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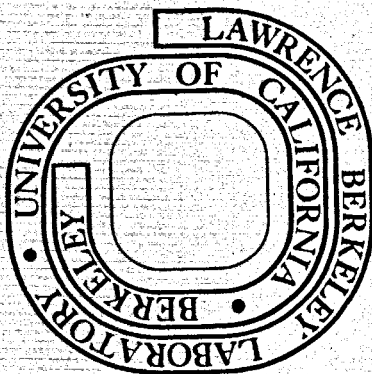
TREATMENT METHODS FOR GEOTHERMAL BRINES

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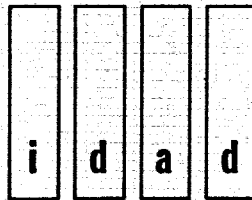
TREATMENT METHODS FOR GEOTHERMAL BRINES

By

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April 1979

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ABSTRACT

A survey is made of commercially available methods currently in use as well as those which might be used to prevent scaling and corrosion in geothermal brines. More emphasis is placed on scaling. Treatments are classified as inhibitors, alterants and coagulants; they are applied to control scaling and corrosion in fresh and waste geothermal brines. Recommendations for research in brine treatment are described.

Introduction

During the past ten years much progress has been made in the United States to develop geothermal energy and to construct power plants. Current electrical power produced is 608 MWe at the Geysers in California, which obtains steam to drive turbines from steam wells. However, the major new sources of geothermal energy in the next decade are expected to be hot brine systems located in the western United States. A problem in utilizing these hot water resources is the dissolved gases and minerals which cause scaling and corrosion of wells, piping, heat exchangers and other components of the power plant (Ref. 1).

Methods for treating brines to control scaling and corrosion in production and injection wells, and within the power plant, are needed to: (1) permit utilization of sites with high scaling potential such as the Salton Sea which contains as much as 30,000 ppm total dissolved solids, and (2) lower the cost of maintenance of power plants by reducing the rate of corrosion and formation of scale at each site.

The control of scale formation and corrosion has a long history of careful empirical testing, research and maintenance. Scale is typically removed by scraping and reaming; often acid is added prior to scraping and the products removed by washing with water. These are effective methods for removing scales once they have formed (Ref. 2).

Currently used methods to control scaling in geothermal plants are centered around mechanical means such as wire brushes to remove scale from pipes and acidizing or reaming of wells. Scale removal is considered as a maintenance problem and scheduled as needed.

Since about 1950, research has been in progress in the oilfield and boiler water areas to develop means to control scale and corrosion by adding chemical substances. Treatment methods are devised for both the fresh fluid (e.g., water, petroleum) prior to use for example in power generation or refining; and for the spent brines prior to injection into the ground or other method of disposal. The treatment methodology of geothermal brines parallels that for oilfield and other brines, and those portions that appear relevant are included here.

The increasing availability of basic data for solubility and kinetics of corrosion and scaling parameters, as well as the development of computer methods, has made it possible to examine increasingly complex scaling problems. The computer calculations are based on solubility and equilibrium data for mineral solutions and other substances, as well as flow rates and temperatures.

Treatment methods to control geothermal and other scaling can be classified in a number of ways. It is convenient to separate them as follows: (1) inhibitors, (2) alterants, and (3) coagulants. Inhibitors are substances added to brines usually at the ppm level to retard the growth of scale; they are generally added to the fresh brine. Alterants are added to the brine with a resulting change in the chemistry; examples are the addition of hydrochloric acid to lower the pH, and removal of metals by ion-exchange. The third class covers coagulants and flocculants which are added to remove precipitates or suspended substances; they are generally added to waste waters as a pretreatment method prior to disposal, for example, by injection. Table I lists these three classes of methods commonly used to treat geothermal

and other waters.

It is not possible to cover both scaling and corrosion in detail for this report. Although emphasis here is on geothermal scaling, research in other areas such as oilfield scaling which might be applicable to the control of geothermal scale formation is also included. Information on geothermal and other corrosion can be found in A Study of Brine Treatment (Ref. 2), Underground Waste Management and Environmental Implications (Ref. 3), Corrosion Inhibitors (Ref. 4), Salt Water Disposal (Ref. 5), Brine Disposal Treatment Practices Relating to the Oil Production Industry (Ref. 6), Scale Prediction in Geothermal Operations (Ref. 7), Brine Chemistry and Combined Heat/Mass Transfer (Ref. 8), Water Quality and Treatment (Ref. 9), and Conference on Scale Management in Geothermal Energy Development (Ref. 10).

In this report, we cover scale formation and treatment for both the fresh brine from production wells which is flashed to steam and used to drive a turbine, and for the spent fluid which is treated prior to disposal, for example, via injection wells. More emphasis is placed on treatment of fresh fluids where the current state of the art is not as well developed as that for spent brines.

Geothermal Scale

Scale formation is common in geothermal hot water systems, and arises from deposition and adhesion of soluble or suspended constituents such as silica and calcite onto pipes, walls and other components of power plants. The need to control scaling stems from three major concerns: (1) plugging and clogging of wells and pipes transporting the brine, (2) decrease in the efficiency of turbines and heat exchangers, and (3) freezing of valves and rendering instruments inoperative. The second problem covered here is corrosion of metallic components in contact with the hot brine. Geothermal brines contain dissolved gases and salts, for example CO_2 , H_2S , NaCl , that are generally more corrosive to materials of construction than other environments common to power production.

Table II shows that the scale constituents commonly found in geothermal systems are silicate, carbonate and sulfide. Depending on the power plant location, the source of the scale is fresh brine, flashed steam from the brine, or spent fluid condensate. The composition of typical brines is shown in Table III.

