Oilfield brines[5]	
					High-salinity	Low-salinity
SiO_2	400	770	470	6.4	-	-
Al	4.2	(6)	-	.01	-	-
Fe	2,290	-	-	.01	-	-
Mn	1,400	-	-	.002	-	-
As	12	-	-	.003	-	-
Sb	.4	-	-	.0005	-	-
Ca	28,000	390	14	400	44,440	630
Mg	54	6	2	1,350	4,340	40
Sr	400	-	-	8.0	-	-
Ba	235	-	-	.03	-	-
Cu	8	-	-	.003	-	-
Pb	102	-	-	.00003	-	-
Zn	540	-	-	.01	-	-
Na	50,400	6,100	1,230	10,500	74,000	5,640
K	17,500	1,860	200	380	4,410	50
Li	215	17	13.5	.17	370	2
Rb	135	-	2-3	.12	-	-
Cs	14	-	2-2.5	.0005	-	-
NH_4	409	-	-	(4)	-	0
HCO_3	>150	890	46	140	95	500
SO_4	5.4	.0	37	2,650	220	120
Cl	155,000	11,750	2,110	18,980	202,050	8,350
F	15	-	8	1.3	-	-
Br	120	14.3	-	65	5,725	70
I	18	-	-	.06	15	5
B	390	(7)	(8)	4.6	200	10
Sulfide as H_2S	16	-	-	(4)	-	-
pH (20° C)	5.2	-	-	-	-	-
T, ° C	340	-	-	-	-	-
Total	258,973	[7]21,915	4,237.5 to 4,239.0	34,486	335,865	15,417

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[1] (64, table 1). Presently considered best values, mainly from samples of erupted brines and condensed vapor collected 4/21/66, analysis by D. E. Donaldson and C. E. Roberson, USGS. Contents reported for As, Cu, and I from analysis of White (63) 1965 decreased by 18.8 percent because of selective loss of steam and other gases, previously suspected, now confirmed. Other constituents in ppm: Ag-1.4, Sn-0.5, Hg-0.006, Tl-1.5, Cd-2.0, Au-0.0.

[2] From table II, attached to memo from Karl Starch, Economist, Intermountain Field Operation Center, Denver, Colo., to J. B. Rosenbaum, Research Dir., Salt Lake City Met. Res. Center, Aug. 6, 1971; well analyses apparently from AEC report on preliminary investigation of desalting geothermal brines in Imperial Valley, ORNL-TM-3021, by Spiewak, Hise, Reed, Thompson, date unknown.

[3] (27). Concentrations are given in ppm by weight for water separated from the bore discharge at atmospheric pressure.

[4] Ocean water composition from White (64, table 1) who cites E. C. Goldberg, 1965. Minor Elements in Sea Water, pp. 163-196 in J. P. Riley and G. E. Skirrow, eds., Chemical Oceanography, Academic Press, Inc., New York, v. 1, 712 pp. NH_4 and H_2S absent from open oceans but present in local reducing environments.

[5] (10, table 2), high = brine No. 3, low = brine No. 30.

[6] Constituents marked "-" were not analyzed.

[7] H_3BO_4 = 115 ppm (this would be 16.2 ppm boron, but Muffler (35) says boron = 0.7 ppm at Cerro Prieto); not included in total. Sample represents brine makeup before flashing.

[8] HBO_2 = 103 ppm included in total.

Nongeothermal brines include those of the ocean, inland seas or lakes, oilfields, and near-surface brines that saturate sediments beneath playas (intermittent lakes in arid basins) such as at Searles Lake, Calif., or Silver Peak, Nev. Table 1 lists three analyses for nongeothermal brines: A complete analysis for ocean brine and partial analyses for high- and low-salinity oilfield brines. Note the consistently dominant Cl and Na ions in these brines and the large variation of SO_4 ion. Processes developed for seawater and salt deposit brine mineral extraction should be applicable in extracting minerals from geothermal brines. The main differences are the higher temperatures, greater SiO_2 and K content, and lower Mg and SO_4 content of geothermal brines.

Mineral Resources Potential

The major chemical constituents of enriched brine from the Imperial Valley at Niland are Cl, Na, K, and Ca (table 1). As expected, the major minerals to precipitate from these brines are the simple chlorides: NaCl (halite), KCl (sylvite), and $CaCl_2$ (hydrophilite). Solar ponds and plant evaporators produced these minerals during geothermal exploration in this area. Minor constituents could precipitate as small amounts of other minerals, such as chlorides of Li, Mg, Ba, Sr, Zn, and Rb.

