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CHARACTERIZATION OF GEOTHERMAL SOLID WASTES

W.F. Morris
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July 1981

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Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under Contract W-7405-Eng-48.

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INTRODUCTION

The major known geothermal resource areas (KGRA) in the United States are located in California in The Geysers area 100 miles north of San Francisco and in the Imperial Valley, 120 miles east of San Diego adjacent to the Mexican border. Both areas are classified as hydrothermal resources. The Geysers is a dry steam field with steam temperatures of about 250°C and enthalpy of 1200 Btu/lb. The Imperial Valley contains five distinct geothermal fields identified as the Salton Sea, Westmoreland, Brawley, Heber, and East Mesa KGRA's. The reservoirs contain hot fluids ranging in temperature from about 170°C to 365°C and enthalpy up to approximately 450 Btu/lb.

The Geysers, located in a remote, sparsely populated area of the state, has been exploited extensively for the generation of electricity and at the present time produces about 1100 MW of power. Abatement of H_2S constitutes the principle environmental control technology. Disposal of liquid and solid wastes is not considered to be a significant problem because the resource is relatively clean, dry steam. Condensed fluids associated with steam gathering and power plant cooling are injected into the subsurface resource. Liquid and solid wastes associated with the iron catalyst H_2S abatement process are disposed of in an approved land-fill disposal site, while by-product solids from the Stretford H_2S abatement units are recovered for commercial use.

Unlike The Geysers, the Imperial Valley KGRA's are located near populated communities (Fig. 1). More importantly the resources underlie one of the richest and most intensively worked agricultural areas in the world. Also, unlike The Geysers, the Imperial Valley resources are "liquid dominated" containing fluids of varying enthalpy and dissolved solids content (Table 1).

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Fig. 1. Imperial Valley communities in relation to KGRAs (Layton and Ermak, 1976).

TABLE 1. Characteristics of Imperial Valley geothermal fluids.^a

KGRA	Temp., °C	Enthalpy, BTU/lb	TDS, ppm
Salton Sea	340	450	300,000
Westmorland	300	400	220,000
Brawley	260	350	100,000
Heber	220	300	20,000
East Mesa	200	260	15,000

^a Approximate maximum values for fluid temperature, enthalpy, and total dissolved solids (TDS).

Large-scale production of geothermal energy is not yet a reality in the Imperial Valley, however, it is estimated that over a period of 30 years, the electric power production potential of the resources can be developed to greater than 3000 MW (Ermak, 1978). The principal approaches proposed for converting Imperial Valley resource heat into electrical energy are the flashed-steam and binary fluid conversion cycles (Layton, D. Ed., 1980). In generating electricity by the flashed-steam process, steam can be separated from the geothermal fluid and expanded through a turbine to run a generator. The steam exhausted from the turbine can be condensed by a direct contact or surface condenser and used as makeup water in a wet cooling tower for subsequent circulation through the condenser. Alternatively, the condensate can be disposed of by subsurface injection along with spent geothermal fluid from the separators.

The binary fluid conversion process is designed to use geothermal fluid in a heat exchanger to transfer heat to a secondary fluid that vaporizes at a much lower temperature than water and can be used to drive a turbogenerator. After passing through the heat exchanger the geothermal fluid may be disposed of by subsurface injection. The binary fluid vapor is condensed after the turbine and circulated back through the heat exchanger.

Of the two approaches for generating electricity from hot water resources, only the flashed-steam process has been implemented on a commercial scale (Cerro Prieto, 1981). To date, no commercial-scale geothermal power plants have been constructed in the Imperial Valley. Only the test facilities and demonstration plants summarized in Table 2 have been implemented or are under development. For purposes of identifying and estimating the amount of geothermal wastes for this study, the flashed-steam process is used as a reference.

TABLE 2. Geothermal test facilities and demonstration power plants in the Imperial Valley.

Location	Facility ^a	Utilities and Developers ^b	Status ^c	Reference ^d
Salton Sea	• Power Plant, 10 MW	SCE, Union Oil	UC	NGS 9/26/80
	• Power Plant, 49 MW	SDG and E, Imperial Magma	FD	NGS 5/22/81
	• Power Plant, 28 MW	SDG and E, Imperial Magma	FD	NGS 5/22/81
	• GLEF (Power plant 10 MW)	SDG and E	SD	NGS 5/22/81
	• Power Plant, 49 MW	Republic Geothermal	FD	GRC Bull., 12/80
Brawley	• Power Plant, 10 MW	SCE, Union Oil	OP	GRC Bull, 10/80
	• Power Plant, 45 MW	DWR, MCR, GKI	ENG, FD	NGS 7/18/80, 1/30/81
	• Sugar Processing	Holly Sugar, TRW	UC	NGS 12/5/80
Heber	• Power Plant, 45 MW	SCE, Chevron, USA	PER	GRC Bull., 12/80
	• Power Plant, 45 MW	SCE, SDG and E, DWR	ENG	CEC New 5/80
		IID, EPRI, DOE		
East Mesa	• Power Plant, 10 MW	SDG and E, Magma Power Co.	OP	GRC Bull, 12/80
	• Power Plant, 10 MW	Republic Geothermal	PER	NGS 1/30/81
	• Power Plant, 500 KW	Westec Services	OP	GRC Trans., 9/80, p518
	• GCTF	Westec Services, DOE	OP	
Westmorland	• Power Plant, 50 MW	MAPCO, Republic Geothermal	FD	NGS 1/30/81
El Centro	• Space Heating Project	DOE, Westec Services, City of El Centro	ENG	GRC Trans., 9/79, p647