Brine Treatment Systems

The developers of systems for treating geothermal brines are faced with a large selection of possible treatment additives, corrosion-resistant materials and disposal options. The selection of an optimum treatment method is further complicated by the combined needs of preventing scale while not affecting the temperature and flow rate of the production fluid. The waste brines must be treated for both compatibility with the injection well and receiving formation and to prevent undesirable pollutants (e.g., boron, arsenic) from mixing with surface waters. Besides these, large

quantities of brine and solids such as sludge must be treated and disposed.

The developer needs to consider that in treatment systems the following basic functions must be provided: chemical analysis, holding tanks, coagulants and filters, pumps, and associated piping. Each function is important and the entire treatment system must be considered in order to realize the full operation capabilities of the system. The discussion which follows applies mainly to the step in which material, e.g., inhibitor or coagulant, is added to the brine.

Besides the addition step, a system will need one or more of the following components: sample methods for fresh and spent brine; samples of steam and condensate; pipes to carry the inhibitor or alterant; mixing and storage tanks; coagulation and sedimentation facilities; sludge disposal sites; pumps for injection wells and for the addition of additive; instrumentation to measure pH and other important parameters; chemical analysis of the waste brine and fresh brine; regulatory requirements; data on the injection (receiving) formation; and fluid flow rates.

Both the discussion which follows and specific examples given will center around the more important geothermal scale components: silica, calcite and sulfide. Treatment methods covered include those currently used in geothermal plants as well as those commonly used in other industries such as those given in Water Quality and Treatment (Ref. 9), Salt Water Disposal - East Texas Oil Field (Ref. 5), Brine Disposal Treatment Practices Relating to the Oil Production Industry (Ref. 6), A Study of Brine Treatment (Ref. 2), "An Evaluation of Scale Inhibitors" (Ref. 11), and "Enhanced-Oil-Recovery by Injection Waters" (Ref. 12).

Scale Inhibitors and Seeding

Prevention of scale formation by addition of inhibitors to fresh brines is largely done on a trial and error basis. Both proprietary and other chemicals are screened by treating the brine and noting the effect on the thickness of the resulting scale or change in the scale composition (Ref. 21,26). The methods commonly used are seeding and scale inhibitors.

Seeding

The idea of seeding is to initiate precipitation of the scale forming substance at selected places under controlled conditions, thereby removing these components before they can deposit as scale in undesired locations. In this treatment method, a finely divided solid is introduced to the brine to help crystallize the soluble material. The method has been used for seawater (Ref. 14), geothermal brines (Ref. 13,15), and in basic studies on seeding with CaCO_3 (Ref. 16,17).

At the East Mesa area in California, seeding was considered in fresh brine as a means of preventing scaling in process equipment, including a vertical tube evaporator. The method involving addition of lime and magnesium oxide to precipitate CaCO_3 , Mg(OH)_2 and silica was not judged attractive because the brine temperature would drop and large amounts of sludge were generated -- estimated at 300 to 600 tons per day for a 1,000,000 gallon per day flow rate (Ref. 15).

At the Niland geothermal area, a wet sludge suspension composed of 20% by weight of sediment (mainly silica) from the geothermal loop experimental facility (GLEF) was metered into the fresh brine at 210°C, and the concentration of dissolved silica measured. Before the addition

of sludge, the silica was 453 mg/kg; sludge was metered in at 0.3 gpm and 0.15 gpm, with silica contents in the treated brine measured as 431 and 416 mg/kg respectively (Ref. 13).

In summary, seeding to control scaling from fresh brines by addition of sludge or lime has been investigated at East Mesa and Niland.

Inhibitors

As used here, the term inhibitor refers to a substance which when present at ppm concentration levels retards significantly the growth of scale or formation of a precipitate. The inhibitors are tested and ranked in order of effectiveness, cost and stability at high temperatures. This testing and ranking procedure must be done at each site because the brine properties and flow conditions vary for each geothermal site.

The inhibitor is generally thought to prevent deposits by preferentially forming a film on the growing scale crystal, thereby retarding further growth of the crystal (Ref. 18). For example, CaCO_3 deposition is prevented by phosphate inhibitors which adsorb on the surface. Table IV lists commercially available inhibitors which have been used to control scaling in geothermal systems, and selected inhibitors applied in other areas and which appear useful in geothermal energy utilization. Reference 26 contains a listing of over 30 inhibitors tested for their effectiveness for inhibiting the precipitation of silica from hypersaline geothermal brines.

Inhibitors of the film type are generally polyphosphates (e.g., sodium pyrophosphate), salts of acrylic and methacrylic acids, and aminoethyl and aminoethylene phosphonates (Ref. 15).

Scale inhibitors are commonly classified as chelating agents, threshold inhibitors and crystal distortion inhibitors (Ref. 22). Depending on the pH and presence of anions, chelating agents such as EDTA are effective for preventing scale due to Ca and Fe by forming strongly bound soluble metal complexes. However, stability at geothermal temperatures and pressures is an important factor.

Threshold inhibitors are chemicals such as phosphonates added to the treatment water at concentrations just sufficient to retard scale formation. They are the most widely used. Crystal distortion inhibitors limit the size of the scale crystals to produce small particles which remain suspended in the water. An example is the addition of Pb^{++} to distort the growth of $CaCO_3$ by forming $PbCO_3$ (Ref. 23).

Alterants

In the alterant method of scale control, a brine property is modified by continuous or semi-continuous injection of a selected substance or by mixing. Ideally, the brine property is changed from its initial value to another value wherein the scale or corrosion is prevented. Alterants are gases, liquids, change in temperature or pressure, or ion-exchange solids. See Table V.

