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Geochemistry of geothermal fluids and well scales, and potential for mineral recovery

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Abstract

Although the potential use of geothermal brines for simultaneous energy and mineral production is significant, only a few mineral recovery systems are currently in commercial operation. Selected metal concentrations reported in fluids and scale deposits that are of interest to economic geologists include the following.

Metal	Fluid range, mg/kg	Scale range, wt.%
Ag	0–1.4	0–89
As	0–114	0–12
Au	0–0.08	0–6.4
Cu	0–8	0–21
Zn	0–1160	0–15.9
Pb	0–650	0–55.8
Pd	0–0.002	0–0.0024
Pt	0–0.05	0–0.016

Geothermal fluids and scale deposits vary considerably in composition. Hyper-saline geothermal fluids encountered primarily in sedimentary basins exhibit significant concentrations of minerals. In many locations near active volcanoes, concentrations of valuable metals are too low to be detected or have not been reported. Metal transport and mobility in geothermal fluids is commonly constrained by concentrations of ligands, temperatures, pH and redox state. Natural or controlled precipitation of minerals from geothermal fluids commonly occurs by decreasing temperature/boiling, dilution, increasing pH, reaction with sulfides and redox reactions. To date, the vast majority of mineral recovery projects have been conducted at the laboratory and pilot scale. New processes and technologies to recover minerals from geothermal fluids may be developed in the future in an effort to improve the economics, development and sustainability of geothermal resources.

Keywords: geochemistry; geothermal fluids and well scales; mineral recovery

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1. Introduction

Geothermal fluids have been recognized for many years as important sources of a variety of mineral resources. It is believed that most hydrothermal solutions obtained these dissolved components by reaction of water with cooling magmas or reactions with rocks through which water passed. Some examples of mineral-rich, modern hydrothermal systems are the Salton Sea geothermal brines in southeastern California, geothermal brines beneath the Cheleken Peninsula on the Caspian Sea, and oilfield brines of the Mississippi Salt Dome Basin (White, 1981). Table 1 presents representative compositions of these hydrothermal solutions, together with a number of geothermal brines containing low concentrations of metals encountered worldwide. All of the brines are aqueous solutions containing primarily sodium, potassium, calcium and chloride. They contain significant, but lesser, amounts of other alkali metals, alkaline-earth metals, and halides. As shown in Table 1, ore metals, such as iron, manganese, zinc, lead, and copper are present in a few brines. However, the majority of geothermal, geopressurized and high temperature oilfield brines exhibit lower salinities and lower ore metal concentrations than the three cases mentioned above (Ellis and Mahon, 1977). This paper will focus primarily on the geochemistry

Table 1
Analyses of geothermal fluids (by AA, ICP, IC and wet methods)

mg/kg	1	2	3	4	5	6	7	8	9	10	11	12
Li	194	219	327	45	2	27	27	6	44	0.3	11.7	13.2
Na	53,000	47,600	65,500	2850	407	2190	8300	2300	4800	212	1050	1250
K	16,700	12,600	12,450	927	64	400	2210	300	800	27	210	210
Rb	170	67					11	1		0.04	2.2	2.9
Cs	20	19					39	0.7	17	< 0.02	1.7	2.5
Mg	33	114	400	< 0.35	0.007	0.3	0.5	0.7	0.7		0.1	0.04
Ca	27,400	21,500	23,700	75	8	10	521	60	250	1.5	2.2	12
Sr	411	1043		2.8	0.4	1.4	16					
Ba	203	992	2260				11					
Fe	1560	3733	4160		< 0.01		1.5			0.1	< 0.01	< 0.01
B	257	221	282	119	9.9	27	9.4	60	206	0.6	48	29
Al	2	0.5	4.2		1.5		0.05					
SiO_2	> 461	> 430	> 510	> 711	> 599	> 650	> 864	> 600	> 740	> 480	> 805	> 670
NH_3	333	725		4	1.8			1.7		0.1	2.1	0.2
F	15	0.5		2	15.5	5	2.4	1.6	3	1.9	7.3	8.4
Cl	151,000	134,000	131,000	5730	438	3650	16.03	3950	9000	197	1740	2210
Br	99	87			0.32	2	17.7			0.45	5.7	5.5
I	20	6					0.6				0.8	0.3
CO_2	1600	14,600		7800	4300		44		5500	55	128	17
H_2S	15	45		160						7.3	< 1	1
SO_4	64	25		5	196	69	2	60	30	61	8	28