^a GLEF - Geothermal Loop Experimental Facility, GCTF - Geothermal Component Test Facility

^b SCE - Southern California Edison, SDG and E - San Diego Gas and Electric, MCR - MCR Geothermal, GKI - Geothermal Kinetics Inc., TRW - TRW Engineering, DWR - California Department of Water Resources

IID - Imperial Irrigation District, EPRI - Electric Power Research Institute, DOE - Department of Energy

^c UC - Under Construction, ENG - Engineering phase, OP - Operating, PER - In permit process, FD - Field development, SD - Shutdown

^d NGS - National Geothermal Service, Petroleum Information Service, Bakersfield, CA 93389

GRC Bull. - Geothermal Resources Council Bulletin, Davis, CA 95617

GRC Trans. - Geothermal Resources Council Transactions, Davis, CA 95617

CEC News - California Energy Commission, Sacramento, CA 95825

This study is intended to determine if potential geothermal wastes identified here and in earlier studies (Layton D. Ed., 1980; Morris and Hill, Ed., 1980) are hazardous as defined in the regulations under the Resource Conservation and Recovery Act (RCRA) of 1976. The Act constitutes "cradle to grave" legislation aimed at controlling the disposition of solid wastes. At the present time wastes generated by geothermal energy development and production are exempt from RCRA while efforts proceed to characterize them.

GEOHERMAL WASTES

Liquid and solid wastes can be generated from a variety of sources during construction and development of geothermal energy plants and throughout the course of their production lifetime. For example, a 50 MW power plant requires about 2×10^6 kg/h of 275°C fluid to produce its specified electrical energy output. Over the course of a year approximately 1.6×10^{10} kg of fluid will have been utilized in such a facility and require disposal in an environmentally safe manner. After energy extraction the enormous volume of spent fluid must be disposed of in an environmentally safe manner. The method of choice is expected to be underground injection because of the large volumes of fluid involved and in deference to Imperial County policy requiring injection of all fluids withdrawn from geothermal resources (Imperial County, 1977).

Experience at the Geothermal Loop Experimental Facility (GLEF) located at Niland in the Imperial Valley has demonstrated that solids will precipitate from hypersaline brine when it is flashed from a reservoir temperature exceeding 300°C down to the facility exit temperature of 90°C (Quong et al., 1978). The precipitated solids seriously impede injection of spent fluids and consequently must be separated before injection takes place.

Experiments conducted on Magmamax No. 1 effluent brines at the GLEF show that precipitated solids average about 500 ppm in the spent brine and are composed for the most part of SiO_2 (Harrar et al., 1979). Separation of solids at this concentration from spent production fluid in a 100 MW power plant could produce about 4 acre feet (a.f.) of waste per year.

Large volumes of cooling water will be required in geothermal power plants because of their low thermal efficiency resulting from the relatively low temperature and pressure of hydrothermal resources. For example, the conversion efficiency of a geothermal plant utilizing 180° steam at approximately 100 psi is only 15% compared to 33% for a modern coal-fired power plant using 540°C steam at 2400 psi. Approximately 60 a.f./MW-y of makeup cooling water will be required for a flashed-steam geothermal facility compared to 14 a.f./MW-y for a coal-fired plant. The principal sources of cooling water for geothermal power plants in the Imperial Valley are: irrigation water from the Colorado river, steam condensate from the flashed-steam process, and agricultural drainage water. Current commitments of irrigation water for use in agriculture and county policy with regard to the use of steam condensate restrict the use of these two sources (Layton, 1978). Consequently, agricultural drainage water may constitute the only major source of power plant cooling water. The annual flow of agricultural drainage water in the Imperial Valley amounts to about $1.23 \times 10^9 \text{ m}^3$. The water contains between 2000 to 4000 mg/l total dissolved solids (TDS) and from 200 to 500 mg/l of undissolved solids. If water of this poor quality is utilized for power plant cooling, then large amounts of waste will accumulate from pretreatment processes and from periodic discharge of concentrated salt-laden water or blowdown from the cooling tower basin. If the wastes are accumulated

by ponding and evaporation, as much as 4 a.f./y of pretreatment solids and 36 a.f./y of blowdown solids will be produced in the operation of a 100 MW plant.

Additional wastes will be generated by other geothermal operations such as well drilling, removal of scale from pipelines and equipment, and operation of H₂S abatement processes. The amounts of the different types of wastes that are expected from the development and operation of a 100 MW flashed-steam geothermal power plant in the Imperial Valley are given in Table 3.