In an experiment at Niland, HCl injection was found beneficial in controlling silica scale formation using brine from Magmamax well No. 1. The pH of unmodified brine was 5.5 to 5.8. The dissolved solids content of the brine prior to and after expansion through nozzles was 18 to 22%w. Nominal scaling composed of copper sulfide, native silver, and iron-rich amorphous silica from unmodified brine resulted in closure of up to 10%

of the cross-sectional areas of nozzle throats. Scale formed on wearblades ranging in thickness from 0.019 mm to 0.04 mm. However, when brine was acidified to pH 1.5, 2.3, and 4.0 with HCl, scaling in the nozzles was eliminated and substantially reduced on the wearblades. Acidified brine effluents remained clear several hours after collection, while the unmodified brine was slightly turbid when collected, with precipitates forming a few minutes after samples were taken (Ref. 2).

Water Dilution

The addition of water to the fresh fluid was successful in reducing silica scaling at Namafjall, Iceland. Before dilution, scale was deposited from 95°C water as loose, leaf-like flakes which grew to 15 to 30 mm inside an 8 inch pipe. The scaling was reduced by mixing unflushed fluid from the drillhole to a 35% dilution with cold water at atmospheric pressure. Addition of dilution water reduced the silica content of the fresh fluid from 347 ppm to 188 ppm (Ref. 2).

Before relying on dilution to reduce silica precipitation, one needs to consider that the diluent must be chemically compatible with the brine. For instance, attempts to reduce scaling in the GLEF at Niland by addition of steam condensate to the brine actually resulted in higher rates of scale and solids formation. This was a result of the high ammonia and carbonate content of the condensate and its correspondingly high pH (9-10). The problem is that when steam containing noncondensibles is cooled, re-distribution of species occurs with most of the ammonia redissolving. This raises the pH of the condensate and promotes dissolution of CO₂ into the condensate (Ref. 2).

Oxidation and Aeration

Oxidation of sulfide to sulfur or sulfate has been proposed as a means of controlling sulfide scale deposition (Ref. 2). A problem here is cooling of the brine and formation of insoluble metal sulfates (e.g., CaSO_4) and elemental sulfur, which cause erosion of piping and plugging of injection systems. Addition of a dispersing agent may be needed to prevent the solids from settling out.

In water quality treatment, diffused-air aerators are used to remove gases such as H_2S and CO_2 and to oxidize Fe^{++} and Mn^{++} to form precipitates. The method utilizes injection of compressed air through a perforated pipe or similar system to produce fine bubbles. The CO_2 is exchanged from the water phase to the gas phase; H_2S is oxidized. An advantage of aeration for H_2S removal is the low cost of air used in aeration. However, aeration can cause formation of sulfate and subsequent deposition of insoluble metal sulfates as well as corrosion due to the introduction of excess dissolved oxygen.

Coagulants

Coagulants are chemicals such as aluminum sulfate, ferrous sulfate and sodium aluminate added to waters and waste waters to speed up the settling and deposition of suspended solids. Flocculants to aid coagulations are often added. The method has been used to treat spent brines prior to disposal. See Table VI.

The preferred method for disposal of geothermal waste brine is by injection into wells beneath the surface of the earth to prevent mixing of the spent fluid with water that will be used for irrigation or drinking

purposes. An important consideration in waste brine injection is pre-treatment to prevent precipitation or other reactions between the brine and the injection well system which will cause scale, corrosion or solids deposition.

Laboratory studies are needed for designing a treatment and injection disposal system. The required data include the following: (1) chemical composition of the brine; (2) pH; (3) scale forming potential; (4) compatibility of the brine and water in the aquifer; (5) necessary treatment to stabilize the brine for injection into the desired subsurface formation (Ref. 2,5). The laboratory studies should provide data on the kind of treatment needed; an extensive treatment system could require the following steps:

<u>Treatment Method</u>	<u>Comment</u>
1. Storage of spent brine	Open or closed storage container
2. Corrosion control	pH adjustment; inhibitors
3. Solids separation	Gravity, sedimentation, coagulation, filtration
4. Slime control	Biocide, chlorine
5. Oxidation	Arsenic removal as As(V)
6. Aeration	Remove CO ₂ , H ₂ S to reduce corrosion
7. Ion-exchange, adsorption	Boron control

A Specific Example

Treatment Methods for Removal of Boron From Geothermal Brines

The presence of boron in geothermal brines at concentrations ranging up to several hundred ppm (Ref. 27), represents a potential hazard from the environmental standpoint. Boron in the form of boric acid and its water soluble salts is an essential trace element in the normal growth of all higher green plants (Ref. 28). However, as is the case with most trace-element nutrients, excessive amounts become toxic and lead to plant death. Some boron-sensitive plants and crops show toxic effects when irrigated with water containing boron concentrations as low as 1 ppm (Ref. 29).

The development of economically feasible methods for removal of boron at the ppm level from waste waters -- industrial, agricultural and geothermal -- is still in progress (Ref. 38). Various approaches have been employed with varying degrees of success as outlined below.

Adsorption of boric acid onto hydrated aluminum oxide and iron oxide sites in clays and clay-components of soils could provide an effective method for boron removal under certain circumstances (Ref. 30,31,38,39). Unfortunately, the adsorptive capacities of clays and related materials are low (0.1mg/gm) even under optimum conditions. From the plant engineering standpoint, prohibitively large amounts of adsorbate would be required in most cases. However, adsorption processes are an important consideration in the removal of boron by soils in situ following a spill or other accidental contamination.

Precipitation methods commonly used in the water treatment industry, i.e., those involving lime, aluminum hydroxide and iron hydroxide, are

ineffective in removing boron (Ref. 31,32). In addition, the conventional sedimentation and biological treatment processes employed in sewage treatment plants have little or no effect on boron levels (Ref. 33).