Minerals of academic but probably not economic interest are the precipitated mineral scales that were deposited from the enriched brines in wellhead pipes at some flowing wells in the Niland area. White and others (66) described a dark scale deposit with the following analysis, in weight-percent: Si--major constituent; Cu--20; Fe--7; Ag--2; Na and K--1 each; Ca and Al--0.7 each; and Sb--0.3. In a 3-month period an estimated (66) 5 to 8 tons of scale were deposited from a well discharging 500,000 pounds of brine per hour and flowing about 60 percent of the time (49). This calculates to 324,000 tons of brine in 3 months; or 0.002 percent of the brine flow was deposited as scale, while the bulk of the dissolved solids remained in solution. Minerals comprising the scale were found (52) to be: Amorphous opaline silica; sulfides of copper, iron, silver, arsenic, antimony, and zinc; and some metallic silver. According to Skinner and others (52), the brine is saturated with respect to sulfide components, and addition of more sulfide ion would cause precipitation of sulfides.

Although few U.S. geothermal areas have been explored enough to allow estimating their mineral resources magnitude with fair accuracy, some idea of the mineral resources potential can be ascertained by estimating the amount of dissolved mineral constituents contained in the fluids at the more completely explored areas. Not predictable at this time are (1) the process for extraction; (2) the recovery ratio expected; (3) the purity and market value of the products; and (4) in some cases, the form in which it would precipitate.

The volume of recoverable water with salinity less than 35,000 ppm in the Imperial Valley has been estimated at 1.1 billion acre-feet of which 200 million acre-feet is at a temperature of 150° C or above (13). D. R. George (18) calculated the amount of two chloride salts that might be obtained upon evaporating 3 million acre-feet of brine per year containing 2 percent of dissolved salts, based on the average composition of wells M-5 and M-8 from Cerro Prieto, Mexico. The 60 Mst (million short tons) of NaCl and 13.5 Mst of KCl calculated are considerably more than the U.S. apparent consumption in 1969 (57) which was 46.8 and 4.7 Mst, respectively.

Another approach to estimating the mineral resources potential is to calculate the amount of solids dissolved in a brine of probable composition at a given flow rate. In a Bureau of Reclamation program proposal (60), 72 wells would be drilled and operated in the Imperial Valley to supply geothermal fluids to a Demonstration Stage Plant. It was estimated that each well would produce 600,000 pounds of brine (before any flashes to steam) per hour. (The Bureau of Reclamation Deep Geothermal Test Well on the East Mesa anomaly presently is producing only 50,000 pounds of brine per hour.) With 36 days shutdown per year for maintenance, the expected brine flow is about 170 times 10^6 short tons per year or about 125,000 acre-feet. Composition of a probable brine (table 2) is based on one-half of the Cerro Prieto well M-8 partial analysis. Additional constituents in the supplemental column were obtained from another source as footnoted. Large tonnages of Na, Ca, and K chlorides and precipitated SiO_2 would be produced, as would smaller, but significant, amounts of other elements or compounds. However, these constituents would have to be separated and purified before being marketable, if a market did exist.

TABLE 2. - Probable average brine analysis for Imperial Valley, Calif., with quantity of potential mineral constituents from 72 wells flowing for 1 year[1]

Constituent	Partial analysis, ppm[2]	Supplemental analysis, ppm[3]	Quantity, short tons per year	Constituent	Partial analysis, ppm[2]	Supplemental analysis, ppm[3]	Quantity, short tons per year
SiO_2..	385		65,450	HCO_3......	445		75,650
Fe....		0.1	17	SO_4.......	.0		0
Mn....		.32	54	Cl........	5,875		998,750
As....		1	170	F.........		1.5	255
Ca....	195		33,150	Br........	7.15		1,215
Mg....	3		510	I.........		1	170
Si....		5	850	B.........	[4]8		1,360
Ba....		6	1,020	P.........		2.5	425
Cu....		.0025	.4	Sn........		.04	6.8
Pb....		.0023	.4	Total	10,876.65	17.4678	-
Zn....		.003	.5				
Na....	3,050		518,500				
K.....	930		158,100				
Li....	8.5		1,445				

[1] Flow of each well estimated to average 600,000 pounds brine/hour under conditions described in text.

[2] For each constituent, at suggestion of Rex (49), the partial analysis of Cerro Prieto, Mex., well M-8 is halved. Anal. from Spiewak and others (53).

[3] For each constituent, at suggestion of Rex (49), the supplemental analysis is 50 percent of the analysis of water flowing from Cerro Prieto, Mexico, wells Taken from table 1, p. 11, of a technical report by W A Klemm and N. R. Fetter, in the Geothermal Resources Program of the Institute of Geophysics and Planetary Physics, University of California, Riverside, Calif., 1972.