Geothermal development in the Imperial Valley is expected to grow significantly over the next 30 years. Ermak (1978) proposed geothermal electric power growth rate scenarios of 40, 100, and 250 MW/y based on historical data and estimates of the size of the Imperial Valley resources. Wastes accumulated over 30 years based on the intermediate growth rate projection of 100 MW/y are given in Table 4 (Morris and Hill, Ed., 1980).

REGULATIONS

The passage of the Resource Conservation and Recovery Act (RCRA) by the Congress in 1976 and promulgation by the Environmental Protection Agency (EPA) in 1980 of regulations (USEPA, 1980) to implement the act have directed more serious attention to the problem of waste generation, the nature of the wastes, their handling and disposal. The stated objectives of RCRA are to protect health and the environment and to conserve material and energy resources. The regulations under the law are intended to provide a management system for hazardous and non-hazardous wastes and to promote resource recovery and the reduction of waste volumes requiring permanent disposal.

TABLE 3. Wastes from development and one-year operation of 100 MW geothermal power plant.

Liquid Wastes	Amount ^a
Brine from well-flow tests	650 ^{b,c}
Spent brine from production plant	20,000 ^c
Blowdown fluid from cooling tower	2000
Solid Wastes	Amount ^a
Drilling mud, well-bore cuttings	3.3
Dried brine, well-bore debris	3.7
Separated solids from brine preinjection treatment	3.6
Scale from process lines, separators, etc.	1.3
Solids from ponding and evaporation of blowdown fluid	36 ^d
Solids separated from pretreatment of cooling tower makeup water	4
By-product from H ₂ S abatement (ammonium sulfate)	.14

^a Acre feet per 100 MW per year

^b Assumes 16 wells per 100 MW plant, each flow tested for 30 days at average rate of 35% of full flow.

^c Disposal expected to be subsurface injection.

^d In the event blowdown cannot be injected, it may be discharged to a pond for evaporation and eventual disposal as solid waste.

TABLE 4. Solid wastes accumulated from geothermal power plant operations in the Imperial Valley over 30 years^a

Solid Waste	Amount in acre feet
Drilling mud, well-bore cuttings	700
Dried brine, well-bore debris	730
Separated solids from brine preinjection treatment	1200
Scale from process lines, separators, etc.	1500
Solids from ponding and evaporation of blowdown fluid	10,500
Solids separated from pretreatment of cooling tower makeup water	400
By-product from H ₂ S abatement (ammonium sulfate)	80

^a Based on geothermal power growth rate of 100 MW per year for 30 years (Ermak, 1977).

Sources and amounts of solid wastes are described by Layton et al., 1980 and Morris et al., 1980.

As defined in the regulations, a solid waste is "---any garbage, refuse, sludge or any other waste material---any solid, liquid, semi-solid or contained gaseous material, resulting from industrial, commercial, mining or agricultural operations, or from community activities that is discarded, accumulated, stored or physically, chemically or biologically treated prior to being discarded---is a manufacturing or mining by-product and is sometimes discarded. A material is discarded if it is abandoned---by being disposed of---incinerated---treated---. A material is disposed of if it is discharged, deposited, injected, dumped, spilled, leaked or placed into or on any land or water so that such material or any constituent thereof may enter the environment or be emitted into the air or discharged into ground or surface waters."

A solid waste is hazardous, according to the law, "---if it is listed (in the regulations), ---is a mixture of solid waste and one or more of the listed hazardous wastes---, exhibits any of the characteristics of hazardous waste identified in the regulations."

The characteristics that establish a solid waste as hazardous are ignitability, corrosivity, reactivity and EP (Extraction Procedure) toxicity. These characteristics are determined through the application of standard physical tests. EP toxicity, for example, is determined by performing an extraction of the solid waste sample and comparing the concentrations of constituents found in the extract with listed maximum allowed levels of toxic metals and organic compounds.

At the present time "drilling fluids, produced waters, and other wastes associated with the exploration, development, and production of geothermal energy" are excluded from regulation and are deemed not to be hazardous under Subtitle C, Part III, Subpart A, Section 261.4(b) of the Hazardous Waste and Consolidated Permit Regulations. However, in spite of this, the wastes are

subject to control under Subtitle D which assigns management of solid waste to state and local control. Whether the exclusion of geothermal solid wastes from regulation will be long-term or temporary depends upon the outcome of characterization studies intended to determine if they are hazardous or not. The investigation reported here constitutes an initial effort in making that determination.

OBJECTIVES OF THE STUDY

The principal objective of this study is to determine if certain geothermal wastes are hazardous according to the characteristic of EP toxicity as defined in Subtitle C, Part III, Subpart A, Section 261.24 of the Hazardous Waste and Consolidated Permit Regulations. The specific intent is to determine if the metal contaminants Ag, As, Ba, Cd, Cr, Pb, Hg, and Se are present in liquid extracts of solid wastes at or above specified maximum concentration levels (Table 5) that characterize the wastes as toxic and therefore hazardous.