(1) Salton Sea USA; McKibben and Hardie, 1997.
(2) Brawley USA; Gallup, unpublished results.
(3) Imperial USA; McKibben and Hardie, 1997.
(4) Coso USA; Moore et al., 1989.
(5) Dixie USA; Bruton et al., 1997.
(6) Roosevelt USA; Unocal well file, 1980.
(7) Cerro Prieto, Mexico; Mercado and Hurtado, 1992.
(8) Miravalles, Costa Rica; Vaca et al., 1989.
(9) El Tatio, Chile; Ellis and Mahon, 1977.
(10) Hvergerdi, Iceland; Ellis and Mahon, 1977.
(11) Broadlands, New Zealand; Ellis and Mahon, 1977.
(12) Wairakei, New Zealand; Ellis and Mahon, 1977.
(13) Rotokawa, New Zealand; Ellis and Mahon, 1977.

of geothermal fluids and wells scales and the potential for mineral recovery at active geothermal energy extraction systems. For a comprehensive review of mineral recovery from other sources, see the work of Barnes (1997) and references therein.

2. Discussion of geothermal energy resources

Masses of throughput at geothermal energy extraction or oil-field production facilities, coupled with high concentrations of metals in solution, have made mineral recovery from these fluids attractive. Geothermal power generation facilities produce (1) steam only, (2) steam and water, and (3) water only from deep wells. The fluids are processed through energy extraction systems at the surface before being injected back into the geothermal reservoir through offset injection wells (Fig. 1). This process is somewhat analogous to solution mining and oil recovery waterflooding technology, except that substantially greater volumes of fluid are produced through surface handling equipment (Anderson and Richie, 1968). As an example, in the process of generating 250 MWe from a liquid-dominated geothermal steam flash plant, up to 175,000 m^3 of brine may be processed per day. At a concentration of only 1 mg/kg, ~150 kg of a metal passes through the example plant each day. Such amounts of metals have attracted the attention of mining engineers and economic geologists (Barnea, 1979).

13	14	15	16	17	18	19	20	21	22	23	24	25
10.2		4.7				17	21.9		81		215	
1525	282	1210	1730	1300	2800	5000	1977	29,000	31,500	43,000	76,140	59,200
176	54	137		225	625	990	558	5500	9500	270	409	538
						5	2.1					
						4.5	0.7				14	
	89	0.1	149	0.03	0.05	0.1	< 0.5	30	4	620	54	1730
50		46	580	21	53	320	128	18,500	4380	1620	19,710	36,400
						4.5	2.4		70	680	400	1100
						0.3			37		235	61
	1370	0.03	167			< 0.4	1.6		19		2290	298
102				58	57	312	7300		125		390	
		0.28				0.1	0.31					
> 430	> 170	> 460	92	> 610	> 600	> 510	> 700	> 470	> 950	> 110		
3.2						4	439				409	39
6.6						0.9			4			
2675	1220	1750	4630	2200	4800	9100	4135	81,000	65,400	67,000	157,000	158,200
							8.4				120	870
0.2							4.1					
55			28			5000			280	1250	32	
	1.7					1.5			2.4			
120	1460	138	33	28	16	7	26	470	20	210	309	310

(14) Tatun, Taiwan; Ellis and Mahon, 1977.
(15) Ohtake, Japan; Ellis and Mahon, 1977.
(16) Onikobe, Japan, Sanada et al., 1995.
(17) Mak-Ban, Philippines; Gallup, unpublished results.
(18) Tiwi, Philippines; Gallup, unpublished results.
(19) Salak, Indonesia; Gallup, unpublished results.
(20) Mote Amiata, Italy; Vitolo and Cialdella, 1995.
(21) Asal, Djibouti; Hirsch, 1997.
(22) Milos, Greece; Karabelas et al., 1989.
(23) Geopressurized well, USA; Unocal well file, 1980.
(24) Cheleken, Russia; Barnes, 1997.
(25) Mississippi Salt Dome Basin oilfield USA; Carpenter et al., 1974.