[4] H_3BO_4 = 115 ppm; B = 11/78 × 115 ÷ 2 = 8 ppm. (See footnote 7 of table 1, this IC.)

Brines from the Niland area, Imperial Valley, contain about 25 times as much total solids as the probable brine of table 2, and the mineral production would be correspondingly higher. Hot water from Casa Diablo carries only about one-tenth the constituents of the probable brine. Casa Diablo fluid is not considered a true brine since its value of 1,092 ppm dissolved constituents is only twice that of potable water which may contain up to about 500 ppm.

Still another approach to estimating mineral market potential of a geothermal brine would be a method first worked out on desalination brines by Christensen and others (9). This method was modified and applied to oil well brines by Collins and Crocker (10). Their estimates of brine value and worth were made by assuming (1) the type of product recovered and (2) an arbitrary marketing cost of 75 percent of the value of the product based on current prices. Collins and Crocker estimated brine value and worth for 42 brines (sea water + 41 oilfield disposal brines). They also calculated a ratio for easy comparison of brines; this ratio is the brine value of commercial brine over that of the oil well disposal brine. Since some chemicals are recovered from seawater, any brine which is disposed of in large volumes, and having a ratio less than 20 (that for seawater), may warrant investigation as a source of minerals. Calculations were not carried out for geothermal brines, but the oil well disposal brine No. 6 (that with most similar content of Li, Br, and I, and total dissolved solids, to the probable Imperial Valley geothermal brine of table 2) had a ratio of 39, indicating insufficient mineral values to be commercially attractive under recent market conditions.

Steam

Analyses

Geothermal steam may be "dry" as at The Geysers, Calif., where all water is in the vapor phase. Table 3 shows that noncondensable gases make up no more than 2.0 percent of the total volume. Mineral constituents in The Geysers steam condensate are presented in a section that follows (table 4). At Wairakei, New Zealand, the gas contents of total discharge are in the range of 5 to 30 millimoles per 100 moles of H_2O, the gas being mainly CO_2 with the CO_2/H_2S ratio usually between 15 and 40 (32). At Lardarello, Italy, the average vapor composition in percent is H_2O - 95; CO_2 - 4.3; H_2S - 0.9; boric acid - 0.3; NH_3 - 0.3; CH_4 - 0.15; and H_2 - 0.04 (50).

TABLE 3. - Analysis of gases at The Geysers, Calif., in volume-percent[1]

Sample	H_2O	CO_2	H_2	CH_4	N_2+A	H_2S	NH_3	N_3BO_3	Total
Total vapor including H_2O.........	98.0	1.242	0.287	0.299	0.069	0.033	0.025	0.0018	100.002
Gases excluding H_2O.........	-	63.5	14.7	15.3	3.5	1.7	1.3	.09	100.69

[1] From White and others (67, table 2).

TABLE 4. - Potential mineral constituents present in steam condensate at The Geysers and at Casa Diablo, Calif.

Constituent	The Geysers, condensate mineral matter				Casa Diablo condensate analysis, ppm[4]
	Average condensate analysis from wells, ppm[1]	Constituents from one average well, pounds[2]		Total from 40 wells,[3] short tons per year	
		1 month (30 day)	1 year		
SiO_2........	0.40	288	3,450	69	0.8
Ca..........	.13	94	1,130	23	-
Mg..........	.04	29	348	7	-
Sr..........	<.08	<57	<685	<14	-
Na..........	.11	79	950	19	5
K...........	<.10	<72	<864	<17	-
Li..........	.003	2	24	.5	-
NH_4.........	225	162,000	1,944,000	38,900	[5].5
HCO_3........	732	527,040	6,324,480	126,240	-
CO_3.........	.37	266	3,192	64	[6]205
SO_4.........	14.03	10,100	121,200	2,420	2
Chloride....	13	9,360	112,320	2,250	5
Fluoride....	<.10	<72	<864	<17	-
B...........	1.68	1,210	14,520	290	.3

[1] Average analysis of 3 wells (thermal #7; DX State 3395-1; and Sulfur Bank 14). Samples collected Oct. 28-29, 1970. (62, p. C-5)

[2] Assumes that condensate is 100 percent of the steam produced at each well; steam per well averages 100,000 pounds per hour (62, p. C-4).

[3] Estimate 40 wells producing at average rate based on proposed 192 MW electric power production as explained in text.

[4] Mono Lake--Long Valley area; well Endogenous No. 4, condensate of steam sample taken during flow test (62, p. D-5).

