A STUDY OF TREATMENT METHODS FOR GEOTHERMAL FLUIDS

https://escholarship.org/uc/item/6t72b6ck

Phillips, S.L.
Mathur, A.K.
Doebler, R.E.

1977-05-01
A Study Of Treatment Methods For Geothermal Fluids

Sidney L. Phillips, Ashwani K. Mathur, and Raymond E. Doebler

May 1977

Lawrence Berkeley Laboratory University of California/Berkeley

Prepared for the U.S. Energy Research and Development Administration under Contract No. W-7405-ENG-48

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.
A SURVEY OF TREATMENT METHODS FOR GEOTHERMAL FLUIDS   SPE 6606

Treatments of the fluids by chemical or physical methods could reduce scaling in the power cycle and plugging in the injection cycle. The problem is compounded by the large volume of fluids required for geothermal power production. As a result many chemical treatment systems which can be devised to control scaling and corrosion might be uneconomical.

The purpose of this study was to compile the current information on brine treatment technology for use by the geothermal power industry. The literature on treatment of geothermal brines to control scaling and corrosion with information widely scattered and incomplete. For this reason, we have drawn on the relevant data from other industries (e.g., boiler water, oilfield brines) to provide additional information which may be useful to the geothermal brine treatment methodology.

Scale incrustation is a fairly common occurrence that arises mainly from the deposition of soluble or suspended constituents of geothermal brines in piping and other components of power plants. The interest in controlling scaling stems from two major concerns: (1) plugging of well casings and pipes transporting geothermal hot water, and (2) decrease in the efficiency of heat exchangers. The other main problem related to geothermal hot water utilization covered here is corrosion of metal which is in contact with the fluid. The corrosion process is complicated and related to a number of parameters including the following: material of construction, chloride concentration, pH, partial pressure, partial pressure, and temperature of the brine. Current methods of dealing with corrosion center around either scheduled replacement of plant components or the selection and choice of suitable resistant materials. Table 1 lists the principal parameters affecting geothermal scaling and corrosion.

Included in this study are current, developing, and suggested means for the treatment of geothermal hot water with the idea of starting scaling incrustation prior to: (1) utilization for electric power production (fresh fluid), and (2) disposal of the spent fluid, e.g., to injection wells or holding ponds. The brine treatment study centers around the three principal formulas of deposits which are commonly found in geothermal scales: silica, carbonate, and sulfide. It is recognized that a geothermal scale is likely to be composed of a mixture of these main deposits as well as metals (e.g., Fe, Pb) so that brine treatment methods specific to calcite, silica, or sulfides may have to be modified for application to mixed scales. The corrosion section covers mainly desalination and material selection which are the principal methods used or suggested to control the rate of corrosion for geothermal brines.

For additional background information on geothermal scaling and corrosion, the reader is referred to the following: A Study of Treatment Methods for Geothermal Fluids,1 Economic Impact of Corrosion and Scaling Problems in Geothermal Energy Systems,2 and Silicate Scale Control in Geothermal Brines—Final Report.3

CURRENT SCALE TREATMENT METHODS

In this section we discuss methods currently being used to remove scale in wells and power plant equipment. There are several approaches for removing deposited scale, depending on the location and composition as described below. (See Table 2.)

A. Chemical Methods

Chemical methods include use of either acid (acidizing) or base to dissolve an existing scale. Acidizing is used to clean boreholes of scale by injecting an acid into the borehole. The type of acid used depends on the composition of the deposit, e.g., HCl for CaCO3 deposits, HF for sand. Calcite dissolves in HCl:

\[
CaCO_3 + 2HCl \rightarrow Ca^{++} + H_2O + CO_2 + 2Cl^{-}
\]

Acid cleaning of CaCO3 deposits with HCl was used in East Mesa Geothermal Well 5-1 by pumping 19,000 liters of inhibited 15% HCl into the bore.1 On acidizing, sufficient deposit was removed to permit lowering of small diameter downhole instruments into the bore; this previously was prevented by CaCO3 scale.