Reverse osmosis (through cellulose acetate) would appear to have but limited application in the removal of boric acid from waste waters. At an operating pressure of 500 psi, only 20-30 percent of the boron in sea water is rejected as compared to over 95 percent of the sodium chloride (Ref. 34,35).

Of the waste water treatment processes, those involving ion-exchange resins appear to be the most promising (Ref. 36,37). It is recognized, of course, that the complete de-ionization of water by strongly basic ion-exchange resins such as Amberlite IRA-400 and Dowex 2, does not represent an economical approach for removal of boron from waters containing appreciable concentrations of other exchangeable anions such as chloride ion. However, the strongly basic resins might be employed economically in the removal of boron from geothermal steam condensates which are relatively low in total salinity. Similarly, the Amberlite IRA-400 and Dowex 2 resins could be used in the removal of boron from brackish waters previously treated by one or more reverse-osmosis cycles.

However, it appears that the most direct and economical method for removal of boron from geothermal brines may be the use of the recently developed boron-specific resin, Amberlite XE-243 (Ref. 37,39). This is a crosslinked microreticular gel-type polymer derived from the amination of chloro methylated styrene-divinyl benzene with N-methylglucamine. The resin exhibits equilibrium boron capacities in the range 5mgB/gm with good hydrodynamic properties and chemical stability. The boron selectivity

of Amberlite XE-243 is not affected by high concentrations of various other salts including sodium chloride. It has been estimated that over-all costs for the lowering of boron concentrations from 10 ppm to 1 ppm in irrigation waters would be below \$0.03 per thousand gallons. An extensive study of the applicability of Amberlite XE-243 in the deboronation of geothermal brines appears warranted.

Corrosion

The treatment methods currently in use or which might be useful in controlling geothermal corrosion generally fall into one of two categories: (1) removal of brine constituents which cause corrosion, and (2) development of corrosion-resistant materials.

Corrosion rates in geothermal fluids which are complex solutions containing many different chemical species are dependent primarily on the following most significant species: H^+ , Cl^- , H_2S , CO_2 , $CO_3^{=}$, HCO_3^- , NH_3 and $SO_4^{=}$. Other less common or aggressive chemical species which can also produce corrosive effects in some geothermal fluids are: F^- , heavy metals, B and O_2 . In addition, the presence of heavy or transition metal ions can also be corrosive. See Table III (Ref. 40).

Aeration, a process used in "open-type" systems, involves a mass transfer between the water and gas phases to speed up the removal of acidic gases (e.g., H_2S and CO_2), by producing a large contact surface area between air and water. Typical aeration equipment include cooling towers, spray nozzles, and forced draft blowers.

Chemical degasification is used to remove oxygen selectively from the water by adding a chemical such as sodium sulfite or hydrazine to remove O_2 from oilfield brines and boiler feed water. Sodium sulfite (10 ppm Na_2SO_3 per 1 ppm O_2) was added to the 86°C water in the Reykjavik Municipal Heating System, Iceland, to reduce oxygen and thereby control internal corrosion of metals in the heating systems (Ref. 40).

Current methods of corrosion control are centered around planned replacement of turbine blades, piping and other plant components and the

development of materials with improved corrosion resistance. Table VII presents a list of materials tested for their performance in liquid dominated resources. The reader is referred to Ref. 25 and 41 for a thorough review of corrosion resistance of various metals and alloys in hot brines.

Computer-Assisted Calculations of Scaling Rates

Computer assisted calculations are finding increased use to the prediction of scaling and corrosion. A great advantage is the ability to simulate the effects of changes in brine variables such as temperature and composition, and the likely result on scaling and corrosion. See Table VIII.

The need is to estimate scaling and corrosion rates at various points in a power plant. Input data is based on brine chemistry and flow, and the code provides the following: flow rate, temperature, velocity at points from bottom of production well through the plant to the waste injection system (Ref. 8,19,24).

Valid analytical expressions and supporting rate data are needed to calculate scaling. The general approach to scaling rate is to equate the rate of buildup to the degree of insolubility or supersaturation of a mineral minus the rate of mechanical removal. For example, the EQUILIB GEOTHERM computer code calculates the degree of mineral precipitation from the temperature, volume, composition, pH, and gas content of the brine (Ref. 8).

Summary and Conclusions

In summary, currently used methods to control scaling in geothermal plants are mainly centered around mechanical means such as wire brushes to remove scale from pipes, and acidizing or reaming of wells. Scale removal can be considered as a maintenance problem, and scheduled as needed. A research and development program with the idea to prevent the formation of scale might include the following:

1. Control of calcite formation in production wells by maintaining the downhole pressure to prevent loss of CO_2 by flashing. Maintaining the pressure keeps CO_2 dissolved in the brine as bicarbonate and prevents formation of insoluble calcium carbonate. Development of downhole pumps is currently in progress.
2. Test equipment is needed to provide empirical data on methods to control geothermal scale formation, for example, evaluation of various commercial additives. The equipment should preferably be convenient for use at the laboratory bench and provide test results under simulated field conditions within a short time, e.g., 2-3 days, using standard testing methods.
3. Fundamental studies are needed on the growth and inhibition of geothermal scales (e.g., FeS , SiO_2 , CaCO_3). The studies should include both heterogeneous scale formation on solid surfaces such as pipes and turbines, and homogeneous nucleation and formation of the main scaling substances within the geothermal brine. The results of some laboratory studies for silica and calcite formation are available.