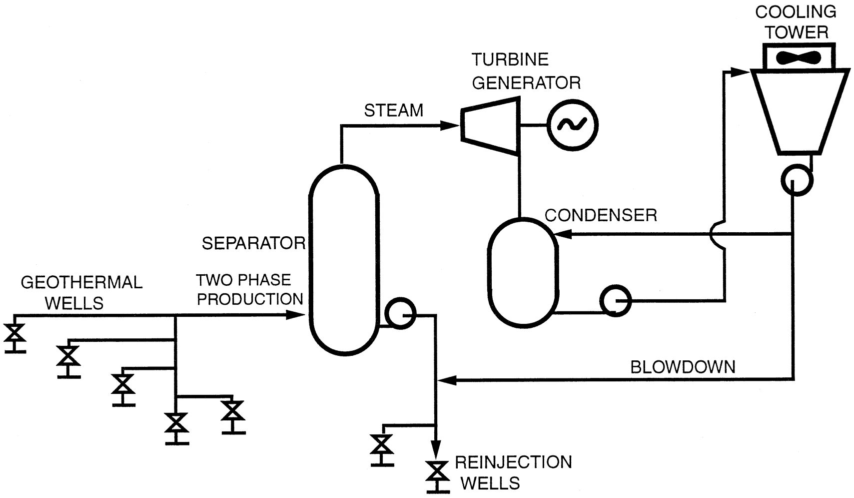

Fig. 1.

Over the past 30 years, electric power production from geothermal sources has blossomed into a mature industry in many countries. The current capacity of geothermal electric production is about 9000 MWe (Huttrer, 1995). The earliest commercial, geothermal mineral recovery process consisted of boric acid 'mining' from steam wells at the Lardarello, Italy field at the beginning of the century (Cataldi et al., 1970). Hyper-saline brines, such as those that have been produced at the Brawley, CA, Imperial, CA, Salton Sea, CA, Milos, Greece and Asal, Djibouti geothermal fields, typically contain the highest concentrations of base and precious metals (Skinner et al., 1967; Clark and Williams-Jones, 1990). Mineral scales deposit from most geothermal brines at some stage of processing. These scales may contain intriguing concentrations of potentially valuable metals, even though the brines from which they precipitate may be rather dilute.

The discovery of metals in geothermal brines and precipitates has led to a plethora of metal value estimates, research studies, and proposed and developed processes. However, to date, very few commercially viable processes have been utilized to recover minerals simultaneously with energy (Hoyer and Ferrell, 1984). This paper summarizes the occurrence and concentrations of precious and base metals in brines and scales, and reviews the present status of mineral recovery endeavors in the geothermal energy industry. A brief summary of origins, and mechanisms of transport and precipitation of these metals are also provided.

3. Discussion of mineral recovery

3.1. Precious metals

Precious metals, silver, gold, palladium and platinum, are generally present in geothermal brines in trace concentrations (low $\mu g/kg$ range). These metals may be sufficiently low in concentration to escape detection. Methods employed in precious metal analyses of geothermal brines and scale deposits have included: (1) neutron activation; (2) fire assay; (3) atomic absorption, AA; (4) emission spectrography, ES; (5) inductively-coupled argon plasma, ICP; (6) ion chromatography; and (7) evaporative or adsorption concentration of brine followed by the above techniques (Harrar and Raber, 1984; Paramonova et al., 1987). Tables 2 and 3 present the concentrations of precious metals reported in various geothermal brines and precipitates, respectively.

