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## SURVEY OF GEOTHERMAL SOLID TOXIC WASTE

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#### SUMMARY

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Geothermal energy resources have the potential for substantial development within the next few decades. This will involve the use of large volumes of geothermal working fluids for this energy utilization. These working fluids may contain substantial amounts of dissolved solids which may precipitate during the energy extraction process. Thus, large quantities of solid wastes, some of which may be toxic, are expected from development of geothermal resources.

The current literature was examined to determine the kinds and amounts of solid wastes expected. Data available to date indicate that these solid wastes were not highly toxic; however, additional work is needed to better characterize them. In a typical case, brine precipitate constitutes about one-half of the total solid wastes, well cuttings and drilling mud one-quarter, and the balance from scale and sludges. Total solid wastes were estimated to be about 30,000 tonnes per year for a hypothetical 100-MWe geothermal electric plant operating with 285<sup>o</sup>C geothermal brine typically found in the Salton Sea, California, area.

Techniques available for processing and disposal of the brine effluent are discussed. These include ponding-landfill, conventional wastewater treatmentlandfill, and minerals byproduct recovery. It appears that experience from related and mature water treatment technologies can be drawn upon and adapted for use in geothermal applications. Laboratory-scale and bench-scale studies with geothermal brine effluents are needed. The mature technology available for the handling of coal ash from fossil-fired power plants would appear to be transferable in part to treatment and disposal of solid geothermal wastes since, surprisingly, the quantities and composition of these solid wastes are similar. Data available from conventional water treatment and from disposal of coal ash have been used to estimate the costs of disposal of solid wastes from a hypothetical 100-MWe geothermal power plant. The cost for disposal of the solid waste amounts to 3 mil/kW•h. This assumes that the solid wastes will be shipped by truck to a landfill site which has been specifically prepared for geothermal

solids. The cost for a clarifier/filter brine disposal system was estimated to be 3 mil/kW•h, giving a total solids waste treatment cost of 6 mil/kW•h. This corresponds to 8% of the costs of geothermal energy at 7¢/kW•h. This preliminary study is encouraging. It appears that further conceptual engineering studies, drawing upon these mature technologies, would be beneficial in solving the solids waste disposal problems in geothermal energy development.

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The recovery of metals and minerals from geothermal solid wastes was also investigated. Calcium silicate (CaSiO<sub>3</sub>) is potentially of some value, but requires the addition of lime in a clarification/filtration step. The recovered CaSiO<sub>3</sub> has a potential value approximately equal to the costs of the lime used by this water purification process. The total potential value of iron, manganese, zinc, lead, and silver from spent Salton Sea geothermal brine was estimated to be about 53 mil/kW·h based upon 100% minerals recovery; however, this estimate does not account for costs involved in brine treatment to recover, separate, and purify these metals. More data are needed to obtain a better estimate of the potential value of recovered minerals from geothermal brines. Priority should be given to the accumulation of more data on the composition of solids produced from geothermal processing, with emphasis on the levels of toxic materials that are found in these solids.

#### I. INTRODUCTION

#### A. STATEMENT OF PROBLEM

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Geothermal energy resources have the potential for making substantial contribution to the energy needs of the U.S. within the next few decades.<sup>1</sup> Geothermal energy will probably receive its greatest use for generation of electric power because of the relative ease of transportation of electric energy and the remoteness of geothermal resources to major population and industrial centers. However, geothermal energy also has the potential in utilization for industrial process heat and for space heating.

Geothermal resources are of relatively low temperature compared to the operating temperatures of modern fossil fuel or nuclear power plants. This will necessitate the use of large volumes of geothermal working fluids for this energy utilization. These working fluids may contain substantial amounts of corrosive elements or compounds either as dissolved gases or solids. The very nature of energy extraction processes lowers the temperature and pressure of the geothermal working fluid. This results in the dissolution of gases and, in many cases, the precipitation of solids during the energy extraction process. Thus, any major utilization of geothermal energy is expected to produce large quantities of byproduct gases or solids. Some of these gases (e.g.,  $H_2S$ ) or solids (e.g., arsenic, cadmium, mercury) are corrosive or toxic and are harmful to the environment if released. Since it may not be practical or feasible to inject these wastes back under ground, provisions must be made for their removal or treatment, and subsequently, their ultimate disposal.

#### B. OBJECTIVES

It is the objective of this report to examine the literature to determine the kind and amounts of solid toxic wastes expected from development of geothermal resources--in particular, to look at the various stages of a typical geothermal energy utilization process in order to identify the types and amounts of toxic

wastes generated. A search was made to identify mature, developed technologies which potentially can be modified or adapted for the treatment and disposal of the wastes generated in geothermal energy development. This approach has been most helpful in obtaining estimates for solid and fluid waste disposal costs which are not generally available from the fledgling geothermal industry. The potential for recovery of minerals and/or metals from these wastes was also investigated. Areas where more research and/or further studies are needed toward solution of solid toxic waste treatment and disposal are indicated.

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#### II. SOURCES OF GEOTHERMAL SOLID WASTES

#### A. SOURCES

A list of sources of the solid wastes that may be produced by geothermal power generation is given. Sources typically are (1) production well filter wastes, (2) well drilling wastes, (3) pipe scale wastes, (4) flash tank solid wastes, (5) settling pond solid wastes or brine precipitate, (6) injection well fluid wastes, (7) H<sub>2</sub>S removal/treatment wastes, (8) cooling tower treatment/ blowdown wastes, and (9) solid wastes from treatment of makeup water. The sources of these solids wastes from typical geothermal power operation are shown schematically in Figure 1. An approximate distribution of the solid wastes generated from a liquid-dominated geothermal resource is shown in Figure 2. Brine precipitates resulting from temperature and chemical changes in the brine from extraction of energy constitute about half of the solid waste generated; well cuttings and drilling mud constitute about one-quarter; with scale, solids from cooling water treatment,  $H_2S$  abatement, and other miscellaneous sources making up the balance. Some of the constituents in these solid wastes may be toxic and therefore require special disposition and/or treatment to protect the environment. The composition, treatment, and disposition of these solid wastes will be discussed in further detail in subsequent sections of this report.

Geothermal resources may be conveniently categorized, based upon the thermodynamic state of the thermal system, into vapor-dominated and liquid-dominated resources.

#### 1. Vapor-Dominated Resources

Vapor-dominated resources have been developed to a greater extent at this time (principally at The Geysers in California) than have liquid-dominated resources, although liquid-dominated resources occur over a wider geographical area and potentially represent a more abundant resource.<sup>1</sup> Power generation from vapor-dominated resources produces relatively small quantities of solid wastes,