4. Scale inhibitors specifically designed and developed for geothermal applications are needed. These should be tested for possible use at each location because brine composition and flow rates can vary from site to site. A program is in progress to evaluate commercially available scale inhibitors which have been developed mainly for non-geothermal fluids.
5. Studies on the adhesion of geothermal scales could provide information on methods to prevent scales from depositing onto pipes, turbines, instruments and other equipment.
6. A database containing data on the rate of formation of scale substances, e.g., Sb_2S_3 , As_4S_3 , $CaCO_3$, SiO_2 , FeS , would be valuable for predicting the likelihood of scale formation. The data is needed for incorporation into existing computer data bases which currently contain mainly equilibrium values.
7. Instrumentation is needed to monitor geothermal plant parameters in situ to measure scale build-up. The instruments should be rugged and able to function in a high temperature environment; self-cleaning features to remove scale or the ability to measure without being in contact with the brine are desirable features. Instruments of this type are available for monitoring waste-waters at low temperatures.
8. Treatment methods are needed to remove selected constituents such as boron from waste fluids which are not removed by conventional methods, for example, by holding tanks and coagulants, and to hasten precipitation of silica. In the latter case, seeding with brine solids is being studied.

Acknowledgment

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Tables

- I. Typical Treatment Methods to Prevent Scaling of Fresh and Spent Geothermal and Other Brines
- II. Scale Compositions Commonly Found in Geothermal Sites
- III. Typical Concentrations of Key Chemical Species in Fluids from Seven Geothermal Sites
- IV. Typical Commercially Available Scale Inhibitors for Geothermal and Other Waters
- V. Selected Commercially Available Alterants
- VI. Selected Commercially Available Coagulants and Flocculants
- VII. Commonly Used Methods for Controlling Corrosion
- VIII. Selected Computer Codes for Geothermal and Other Waters

Table I. Typical treatment methods to prevent scaling of fresh and spent geothermal and other brines.

<u>Treatment Method</u>	<u>Prevents or Controls</u>
<u>Inhibitors</u>	
Lime slurry	calcite
Phosphonate + polymer	silica scale; mixed scales
Ethylene Oxide Polymer	silica; corrosion
Hydroxethylcellulose	silica deposition; corrosion
Low molecular weight carboxylic acid	silica; corrosion
Amine	silica; corrosion
Sludge	silica; corrosion
Phosphoric acid	calcite
Polymeric carboxylic acid	calcite
Seeding with scale	calcite
EDTA	calcite
Polyacrylate	scales
Dispersant (highly carboxylated polymers)	calcite
Phosphate + sand	calcite; BaSO ₄ ; CaSO ₄
Solutions of amines, amides, carboxylic acids	scales, inhibits to 400°F
Molybdate	scales
<u>Alterants</u>	
Hydrochloric acid	silica; calcite
Hydrogen peroxide; nitric acid	H ₂ S
Fresh water diluent:	silica
Heavy diesel oil	silica; FeS; borate
CO ₂ pressure	calcite
Temperature	silica; calcite
Air, oxygen	H ₂ S, Mn ⁺⁺ , Fe ⁺⁺
Chlorine	H ₂ S, biogrowth
Ion exchange resin	dissolved metals; borate
<u>Coagulants and Flocculants</u>	
Anionic polyelectrolyte	flocculant
Slaked lime + hypochlorite	silica, arsenic
Aluminum sulfate; ferrous sulfate	suspended solids; colloids
Cellulose xanthate	heavy metals
<u>Other</u>	
Metallic core piping	scale; corrosion
UV light	biogrowth

Table II. Scale compositions commonly found in selected geothermal sites.

Site	Major Components, %w						
	CaCO ₃	CaO	SiO ₂	S	SO ₄	Fe	Other
<u>Matsukawa</u>							<u>Al</u>
Well No. 1 (pH5.0)	--	0.30	17.75	3.20	40.84	12.20	0.83
Well No. 2 (pH7.5)	--	0.59	90.45	--	2.25	0.35	0.84
Power Plant Generator	--	1.5-1.7	59-61	0.05-53	10.2- 13.8	3.8-46.9	--
Control Valve	--	1.2- 1.60	44.4- 69.28	--	17.56- 32.82	1.00-2.01	--
Ejector	--	0.49	40.6	2.1	15.5	27.4	--
<u>Cerro Prieto</u>							<u>FeS</u>
Well Casing, M-5	1.5	--	15.1	--	--	--	83.4
Well Casing, M-7	93.0	--	1.8	--	--	--	1.2
Production Pipe, M-9	75.56	--	12.51	--	--	--	9.46
<u>Otake</u>							<u>Fe₂O₃</u>
Disposal Pipe: Entrance	--	--	78.45	--	--	--	3.22
3863m from Entrance	--	--	93.25	--	--	--	0.15
<u>East Mesa</u>							
Well 38-30 Vertical Tube Evaporator	Major	--	--	--	--	--	--
	Major	--	--	--	--	--	--
<u>Salton Sea/Niland</u>							<u>Ca</u>
Teflon Coupon	--	--	83	0.3	--	--	0.45
<u>Heber</u>							<u>Si</u>
Heat Exchanger, Steel	--	--	--	19-41	--	18-62	1-21
Heat Exchanger, Titanium	--	--	--	15-45	--	0.5-4	1-11
<u>Lardarello</u>							<u>FeS</u>
Turbine	Present	--	--	--	Present	--	Present
<u>Hveragerdi and Namafjall</u>							<u>Fe₂O₃</u>
Heat Exchanger	--	--	61-73	--	--	--	0.3-4

Table III. Typical concentrations of key chemical species in fluid from seven geothermal sites.