The reported concentrations of precious metals in geothermal brines generally agree with calculated concentrations derived from experimental solubility data (McKibben et al., 1989). Some important solubility studies of precious metals that potentially re-

Table 2
Precious metal values in geothermal brines

Location	μg/kg				Reference	Method
	Ag	Au	Pd	Pt		
Salton Sea, USA	1400				Ellis and Mahon, 1977	AA—atomic absorption
	45	< 0.06		50	Harrar and Raber, 1984	Fire Assay/AA
		0.4	< 0.2	0.3	McKibben et al., 1990	ICP-MS
		0.5	1.3	0.5	McKibben et al., 1990	ICP-MS
	240	80	< 20	< 20	Gallup, unpublished results	ICP-MS
	160	10	< 2	< 2	Gallup, unpublished results	ICP-MS
Brawley, USA	65	< 2	< 2	< 2	Gallup, unpublished results	ICP-MS
Raft River, USA	< 380	0.082		< 5	Harrar and Raber, 1984	Fire Assay/AA
Mississippi Salt Dome	< 4	< 0.1			Saunders and Rowan, 1990	ICP-MS
Milos, Greece	200				Karabelas et al., 1989	AA
Cerro Prieto, Mexico	4				Ellis and Mahon, 1977	AA
Cheleken, Russia	0.62				Paramonova et al., 1987	Extraction/AA
Rotokawa, New Zealand		1.5			Brown and Roberts, 1988	AA
Broadlands, New Zealand	0.5				Ellis and Mahon, 1977	AA
	8	1.5			Brown, 1986	AA
	18.9	1.03			Brown et al., 1996	ICP
	5.7	0.5			Brown et al., 1996	ICP

late to geothermal brines include: Au in sulfide solutions (Seward, 1973; Shenberger and Barnes, 1989); Au in sodium chloride and hydrogen sulfide solutions (Hayashi and Ohmoto, 1991); Ag in chloride solutions (Seward, 1976; Gammons and Williams-Jones, 1995); Ag in sulfide solutions (Gammons and Barnes, 1989); and Pd and Pt in chloride solutions and geothermal brines (McKibben et al., 1990; Hsu et al., 1991).

Precious metals may be transported in geothermal brines as chloride or bisulfide complexes depending on the relative concentrations of the appropriate lig-

Table 3
Precious metal values in geothermal scale deposits

Location	mg/kg				Reference
	Ag	Au	Pd	Pt	
Salton Sea, USA	70,000				Skinner et al., 1967
	3400				Maimoni, 1982
		15.7	0.012	0.013	McKibben et al., 1990
	50,000	14	24	158	Gallup, unpublished results
	174,000				Gallup, 1995a
	890,000	820	< 10	< 10	Gallup, unpublished results
	70,000	< 10	< 10	< 10	Gallup et al., 1995
Brawley, USA	17,200	2	0.4	< 0.2	Gallup, unpublished results
Mississippi Salt Dome	110	< 0.005			Saunders and Rowan, 1990
Milos, Greece	5000				Karabelas et al., 1989
Cerro Prieto, Mexico	22,900	270			Clark and Williams-Jones, 1990
Rotokawa, New Zealand	30	70			Ellis and Mahon, 1977
Broadlands, New Zealand	200	55			Ellis and Mahon, 1977
	174,000	54,000			Brown, 1986
Kawerau, New Zealand	294,000	64,000			Brown, 1986

ands in solution (Seward, 1982; Brown, 1989; Krupp and Seward, 1987). Studies suggest that bisulfide complexes, $M(HS)_x^y$, predominate in most geothermal brines, where M is Ag, Au, Pd or Pt. However, chloride complexes, MCl_x^y, become more important in the hyper-saline brines. Complexation of silver in ammonia-rich brines, $Ag(NH3)_x^+$, also cannot be discounted (McKibben and Hardie, 1997). According to Seward (1982), precious-metal chloride complexes may be de-stabilized upon: (1) decreasing temperature, (2) dilution, (3) increasing pH, and (4) reduction, resulting in metal deposition. In contrast, precious metals may deposit when bisulfide complexes are de-stabilized by any process that decreases reduced-state sulfur activity, i.e., boiling, metal sulfide precipitation, dilution, oxidation, and simultaneously decreasing pH and oxidizing hydrogen sulfide, H_2S. Details of precious and base metal geochemistry are discussed in the work of Barnes (1997).