[5] NH_3.

[6] CO_2.

At Niland in California's Imperial Valley, 15 to 20 percent by weight of the brine flashes to steam, and at Cerro Prieto, Mexico, the percentage is higher owing to lower salinity of the fluid (28). Noncondensable gases in the Niland steam consisted of CO_2, O_2, CH_4, N_2, H_2S, and CO (33).

Mineral Resources Potential

At Lardarello, Italy, after generating electric power, the geothermal steam is condensed to a brine from which the following chemicals have been produced: Dry ice (CO_2), liquid NH_3, $(NH_4)_2CO_3$, NH_4Cl, sodium perborate and manganese borate. Bullard (7) reported that, around 1940, the annual production at Lardarello was 8,000 tons of boric acid and 4,500 tons of borax. Market conditions in 1971 were such that no borax was being extracted, since it was more economical to use the steam to refine borax from imported materials (35).

According to White and others (67), common metal chlorides have negligible volatility and solubility in low-pressure steam. The only chlorides that are volatile enough to be steam-transported at low temperatures and pressures are HCl and NH_4Cl. Mercury occurs as cinnabar (HgS) and metacinnabar (also HgS) mainly around hot springs which have high (SO_4) content. However, Hg seems to be virtually absent in hot-water-systems with chlorides, for example Hg = 0.006 ppm in IID, No. 1 well, footnote 1 of table 1, this IC.

The Geysers

The most information on geothermal steam in the United States has been collected at The Geysers, which has produced steam electric power since 1960. "Dry" steam here contains the gases listed previously in table 3, plus small amounts of mineral constituents shown in table 4. The first column of table 4 lists the average of each mineral constituent in condensates from three wells. The amount of each constituent present for various periods of steam flow was calculated for one well at an average production rate of 100,000 pounds per hour (62, p. C-4). This assumes no evaporation loss up to the point of condensate sampling. During a 10-hour period, 1 million pounds of steam are produced; therefore, the pounds of each constituent produced are the same as the ppm figures. Columns two and three list such amounts in 1 month and 1 year, respectively. Column four lists the number of short tons contained in condensate from a total of 40 wells during 1 year. Forty wells is an estimate of the number required to produce 192 MW of power scheduled for 1972 production at The Geysers. It is based on the June 1960 operation of the 12.5-MW powerplant, which used 250,000 pounds of steam per hour, or 20,000 pounds of steam per MW (62, p. C-4). The tonnages shown in table 4 for most constituents are either too small to justify considering their recovery or there is no market for the product. However, the large amounts of ammonia and bicarbonate might have potential for the fertilizer and chemical markets, respectively. The amount of boron reported in the condensate water, after water loss of 75 to 80 percent in the cooling towers, is reported to be 20 to 40 ppm (3). This is between two to five times as much as the 8.4 ppm obtained using a five-fold concentration of the table 4 figure (1.68 ppm). Differences in analyses, as in this example, make it difficult to calculate meaningful quantities of constituents.

Casa Diablo

At Casa Diablo Hot Springs, in the Mono Lake-Long Valley area, shallow wells produced hot water, but four wells drilled to 1,200 feet produced hot water and steam, the steam representing about 10 percent of the total production. Flow rates of steam per well varied from 19,000 to 69,000 pounds per hour (62, p. D-4). The median value, 44,000 pounds per hour, is less than half that of the average well at The Geysers. A partial analysis of Casa Diablo steam condensate is shown in the last column of table 4. This incomplete analysis, upon comparison with that at The Geysers, suggests that the mineral potential of Casa Diablo steam is insignificant.

Imperial Valley

Imperial Valley brine is known to flash about 20 percent by weight to steam (60, 62). Theoretically, each of the 72 wells proposed by the Bureau of Reclamation would produce 120,000 pounds of steam per hour. Therefore, total steam per hour from all wells would be 8,640,000 pounds, slightly more than twice the calculated steam production (4 million pounds) at The Geysers with 40 wells at 100,000 pounds per hour. It seems reasonable to expect that, while gaseous constituents would enter the flashed steam in large proportions, only small proportions of mineral constituents would do so, with most remaining in the 80 percent unflashed brine. Consequently, mineral potential of flashed steam from the Imperial Valley is much less than that of the unflashed brines as calculated in table 2.