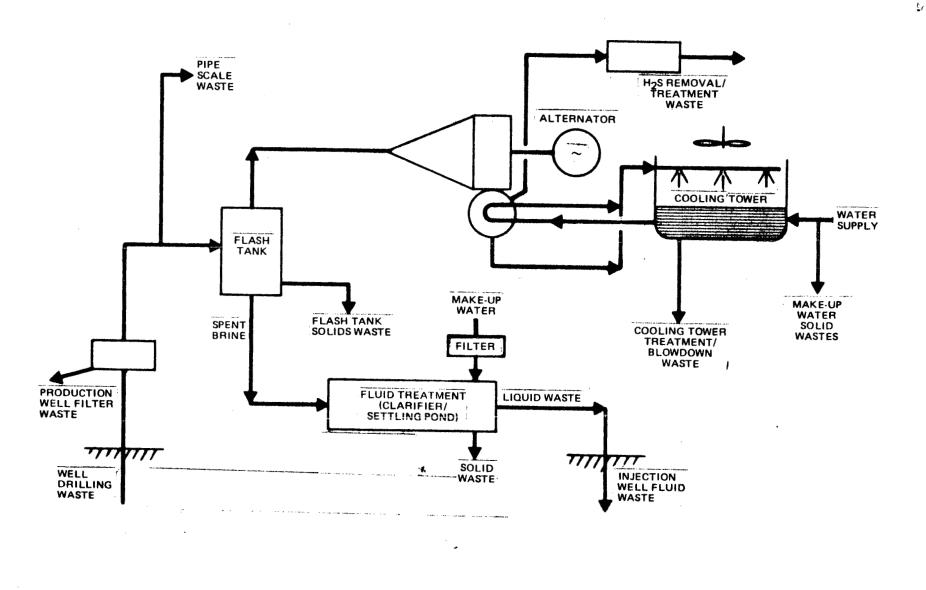


Figure 1. Sources of Geothermal Solid Wastes

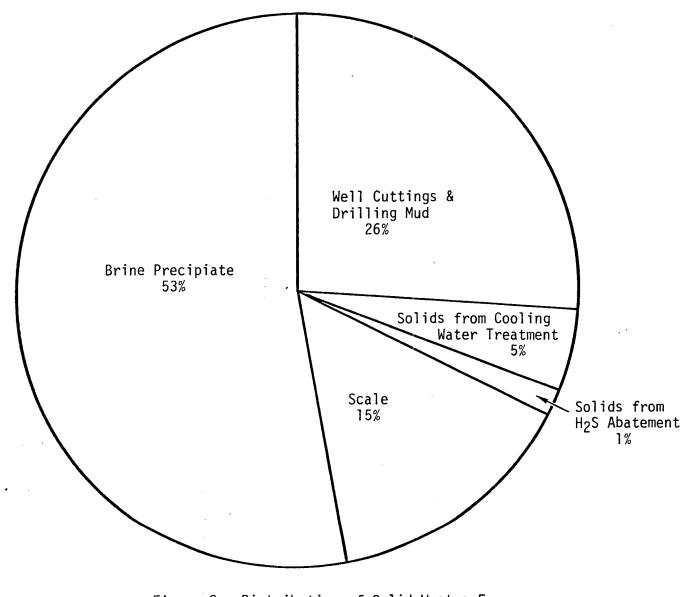


Figure 2. Distribution of Solid Wastes From Development of a Liquid-Dominated Geothermal Resource

primarily because of the nature of the vapor transport mechanism of this kind of system, wherein mostly volatile materials are carried to the surface. Toxic components which could result in the generation of solid wastes from a vapordominated geothermal resource are given in Table 1. The quantities shown are typical inputs to a 100-MWe power plant at The Geysers, California.

Constituent	Average Input Flow for 100 MW of Power Generation (1b/h)
Hydrogen sulfide (H <sub>2</sub> S)	360
Boric acid (H <sub>3</sub> BO <sub>3</sub> )	150
Arsenic (As)	0.032
Mercury (Hg)	0.008

	TABLE 1						
TOXIC	CONSTITUENTS	0F	STEAM	AT	THE	GEYSERS <sup>1,2</sup>	

Boric acid is seen to constitute the largest source of solid toxic waste. The amount and kind of solid toxic waste from  $H_2S$  would depend upon the abatement system utilized. Some of these  $H_2S$  abatement systems generate toxic materials such as sludges, copper sulfate, or metal sulfides.

#### 2. Liquid-Dominated Resources

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Liquid-dominated geothermal resources in general contain much higher concentrations of solids than are found in vapor-dominated resources. As a rule, the concentration of toxic components increases as the concentration of total dissolved solids increases. Geothermal brines containing up to 300,000 ppm dissolved solids have been reported.<sup>1,2</sup> Table 2 shows a typical composition of potentially toxic constituents contained in brine from a Salton Sea, California, geothermal source.<sup>3</sup>

Constituent	Concentration of Dissolved Solids (ppm)
Manganese (Mn)	3030
Boron (B)	2240
Barium (Ba)	1520
Zinc (Zn)	1280
Lead (Pb)	310
Arsenic (As)	56
Copper (Cu)	5

	TAE	BLE	2		
TOXIC	CONSTITUENTS	IN	SALTON	SEA	brine <sup>3</sup>

In current practice, thermal energy for power generation is extracted from liquid-dominated geothermal resources by (1) flashed steam/steam turbine cycles or (2) by use of organic Rankine binary cycles, particularly in the case of low-grade, i.e., low-temperature, energy sources.

Considerable variability is found in fluid temperature and composition from field to field and, in fact, from well to well in some fields.

#### B. WASTES FROM GEOTHERMAL ACTIVITIES

The wastes generated in the various activities from development of geothermal energy resources are discussed below.

#### 1. Well Cuttings and Drilling Muds

Assumptions based on drilling experience in the Imperial Valley suggest that 600 tonnes of drilling mud and well cuttings will be produced in creating a typical 1,500-m well.<sup>4</sup> This is based upon an estimate of 50 production wells in operation at one time. Injection of 100% of the spent brine (or brine makeup

water equivalent) is assumed in order to inhibit land subsidence. This is estimated to require 15 injection wells to dispose of the spent brine. Over a projected 30-year lifetime of the facility, it is expected that both the production and injection wells will have to be replaced from time to time. Between exploration, initial well drilling, injection monitoring wells, and replacement wells over the life of the power plant, approximately 13 wells would be drilled in an average year, resulting in 8,000 tonnes of drilling mud and well cuttings. The composition of a typical drilling mud is given in Table 3.<sup>5</sup>

COMPOSITION OF DRILLING MUD <sup>og</sup> Percentage Component Formula (volume)						
Bentonite	Na0.33 <sup>A1</sup> 2.67 <sup>S1</sup> 3.6 <sup>0</sup> 20 <sup>(OH)</sup> 2	5.39				
Quebracho	Organic, wood extract	0.45				
Caustic soda	NaOH	0.32				
Lignin (tannathin)	C <sub>212</sub> H <sub>171</sub> O <sub>41</sub> N <sub>3</sub> S	0.12				
Sodium bicarbonate	NaHCO <sub>3</sub>	0.09				
Cottonseed hulls*	Organic					
Walnut shells*	Organic					
Mica*	KA1 <sub>3</sub> Si <sub>3</sub> 0 <sub>10</sub> (OH) <sub>2</sub>					

TABLE 3 COMPOSITION OF DRILLING MUD<sup>5</sup>

\*Materials added to control loss of circulation by plugging the fissures causing the loss.

The well cuttings are not likely to be hazardous in themselves but may be sufficiently contaminated with brine and drilling mud to require disposal as a hazardous waste. Acurex<sup>6</sup> has sampled drilling muds and cuttings at six locations. A summary of the results from the analysis of these samples is given in Table 4. In only one case (mud from a well near Westmoreland, California, where the Ra-226 activity exceeded 5.0 pCi/g), did these residues exceed the Resource Conservation and Recovery Act (RCRA) criteria for hazardous wastes.<sup>7</sup> Drilling muds are variable and often of a proprietary formulation, with typical muds containing metals such as barium or chromium and organics that may decompose to yield toxic substances.<sup>4</sup>

Acurex Sample No.	Location	рН	Radioactivity (pCi/g)	As	Ba	Cd (Nei	Cr utral l (µg,	Pb Extract /L)	Hg t)	Se	Ag
G-6	East Mesa, CA	12.0	1.0	<20	<300	<5	<20	<20	<1	<20	<20
G-9	Niland, CA	8.4	2.1	<20	<300	<5	<20	<20	<1	20	<20
G-16	Westmoreland, CA	8.8	5.9	41	6800	<5	<20	<20	<1	120	<20
G-27	The Geyers, CA (near Unit 13)	9.6	0.4	20	<300	<5	<20	<20	<1	<20	<20
G-30	Steamboat, NV	9.3	1.0	260	<300	<5	<20	<20	<1	<20	<20
G-31	Humboldt, NV	9.8	1.6	140	500	5	27	400	<1	<20	<20
G-32	Desert Peak, NV	9.1	1.5	<20	<300	<5	39	<20	<1	<20	<20

 TABLE 4

 SUMMARY OF ANALYSES FROM DRILLING MUDS<sup>6</sup>

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#### 2. Production Well Filterable Solids

The filtrate from production wells may consist of sand and/or other small aggregates small enough to be carried up by the production well fluid flow. It may also contain some dislodged pipe scale. No analytical data appears to be available for the composition of this type of solid waste.

#### 3. <u>Scale</u>

Estimation of scale formation rates is difficult due to a combination of site dependency, process dependency, and the results of any pretreatment applied. A value of ~4,500 tonnes/year may be derived based on an assumption that 0.014 wt. % of the brine will deposit as scale.<sup>8</sup> The compositions of these scales can be expected to be predominantly calcium carbonate and amorphous silica with a variety of metals co-deposited.<sup>3</sup> Table 5 gives the composition of geothermal scale for the Geothermal Loop Experimental Facility (GLEF) at Salton Sea, California.<sup>9</sup> Some of the metals incorporated into the scale, such as barium, may be present at levels deemed to be hazardous.