Precious metals have been recovered from geothermal brines in naturally-occurring scale deposits, by use of reducing agents and by adsorbents. Only traces of palladium and platinum have been reported in geothermal scale deposits or precipitates (Table 3). On a pilot scale, a carbon adsorption process was developed to recover platinum from Salton Sea brines (Gallup and Ririe, 1994). Brown (1986) discovered gold and silver in scale deposits from New Zealand geothermal brines containing very low concentrations of metals. Gold and silver recovery were enhanced by passing brine across steel and copper plate collectors (Brown and Roberts, 1988; Brown et al., 1996). Recovered metal values from these brines have generally been insufficient to merit commercial process installation, however. Silver was observed to co-precipitate with metal sulfide and iron silicate scales at the Brawley and Salton Sea fields, respectively (Gallup, 1995a; Gallup et al., 1995). Forms of silver detected in these scale deposits included the native metal, Ag, cerargyrite, AgCl, and dyscrasite, Ag_3Sb. High concentrations of arsenic and antimony in the scales were a serious obstacle to extracting silver. Low concentrations of silver are deposited in barite scales from the oilfield brines of the Mississippi Salt Dome Basin (Saunders and Rowan, 1990).

Similar to the New Zealand experience described above, scale deposits collected at a geothermal field were recently found to be enriched in silver and gold, even though the metal concentrations in brine are below reporting limits (Table 4) (D.L. Gallup, unpublished results). In this example, gold and silver were deposited in flash-separator vessels where apparently de-stabilization of $Au(HS)^{2-}$ and $Ag(HS)^{2-}$ complexes occurred. The native metals were associated with galena, PbS, and magnetite corrosion product, Fe_3O_4, suggesting reduction by metal sulfides and/or by steel surfaces, respectively (Hyland and Bancroft, 1989). Precious metals were not detected in scales deposited in production wells or re-injection piping at this field. This result implies that metal precipitation may be variable within a given field or brine-handling process.

Precious metals have not been reported in brines or scales produced from many geothermal fields (Peralta et al., 1996). Brines commonly contain precious metals below analytical reporting limits (typically < 20 μg/kg). Thus, the presence of traces of precious metals in geothermal brines and scale deposits may be easily overlooked. Whether this is due to lack of analyses of precious metals in brines and scale deposits, analytical errors/uncertainties, or real absences of the metals is unknown.

The potential for precious and/or other metal recovery from geothermal fluids varies considerably

Table 4
Some geothermal scale compositions from a field in Southeast Asia

Analyte	wt.%		
	Composite 1	Composite 2	Composite 3
Al_2O_3	6.4	8.18	8.11
CaO	1.79	6.74	2.32
K_2O	1.88	1.97	1.9
MgO	0.36	4.37	0.11
Na_2O	3.25	1.79	1.56
Fe_xO_y	2.25	6.01	2.89
SiO_2	54.2	55.4	54.3
Cl	1.87	0.29	0.13
MnO	0.11	0.79	0.14
TiO_2	< 0.01	0.03	0.01
CuS	1.8	0.95	4.45
PbS	0.94	0.86	3
Sn	1.07	Not determined	Not determined
ZnS	1.63	0.94	1.34
Ag	12.09	8.33	10.6
Au	0.7	0.06	0.34
Total	90.34	96.71	91.2