KGRA	Properties of the Geothermal Resource									
	Temperature °C and location	Concentration of Key Species in the Fluid (ppm)						Fluid Description	SiO ₂	TDS
		pH	Cl ⁻	Total CO ₂	Total H ₂ S	Total NH ₃	SO ₄ ⁼			
Salton Sea, Ca.	250 (bore-hole)	5.2	115,000	1,000	10-30	300	20	unflashed well-head fluid	500	120,000- 250,000
East Mesa, Ca.	180-200 (bore-hole)	5.7	11,000	800	3	41	20	unflashed well-head fluid	330	3,000
Heber, Ca.	180-200 (bore-hole)	7.1	9,000	180	~2	13	152	unflashed well-head fluid	--	14,000
Mono-Long Valley, Ca.	175 (bore-hole)	6.5	227	180	14	0.1	96	unflashed well-head fluid	--	--
Baca (Valles Caldera) N.M.	171 (well-head at 110 psig)	6.8	3,770	128	6	--	59	flashed fluid	--	--
Beowawe, Nev.	132 (well-head)	9.3	50	209	6	3	89	flashed fluid	329	1,200
Raft River, Id.	146 (bore-hole)	7.2	780	60	0.1	2	61	unflashed fluid	--	1,204- 3,360

Table IV. Typical commercially available scale inhibitors for geothermal and other waters.

Manufacturer	Inhibitor	Comment
American Can Co.	Marasperse N-3	Cellulose compound
American Hoechst	Tylose MHB	Cellulose compound
Dow Chemical Co.	XFS-43075	
Union Carbide Corp.	Cellosize QP-09-L; Carbowax 350	Hydroxyethylcellulose; ethylene oxide polymer
A.E. Staley	Starpol 100	Substituted starch
Air Products	Surfynol 485	Acetylenic glycol
E.I. DuPont	Zonyl FSN, FSB	Fluorinated surfactants
Drew Chemical Corp. Calgon Corp.	Drewplex 502 Calgon CL-77W Calgon SL-500	Tested at East Mesa Tested at East Mesa Chelating type, tested at East Mesa
Monsanto Chemical Co.	Dequest 2060 (diethylenetriamine-penta-methylenephosphoric acid)	Tested at East Mesa
Hercules, Inc.	Natrosol 250LR (hydroxyethylcellulose)	Tested at Salton Sea - Niland
Dearborn Chemical Corp.	Geomate 256 (phosphonate + polymer); Geomate 259	Tested at Salton Sea - Niland
Calgon Corp.	CL-165 (polymer mixture)	Tested at Salton Sea - Niland
Drew Chemical Corp.	Drewsperser 747 (phosphonate + polymer)	Tested at Salton Sea - Niland
Betz Laboratories	Betz 419 (phosphonate + acrylic polymer); Polysperse Plus	Tested at Salton Sea - Niland
Far-Best Corp.	Thermosol APS (polyalkylphosphonate)	Tested at Salton Sea - Niland
C-E Natko	S-404 (organic polymer)	Tested at Salton Sea - Niland
Southwest Specialty Chemicals	SC-210 (low molecular weight carboxylic acid)	Tested at Salton Sea - Niland
Champion Chemicals	Cortron R-16 (filming amine)	Tested at Salton Sea - Niland
National Starch & Chemical Magma Corp. (Aquaness Div.)	Versa-TL3 Calnox Polyacrylates (214DN)	Used in boilers Carbonate and sulfate scale control
Wright Chemical Corp. CIBA-GEIGY	Molybdate base Belgard EV (polymeric carboxylic acid)	Scale control Seawater

Table IV. Typical commercially available scale inhibitors for geothermal and other waters. (continued)

<u>Manufacturer</u>	<u>Inhibitor</u>	<u>Comment</u>
Allied Colloids, Inc. (General Industries Div.) Hercules, Inc.	ANTIPREX A (sodium polyacrylate) SP-944, lime slurry additive	Developed for boilers and evaporators Prevents CaCO ₃
Colloid-A-Tron, Inc.	Colloid-A-Tron	Piping which contains metallic core to prevent scaling/corrosion
Petrolite Corp. (Tetralite Division) Nalco Chemical	Tolsperse 133 NALCOOL	Organic polyphosphonate Dispersive corrosion inhibitor
Oakite Products, Inc.	Enprox	Non-chromated inhibitors for scale and corrosion

Table V. Selected commercially available alterants.

Manufacturer	Alterant	Comment
FMC Corp.	Hydrogen peroxide, oxygen	
Pentech Div. (Houdaille Industries, Inc.)	JAC oxyditch systems	Aerator system
Permutit	Air system	Aeration
Wallace and Tiernan (Pennwalt Corp.)	Chlorination	
Capital Controls Co. (Dart Industries)	Chlorination	
IMC Chemical Group	AMP-95	Neutralizing amine for CO ₂
C-E Bauer (Combustion Engineering, Inc.)	Airpact air diffusers	Aerator system
Xodar Corp.	360 system	Aerator
Rohm and Haas	Ion exchange	Metals removal
Various Manufacturers	Hydrochloric acid	Reduced scale at Salton Sea
DuPont Co.	TYSUL WW, hydrogen peroxide	
Ionac Chemical Co.	Ion exchange	
Dow Chemical Co.	Ion exchange	

Table VI. Selected commercially available coagulants and flocculants.

<u>Manufacturer</u>	<u>Coagulant</u>	<u>Comment</u>
Allied Colloids	Percol 726 (anionic high molecular weight polymer bead)	Flocculant
Hercules, Inc.	Hercofloc organic polymers	Flocculant for suspended solids
ARRO Laboratories, Inc.	ARRO-CX (cellulose xanthate)	Removes heavy metals
Petrolite Corp.	Tolfloc 352; 300	Flocculant; cationic polyelectrolyte
Nalco Chemical Co.	Instant polymers	Flocculant
Narvon Mining	Zeta Flocc WA	Polyelectrolyte flocculant
Swift Environmental Systems Co.	Lectro Clear (alum) Watcon 1355	Electrocoagulation High molecular weight cationic flocculant
Oakite Products, Inc.	Enprox	For coagulation
Dow Chemical	Purifloc	

Table VII. Commonly used methods for controlling corrosion.