#### 4. Precipitated Solids/Clarifier Solids

The largest source of solid wastes from liquid-dominated geothermal power operations is generally from the precipitation of supersaturated species from the spent brine. In order to minimize plugging of injection wells, it will be necessary to eliminate the supersaturated condition by promoting precipitation and filtering out suspended solids. The magnitude of these compounds has been estimated at 0.05 wt. % of the brine required. For a 100-MWe plant, this solid waste amounts to 16,000 tonnes/year.<sup>10</sup> This waste may be expected to contain silica, heavy metal sulfides, calcium carbonate, entrapped salts, and possible contributions from additives to promote precipitation.<sup>11</sup> The composition of the precipitated solids<sup>3</sup> is shown in Table 6. The composition of solids from clarifier operation<sup>12</sup> is also shown in Table 6. Toxicity is expected to derive from the heavy metal sulfides containing antimony, arsenic, and mercury, and from the substantial salinity content.<sup>6</sup>

Constituent	Geothermal Scale
Major Component	cs (wt. %)
SiO <sub>2</sub> Al Fe Ca Mg Na K Ba S C1 Mn Pb Zn	25.8-70.3 $0.03-1.0$ $0.88-17.7$ $1.08-4.4$ $0.01-1.0$ $2-10$ $0.58-1.7$ $0.010-5.3$ $0.24-2.6$ $0.89-4.8$ $0.67-1.2$ $0.32-1.6$ $0.06-1.02$
Minor Componen	
As Sb Ag Sr Cu Li Rb Cs B Ni Mo Se Ti Th Cr U V Ga Be	100-400 50-1200 80-1200 200-1100 400-3800  40-50  200-700 3-100 3-30  80-800  3-30  

TABLE 5 COMPONENTS OF GEOTHERMAL SCALE<sup>9</sup>

Constituent	Dissolved Solids <sup>3</sup>	Precipitated Solids <sup>3</sup>	Clarifier Solids <sup>12</sup>				
Major Constituents (wt. %)							
Si0 <sub>2</sub>	0.238	96.9	74.4				
AL	0.005	0.02					
Fe	0.102	0.98	5.44				
Ca	10.16	1.15	2.29				
Mg	0.037	0.003					
Na	25.92	0.10	0.26				
K	4.57	0.60	0.27				
Ba	0.152	0.05	4.80				
S		0.1	2.12*				
C1	57.84	0.1	8.6				
Mn	0.303	0.80	0.35				
Pb	0.031	0.029	0.1				
Zn	0.128	0.170	0.1				
Minor Constituents (ppm)							
As	56	200					
Sb							
Ag		20					
Sr	1730	30	30,200				
Cu	5	160	5,000				
Li	630	10					
Rb	265	20					
Cs	55						
В	2240	600					
Ni	1						
Мо	20						
Se							
Ti							
Th							
Cr							
U							
V	3						
Ga Be							
De		<b></b>					

# COMPOSITION OF DISSOLVED SOLIDS, PRECIPITATED SOLIDS, AND CLARIFIER SOLIDS FROM A LIQUID-DOMINATED GEOTHERMAL SOURCE<sup>3,12</sup>

TABLE 6

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\*All of the sulfur in the geothermal clarifier solids is in the form of sulfate,  $SO_4$ .

#### 5. Injection Well Fluid Wastes

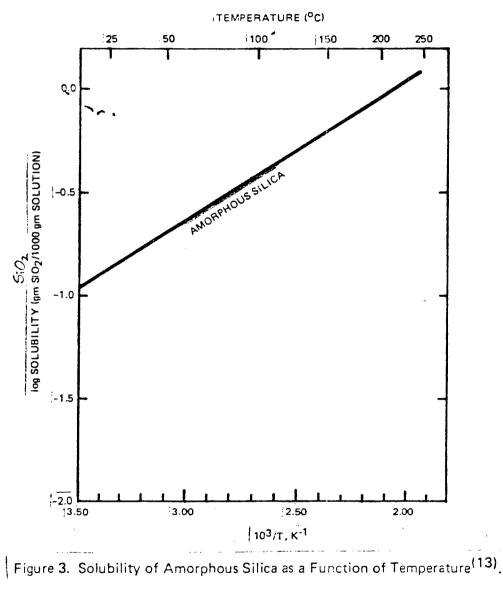
The reject fluid from the geothermal power plant potentially can serve as a vehicle for disposal of most of the dissolved solid toxic wastes when injected back into an aquifer. From data in Table 2, it can be determined that, in general, concentrations of the toxic elements are considerably below saturation, even at ambient temperature.\* Thus, injection of the spent brine is a convenient means for disposal of these solid toxic wastes. Furthermore, 100% or near 100% injection may be required to mitigate subsidence and, on the other hand, may aid in recharge of the producing aquifer.

Brine injection is complicated by precipitation of silica in the utilization, and subsequent cooling, of the geothermal fluid. Figure 3 shows the solubility constant for amorphous silica as a function of reciprocal  $(1/T, K^{-1})$ temperature.<sup>13</sup> For example, in a brine at a well-head temperature of  $200^{\circ}$ C, utilized and rejected at  $100^{\circ}$ C, the solubility of amorphous silica decreases from about 1 g per 1000 liters to about 0.3 g per 1000 liters during this temperature decrease. Thus, the amount of silica that will precipitate (or exist in a supersaturated state) is appreciable. Further precipitation or supersaturation will occur if the reject brine is reduced to ambient temperature in the clarifier/ settling pond operation. The precipitation of silica has the tendency to occlude or cause co-precipitation of other dissolved ions present in the brine. Thus, the silica precipitate may, in this manner, contain heavy metals at concentrations sufficiently high to be considered toxic (see Table 6).

# 6. <u>Solid Wastes from H<sub>2</sub>S Abatement</u>

Hydrogen sulfide abatement operations from vapor-dominated geothermal power plant operations, such as The Geysers, California, generate significant amounts

<sup>\*</sup>However, precipitation of the toxic elements may occur due to chemical changes in the geothermal brine caused by loss of noncondensables such as CO<sub>2</sub>, changes in H<sub>2</sub>S concentration, or the use of additives.



of sulfur or sulfur-containing solid wastes. Some of these wastes such as sludges, copper sulfate, and metal sulfides are toxic and therefore require special handling for their disposal.

Brines from liquid-dominated geothermal resources such as found in Imperial Valley, California, contain substantially less hydrogen sulfide than present in fluids at The Geysers, but the quantities are still significant. The Brawley-Salton Sea area yields fluids containing ~3 mg of hydrogen sulfide per kilogram of brine.<sup>4</sup> For a 100-MWe power plant, this would represent an annual release of 100 tonnes. There are numerous competing processes for removal of hydrogen sulfide. If, for example, it is abated with 95% efficiency by the copper sulfate process (EIC, Inc.)<sup>14</sup> the resultant ammonium sulfate will contribute ~400 tonnes of solid waste. The product will probably be contaminated with boric acid but  $H_3BO_4$  does lend itself to recovery rather than disposal as a toxic substance.

#### 7. Wastes from Treatment of Makeup Water

One hundred percent fluid injection is required in many locations where geothermal power plants are to be located. Makeup water will be required to compensate for water losses in the power plant operation. Treatment of this makeup water may be required to prevent material problems within the plant and/or to maintain the injectivity with respect to the aquifer. These water treatment operations would be expected to generate solid wastes such as filterable insoluble solids and chemicals used in the treatment operation. These solid wastes would be expected to be similar to those generated by the usual or customary domestic water treatment operations. These solid wastes would not, in general, be considered toxic.

#### III. DESCRIPTION OF SOLID TOXIC WASTES

#### A. QUANTITY

The sources of solid waste from geothermal power were described in Section II. These sources were found to be drilling muds, precipitated solids from the brine, scale, and cooling water-treatment solids.

In order to illustrate the amounts of solid wastes involved in geothermal development, this study has selected a representation of conditions which might be found in the Brawley-Salton Sea area and incorporates values reported in "An Assessment of Geothermal Development in the Imperial Valley of California."<sup>4,15</sup> A 100-MWe generating station operating 6,500 h/year and utilizing brine at a downhole temperature of  $285^{\circ}$ C and a flow rate of 50 kg of brine per kilowatt-hour produced is assumed. The brine is assumed to contain 80,000 ppm total dissolved solids and 0.05 wt. % precipitatible solids.<sup>10</sup> The average annual amounts of solid wastes generated by this hypothetical power plant are shown in Table 7.