as a function of host rock. In sedimentary basins, such as Salton Sea and Asal, basaltic rocks are potential sources of precious and platinum group elements. McKibben et al. (1990) detected precious metals in hematite-epidote-rich veins, mudstones and sandstones at Salton Sea. Gold in orebodies on the edges of the Salton Trough is hosted by metamorphic gneisses interlayered with schists and intruded by granite. By contrast, gold-depositing geothermal systems in the Taupo, New Zealand volcanic zone are hosted by rhyolites, greywackes and andesitic lava flows (Krupp and Seward, 1987). Other fields, where precious metals have not been detected in brines or precipitates, commonly are located near recent volcanic activity. These fields generally contain host rocks dominated by andesitic flows, lahars, breccias and their tuffaceous equivalents (Sussman et al., 1993; Halbouty, 1981; White, 1981). Although no one rock type appears to be enriched in gold, silver or platinum group metals, chemical sediments occurring as interflow units in volcanic terranes and iron-formation typically lack these precious metals (Romberger, 1988).

3.2. Base metals

Similar to precious metals, base metals are generally present in geothermal brines in trace concentrations (low mg/kg range). The exception is the hyper-saline brines, vide supra. Tables 5 and 6 present the concentrations of selected base metals reported in various geothermal brines and precipitates from around the world, respectively. Geothermal brines may also contain the metals, antimony, arsenic, cadmium, chromium, cobalt, iron, mercury, molybdenum, nickel, selenium, thallium, tin, titanium, vanadium, etc., albeit typically at trace concentrations (Maimoni, 1982).

Base metals may also be transported in produced geothermal brines as chloride or bisulfide complexes depending on the concentrations of ligands in solution (Hemley et al., 1992). In the majority of geothermal brines, manganese, lead and zinc are present in greater concentrations than copper. The former metals are expected to be present dominantly as chloride complexes (Wood et al., 1987; Bourcier and Barnes, 1987; Seward, 1984). Copper forms both chloride and bisulfide complexes in most geothermal brines (Crerar and Barnes, 1976). In hyper-saline brines, most base metals likely speciate as chloro-complexes (Barrett and Anderson, 1988). The deposition of base metals from geothermal brines, primarily as sulfides, may occur during production and handling of geothermal brines. Chloride and/or bisulfide complexes of the base metals may be de-stabilized as a result of, (a) reduction in brine

Table 5
Base metal values in geothermal brines (by AA or ICP)

Location	mg/kg						Reference
	As	Cu	Mn	Pb	Sb	Zn	
Salton Sea, USA	12	5.5	1400	91		520	Ellis and Mahon, 1977
			1390	91		506	Duyvesteyn, 1992
	10	4	760	70	1	280	Gallup, 1995a
		8	1560	84		790	Skinner et al., 1967
Brawley, USA		1.2	1340	240		825	Gallup, unpublished results
Imperial, USA			1280	650		1160	Duyvesteyn, 1992
Mississippi Salt Dome	< 0.3	< 0.02	64	53	< 0.075	222	Saunders and Rowan, 1990
Asal, Djibouti			131	3		32	Hirsch, 1997
Milos, Greece		0.2	30	2		3	Karabelas et al., 1989
Monte Amiata, Italy	114				10.3		Vitolo and Cialdella, 1995
Cerro Prieto, Mexico		0.005	0.64	0.005		0.006	Ellis and Mahon, 1977
Wairakei, New Zealand		0.001	0.001	0.001		0.002	Ellis and Mahon, 1977
Broadlands, New Zealand		0.0006	0.001	0.0008		0.0006	Ellis and Mahon, 1977
Cheleken, Russia	1	1.4	46.5	9.2		3.1	Ellis and Mahon, 1977
Matsao, Taiwan		0.035	28	0.5		8.8	Ellis and Mahon, 1977