Site	Method	Comment
Raft River, Well No. 1	Materials evaluation: bronzes, brasses, stainless steels, nickel-based alloys, cobalt-based alloys and titanium had lowest corrosion rates	Major brine constituents for corrosion: Cl, HCO ₃ , CO ₃ , S, CO ₂ , H ₂ S, Fe, Ca, Mg, SiO ₂
Salton Sea, Magmamax No. 1	Materials testing: low Cr-Mo steels had lowest rate	
Desalination	Deaeration, pH control, polyphosphate addition, materials (titanium, polymers)	Chromate and phosphate mixtures promising
Oilfield Fouling	Antifoulants composed of mixture of dispersants, antioxidants, corrosion inhibitor	See reference 4 for detailed discussion
	Pre-Krete G-8 and C-17 blocks	Available from Pocono Fabricators (Patterson-Kelley Co.)
	Water soluble Molybdates	Climax Molybdenum Co.
*East Mesa	≤1 mpy corrosion for AISI type 302, type 430, Hastelloy S, titanium	Data for wellhead fluid
*Heber	≤1 mpy corrosion for AISI 316L, titanium, Hastelloy G, Inconel 625	Data for wellhead fluid
*Baca Location No. 1	Materials testing: ≤1.0 mpy for AISI type 316 Carpenter 20Cb3, Carpenter 7Mo, Inconel 600, Incoloy 825, titanium; >10 mpy for carbon steel	Data for flashed wellhead fluids

*See Reference 25 for additional data.

Table VIII. Selected computer codes for geothermal and other waters.

<u>Code</u>	<u>Comment</u>
Helgeson-Herrick	Prediction of sulfide-silicate precipitation from Salton Sea brine
EQUILIB	Predict control of scale formation on adding acid; equilibrium scale formation
FLOSCAL	Kinetics of scaling
PLANT	Impact of scale build-up
GEOSCALE	Identify plant scale problems
BROP7	Thermodynamic properties of brine and vapor
WELLFLOW	Wellhead flow for geothermal well
CALGUARD	Predicts corrosion and deposition, along with appropriate treatment in operating cooling systems

References

1. A Recommended Research Program in Geothermal Chemistry, Lyon, R.N. and Kolstad, G.A., Cochairman, Wash-1344, October 1974, Atomic Energy Commission (Department of Energy), available from National Technical Information Service, Springfield, VA 22151
2. Phillips, S.L., Mathur, A.K. and Doebler, R.A., A Study of Brine Treatment, EPRI ER-476 and LBL-6371, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, November 1977, available from Electric Power Research Institute, Palo Alto, CA 94304
3. Underground Waste Management and Environmental Implications, Cook, T.D., ed., Memoir 18, Proc. Symp., Dec. 6-9, 1971, Houston, TX (1972), available from the American Association of Petroleum Geologists, Tulsa, OK
4. Corrosion Inhibitors, Nathan, C.C., ed., Second Printing, National Association of Corrosion Engineers, P.O. Box 1499, Houston, TX 77001 (1974)
5. Salt Water Disposal, East Texas Oil Field, Second Ed., East Texas Salt Water Disposal Co., Kilgore and Tyler, TX (1958), available from the Petroleum Extension Service, The University of Texas, Austin, TX
6. Reid, G.W., Streebin, L.E., Canter, L.W., Smith, J.R., Brine Disposal Treatment Practices Relating to the Oil Production Industry, University of Oklahoma Research Institute, Norman, OK 73069, EPA-660/2-74-037 (May 1974), available from U.S. Government Printing Office, Washington, D.C. 20402
7. Vetter, O.J., "Scale Prediction in Geothermal Operations - State of the Art", International Symp. on Oilfield and Geothermal Chemistry, Paper No. SPE 6593, La Jolla, CA, June 27-28 (1977), P.37-44
8. Shannon, D.W., Walter, R.A. and Lessor, D.L., Brine Chemistry and Combined Heat/Mass Transfer, Vol. I and Vol. II, Battelle Pacific Northwest Laboratories, Richland, WA 99352, EPRI ER-635, January 1978, available from Electric Power Research Institute, Palo Alto, CA 94304
9. Water Quality and Treatment, A Handbook of Public Water Supplies, American Water Works Association, 3rd Ed. (1971), McGraw-Hill, Inc., New York, NY
10. "Conference on Scale Management in Geothermal Energy Development", C00-2607-4, San Diego, CA, August 2-4, 1976, available from National Technical Information Service, Springfield, VA 22161
11. Vetter, O.J., "An Evaluation of Scale Inhibitors", J. Pet. Technol., P.997-1006 (1972)
12. Collins, A.G., "Enhanced-Oil-Recovery Injection Waters", International Symp. on Oilfield and Geothermal Chemistry, Paper No. SPE 6603, La Jolla, CA, June 27-28 (1977), P.37-44