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AVERAGE ANNUAL SOLID WASTES GENERATED IN SUPPORT OF A 100-MW POWER PLANT\*

Solid Waste	Tonnes <sup>†</sup> /Year
Drilling mud & well cuttings	8,000
Scale	4,500
Brine precipitate	16,000
H <sub>2</sub> S abatement	400
Cooling water treatment	1,500
Total	30,400

\*Assuming 6,500 hours of operation per year using typical Salton Sea brines requiring 50 kg of brine per kilowatt-hour. \*1 tonne = 1000 kg = 2200 lb The total amount of solid wastes from this 100-MWe plant was estimated to be 30,400 tonnes/year. The quantities from the various operations of this 100-MWe Salton Sea geothermal power plant are shown in Figure 4. In this figure, the annual rates of production of waste solids have been averaged over 6,500 hours of operation per year. This average hourly rate assumes a continuous source of solids, such as the clarifier solids; it is not properly representative of an intermittent source, such as the well-drilling solids. However, it provides a ready means of comparing the relative magnitudes of the solid waste streams and the flow rate of the hot brine. For example, the clarifier solids production rate, 2,500 kg/h, is the predominant solids source. However, this value is quite small compared to the 5,000,000 kg/h of hot brine that are processed.

The geothermal power plant solids production shown in Figure 4 includes the entire geothermal power process from production wells to the injection wells. A byproduct recovery step has been included in the plant as a potential means of improving the overall economics of the plant by recovering mineral values from the brines. The exact type of byproduct recovery system that would be used is yet to be developed. At the present time, the most likely minerals that would be recovered are lead, zinc, silver, iron, and manganese.<sup>16</sup> The use of a byproduct recovery step is an option that will be very dependent on the economics of the recovery process. A settling/clarification step is used to separate the precipitated solids (mainly silica) from the brine. A clarifier is presently being used for this purpose in demonstration-scale facilities in the Imperial Valley.<sup>1/</sup> The clear overhead liquid from the clarifier is mixed with about 10% makeup irrigation water and injected into the geothermal source.<sup>18</sup> However, care must be exercised in maintaining chemical compatibility between the makeup water and the geothermal brine (particularly sulfates) to prevent plugging the aquifer formation.

It is informative at this time to compare some of the features of undeveloped geothermal power with a mature technology such as power generation from a fossil fuel such as coal, where much data are available. A comparison of the solid waste production from a 100-MWe coal-fired power plant with a hypothetical geothermal plant is made in Table 8. Data for two high-sulfur eastern coals,

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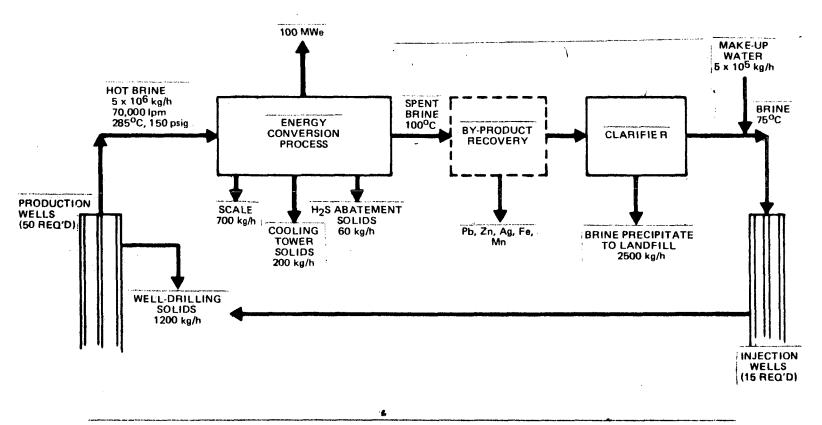


Figure 4. Solids Production From a 100-MWe Salton Sea Geothermal Power Plant\*

\*HOURLY RATES ARE BASED ON ESTIMATED ANNUAL PRODUCTION AVERAGED OVER 6500 OPERATING HOURS PER YEAR

	Estimated Solid Waste Production (tonnes/year)						
Energy Source	Ash	Sulfur Abatement <sup>a</sup>	Total				
Illinois No. 6 coal <sup>b</sup> (10,750 Btu/lb, 10 wt. % ash, 4 wt. % sulfur)	28,000	45,000	73,000				
Kentucky No. 9 coal <sup>b</sup> (13,100 Btu/1b, 11 wt. % ash, 4 wt. % sulfur)	25,000	37,000	62,000				
Montana Rosebud coal <sup>b</sup> (8,750 Btu/lb, 8.5 wt. % ash, 0.75 wt. % sulfur)	29,400	10,400	40,000				
Niland-type geothermal brine (high-salinity)	8,000 (drilling) 16,000 (prec. solids) 4,500 (scale) 1,500 (cooling water)	400	30,400				
East Mesa geothermal brine (low-salinity)	8,000 (drilling) 4,500 (scale) 1,500 (cooling water)	<b>40</b> 0	14,000				

TABLE 8 COMPARISON OF COAL AND GEOTHERMAL SOLID WASTE PRODUCTION - 100-HWe SITE

<sup>a</sup>Based on dry flue gas desulfurization product equal to four times the weight of sulfur burned.<sup>20</sup> <sup>b</sup>Based on 33% conversion efficiency of coal to electricity; composition from

"Based on 33% conversion efficiency of coal to electricity; composition from Reference 21.

Illinois No. 6 and Kentucky No. 9, and a low-sulfur western coal, Montana Rosebud, are included in Table 8. The solid waste production for coal is estimated on the basis of the coal ash that would be produced and the solids that are introduced by dry flue gas scrubbing of the sulfur in the coal. The solid waste from geothermal brines is estimated on the same basis as described previously in Table 7. It is found that the total amount of geothermal waste solids is about equal to the amount of solids that are produced just from the ash in coal burning. The amount of solids that are produced from high-sulfur eastern coals is approximately twice that of geothermal brine solids. The burning of Illinois No. 6 coal produces 73,000 tonnes/year of solid waste, and 62,000 tonnes/year are estimated to be produced from the burning of Kentucky No. 9. A low-sulfur western coal produces approximately 40,000 tonnes/year. A high-salinity geothermal brine such as the Niland type will produce about 30,400 tonnes/year of total solids, with about a little over half of these solids coming from the precipitated solids from the brine. A low-salinity geothermal brine such as the East Mesa type has very little precipitated solids. It is estimated to produce only 14,000 tonnes/year of waste solids. On the basis of this general comparison, it can be seen that the magnitude of the problem of disposal of geothermal solids does not significantly differ from that of burning coal. The technology from handling waste solids from coal burning has been well developed and could be applied to the disposal of geothermal solids.

#### B. COMPOSITION

The composition of geothermal brine has been studied by a number of investigators and is well documented.<sup>19</sup> However, the composition of the solids which are expected to be produced from processing of geothermal brines is not readily available. The composition of these solids is important to the estimation of the toxicity of the waste. There are some data available from the Niland site in the Imperial Valley. These data have been presented in Tables 5 and 6 and are also compared in Table 9, along with composition of waste solids from coal fly ash. The coal fly ash data have been included to provide a means of comparison of the expected geothermal solids with solids produced from use of other energy sources.

Two different solids compositions are available for geothermal solids. The first is the composition of precipitated solids from fresh geothermal brine that has been allowed to cool and settle. The second is the composition of solids that has been clarified and filtered such as that at the GLEF near Niland. The composition of these two solids differs significantly, especially in concentrations of silica, iron, barium, and strontium. This is probably due to some air oxidation which occurred during processing of the clarifier solids. This air oxidation produced the insoluble salts, iron hydroxide and barium and strontium

sulfate. However, the clarifier solids are most representative of solids which would go to a landfill site, and additional data on nonoxidized solids are not available.

In general, the precipitated solids from geothermal processing are very high in concentrations of silica, with minor amounts of iron, calcium, and manganese. This is also true for the scale that is produced in geothermal processing. These quantities are different from the coal ash in that very little alumina is present in the geothermal solids. In addition, the geothermal solids are high in zinc, arsenic, and lead. These quantities are much higher than are found in normal coal fly ash. The geothermal solids are very low in titanium, which is found in high quantities in coal fly ash. The high concentration of silica in the geothermal solids may be used as an advantage in that it may be recovered for industrial uses as silica or calcium silicate. This may require some processing of the solids to remove some of the trace elements such as arsenic and lead. In addition, the high quantity of zinc in the solids may be recoverable. It should be noted that the geothermal data presented in Table 9 come from only one site. Since geothermal sites vary significantly in solids concentration, more studies should be made on precipitated solids and scale from other sites; in particular, evaluating the concentrations of trace metals such as arsenic and lead to provide a sounder basis for an evaluation of solids treatment processes.