Table 6
Base metal values in geothermal scale deposits

Location	wt.%						Reference
	As	Cu	Mn	Pb	Sb	Zn	
Salton Sea, USA			0.42	0.011			Skinner et al., 1967
		1	0.67	1.3		0.11	Maimoni, 1982
		0.02	0.03	76		0.07	Maimoni, 1982
		0.1		55.8		1	Gallup et al., 1990
		0.4		6.1		13.7	Gallup et al., 1990
		0.3	3.9	6.3		15.9	Gallup and Featherstone, 1992
	9	30	0.1	0.1	6	0.1	Gallup et al., 1995
	1	2	0.1	0.1	14	0.1	Gallup et al., 1995
Brawley, USA		0.2	0.1	0.4		12.8	Gallup, unpublished results
				80		3	Gallup, unpublished results
Mississippi Salt Dome	0.0006	0	0.0032	2	0.0012	0.48	Saunders and Rowan, 1990
El Tatio, Chile	12			0.01	1.5	0.01	Ellis and Mahon, 1977
Asal, Djibouti		Present		Present		Present	Hirsch, 1997
Milos, Greece		3	0.2	33.8		15.5	Karabelas et al., 1989
Cerro Prieto, Mexico		13		8.3		8.9	Clark and Williams-Jones, 1990
Rotokawa, New Zealand		0.0025		0.02		0.015	Krupp and Seward, 1987
	0.4			0.005	30	0.01	Ellis and Mahon, 1977
Broadlands, New Zealand		21.2				0.79	Brown, 1986
	8			0.005		0.02	Ellis and Mahon, 1977
Kawerau, New Zealand		13		1.1		0.35	Brown, 1986

temperature and (b) exsolution of acidic gases during steam flashing (Karabelas et al., 1989). Sulfides, arsenides and silicates of base metals deposit as scales in wells and surface equipment primarily as a result of decreasing temperature and increasing pH (Gallup et al., 1990; Gallup et al., 1995). Base metal alloys are present as a result of reducing reactions in barite-rich scales retrieved from Mississippi Salt Dome Basin oilfield tubular scales (Saunders and Rowan, 1990).

Base metals have been recovered from geothermal brines in naturally-occurring sulfide scale deposits. At the Brawley geothermal field, metal sulfide scale, consisting of sphalerite, galena and pyrrhotite, was mechanically drilled out of production well retrievable liners and surface piping. The scale was then sent to a smelter as ore feedstock (Messer, 1983). Metals may also be recovered from scales by selective leaching (Wong and Shugarman, 1987) and bio-leaching (Premuzic et al., 1992).

A variety of processes have been developed to recover base metals, especially from hyper-saline brines. These processes include: (1) selective precipitation of the hydroxides using lime or caustic (Berthold, 1978), or high pH steam condensate (Gallup and Featherstone, 1992); (2) sulfide precipitation using sulfide or polysulfide solutions, or hydrogen sulfide in steam (Bartlett et al., 1980; Schultze, 1984); (3) cementation with active metals (Maimoni, 1982); (4) selective electrodeposition with varying current (Gallup, 1993); and (5) solvent extraction or ion exchange (Byeseda and Hunter, 1985; Duyvesteyn, 1992). Although these processes have been tested in the laboratory and at the pilot scale, none has yet to be fully commercialized. However, solvent extraction of zinc from Salton Sea brine will likely be the first full-scale, commercial, base metal recovery process to be utilized in the geothermal industry (J.L. Featherstone, 1997, personal communication). Estimated net revenue accruing from this zinc recovery process ($4,800,000/year) is significant when compared with electric power net revenue ($11,000,000/year) for a typical Salton Sea power plant (Duyvesteyn, 1992). Silver and manganese recovery is also contemplated at Salton Sea, in addition to zinc recovery. Revenues generated from recovery of these three metals may eventually be as important as power generation revenues.

Owing to differences in host rocks at geothermal fields, base metal concentrations are generally higher in sedimentary basin brines than igneous (basaltic) basin brines. McKibben et al. (1990) present compelling evidence for base metal dissolution from shales in the Salton Sea reservoir. Zinc, lead and copper were originally incorporated in detrital and diagenetic carbonate minerals and then released during shale metamorphism. Similar origins of base metals likely occur at the Brawley, Imperial, Asal, Milos and Cheleken fields (Lebedev, 1973). Sands and shales also host the lead and zinc-rich brines from the Mississippi Salt Dome Basin (Carpenter et al., 1974).