There are other objectives of this study that are not required under the regulations of the RCRA but have been undertaken to determine metals such as B, Be, Cu, Li, Ni, Sb, Sr, and Zn that are of interest in EPA surface and ground water programs. In addition, the objectives are: to determine the general inorganic composition of the various wastes, to measure the concentrations of the toxic and other metal contaminants in the original wastes before extraction, to evaluate the data, and recommend any additional sampling and analysis needed to verify the results and more definitively characterize geothermal wastes.

TABLE 5. Maximum allowed toxic metal concentrations in extracts of solid wastes.^a

Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

^a Reference USEPA, 1980
Numbers = milligrams per liter

DESCRIPTION OF WASTE SAMPLES

Although commercial-scale power plants have not been implemented to date in the Imperial Valley, it has been possible to collect samples of each of the different types of geothermal wastes described earlier in the text (Table 3).

The collected samples include:

- Well-drilling mud and cuttings from sites in The Geysers and the Imperial Valley,
- Brine samples from three sites in the Imperial Valley,
- Separated solids from the reactor-clarifier experimental unit designed to remove solids from spent brine prior to injection (Van Note, Featherstone, and Pawlowski, 1978),
- Scale from the Geothermal Loop Experimental Facility (GLEF) at Niland,
- Solids separated from agricultural drainage water (a potential source of cooling tower water).

WELL DRILLING MUD AND CUTTINGS

Well-drilling mud and cuttings were obtained from the Neasham No. 1 and Federal Lease sites of Occidental Geothermal, Inc. in The Geysers resource area. Samples were taken from fan-like tailing areas where mud and cuttings were discharged into the reserve pits at the two well sites. The samples were removed from the tailings at depths of 1 to 1.5 feet using a narrow spade. The cross-sectional appearance of all samples was similar, exhibiting varied layers of mud and cuttings saturated with water and oil.

Samples of mud and cuttings from the Republic Geothermal, Inc., Fee No. 1 and MAPCO, Inc., Courier No. 1 well sites in the

Imperial Valley were obtained through Acurex Corporation, Mountain View, CA. Acurex, in carrying out a sampling and analysis study of geothermal wastes for EPA, made composites of individual samples from four corners of the reserve pits at the Fee No. 1 and Courier No. 1 sites. A hand trowel was used to obtain the samples 3 to 6 inches below the surface.

BRINE SAMPLES

Brines from the Fee No. 1 and Courier No. 1 geothermal wells were also obtained through Acurex Corporation. The brines, accumulated from well flow tests at the two sites, were stored in a brine pit and brine storage tank, respectively. Samples were taken by dipping a beaker fastened to an extension rod into the brine fluid.

A third brine sample was obtained by LLNL from the Imperial Magma Co., Magmamax No. 1 well. Replicates of this sample were used originally by LLNL to study brine chemistry and scaling phenomena (Harrar, et al., 1979).

SOLIDS SEPARATED FROM SPENT BRINE

A sample representing solids separated from spent brine prior to injection was obtained from the reactor-clarifier experiment conducted at the GLEF by VanNote, Featherstone, and Pawlowski (1978). The experiment tested a treatment system in which precipitated solids were separated and the spent brine was stabilized to permit injection. The sample was one of two pressed filter cakes originally obtained by LLNL for solid waste characterization studies (Morris and Hill, Ed., 1980).

GEOHERMAL SCALE

A sample of geothermal scale retained from experiments conducted at the GLEF was utilized for this study. The sample, stored in a sealed packet, was one of several that were obtained originally for use in scale dissolution experiments (Deutscher, et al., 1980). The scale was taken from the second stage separator of the GLEF where brine temperature was approximately 120°C. It is anticipated that this type of low temperature scale will represent the major fraction (>90%) of waste scale that will require disposal after removal from separators, downstream components, and injection well pipelines in future power plants.

COOLING WATER WASTES

Samples of agricultural waste water were obtained from the New and Alamo rivers which are the principal drainage tributaries for agricultural water runoff in the Imperial Valley. The samples were taken at four locations on each of the two rivers at locations equidistantly spaced along the lengths of the rivers from the Salton Sea to the Mexican border. Solid material intended to represent the sediment and suspended solid wastes removed during cooling tower water makeup operations were separated in the laboratory by passing the water sample through a 0.45 μ m membrane filter. Samples intended to represent concentrated blowdown solid waste were prepared by evaporating the filtered river water samples to dryness at 108°C.

SAMPLE PREPARATION AND ANALYSIS METHODS

Emission spectrographic and x-ray fluorescence methods were used to analyze both the bulk waste samples prior to extraction and the extracts that were prepared by the recommended EP toxicity test procedure. Atomic absorption spectrophotometric methods were also used to determine toxic metals in the extracts. The approximate general compositions of the bulk samples and the extracts were determined in addition to the toxic metals listed in the RCRA regulations and the other elements of interest to EPA ground water programs. The pre-extraction analyses provided data to calculate the maximum concentrations of metals potentially extractable from the waste samples for comparison to the actual amounts extracted.