#### C. TOXICITY

There are very little data available on the toxicity of solids that are produced from geothermal energy production. Acurex<sup>6</sup> has made one study of a variety of solid and liquid samples from various geothermal sources. The focus of this program was to evaluate solid wastes in comparison to the RCRA hazardous waste characteristics. Of 20 samples which were selected for analysis, only 5 exhibited corrosivity, radioactivity, toxicity, or bioaccumulation values which exceeded proposed or promulgated RCRA criteria for being considered hazardous solid wastes. The analyses of these five samples are presented in Table 10. These samples all came from Imperial Valley, California, sites. (Samples from

Constituent	Geothermal Brine, Dissolved Solids <sup>3</sup>	Geothermal Brine, Precipitated Solids <sup>3</sup>	Geothermal Brine, Clarifier Solids12	Geothermal Scale <sup>9</sup>	Coal Fly Ash22
**** <u></u>		Major Constitue	ents (wt. %)		
SiO <sub>2</sub> Al Fe Ca Mg Na K Ba S Cl Mn Pb Zn	0.238 0.005 0.102 10.16 0.037 25.92 4.57 0.152  57.84 0.303 0.031 0.128	96.9 0.02 0.98 1.15 0.003 0.10 0.60 0.05 0.1 0.1 0.80 0.029 0.170	74.4  5.44 2.29  0.26 0.27 4.80 2.12* 8.6 0.35 0.1 0.1	$\begin{array}{c} 25.8-70.3\\ 0.03-1.0\\ 0.88-17.7\\ 1.08-4.4\\ 0.01-1.0\\ 2-10\\ 0.58-1.7\\ 0.010-5.3\\ 0.24-2.6\\ 0.89-4.8\\ 0.67-1.2\\ 0.32-1.6\\ 0.06-1.02\end{array}$	57.4-63.4 13.8-14.2 2.5-3.2 2.1-3.8 0.47-0.63 1.2-1.9 0.74-0.82 0.17-0.41  0.007-0.075 0.007-0.028 0.007-0.075
		Minor Constitu	uents (ppm)		
As Sb Ag Sr Cu Li Rb Cs B Ni Mo Se Ti Th Cr U	56  1730 5 630 265 55 2240 1 20  	200  20 30 160 10 20  600   	 30,200 5,000        	$   \begin{array}{r}     100-400 \\     50-1200 \\     80-1200 \\     200-1100 \\     400-3800 \\     \\     40-50 \\     \\     200-700 \\     3-100 \\     3-30 \\     \\     80-800 \\     \\     3-30 \\     \\     3-30 \\   \end{array} $	14-132 3-26  410-700 56-137   25-43 9-50 19-198 6200-7800 26-30 28-71 9-29
V Ga Be	 3 			  50-100	86-327 43-178

i	A	R	.E	9	

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COMPARISON OF SOLIDS FROM GEOTHERMAL AND COAL ENERGY PRODUCTION

\*All\_of the sulfur in the geothermal clarifier solids is in the form of sulfate,  $SO_4^{-1}$ .

Characteristic: Analysis:	Corrosivity pH	Radioactivity Ra-226 ≥5 pCi/g or	EP Toxicity (mg/L)*			Bioaccumulation					
RCRA Limit:	$\leq 2$ or $\geq 12.5$	50 pCi/L	As	Ba	Cd	Cr	Рb	Hg	Se	Ag	- Potential Log P > 3
Clarifier sludge (GLEF near Niland)		78 pCi/g									
Brine (well near Niland)	1.6			363							
Solids (landfill, Imperial County)											Positive
Brine (well in northern Imperial Valley)		1320 pCi/L	14		4		83		5.1		
Mud pit (northern Imperial Valley)		5.9 pCi/L									

TABLE 10

EXAMPLES OF GEOTHERMAL BRINE AND SOLIDS WHICH EXCEED RCRA CRITERIA FOR HAZARDOUS WASTES<sup>6</sup>

\*Acid extracts and liquid sample filtrate

.

The Geyers geothermal steam fields and northern Nevada sites were not found to exceed RCRA limits in any category. The hazardous nature of the Imperial Valley samples is due to the high salinity of the brine at these sites.) However, the solids noted in Table 10 (clarifier sludge, landfill solids, and mud pit) are only hazardous due to high radioactivity or bioaccumulation potential. The chemical toxicity of these samples did not exceed RCRA limits.<sup>7</sup> Relatively low barium and strontium levels may be due to the formation of barium sulfate and strontium sulfate in the clarifier solids. These sulfates are considered nontoxic due to their extremely low solubility.<sup>23</sup> According to EPA hazardous waste regulations,<sup>7</sup> a solid waste exhibits the characteristic of EP toxicity if the extract from a representative sample of the waste contains any of the contaminants listed in Table 11 at a concentration equal to or greater than the maximum concentration given in Table 11. The waste will be designated by the EPA hazardous waste number of the toxic contaminant which causes it to be hazardous. The maximum allowable EP concentrations for the principle heavy metals found in geothermal solids are listed in Table 11.

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (milligrams per liter)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0

MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY<sup>7</sup>

TABLE 11

The Acurex study<sup>6</sup> provides only a limited amount of data on the toxicity of geothermal solids. In particular, much more data should be taken from high-salinity brine sources such as near the Salton Sea. In particular, the solid wastes produced at these sites should be more thoroughly studied.

#### IV. SOLID WASTE TREATMENT AND DISPOSAL

Current practices for treatment and/or disposal of solid wastes generated from geothermal power operations are discussed. Areas where current and mature practices from other technologies can potentially be applied for the disposal of toxic solid wastes from geothermal operations are pointed out. Potential byproduct minerals recovery from geothermal-derived solid wastes are also discussed, and finally, recommendations are made for further studies in areas where data are needed for solutions to the disposal of toxic solid wastes.

#### A. WELL CUTTINGS AND DRILLING MUDS

In current practice, solid wastes consisting of well cuttings are screened from the drilling fluid/mud during the drilling operation, and the drilling mud is circulated down the hole. In some cases, air or foam has been used as the drilling fluid.<sup>1</sup> The well cuttings go to a pit. If they are not contaminated, they may be buried at the location or else hauled to a conventional landfill. However, the cuttings may be contaminated with brine or, in some cases, brine containing toxic components such as boron, arsenic, lead, etc.<sup>8</sup> In this case, the cuttings should be hauled to a suitable disposal site. Drilling muds are customarily dried and then hauled to a landfill site or another suitable disposal site, depending upon their toxic material content.

#### B. PRODUCTION WELL FILTERABLE SOLIDS

The sand, small aggregates, dislodged pipe scale, etc., in this filterable solid residue would not be expected to contain sufficient toxic materials to require treatment or special handling unless the pipe scale is contaminated. In such an event, this solid waste could be combined with the scale waste for disposal.

#### C. SCALE

As indicated in Figure 2, scale can constitute approximately 15% of the solid wastes requiring disposal. Typical composition of scale was given in Table 5. Many factors influence the deposition of scale, <sup>3</sup> i.e., temperature, pH, chloride and sulfate ion concentration, and dissolved gases  $(CO_2, H_2S, NH_3)$ . In actual practice, scaling and plugging may result from one or more of the following: (1) precipitation and polymerization of silica and silicates; (2) precipitation of alkaline earths as insoluble carbonates, sulfates, and hydroxides; (3) precipitation of heavy metals as sulfides; and (4) precipitation of redox reaction products, e.g., iron compounds.

One of the major problems in geothermal energy conversion and injection systems is silica precipitation and scale formation. Monomeric silica in solution will not precipitate nor adhere until it starts to polymerize. The tendency to lessen polymerization can be achieved in several ways:

- . By maintaining a sufficiently high temperature to keep the silica solubility above saturation
- . By reducing turbulence in order to avoid fluctuations in the velocity gradients and collision of particles
- . By lowering the pH of the solution--a reduction in pH below 6.5 causes a substantial decrease in polymerization.

Many of the processes leading to deposition of scale from an aqueous solution would be expected to be reversible; thus, it is very likely that scale would exhibit some solubility to surface waters under ambient conditions. Thus, it is possible that any toxic substances present in the scale would be potentially leachable.