Market Potential

Minerals whose constituents are present in large amounts in geothermal brines (and in lesser amounts in gases) such as the chlorides will face stiff competition in the market because of oversupply and product quality problems, resulting in low prices. For example, each year thousands of tons of excess $CaCl_2$ are discarded as a byproduct from soda ash manufacturing by the Solvay process (17). The United States demand for potash (usually as KCl) fertilizer materials may not catch up with current oversupply until 1974 or 1975, with Canadian producers supplying 60 to 90 percent of this potash. If the U.S.S.R. supplies the free world with potash, the surplus may last until 1981 (58). Fertilizer chemical composition may offset the advantage gained by market proximity. Thus, fertilizers made with KCl are rejected by citrus and tobacco growers in favor of those made with K_2SO_4. KCl is suspected of staining the tobacco plant leaf (17) and reducing the quality and quantity of tree and plant growth (8). Irrigation waters in cultivated parts of the Imperial Valley contain more chloride ion than desirable, so fertilizers with KCl are not used there. Uses, cost per ton from various sources, and amount of salt consumed by the large chloride-alkali industry of the United States were presented by Grotheer and Currey (21). Table 5 lists 10 brine compounds and their recent market values. The low prices of the Na, Ca, and K chlorides are in sharp contrast to the high prices of LiCl and NaI.

TABLE 5. - Brine products and recent prices[1]

Product	Dollars per short ton	Product	Dollars per short ton
NaCl............	6.45	$Na_2B_4O_7 \cdot 10H_2O$...	50.25
$CaCl_2$	39.50	NaBr............	800.00
$MgCl_2$...........	60.00	NaI.............	7,000.00
KCl.............	28.00	$MgSO_4$	62.80
LiCl............	1,700.00	$NaHCO_3$..........	53.55

[1] Collins and Crocker (10, table 5).

On the Pacific Coast there are at least two areas where ocean salts are extracted. One is in San Francisco Bay and furnishes about 1 million tons per year of salt to the West Coast market from one "crop" per year. The other is at Black Warrior Lagoon, on the Pacific side of the Baja Peninsula. Solar ponds are used to extract only NaCl, which is screened, dried, and exported to Japan and also to the U.S. West Coast (probably to the Los Angeles area) where it furnishes about 50 percent of the consumption. Because of the warmer temperatures, Baja salt is a continuous crop. It is unlikely that any is shipped to Mexico. Salts produced at Great Salt Lake and other desert areas in the Western United States usually go to Arizona and Nevada markets and do not enter the California market (26).

Summarizing domestic geothermal mineral potential, the brines are more abundant and carry more mineral constituents than geothermal steam. The major mineral constituents have a low market price and are subject to foreseeable oversupply. Some of the less abundant constituents, as products in purified form, would have attractive prices, but their extraction and purification costs are not known. At the present time, extraction of minerals from domestic geothermal brines or steam is considered uneconomical.

TECHNOLOGY FOR RECOVERING GEOTHERMAL MINERALS

Brine Mineral Recovery

The science of extracting minerals from brines dates from early civilizations, where solar evaporation of seawater produced common salt (NaCl) and a few other simple salts. Modern mineral extraction from brines seems simple and the chemistry easily understood. However, each brine of different composition must be treated with its own sequence of steps to extract the desired ions with the best efficiency and crystal purity desired. The complexity of brine extraction becomes apparent when the chemist tries to understand and control the process.

Geothermal Brines

Kennedy (27) described laboratory and pilot tests done on brine at Wairakei, New Zealand. This chloride brine has a low salinity (0.42 percent solids) as shown in table 6 and has potential for recovery of chlorides of Na, K, and Li. Ion exchange and multiple-effect evaporation were found to be technically feasible but economically unattractive. A combined electrodialysis-evaporation process was laboratory- and field-tested for removing salt, potash, lithium carbonate, and possibly borax, rubidium and cesium. Several design problems were judged resolvable but market prices of the products were too low for the process to be economical.

TABLE 6. - Analysis of Wairakei bore water[1]

Ion	Amount, ppm[2]	Ion	Amount, ppm[2]
Na+	1,230	Cl^-	2,110
K+	200	F^-	8
Li+	13.5	$SO_4^=$	37
Rb+	2-3	HCO_3	46
Cs+	2-5.5	HBO_2	103
Ca++	14	SiO_2	470
Mg++	2	Total	4,237.5

[1] Kennedy (27).

[2] By weight for water separated from the bore discharge at ambient pressure.

Morton International explored Imperial Valley geothermal resources from 1964-67, taking over Shell Oil Co.'s work. They operated solar evaporating ponds and a small plant, which has now been dismantled (15). NaCl was precipitated in ponds, then re-dissolved and processed to remove impurities, and finally flashed to dryness using geothermal steam. $CaCl_2$ was recovered by solar evaporation, and KCl was precipitated late in the evaporation stage (28). According to Fiedelman (15), 95 percent of the product shipped was KCl. Details of the chemical process apparently have not been published.