3.3. Miscellaneous minerals

Owing to a wide variety of chemical constituents found in geothermal brines, recovery of non-precious and non-base metals, gases and other elements has been extensively studied or commercially developed (Steingrimsson et al., 1992). Although many studies have been conducted to recover these constituents, commercial recovery has generally been slow to materialize. However, some examples of miscellaneous chemicals that have been recovered or considered for recovery are summarized below. Selective precipitation and evaporation typically recover salts and other compounds, whereas gases are generally recovered by adsorption techniques.

— Wei (1982) conducted a preliminary evaluation of brine mineral values and concluded that promising species for recovery at geothermal fields include Li, B, CO_2, NH_3, Br_2, I_2 and Sr. Proposed methods to recover these species included solvent extraction, refrigeration, brine electrolysis and sulfate precipitation.

— Extraction of potash and other salts from brines at the Cerro Prieto, Mexico geothermal field has been extensively studied over the past two decades in pilot scale tests (Mercado and Hurtado, 1992). Production of up to 100,000 tons per year of KCl is under evaluation.

— Alkali and alkaline-earth salts were recovered unsuccessfully from Salton Sea brines several decades ago in evaporation ponds (Werner, 1970). Salts have also been recovered using evaporators/crystallizers in Iceland and Russia (Kristjansson, 1992).

— Recovery of lithium by solvent extraction, alumina or carbonate precipitation, and MnOH adsorption has been laboratory and pilot tested (Schultze, 1984; Ooi et al., 1986).

— Boron may be recovered from brines or steam condensates as boric acid or borax (Allegrini et al., 1992). Boron is commercially recovered as borax at a rate of 12,000 tons per year at the Lardarello, Italy geothermal field. Using boron-specific ion exchange resin, boron in brines or steam condensates may also be recovered after elution with strong acid. Outside of Italy, efforts to remove boron and arsenic from geothermal fluids have been directed primarily to safe discharge of fluids to the environment (Recepolgu and Beker, 1991; Gallup, 1995b; Buisson et al., 1979).

— Amorphous silica and alumina may be recovered for use in paper, construction materials, detergent, insulation, etc. (Harper et al., 1995; Carter and Hotson, 1992). Biotechnology has been successfully demonstrated to produce high-grade silica from iron-rich Salton Sea sludge (Premuzic et al., 1992). Large-scale silica production has yet to be implemented.

— Carbon dioxide and other gases have been recovered from produced geothermal gases (Lindal, 1992). Elemental sulfur, sulfurous acid and sulfuric acid may be recovered as by-products of hydrogen sulfide oxidation (Hirowatari, 1996). Only small-scale production of gases and products has been achieved.

— Iodine and bromine are reported to be recovered from Cheleken thermal waters in Russia (Lindal, 1992). Warm oilfield brines in the area of Magnolia, AR are also commercial sources of bromine (Barnes, 1997).

— Calcium carbonate, strontium sulfate and barium sulfate may be recovered from geothermal brines by a variety of precipitation techniques (Harper et al., 1992). Commercial production of these minerals is limited.

4. Conclusions

Although a variety of economic analyses have shown that mineral recovery from geothermal fluids is a potential source of revenue, only a few recovery processes have been installed to date. Generally, electric power, thermal power or petroleum productions are the primary sources of revenue in brine-handling operations. Mineral recovery is generally viewed as a secondary revenue source. In an effort to make geothermal energy production more viable and cost competitive with other energy sources, recovery of precious metals, base metals and miscellaneous chemicals has been extensively studied. Until recently, most mineral recovery efforts were conducted on laboratory, pilot and demonstration scales, with only a few processes being commercially operated. Attempts to commercialize new processes and technologies to recover minerals primarily from hypersaline geothermal fluids continue. At a few geothermal fields, mineral recovery projects may become increasingly important in the economics, development and sustainability (decrease of mineral scale precipitation in re-injection piping and wells) of geothermal resources.

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