EXTRACTION PROCEDURE

The extraction procedure described in Part III, Appendix II of the EPA Hazardous Waste and Consolidated Permit Regulations was used. A 100 gram sample of each waste was placed in the extraction apparatus consisting of a 2-liter polyethylene jar and a motor driven paddle for continuous stirring; 1600 ml of H_2O was added and the mixture was stirred for 24 hours. During the 24 hour extraction the acidity was maintained at $pH\ 5.0 \pm 0.2$ using 0.5 N acetic acid as specified. Upon completion of the extraction, the volume was adjusted to 2 liters. The solid and liquid phases were then separated using a nitrogen pressurized filtration apparatus incorporating a $0.45\ \mu m$ membrane (Nucleopore Cat. Nos. 420800 and 142118). The clear filtrate or extract was retained for analysis.

The above extraction and separation steps were used for all of the well-drilling mud and cuttings samples, the geothermal scale, and the reactor

clarifier filter cake. The Magmamax No. 1, Fee No. 1, and Courier No. 1 brines were prepared differently but in accordance with the recommended extraction procedure for fluid samples containing less than 0.5 percent solid residue. The recommended procedure for such samples simply requires the separation of the solids by filtration and retention of the liquid phase as the extract for analysis. No 24 hour extraction is required for samples of this type.

ATOMIC ABSORPTION SPECTROPHOTOMETRY

The graphite furnace technique was used to atomize samples of extract for measurement by a Perkin-Elmer model 603 atomic absorption spectrophotometer. Twenty microliters each of standards and samples were pipetted into a Perkin-Elmer model HGA 2100 graphite tube furnace. Table 6 lists the preprogrammed furnace conditions to achieve optimum drying and charring of the sample followed by atomization of the elements of interest into the source light path.

EMISSION SPECTROGRAPHIC ANALYSIS

Samples of well-drilling mud and cuttings, brines, geothermal scale, and filter cake were prepared for compositional and trace analysis prior to extraction by drying as necessary under an infrared lamp. Each of the samples was then homogenized by grinding in an agate mortar and pestle.

Filtrates from the extraction process were evaporated on a steam bath and the residues were heated to dryness under an infrared lamp. The residues were subsequently homogenized in plastic vials using mechanically agitated plastic ball pestles.

TABLE 6. Programmed time and temperature conditions for operation of the graphite tube furnace.

Temperature, °C - Time, sec.

Element	Dry	Char	Atomize
Arsenic	100° - 20 sec.	250° - 10 sec.	2000° - 10 sec.
Mercury	100° - 20 sec.	150° - 10 sec.	1900° - 10 sec.
Selenium	110° - 20 sec.	300° - 10 sec.	2200° - 10 sec.

All samples and standards were excited in a direct current arc discharge and the spectra were produced and photographed on a Jarrell-Ash 3.4 M emission spectrograph.

X-RAY FLUORESCENCE ANALYSIS

The samples prepared for spectrographic analysis were analyzed for Hg, As, and Se by energy dispersive x-ray fluorescence spectrometry. Samples and standards were placed in cups covered with mylar film windows. The samples were exposed to x-rays from a tungsten x-ray tube; the dispersed energy was measured with a Kevex detector and Tracor-Northern, NS 750 multichannel analyzer.

ANALYTICAL RESULTS

PRE-EXTRACTION ANALYSIS

Samples of well-drilling mud and cuttings, geothermal scale, filter cake solids separated from spent brine, sediment and suspended solids and dissolved solids from agricultural drainage water were analyzed by spectrographic and x-ray fluorescence methods before carrying out the EPA-recommended extraction procedure. The results are summarized in Table 7. EPA-listed toxic metals such as Ba and Pb are present in relatively large amounts in the drilling muds and in the geothermal scale and filter cake solids. However, as will be shown in subsequent data, only small amounts of these two toxic metals are leached from the waste samples into the extracts.

TABLE 7. Pre-extraction analysis of geothermal solid waste samples^a.

	Well-drilling Mud and Cuttings				Scale (GLEF)	Filter Cake (GLEF)	Suspended and Sediment Solids		Dissolved Solids ROE 108°C ^d	
	Occidental Fed. Lease ^b	Occidental Neasham ^b	Republic Fee-1	MAPCO Courier-1			Alamo Rv.	New Rv.	Alamo Rv.	New Rv.
Ag	< 0.3	< 0.3	0.3	0.6	100	10	<1	1	<.3	<.3
As ^c	<10	<10	15	10	150	400	<30	<30	<30	<30
Ba	2000	>10000	10000	3000	100	>10000	500	500	80	80
Cd	<10	<10	<10	<10	<10	<10	<10	<10	<3	<3
Cr	460	460	30	20	<3	<3	50	70	<1	<1
Hg ^c	<2	<2	<2	<2	<2	<2	<20	<20	<20	<20
Pb	<10	35	100	250	4000	250	<10	<10	<3	<3
Se ^c	<2	<2	<2	<2	<2	<2	NA	NA	NA	NA
B	70	100	150	200	500	400	70	80	200	300
Be	<1	<1	2	2	50	20	<1	<1	<.3	<.3
Cu	40	50	30	30	1000	300	35	50	5	3
Li	9	25	70	150	300	500	30	30	100	600
Ni	700	700	20	20	<10	<10	30	50	<1	<1
Sb	<30	<30	<30	<30	200	200	<30	<30	<30	<30
Sr	200	340	300	600	300	600	300	230	1000	1000
Zn	40	46	200	250	500	200	40	20	<10	<10
Al	MC	MC	MC	MC	300	100	MC	MC	30	20
Ca	MC	MC	MC	MC	MC	MC	MC	MC	MC	MC
Co	54	46	2	2	<2	<2	15	10	<1	<1
Fe	MC	MC	MC	MC	MC	MC	MC	MC	10	10
K	MC	MC	MC	MC	MC	MC	MC	MC	>1000	>1000
Mg	MC	MC	MC	MC	300	300	MC	MC	MC	MC
Mn	1100	1200	1000	1200	1200	1300	1000	2000	<1	<1
Mo	<10	<10	<10	<10	<10	<10	<10	<10	3000	3000
Na	MC	MC	MC	MC	MC	MC	MC	MC	MC	MC
Rb	4	10	30	30	10	30	20	20	<1	3
Si	MC	MC	MC	MC	MC	MC	MC	MC	3000	3000
Sn	<10	<10	<10	<10	<10	<10	<3	<3	<3	<3
Ti	4700	4200	5000	5000	<10	<10	3000	4800	<1	<1
V	50	50	50	50	<20	<20	100	150	<10	<10