Union Oil Co.'s Imperial Valley research included designing a pilot plant and process primarily for extracting potash (KCl) by a sequential precipitation using evaporators and crystallizers. NaCl was precipitated first, then KCl and finally $CaCl_2$. This plant was fed by a small amount of geothermal well fluid, while most was reinjected without processing (14, 43-44).

Geothermal development at Cerro Prieto, Mexico, is confined to testing and developing steampower. Brine is discharged into ponds, although there are no plans to recover minerals now (35).

Lindal (31) described the flow diagram of a process plant planned for Reykjanes, Iceland, from which Na, K, and Ca chlorides are to be extracted from a geothermal brine. The natural heat and higher potassium and lithium content of this brine compared with that of seawater make this brine more attractive economically than seawater.

Nongeothermal Brines

Minerals that are known to precipitate from nongeothermal brines are more numerous and complex than the simple chlorides from geothermal brines listed earlier. Nongeothermal brine minerals usually precipitate in a sequence with some overlapping: the first minerals to form are carbonates, then sulfates, and finally chlorides. Single salts are produced at nonoverlapping stages and double or complex salts at overlapping stages of precipitation. Problems of extracting minerals from complex brines include the following: (1) Temperature changes which may affect precipitation of some minerals but not others; (2) changes in concentration of one ion may cause entire concentration equilibrium to change, so that ions in minor concentrations may precipitate along the process path; (3) changes in brine concentration cause changes in solubilities of various ions and then mixed salts can precipitate and alter the entire system; (4) crystals of the wrong composition, which are difficult or impossible to re-dissolve in the brine, may precipitate in a pond; (5) close control is needed for complex brines and this is complicated by difficulty of taking meaningful samples because some brines may require 3 days to reach equilibrium (5).

Minerals that precipitate and processes used to bring this about are discussed in references such as (45, 19, 4, 16, 41, 6). Treatment of a high salinity brine (27 percent dissolved solids) is explained (8), as are the chemistry and problems (22-23) of bitterns (concentrated brine or bitter mother liquor remaining after salt has crystallized out of solution). Industrial and government research on process treatment for mineral extraction or desalination of nongeothermal brines may be found in the following references: (30, 38-41, 46-47, 61). Novel processes for brine mineral extraction include a covered solar evaporator designed to recover both the salts and water from brine. The freezing of brine requires only one-seventh of the energy to distill water, while corrosion and scale are reduced. Water may be cooled by evaporation of immiscible butane in contact with the water, reducing the reliance on heat exchangers (11). About 88 percent of seawater is removed as ice before any other solid phase begins to form (54). The mixing of brines of different compositions and specific gravities can precipitate crystals (48).

In summary, technology for treating nongeothermal brines to recover minerals is fairly well developed and available in literature. Precipitation is well understood theoretically but is complex to control. Each brine requires its own special flowsheet. The controls needed to treat geothermal brines may be quite costly in terms of manpower and equipment, and they must be balanced against the product's value in a company venture but could be balanced against other objectives in a nonprivate venture.

Corrosion

One of the most frequently mentioned and costly problems in geothermal resource utilization is corrosion of metals in the entire operation, from the well casing and wellhead piping to the metal pipes, tubing, and equipment used in brine mineral extracting plants (15, 28, 37, 56, 65). The hot, chloride-rich brine is more corrosive than brines treated near atmospheric temperatures. Main steam lines are usually constructed of carbon steel pipe, while steam condensate lines are frequently made of various stainless steels as protection against the sulfur content (33). Because common brines have been treated in plant evaporators for years, it is expected that alloys to resist brine corrosion in these installations have been fairly well developed.

Corrosion is most severe when oxygen enters the pipelines (56). Research is being undertaken to develop claddings and coatings of 0.003-inch thickness in co-extruded form with an inexpensive base, such as iron (42). Also, very hard and thin cladding a few millionths of an inch thick has been developed for coating mild steel parts used in pumps; and alumina cladding on base metals exhibits great hardness. Other corrosion tests (51) were designed using selected copper alloy tubing in a desalting environment. Results show that most alloys exceed a 25-year life span; the best alloy lasts longer than 39 years; and the corrosion rate drops significantly and increasingly with passage of time.

Scaling

Deposition of a SiO_2 scale in producing wells, surface pipelines and other equipment is most likely to occur where reservoir temperatures are above 250° C; in some lower-temperature reservoirs and wells, the deposition of $CaCO_3$ is the major problem (65). Deposition of SiO_2 occurs as temperature of a geothermal fluid decreases, while carbonate deposition occurs when the pH changes (56). Also, $CaCO_3$ deposition in wells and pipes may increase with time due to pressure and CO_2 losses from the reservoir with resulting pH increase.