#### 1. Scale Removal

Scale removal methods include chipping, chiseling, hammering, and other fracturing methods. In some cases, it may be necessary to remove and discard the entire structure member, i.e., pipe or conduit. Dissolution of scale by use

of acids, solvents, or chemical complexing agents offers an alternative method for removal. Work is needed to investigate the feasibility of this approach.

#### 2. Scale Disposal

Solid waste scale and attached structural members such as pipe, plates, etc., can be disposed of by:

- 1) Hauling to a site suitable for toxic substances
- 2) Hauling to a landfill if nontoxic
- 3) Chemical dissolution with use of acids or complexing agents or thermal dissolution, i.e., autoclaving, or a combination of these techniques. This could be followed by separation of toxic and/or valuable components. The residue could then be disposed of at a suitable site. Here also, more work is needed to investigate this approach for disposal of scale.

#### D. BRINE EFFLUENT/PRECIPITATED SOLIDS

As pointed out in the previous section, the geothermal brines are often of high salinity and contain appreciable concentrations of elements such as arsenic, lead, boron, and fluoride, which may affect human, animal, fish, or plant life.

Most waste geothermal waters to be returned to the reservoir will be supersaturated with silica if there is to be optimum utilization of heat. Although amorphous silica may not deposit readily from water flowing in a pipe, separator, or heat exchanger, it is known to do so on concrete or brick surfaces. It will therefore, reduce the injectivity with time by blocking the aquifer formation, unless the chemical conditions are carefully controlled. Thus, treatment of the brines will have a major impact on the type and amount of solids which must be disposed of.<sup>24</sup> It is necessary therefore to adequately treat this brine effluent in order to maintain its injectability in the accepting aquifer. This will require treatment procedures to rectify its supersaturated condition with respect to dissolved solids.

# 1. Waste Processing Techniques

The ideal method for disposing the spent brine from geothermal power production would be the injection of all of the brine and its constituents back under ground. However, due to the temperature coefficient of solubility of solids in the brine, particularly silica, see for example Figure 3, it can be expected that some solids will come out of these highly saline solutions. Three processing methods which could be used for treatment of geothermal brines are: (1) ponding of the spent brine with injection of the clear liquor back under ground and landfill of any precipitated solids, (2) use of conventional water treatment technology for treatment of the brine so that any precipitated solids and other toxic materials may be removed as a solid product which is disposed of at a landfill site, with the injection of the wastewater, and (3) processing of the geothermal brine in such a way that minerals and useful byproducts may be recovered from the brine wherein solid wastes are disposed in a landfill, and the clear liquid is injected into the aquifer. These options for brine treatment are shown schematically in Figure 5.

#### a. Ponding - Landfill

A holding pond has been used at the East Mesa site for treatment of spent brine.<sup>4</sup> In this application, the brine that leaves the geothermal power plant is added to one end of a large holding pond. This holding pond has sufficient residence time so that liquid withdrawn from the other end of the pond is clear enough so that it may be injected back into the aquifer. Solids which accumulate in the pond may be dredged and then evaporated to dryness and transported by truck to a suitable landfill site. This method of treating the spent brine is successful in those cases where the salinity of the brine is low. At the East Mesa site, the salinity of the brine is low compared to Salton Sea sites. The East Mesa site presently uses a closed-binary system with direct injection of the spent brine.<sup>25</sup>

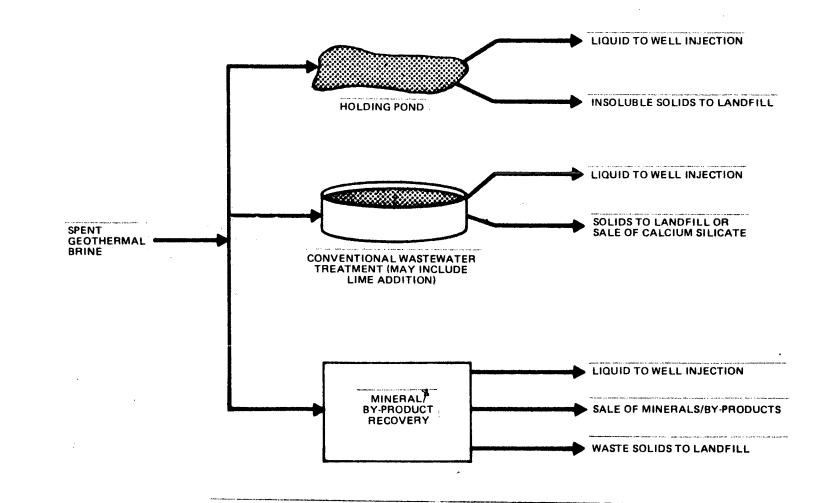


Figure 5. Options for Spent Geothermal Brine Treatment

This technology has been highly developed for solid waste disposal in other industries, for example, the use of an ash pond is the simplest and, historically, the most widely used ash disposal method for coal-fired power plants.<sup>26</sup> Water from any convenient large-volume source (such as from once-through cooling water or directly from power plant water intakes) is used to sluice both fly ash and bottom ash to disposal ponds. The transportation water that flows from the ponds is treated to meet pH requirements and returns to the body of natural water from which it came. As an option, the water may be returned to the power plant for reuse.

The ash pond for a coal-fired power plant is designed to accumulate ash over the entire life of the plant. A typical fly ash pond occupies 200 acres, and the bottom ash pond occupies 60 acres. A detailed study by  $TVA^{26}$  found that the costs of ash ponding are approximately 2 mils/kW·h (1981 \$). Smaller costs could be expected for a geothermal power plant utilizing this option because much less acreage would be necessary. The effluent water in this case would be returned to the aquifer.

### b. Water Treatment - Landfill

In the case of a geothermal brine which may have high salinity and high levels of toxic materials, one useful method of treatment of the brine will be to use conventional water treatment technology.<sup>27-29</sup>

The wastewater treatment technologies which are usually applied are sedimentation, filtration, and chemical precipitation.

### (1) Sedimentation

Sedimentation is a physical treatment operation that removes settleable solids from wastewaters. It is generally applied to raw wastewaters and to wastewaters that have been chemically treated to precipitate constituents. Any one of several configurations of settling ponds, tanks, and gravity separators may be used for sedimentation.

Sedimentation process efficiency is a function of temperature, hence viscosity, of the wastewater, the density and size of suspended particles, the amount and character of the suspended material, and the settling time. Gravity separation can normally remove 50 to 65% of the suspended solids.<sup>30</sup>

# (2) Filtration

Filtration is a solids-liquids separation technique to remove particulate matter from wastewater. It may be used instead of, or in addition to, sedimentation. In filtration, the wastewater to be treated is passed through a porous medium. Solids separation is accomplished largely by sieving action. The mechanisms involved in the removal of suspended or colloidal material from wastewater by filtration are complex and interrelated. The dominant mechanisms depend on the physical and chemical characteristics of the particulate matter and filtering medium, the rate of filtration, and the biological-chemical characteristics of the water. The mechanisms responsible for the removal of particulate matter vary with each treatment system.

Filtration can be accomplished by the use of: (1) microstrainers, (2) diatomaceous earth filtration, (3) sand filtration, or (4) mixed-media filtration. The microstrainer is a screen in the form of a partially submerged rotating drum or cylinder. Water flows continuously by gravity through the submerged portion from inside the drum to a clear-water storage chamber outside the drum. Cleaning is carried out by backwashing with sprays of product water. Removal efficiencies have been reported for the following parameters: suspended solids - 50 to 80%, biodegradable - 40 to 70\%, and turbidity - 60 to 76\%.<sup>30</sup>

### (3) Chemical Precipitation

Chemical precipitation is a chemical treatment process involving chemical addition, particle aggregation, and particle precipitation. This treatment process is used to assist the sedimentation of colloidal and highly dispersed particles in the waste stream by aggregation and coalescence of small particles

into larger, more readily settleable or filterable aggregates. Some dissolved (and unsaturated) inorganic constituents may also be precipitated by chemical coagulants. Thus, if there are dissolved toxic materials in the effluent, they, in all likelihood, will be precipitated in the process, thus perhaps requiring the precipitates to be treated in a toxic waste.

The function of chemical coagulations and mechanical flocculation of wastewater is the removal of suspended solids by destabilization of colloids and removal of soluble inorganic compounds, such as trace metals and phosphorus, by chemical precipitation or adsorption on chemical floc. Coagulation involves the reduction of surface charges of colloidal particles and the formation of complex hydrous oxides or precipitates. Coagulation is essentially instantaneous in that the only time required is that necessary for dispersing the chemical coagulants throughout the liquid. Flocculation involves the bonding together of the coagulated particles to form settleable or filterable solids by agglomeration. Agglomeration is hastened by stirring the water to increase the collision of coagulated particles. Unlike coagulation, flocculation requires definite time intervals to be accomplished.