^a Determinations by optical emission spectroscopy except as noted.

Numbers = micrograms of constituent per gram of sample.

MC = Major constituent, ranging from fractional percent levels to tens of percent.

NA = Not analyzed.

^b Values represent mean of five samples analyzed.^c As, Hg, and Se were determined by x-ray fluorescence spectroscopy^d ROE = Residue on evaporation

CALCULATED MAXIMUM EXTRACTABLE TOXIC METAL CONCENTRATIONS

The maximum concentrations of toxic metals potentially extractable from the original waste samples were calculated using the pre-extraction analysis data and assuming 100-percent extraction of the metals from the waste into the aqueous extract. The calculations are based on the extraction of 100 grams of sample into an adjusted volume of 2 liters of aqueous extract. The calculated values are summarized in Table 8 and are useful for evaluating the maximum extent to which specific constituents could be leached from the different types of wastes.

ANALYSIS OF THE EXTRACTS

The EPA-recommended extraction procedure was applied to all of the samples with the exception of the sediment-suspended solids and dissolved solids samples of agricultural drainage water from the New and Alamo rivers. In the case of the latter samples, insufficient amounts of solids were separated from the available volumes of samples to perform adequate extractions.

Table 9 summarizes the data for the elements determined in extracts of well-drilling mud and cuttings, geothermal scale, and filter cake solids from spent brine. Table 10 lists the data for extracts of Magmamax No. 1, Fee No. 1 and Courier No. 1 brines.

In analyzing the extracts it should be noted that graphite furnace atomic absorption spectrophotometry did not achieve detection levels for Hg and Se equal to or lower than the maximum allowed concentrations specified in the EPA Hazardous Waste and Consolidated Permit Regulations. Levels of detection for Hg lower than those shown in Table 9 were precluded by interferences.

TABLE 8. Calculated maximum concentrations of metals potentially extractable from geothermal solid wastes^a.

	Well-drilling Mud and Cuttings				Scale (GLEF)	Filter Cake (GLEF)	Suspended and Sediment solids		Dissolved Solids ROD 108°C	
	Occidental Fed. Lease	Occidental Neasham	Republic Fee-1	MAPCO Courier-1			Alamo Rv.	New Rv.	Alamo Rv.	New Rv.
Ag	<.015	<.015	.015	.03	5	.5	<.05	.05	<.015	<.015
As	<.5	<.5	.75	.5	7.5	5	<1.5	<1.5	<1.5	<1.5
Ba	100	>500	500	150	5	>500	25	25	4	4
Cd	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.5	<.15	<.15
Cr	13	13	1.5	1	<.15	<.15	2.5	3.5	<.05	<.05
Hg	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<1	<1
Pb	<.5	1.8	5	13	200	13	<.5	<.5	<.15	<.15
Se	<.1	<.1	<.1	<.1	<.1	<.1	b	b	b	b
B	3.5	5	7.5	10	25	20	3.5	4	10	15
Be	<.05	<.05	.1	.1	2.5	1	<.05	<.05	<.015	<.015
Cu	<2	2.5	1.5	1.5	50	15	1.8	2.5	.25	.15
Li	.4	1.3	3.5	.5	15	25	1.5	1.5	5	30
Ni	35	35	1	1	<.5	<.5	1.5	2.5	<.05	<.05
Sb	<1.5	<1.5	<1.5	<1.5	10	10	<1.5	<1.5	<1.5	<1.5
Sr	10	17	15	3	15	30	15	12	50	50
Zn	2	2.3	10	1.3	25	10	2	1	<.5	<.5

^a Calculations are based on pre-extraction analysis data (Table 7) and assume 100 percent extraction of the metals from the waste into 2 liters of aqueous extract.

Numbers = milligrams of constituent per liter of extract.