Although scaling was one of the major problems of geothermal resource utilization mentioned by Fiedelman (15), he explained that Morton International had operated a well in the Imperial Valley for 1 year with only 1 inch of deposit accumulating. Mulkey (37) believes that scaling problems in geothermal resource utilization can be solved technologically and economically. Some remedies for scaling and corrosion problems are (1) to keep air out of the well pipe, wellhead, and piping system; (2) to keep CO_2 in solution by pressurizing the system; (3) to use cooling towers of wood to prevent metal corrosion and scaling; (4) to avoid conditions in which harder forms of SiO_2 are deposited; and (5) to construct equipment so that scale can be removed easily.

According to Tiball and Woodbury (55) current flash distillation techniques for water desalination at temperatures below 300° F cause a scale to form that is composed of the major minerals $CaCO_3$, $Mg(OH)_2$, or $CaSO_4$, and minor minerals $Fe(OH)_3$ and SiO_2. These authors cited a Soviet article suggesting that the best method to combat scale is to introduce seed crystals of the approximate composition of scale formers, let the scale form on these, remove them, and clarify the crystals for re-use. In this way, the heat exchanger surface is kept free from scale.

Reinjection

Reinjecting brines into the producing formations is not a new technique, but it has special considerations for geothermal resource use. Fluid from oil wells contains considerable natural brines, and for many years such brine has been separated from the petroleum and reinjected in nearly unchanged condition except for lowered temperature.

Brine disposal in Western Kansas oilfields was not successful in shallower formations because of plugging and insufficient capacity of the disposal formation. It was successful when reinjected into deeper sand formations through abandoned producing wells. By June 1942, for example, 255 million barrels of brine from 10 producing formations or zones had been reinjected into non-oil productive portions of 14 disposal formations or zones (20).

Reinjection of geothermal brine in the Imperial Valley was undertaken by Union Oil Co. (43). Most of the flow of the River Ranch well (8,100 feet deep and flowing 15,000-16,000 bpd of steam and brine of which 20-25 percent of total mass flow is usable as steam) was used to test production of the fluid which was reinjected into the Hudson well three-quarters of a mile away. The Hudson well was shallower than 7,000 feet and was larger (26,000 bpd) than the test well, so it was not on stream all of the time during reinjection. Initially it was necessary to overcome 200 psi wellhead pressure with a transfer pump. The reinjection rate was about 20,000 bpd and during the 1-year test, about 3 million barrels were reinjected. An estimated 4.5 million barrels of fluid were extracted from the River Ranch well and the difference represents vented or utilized steam. There were no reinjection problems during the year and apparently no detrimental effects on the wells. Otte (43) believes that it was a freely circulating geothermal fluid system because brine chemical composition was essentially unchanged during the year. In the period from the 1964 reinjection to about 1970, substantial deposits were formed in the pore and fracture spaces. Otte believes these deposits were caused by a mixture of irrigation and geothermal fluids and recommends testing chemical compatibility of fluids before reinjection.

At The Geysers, the 20 percent of original steam that is not lost to evaporation contains boron and ammonia which are harmful to plants and fish, respectively. For several years, this waste water has been reinjected into a nonproducing well at the rate of 400 gallons per minute without any difficulty (62).

ENVIRONMENTAL IMPACT OF GEOTHERMAL BRINE EXTRACTION AND DISPOSAL

The wise use of geothermal resources should be planned to consider the effects on the environment of fluid extraction from the reservoir and all intermediate steps up to and including waste disposal. Three major environmental areas with different problems are (1) the subsurface; (2) the surface; and (3) the atmosphere. Several factors that could affect these environmental areas are discussed in the paragraphs that follow. Environmental concern for initial stages of geothermal exploration are presented in reports of the U.S. Department of the Interior and two of its Bureaus (34, 59, 62).

Subsurface

Resource Life

The useful life of a geothermal resource depends upon the rates of extraction and recharge of its heat energy, recoverable water, and dissolved minerals. A long resource life is economically desirable because of costly well and surface pipes and extraction plants. Wise and efficient geothermal resource utilization, therefore, should be carefully planned and monitored so that its heat, water, and mineral constituents are not depleted and the equilibrium of the subsurface environment is disturbed as little as possible. If thermal wells are drawn down too fast, pressure loss may cause flashing to steam below ground, with resulting mineral precipitation and plugging of the reservoir. Therefore, it is necessary to space wells and limit production.