In general, coagulation reactions vary significantly with changes in pH; therefore, pH adjustment of the wastewater may be required to achieve optimum conditions. With proper design of the coagulation/flocculation system and sedimentation tank, removal efficiencies of 80 to 90% of suspended solids and 20 to 40% of dissolved solids can be readily attained.<sup>30</sup>

Silica-laden discharge waters have been successfully treated with slaked lime to precipitate silica and any arsenic, if present. The wastewater in the Otake geothermal field in Japan<sup>31</sup> is treated with slaked lime and ponded for about 1 hour. Colloidal silica is formed, polymerization ceases, precipitation and settling takes place, and the water can then be disposed of.

It has been shown that geothermal waters treated with a minor quantity of slaked lime produce a flocculant precipitate which consists essentially of hydrated calcium silicates.<sup>32</sup> The precipitates, which settle rapidly, can

easily be separated from the waters by decantation or filtration, and can be airdried to amorphous calcium silicates of low moisture content. When ignited, these precipitates give a pure and fine wollastonite. It was discovered that arsenic in the waters was also removed into the calcium silicate precipitate, particularly if the arsenic was first oxidized to arsenate by a small concentration of chlorine.

Extensive work was done at Wairakei and Broadlands on the lime treatment of geothermal waters.<sup>24</sup> It was found that the precipitation of silica by lime was considerably more efficient if the waters were aged to allow polymerization of silica. For Wairakei well waters and a holding temperature of  $85^{\circ}$ F, silica polymerization was almost complete within 2 to 3 h; for Broadlands waters, the time was ~ 30 min.

A continuous-flow pilot plant was operated at Wairakei and at Broadlands to treat 2,000 to 5,000 l/h of well water, and a larger plant to take the discharge of two to three wells was built at Broadlands. The optimum  $SiO_2/CaO$  ratio in the product was found to be 1.7 when the gel produced a high solid content and was easily filterable on a rotary-drum vacuum filter. Of the calcium silicate formed, 93% was recovered, and the treated water had a stable silica concentration of about 100 ppm and a much reduced arsenic concentration.<sup>24</sup>

The calcium silicate material is being evaluated for use as an insulant, an industrial filler, and a paint extender, as well as for use in low-density building blocks and high-temperature ceramics.

Alternative means of removing polluting elements from waters, such as filtering through clay minerals and flocculation with iron hydroxides, are being tried in New Zealand. The latter is particularly effective for arsenic removal.

#### c. Mineral/Byproduct Recovery

Due to the concentration of potentially recoverable minerals in the geothermal brine, there is interest in a viable technology to recover these minerals to improve the economics of geothermal energy development. As an option to clarification/filtration, lime may be added to the brine to bring down calcium silicates. It is estimated that a 100-MWe liquid dominated geothermal plant would require 2,500 kg/h of lime at a cost of 8.6 mil/kW·h. The recovered calcium silicate from this operation potentially has a value of 7.0 mil/kW+h. The wastewater treatment costs of single-stage lime addition with filtration are estimated to be 3.5 mil/kW.h. The actual value of the calcium silicate may depend on the purity and use of the material that is recovered. Recovery of calcium silicate is presently being done at Wairakei, New Zealand.<sup>33</sup> The potential recovered value of calcium silicate greatly exceeds the value of other minerals in the precipitated solids. A comparison of these values is given in Table 12. The value of the iron, manganese, zinc, and lead in the solids is less than 0.6 mil/kW-h.

Mineral	Concentration in Solids <sup>a</sup> (wt. %)	Estimated Annual Production <sup>b</sup> (tonnes)	Price <sup>C</sup> (\$/tonne)	Potential Value (mil/kW•h)
Si0 <sub>2</sub>	96.9	41,200 (as CaSiO <sub>2</sub> ) 21,300 (as SiO <sub>2</sub> ) <sup>3</sup>	100 34	7.0 1.1
Fe	0.98	308 (as Fe <sub>2</sub> 0 <sub>3</sub> )	840	0.4
Mn	0.80	176 (Mn metal)	730	0.2
Zn	0.17	37 (Zn metal)	810	0.05
Pb	0.03	7 (Pb metal)	620	0.1

TABLE 12 VALUE OF RECOVERABLE MINERALS FROM PRECIPITATED SOLIDS

<sup>a</sup>From Reference 3.

Based on a 100-MWe geothermal power plant operating 6,500 h/year. Total precipitated solids account for 500 ppm of the brine. From Reference 34.

The principal difficulty in the recovery of minerals from geothermal brine is the low concentration of valuable materials. In a 1974 literature review of mineral extraction techniques from geothermal brines, Blake<sup>35</sup> found that extracting minerals was technically feasible, but the major mineral products had little or no market value, and there were insufficient amounts of more valuable minor products.

A detailed review of various processes for recovering chloride salts from brines was made by Hazen Research<sup>36</sup> before developing their hydroxide precipitation process. They found that chloride recovery was only economically possible where large holding ponds for solar evaporation could be used. In addition, the requirement for injection of the spent brine back into the aquifer eliminates this possibility in the Salton Sea area and other geothermal sites where land subsidence may be a problem.

Development has been done on processes for the recovery of minerals from spent geothermal brine. Hazen Research developed a process for the Bureau of Mines based on the selective precipitation of iron, manganese, zinc, and lead as hydroxides. The process was based on the initial removal of silica by a thickener, followed by metals recovery by lime addition. Laboratory-scale<sup>37</sup> and pilot-scale tests<sup>33</sup> were run. However, the silica removal step was not very effective, and it was difficult to process the lime precipitates to obtain iron, lead, and zinc in materials pure enough to be of commercial interest. Only about 50% of the precipitated zinc can be usefully recovered from the Hazen process.

The Bureau of Mines has also funded the development of a sulfide-precipitation process by SRI International.<sup>16</sup> In this process,  $Na_2S$  is added to the brine, followed by solids recovery in a thickener. The recovery of Pb, Zn, and Ag as sulfides was demonstrated. However, Fe and Mn sulfides were also recovered (they are considered undesirable) along with about 20 other elements in minor amounts. The recovered product had the composition of 31% ZnS, 5% PbS, 9% FeS, 14% MnS, 41% SiO<sub>2</sub>, and the 20 other elements. This process is currently being studied to improve the sulfide precipitate grain size and to produce a Zn product suitable for industrial Zn reduction.

The potential value from the recovery of iron, manganese, zinc, lead, and silver is not great, as shown by the data in Table 13. The total potential value of these minerals is 53 mils/kW h. This includes no costs for brine treatment or further ore treatment for separation and recovery of the byproduct minerals. A detailed economic analysis of this process should be made.

Brine Constituent	Concentration <sup>b</sup> (ppm)	Price <sup>C</sup>	Recovered Value (mils/kW∙h)
Iron	272	\$0.84/kg Fe <sub>2</sub> 03	11.4
Zinc	207	\$0.81/kg Zn	8.4
Manganese	685	\$0.73/kg Mn	25.0
Lead	53	\$0.62/kg Pb	1.6
Silver	0.5	\$257/kg Ag	6.4
Total			52.8

TABLE 13 POTENTIAL VALUE OF MINERAL RECOVERY FROM SPENT SALTON SEA GEOTHERMAL BRINE<sup>a</sup>

<sup>a</sup>Based on processing 50 kg/kW h with 100% mineral recovery. No costs of recovery have been included. Fe, Zn, Mn, Pb from Reference 18; Ag from Reference 38.

cFrom Reference 34.

Another alternative process has been proposed by Lawrence Livermore Laboratories in which the brine coming from the well is acidified with HCl before going into the geothermal power plant. $^{38}$  This acidification inhibits the precipitation of calcium carbonate and silica. Iron metal is added to provide nucleation sites for the metals in the brine. These metals then accumulate into large enough precipitates that may be recovered by processing the product brine. The pH of the brine must be reduced from 5.6 to about 3 before entering the power cycle. Two disadvantages of this approach are the cost of hydrochloric acid, which is about 1 mil/kW h, and the increased corrosion which will occur on all the wetted parts of the power plant.