^b Not calculated. Se not analyzed in the original sample.

TABLE 9. Metals determined in the extracts of geothermal solid wastes.^a

	Well-drilling Mud and Cuttings				Scale (GLEF)	Filter Cake (GLEF)	Maximum Allowed
	Occidental Fed. Lease ^b	Occidental Neasham ^b	Republic Fee-1	MAPCO Courier-1			
Ag	<.01	<.01	<.01	<.01	.01	.02	5
As ^c	<.5	<.5	<1	<1	<.5	<.5	5
Ba	.3	.5	3	25	3.5	7	100
Cd	<.1	<.1	<.1	<.1	<.1	<.2	1
Cr	<.02	<.01	<.03	<.03	<.02	<.04	5
Hg ^c	<1	<1	<1	<1	<1	<1	.2
Pb	<.1	<.1	.06	.1	7	.07	5
Se ^c	<.5	<.5	<.5	<.5	Int.	Int.	1
B	.02	.1	2	6	4	7	
Bd	<.003	<.003	<.01	<.01	<.007	<.01	
Cu	<.02	.02	.01	.03	.7	1	
Li	.02	.04	3	10	15	30	
Ni	.5	.1	.1	.2	.07	<.02	
Sb	<.1	<.1	<.2	<.3	<.2	<.4	
Sr	1	2	10	25	5	13	
Zn	<.1	<.1	.5	15	.5	.7	
Al	.05	.6	.2	.1	.07	.1	
Ca	MC	MC	MC	MC	MC	MC	
Co	<.03	<.03	<.03	<.03	<.02	<.04	
Fe	2	2	1	1	.2	<.4	
K	5	40	MC	MC	MC	MC	
Mg	10	10	10	15	2	3	
Mn	.4	1.3	4	10	5	10	
Mo	<.03	<.03	.1	<.1	<.1	<.1	
Na	MC	MC	MC	MC	MC	MC	
Rb	<.1	.15	1	2	1	1	
Si	5	30	10	3	2	4	
Sn	<.1	<.1	<.1	<.1	<.1	<.1	
Ti	<.1	<.1	<.3	<.3	<.1	<.1	
V	<.1	<.1	<.1	<.1	<.2	<.4	

^a Determinations by optical emission spectroscopy except as noted.

Numbers = milligrams of constituent per liter of extract.

MC = Major constituent, ranging from approximately 5000 mg/l to higher levels.

^b Values represent mean of five samples analyzed.

^c As, Hg, and Se were determined by atomic absorption spectrophotometry.

Interference on Hg precludes lower detection level for Hg.

Int. = Interference.

TABLE 10. Metals determined in the extracts of geothermal brines^a.

	Imperial MagmaMax-1	Republic Fee-1	MAPCO Courier-1	Maximum Allowed
Ag	.1	.5	.1	5
As ^b	25	<5	20	5
Ba	250	400	1300	100
Cd	<5	<4	<3	1
Cr	<1	<1	<1	5
Hg ^b	<.1	<.2	<.2	.2
Pb	50	200	130	5
Se	NA	NA	NA	1
B	600	400	130	
Be	<.2	<.4	<.3	
Cu	5	10	<.7	
Li	130	2000	1000	
Ni	<1	5	<3	
Sb	<5	<10	<7	
Sr	400	800	1750	
Zn	200	1000	400	
Al	<1	10	70	
Ca	MC	MC	MC	
Co	<1	<1	<1	
Fe	250	1000	650	
K	MC	MC	MC	
Mg	100	400	250	
Mn	400	800	250	
Mo	<2	<4	<3	
Na	MC	MC	MC	
Rb	10	25	17	
Si	300	30	20	
Sn	<4	<4	<4	
Ti	<.5	<10	<10	
V	<4	<4	<4	

^a Determinations by optical emission spectroscopy.

Numbers = milligrams of constituent per liter of extract.

MC = Major constituent, ranging from approximately 2000 mg/l to higher levels.

NA = Not analyzed.

^b Preconcentration using CuS carrier prior to spectrographic analysis.

Adequate detection was achieved for Se in the extracts of the mud and cuttings samples; however, interferences encountered in the scale, filter cake, and brine extracts made it impossible to determine Se.

Hg and As were determined in the brine extracts by emission spectrography; however, it was necessary to perform a preliminary concentration by precipitation with H_2S using Cu as a carrier coprecipitating agent.

EVALUATION OF ANALYTICAL RESULTS

WELL DRILLING MUD AND CUTTINGS

Table 7 lists the results for samples analyzed before performing the EPA recommended extraction. The original samples of mud and cuttings contain relatively high concentrations of Ba, Cr, and Pb; however, as shown in Table 9, the extracts do not contain these toxic metals in concentrations that would characterize the wastes as hazardous.

Virtually all of the constituents found in the original mud and cuttings samples are common to rock formations and drilling muds. In noting the relatively high Cr and Ni in two of the well-drilling wastes (columns 1 and 2, Table 7), a cursory analysis was made of the rock cuttings that were separated from the mud and washed. Most of the Cr and Ni were found to be present in the rock.