Water replenishment could be a major problem if potable water is extracted and then used and discarded into a different recharge basin than that of its source. Dissolved mineral constituents believed to be mostly leached from the rocks with only small amounts supplied by magmatic sources, could become depleted, especially those available only in trace amounts. Such depletion could have a negative effect on mineral recovery but a positive one on disposal of waste brine. Helgeson (24) believes that the Imperial Valley reservoir is so large that proposed extraction of minerals, water, and heat would not result in depletion of these commodities.

Reinjection of untreated natural brines (except for lowered temperature) was discussed under the technology section. If any mineral precipitation took place underground because of supersaturation and lowered temperature, it apparently caused no problems. A geothermal brine, from which some water and heat are extracted, presumably could cause such a problem. Thus, it may be necessary to remove some dissolved ions from a waste brine to prevent plugging, rather than for mineral marketing. Cost of producing a mixed-salt precipitate to prevent plugging should be much less than the cost of producing pure minerals for marketing. Each brine proposed for reinjection should be carefully studied for any treatment needed to prevent plugging of wells and rock pores.

Subsidence

Mare Island Naval Base in the San Francisco Bay area of California has subsided several feet, creating problems because it is almost at sea level. Subsidence is attributed to withdrawal of petroleum from reservoirs beneath the bay. The Great Valley in Central California (the San Joaquin and Sacramento Valleys) has subsided as much as 26 feet in the past 100 years, supposedly from extraction of water drawdown for irrigation purposes (35). Extraction of geothermal fluids without replenishment could cause subsidence with varying effects underground such as closing of permeability channels in the geothermal deeper reservoir and disruption of near-surface potable water reservoirs.

Subsidence in geothermal areas is under study; at Wairakei the subsidence has occurred in an area of about 16 square miles around the geothermal producing field which is about 0.5 square mile in area. Between 1961 and 1968, maximum subsidence was about 2.3 feet which represents 3 percent of the fluid volume lost during the period (25). Subsidence of about 5 inches has occurred at a distance of 7 miles from wells at Cerro Prieto. Because the Imperial and Mexicali Valleys are in a very active tectonic location, it may be difficult to distinguish between tectonic subsidence and subsidence from geothermal resource development. Several leveling surveys are taking place in Imperial Valley to record tectonic activity (about one-fourth of an inch per year subsidence) before geothermal extraction is well developed (35).

Earthquakes

The possibility of triggering earthquakes during geothermal fluid extraction or reinjection of waste products should be carefully considered. Changes in fluid temperature, pressure, volume, or composition are factors in both extraction and reinjection techniques that should be especially examined. Experience in oilfield engineering technology is considered essential to avoid increased seismic activity caused by reinjection of brines.

Surface

Environmental effects of geothermal resource exploitation would be most noticeable at the earth's surface where both land and water may be affected.

Land

Land subsidence would tend to disrupt drainage patterns and in the Imperial Valley might affect canals and slopes of land under cultivation, as well as buildings. Wellheads, solar ponds, pipelines, and final treatment plants should be esthetically designed and maintained to blend with the surrounding scenery. If reinjection is undesirable, a possible means of disposing of the waste products (after steam, water, and/or mineral extraction) would be surface stockpiling of a dry brine effluent cake of the type sought by Office of Saline Water (OSW) research (39-41). Such a stockpile would have to be protected from precipitation to prevent dissolution and possible runoff contamination. Extensive area or height of stockpiles might cause local subsidence. The possibility of underground storage in abandoned mines should be considered, although transportation costs may preclude such disposal if mines are distant.

Water

Groundwater resources, water reservoirs, irrigation water, and streams and lakes would have to be protected from pollution by warm process cooling water or brine waste, whether it is reinjected or stockpiled.

Atmosphere

Noise suppression at geothermal facilities would have to be considered for equipment at the wellhead where steam often is allowed to blow into the atmosphere in flow rate tests. Also noisy, but capable of being suppressed, are steam/brine separators, steam/solid cyclones, pipelines carrying steam or steam-entrained water, large pumps, and plant equipment. Toxic gases such as H_2S, CO, NH_3, HCl, and CH_4 and particulate matter would have to be removed or reduced to levels acceptable for air effluents; particulate matter likewise has to be considered from operations in which steam or hot brine could pollute the atmosphere. However, geothermal power probably would provide less air pollution (especially SO_2) per Btu obtained than a fossil fuel.

The technology to handle most of the environmental problems mentioned is available and good design and cost analysis in the planning stage of any geothermal facility should enable reasonable compliance with reasonable pollution standards and good esthetic practice.

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