### 2. Disposal Costs

Only meager amounts of information are available for the costs of treatment and disposal of geothermal wastes; therefore, cost data from other industries using similar treatment or disposal methods have been used where applicable.

## a. <u>Wastewater Treatment Costs</u>

These wastewater treatment methods have been used in other industries, particularly in the treatment of fly ashes from coal-fired power plants, especially in the case where the power plant is near a populated center. <sup>39</sup> This technology is available and well developed. The costs of conventional wastewater treatment technologies are estimated in Table 14. The most well-developed technique for treating geothermal solids is a combination of clarification and filtration, as demonstrated at the GLEF.<sup>18</sup> This technology will cost about 3 mils/kW+h. For geothermal electricity selling at 7¢/kW+h, this treatment would account for 4% of the power production costs. The clear liquor from the clarifier is filtered and then returned to an injection well. The solids that are accumulated from the clarifier may be allowed to evaporate to dryness and are then hauled by truck to a landfill. More experimental work needs to be performed with geothermal brines to determine if these solid wastes are toxic.

#### b. Landfill Costs

The estimated costs for solids disposal from a 100-MWe geothermal power plant are given in Table 15. These costs have been based on the assumption that all of the solids produced will be shipped by truck to a designated landfill site that has been specifically prepared for geothermal solids. From data available at this time, it appears that solid wastes from geothermal operations are of relatively low toxicity; therefore, it is expected that this landfill site will not require the particular precautions that are necessary for industrial toxic and hazardous chemical wastes. The site will require precautions for the leaching of soluble salts and toxic metals from the solids. These costs do not take into account any minerals or solids recovery values from the solid wastes. The total cost of

Process	\$/1,000 liters @ 100,000 lpm	mils/kW•h <sup>b</sup>
Sedimentation	0.01	0.4
One-stage lime addition	0.02	0.8
Two-stage lime addition	0.01	0.4
Alum addition	0.06	2.5
Ferric chloride addition	0.07	2.9
Filtration	0.06	2.5
Ion exchange	0.09	3.8
Reverse osmosis	0.12	5.0
Electrodialysis	0.30	12.5
Vapor compression evaporation	0.20	8.3
Multieffect evaporation	0.50	20.8
Multistage evaporation	0.50	20.8

TABLE 14 ESTIMATED WASTEWATER TREATMENT COSTS<sup>a</sup>

Adapted from Reference 33. Based on a 100-MWe geothermal power plant processing 5 x 10<sup>6</sup> kg/h (70,000 lpm) of brine.

Source	Production Rate (tonnes/year)	Main Constituents	Cost of Disposal <sup>a</sup> (mils/kW•h)
Drilling muds	8,000	Bentonite Sepiolite	0.6
Solids from spent brine	16,000	Silica Heavy metal sulfides	1.2
Scale buildup	4,500	Silica Calcite	0.4
Solids from H <sub>2</sub> S abatement <sup>b</sup>	400	Ammonium Sulfate	0.03
Cooling tower sludge	1,500		$\frac{0.1}{2.3}$

TABLE	1	5
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ESTIMATED COSTS OF SOLIDS DISPOSAL FROM A 100-MWe GEOTHERMAL POWER PLANT

a At \$50/tonne, operating 6500 h/year bEIC copper sulfate process assumed

disposal of these solids, on the basis of 50/tonne, is estimated to be 2.3 mil/kW·h. A recent study for the disposal of coal ash has been used as a basis for disposal costs for a 1981 power plant which burns coal to be in the range of \$28 to \$35/tonne.<sup>26</sup> In addition, the cost of landfill disposal of hazardous waste from coal gasification and liquefaction has been estimated to be \$18/tonne (1981 \$). It is expected that the cost for disposal of geothermal solids should not be significantly greater than the disposal of coal ash solids. However, even if the disposal of geothermal solids were to increase by a factor of three, this would only make the cost 1¢/kW·h. This would still be small compared to energy costs of ~7¢/kW·h. The costs given in Table 13 do not consider treatment technology economics which would be required, such as clarifiers and filters to separate the solids from the brine. The cost of a clarifier/filtration system was previously estimated as 3 mil/kW·h, giving a total solids treatment cost of 6 mil/kW·h.

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### V. REGULATORY MEASURES

Of the various federal regulatory agencies, it is clear that the Environmental Protection Agency (EPA) will dominate the regulation of geothermal solid wastes. Documents published by the EPA have made it clear that they intend doing so primarily under the auspices of the Resource Conservation and Recovery Act (RCRA).<sup>41</sup> This produces some confusion in that the regulations thus far promulgated under RCRA, Subtitle C, specifically exclude ". . . drilling fluids, produced waters, and other wastes associated with the exploration, development, or production of crude oil, natural gas, or geothermal energy."<sup>42</sup> These same regulations state that materials excluded under Section 261.4(b) of RCRA are subject to control under Subtitle D of the same act. This simply means that state and local laws may be applied.<sup>43</sup> This lack of current federal regulation in the geothermal area is based on the Department of Energy's schedule of providing only regulatory guidance to state and local government during the precommercialization phase.<sup>44</sup> The states may be expected to apply substantially the same definitions of what constitutes hazardous waste as the EPA has implemented under RCRA. ' The characteristics most likely to render a geothermal waste hazardous are corrosivity, radioactivity, EP (extraction procedure) toxicity, and possibly bioaccumulation potential.<sup>6</sup>

The State of California regulates the disposal of solid wastes as described in Title 23, starting with Section 25100 of the California Administrative Code. Section 25143 of this code states that "Any drilling for geothermal resources shall be exempt from the requirements of this chapter because the disposal of geothermal wastes is regulated by the Regional Water Quality Control Boards." Class I dumpsites are regulated under this chapter by the Hazardous Waste Management Branch of the California Department of Health Services.

Another category of landfill to be considered is the Class II-1 site. The Colorado River Water Quality Control Board, which has jurisdiction over the Imperial Valley, will permit wastes containing over 6,000 ppm total dissolved

solids to be disposed of in a Class II-1 dump.<sup>45</sup> Efforts are now being made to establish a large Class II-1 site in the Imperial Valley primarily to service the geothermal industry.<sup>46</sup>

Wastes containing toxic substances such as heavy metal sulfides will have to be deposited in a Class I dumpsite, whereas wastes which are only high in salt content may be taken to a Class II-1 landfill. Some potential wastes, such as suspended solids from agricultural wastewater, may not require disposal to either of these restrictive landfills.

The term "solid waste disposal" generally is taken to mean disposal on land whether the waste deposited is solid, liquid, or a slurry. In this sense, the spent brine may be considered a solid waste unless or until it is injected.<sup>47</sup> In the case of Imperial County, the geothermal element of the county code specifies that all fluids removed from geothermal resources must be fully reinjected.<sup>48</sup> This is motivated largely by concerns over subsidence and may require that losses in geothermal fluids due to diversion of flashed steam or evaporation be made up by injection of cooling tower blowdown or some other water source.

For a given geothermal operation, the impact of the various regulations can only be assessed following a careful analysis of the generated waste forms. In many regions, the geothermal wastes have been found not to be hazardous under RCRA criteria. Even in the Imperial Valley, the majority of wastes studied have been found to be restricted only by their salinity.<sup>8</sup>

## VI. RECOMMENDATIONS FOR FURTHER STUDY

The two most significant problems for the operator of a geothermal power plant will be the inhibition of scale formation on the power plant surfaces and the stability of the water which will be injected back under ground. Both of these problems will affect the amount of solid toxic waste that is produced. Studies have been made of inhibitors which may be used to minimize the formation of scale.<sup>9,40</sup> Further study in this area is recommended. In addition, a top priority should be given to studies which will ensure the stability of the clear liquor from clarification processes and minerals recovery processes that are used in the treatment of spent brine. In addition, studies should be made of conventional treatment technology that has been applied for the treatment of coal fly ash and other types of solid wastes. This treatment technology may be readily converted for the application to geothermal solid wastes. All advantages should be taken of technology that has already been developed. Economic studies should be made for the application of this technology to the geothermal problem. In addition, a first step that should be made on any of the minerals recovery processes is study of the overall effect of the minerals recovery process on the geothermal power plant. In particular, this study should take into account any increase in corrosion or power plant operating difficulty which will come about due to the minerals recovery process. Only those processes with significant economic advantages should be studied. The top priority should also be given to the accumulation of more data on the composition of solids produced from geothermal processing. In particular, these studies should concentrate on the levels of toxic elements that are found in these solids. There are very few data in this area presently available.

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