13. Harrar, J.E., Locke, F.E., Otto, C.H., Jr., Deutscher, S.B., Lim, R., Frey, W.P., Quong, R. and Lorensen, L.E., Preliminary Results of Tests of Proprietary Chemical Additives, Seeding, and Other Approaches for the Reduction of Scale in Hypersaline Geothermal Systems, UCID-18051, Lawrence Livermore Laboratory, Livermore, CA, Feb. 1, 1979
14. Chernozubov, V.B., Zastrovskii, F.P., Shatsillo, V.G., Golub, S.I., Novidov, E.P. and Tkach, V.I., "Prevention of Scale Formation in Distillation Desalination Plants by Means of Seeding", Proc. First Intl. Symp. on Water Desalination, Vol. 1, P.539-547 (1965), Washington, D.C.
15. Lindemuth, T.E., Houle, E.H., Suemoto, S.H., Van Der Mast, V.C., "Experience in Scale Control With East Mesa Geothermal Brine", International Symp. on Oilfield and Geothermal Chemistry, La Jolla, CA, June 27-28 (1977), SPE 6605, P.173-186
16. Tomson, M.B., Nancollas, G.H. and Kazmierczak, T.E., "Controlled Composition Seeded Growth Kinetics of Calcium Carbonate", International Symp. on Oilfield and Geothermal Chemistry, La Jolla, CA, June 27-28 (1977), Paper No. SPE 6591, P. 13-20
17. DeBoer, R.B., "Influence of Seed Crystals on the Precipitation of Calcite and Aragonite", Am. J. Sci., 277 (1), P.38-60 (1977)
18. Metcalf, J.H., "Inhibition and Corrosion Control Practices for Boiler Waters", Corrosion Inhibitors, P. 196-219, National Association of Corrosion Engineers, Houston, TX (1973)
19. "Water Treatment and the Computer", Industrial Water Engineering, 15 (7), P.4 (1978)
20. Zilch, H.E. and Fischer, P.W., "Inhibition of Scale Deposition in High Temperature Wells", U.S. Patent 4,032,460, Abstract No. 149, Geothermal Energy Update, January 1978
21. Harrar, J.E., Lorensen, L.E., Otto, C.H., Jr., Deutscher, S.B. and Tardiff, G.E., "Effects of Organic Additives on the Formation of Solids from Hypersaline Geothermal Brine", Trans., Geothermal Resources Council, Vol. 2, P.259-262 (July 1978), Annual Meeting, Hilo, HI, July 25-27, 1978
22. Hausler, R.H., "Predicting and Controlling Scale from Oilfield Brines", Oil and Gas J., P.146-154 (Sept. 18, 1978)
23. Michels, D.E. and Keiser, D.D., "Molecular Mechanisms of Scale Deposition", Conf. Scale Management in Geothermal Energy Development, San Diego, CA, Aug. 2-4, 1976, P.51-58, C00-2607-4 (1976)

24. Riney, T.D. and Reynolds, S.L., "EQUILIB Simulation of Acidization for Geothermal Scale Control", Proc. Second Geothermal Conference and Workshop, Taos, NM, June 20-23, 1978, EPRI WS-78-79 (Oct. 1978), P.147-150
25. DeBerry, D.W., Ellis P.F. and Thomas, C.C., Materials Selection Guidelines for Geothermal Power Systems, First Ed., Radian Corp., Austin, TX 78766, Report No. ALO-3904-1, September 1978
26. Harrar, J.E., Locke, F.E., Lorensen, L.E., Otto, C.H., Jr., Deutscher, S.B., Rey, W.P. and Lim, R., "On-Line Tests of Organic Additives for the Inhibition of the Precipitation of Silica from Hypersaline Geothermal Brine", UCID-18091, April 3, 1979, Lawrence Livermore Laboratory, Univ. of California, Livermore, CA 94550
27. Bassett, R.L., The Geochemistry of Boron in Geothermal Waters, Ph.D. Thesis, Stanford University (1976)
28. Bonner, J.E. and Varner, J.E., Plant Biochemistry, Academic Press, New York, NY (1976)
29. Bingham, F.T., "Boron in Cultivated Soils and Irrigation Waters", Adv. Chem. Ser., 123, P.130 (1973)
30. Sims, J.R. and Bingham, F.T., "Retention of Boron by Layer Silicates, Sesquioxides and Soil Materials I", Soil Sci., Am. Proc., 31, P.728 (1967)
31. Jasmund, K and Liner, B., "Experiments on the Fixation of Boron by Clay Minerals", Int. Clay Conf. Proc., Madrid (1972)
32. Waggott, A., "An Investigation of the Potential Problem of Increasing Boron Concentrations in Rivers and Water Courses", Water Res., 3, P.749 (1969)
33. Roberts, R.M. and Gressing, L.E., Development of Economical Methods of Boron Removal From Irrigation Return Waters, U.S. Dept. Int. Res. Dev. Report, No. 579, July 1970
34. Lonsdale, H.K., et al., Study of Rejection of Various Solutions by Reverse Osmosis Membranes, U.S. Dept. Int. Res. Dev. Prog. Report, No. 447, July 1969
35. Cruver, J.E., "Reverse Osmosis", Water and Sewage Works, 13, P.74 (1973)
36. Grinstead, R.R. and Wheaton, R.M., Improved Resins for Removal of Boron From Saline Waters, U.S. Dept. Int. Res. Dev. Report, No. 721, Dec. 1971

37. Kunin, R., "A Macroreticular Boron-Specific Ion-Exchange Resin", Adv. Chem. Ser., 123, P.139 (1973)
38. Choi, W.W. and Chen, K.Y., "Evaluation of Boron Removal by Adsorption on Solids", Env. Sci. Technol., 13 (2), P.189-196 (1979)
39. Chemical Technology and Economics in Environmental Perspectives. Task II - Removal of Boron From Wastewater, EPA-560/1-76-007, April 1976, U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.
40. Hermannsson, S., "Corrosion of Metals and the Forming of a Protective Coating of the Inside of Pipes Carrying Thermal Waters Used by the Reykjavik Municipal District Heating Service", Geothermics, Special Issue 2, 2 (2), P.1602-1612 (1970)
41. Banning, L.H. and Oden, L.L., Corrosion Resistance of Metals In Hot Brines -- A Literature Review, Report #1C-8601, U.S. Bureau of Mines, Washington, D.C. (1973)