The major constituents such as Al, Ca, Fe, K, Mg, Na and Si as well as Ba make up the composition of most rocks. They are also present in drilling mud. Variation in the amounts of Na, K, and Ba may be due to the presence of brines in the waste and the addition of specific Na and Ba compounds to the drilling muds.

SCALE

The analysis of the original sample of scale shown in Table 7 shows a relatively high concentration for Pb and lesser amounts of Ag, As, and Ba. Of these, only Pb is extracted. Its concentration in the extract of 7 mg/l (Table 9) exceeds the 5 mg/l maximum amount allowed by the permit regulations.

Deutscher et al. (1980) report that the major component of this type of scale is SiO_2 (57.2%); Na is present at a level of 10%, Ca 2.9%, K 1.09%, and Fe 0.88%. The minor and trace elements shown in Table 7 are in close agreement with those reported by Deutscher.

Virtually all of the elements of interest in EPA surface and ground water programs (B through Zn) are present at several hundred $\mu\text{g/gm}$ in the original scale samples. However, only very small amounts are present in the extracts.

FILTER CAKE SOLIDS SEPARATED FROM SPENT BRINE

The pre-extraction analysis (Table 7) of the precipitated solids from spent brine identified as filter cake shows a high concentration of Ba and significant levels of As and Pb. As shown in Table 9, only a small amount of Ba (7 mg/l) and virtually no As and Pb are detected in the extract. All concentrations are well below the maximum allowed levels.

The elements B through Zn also are not detected in the extract in any appreciable amounts even though they are present in the original sample at levels up to 600 $\mu\text{g/gm}$.

GEOTHERMAL BRINES

No pre-extraction analyses of geothermal brines were performed. It was determined that such analyses were not necessary because the extracts, prepared according to the EP toxicity test procedure, were virtually

equivalent to the original brine samples differing only to the extent that solids, amounting to about .05 percent of the original brine, had been filtered off. Thus only analysis of the brine extracts were performed.

As shown in Table 10, all three brine extracts contain the toxic metals As, Ba, and Pb in concentrations exceeding the maximum levels allowed by the EPA permit regulations. Significant amounts of other metal contaminants such as B, Li, Sr, and Zn are also present.

SOLIDS FROM NEW AND ALAMO RIVER WATERS

Table 7 lists the constituents determined in both the undissolved (suspended and sediment solids) and the total dissolved solids from the New and Alamo Rivers. No unusual constituents or concentrations of constituents were determined in the two types of samples. Extractions were not performed on these samples because of the small amounts of solids available. Nevertheless, even without doing the extractions it is predictable that the maximum allowed concentrations of toxic metals in the extracts as defined in the RCRA regulations will not be exceeded. This is based on the amounts present in the original samples and the calculated maximum extractable toxic metal concentrations listed in Table 8.

CONCLUSIONS

The compositions of 5 major types of geothermal wastes have been determined and samples have been subjected to EPA recommended extraction tests to determine if they contain toxic metals that would classify the wastes as hazardous. Of the samples tested, the extracts of geothermal brines clearly contain levels of As, Ba and Pb exceeding the maximum allowed concentrations that characterize wastes as toxic.

Only one other waste type, geothermal scale, exhibited EP toxicity. Pb was found in the extract of geothermal scale at a level of 7 mg/l, only 2 mg/l over the maximum limit. All of the other types of geothermal waste samples showed levels of toxic metals in the extracts well below the regulated limits.

Because only a limited number of samples have been utilized in this study it is premature to draw conclusions for the long-term regarding the hazardous or non-hazardous nature of the different types of wastes. The well-drilling wastes analyzed in this study apparently do not exhibit EP toxicity and by that criterion are not hazardous according to EPA regulations. However, additional analyses are needed to categorize the wastes under California state regulations. To that end analyses should be performed on well-drilling wastes to delineate those constituents that are part of the rock formation, in contrast to those present in the drilling mud, added to the mud, or present as a result of brine discharge.

The geothermal brines examined in this study exhibit EP toxicity by virtue of the amounts of As, Ba, and Pb present in the extracts. By this finding they are hazardous according to EPA standards under RCRA. Notwithstanding this finding, geothermal brines are toxic by definition under subchapter 15, Title 23 of the California Administrative Code (CAC, 1977).

Before any conclusions can be made about wastes associated with scaling, separation of solids from spent brine, and use of agricultural waste water for power plant cooling, many more samples will have to be analyzed. This current study indicates that even though significant amounts of certain toxic metals such as Ba and Pb are present in the original wastes, only very small amounts below toxic limits are leached into the extracts. Additional samples and tests are needed to determine if this finding is consistent.

Other factors are involved that mandate the acquisition of additional samples from a variety of facilities and locations over a relatively long period of time. These factors have to do with differences in the types of power plants and steam gathering facilities that will be built and new processes that will be developed and utilized for pretreatment of cooling water and treatment of spent fluids and other wastes. Other more fundamental factors are involved as well. These pertain to temperature, pressure, and compositional differences of the resource fluids in the different KGRA's and changes in these characteristics that may occur with utilization of the resources over a long period of time.

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