Acidizing to descale well casings was used in Hungary and inhibited hydrochloric acid in the Kawerau Geothermal Field (New Zealand) to remove calcite deposits from well casing slots. In Otake, Japan, acid cleaning of a bore choked with calcite scale at a depth of 260 meters was carried out using 5000 kg of 35% HCl containing 75 kg of inhibitor.1 Water was injected into the well to maintain a 3-5% acid concentration. Although the deposit was not removed completely, the discharge from the well approximately doubled. Chemical cleaning to remove silica scale from flow control equipment and heat exchangers using ammonium bifluoride was studied at Hveragerdi, Iceland.

Caution is required in selection of the acid; fluoride reacts with certain metals.
ABSTRACT

This paper presents a study of methodology used to control geothermal scaling and corrosion. The information used for this study was screened from the geothermal, oil and gas, wastewater disposal, and boiler water treatment industries. This information was evaluated and the current state of knowledge and methodology concerning the treatment of geothermal brines to control scaling and corrosion in geothermal electric power production was assessed. Currently, geothermal scale in pipes and wells is removed by physical or chemical methods. There is a growing effort on developing methods to control scale formation for both fresh and spent brines, including pH adjustment and application of an electrical potential for fresh fluids, and coagulation to treat spent fluids. Current methods of corrosion control center around planned replacement of piping and other plant components, with efforts focused primarily on development of materials with improved corrosion resistance. Recommendations for additional work include the following:

1. Chemical and physical characterization of brine and scale compositions;
2. Basic data on the mechanism of scale formation and the effects of inhibitors;
3. Development of instrumentation to monitor geothermal brine constituents;
4. Correlation of laboratory results with field test data, and
5. Screening of currently available commercial inhibitors for application to geothermal brines.

INTRODUCTION

Utilization of geothermal energy for power production requires a fluid to extract heat from the earth. Major development of geothermal energy in the next 25 years will be in regions where the fluid occurs naturally as hot water and has been in contact with the country rocks for a considerable period of time. The chemical composition of the fluids will therefore reflect the composition of the country rock and in general be in chemical equilibrium with it. Because of the wide variety in rock types, the composition of geothermal hot water fluids is expected to vary widely, ranging from several thousand to several hundred thousand ppm dissolved solids combined with dissolved gases in an aqueous solution. The fluids can react with the total geothermal power generation system to cause scaling and corrosion, and may plug injection wells and
(e.g., Ca) to form insoluble substances which could precipitate and clog a borehole.

Though very insoluble in water and acid, silica scale dissolves in alkaline solutions to form soluble silicate. As an example, scale containing 90% silica was removed from a well in the Matsukawa Field using sodium hydroxide (NaOH): Here, 125 kg of NaOH was dissolved in 300 liters of water, and the solution placed in the wellhead for 8 minutes. The wellhead was then washed with pure water for 15 minutes, and the process repeated. This resulted in complete removal of scale.1

![Image](image.png)

A disadvantage in scale removal with NaOH is the possibility of precipitating metal hydroxides in the formation.

B. Physical Methods

As used here, the term physical methods means scraping and scratching to clean scale deposits from the wall or casing of a well and from pipelines. In a well, a scratcher or reamer is lowered into the bore and deposits removed by the simultaneous rotary transverse motion of the reamer.

Reaming of geothermal wells to remove calcite was used in New Zealand, Hungary, and Mexico. Borehole reaming can be expensive: A 1974 estimate of the cost of reaming may be obtained from the following data: Low enthalpy wells (400 Btu/1b) at Cerro Prieto are expected to plug with calcite in about one year, and the high enthalpy wells (650 Btu/1b) with silica in three to four years. Reaming a typical plugged-up well by redrilling requires five to ten days at Cerro Prieto and costs about $1200/day. Based on these figures, a rework cost of $10,000 to $30,000 is estimated for a Salton Sea well, assuming that the rework rig was available with no move in or mobilization charge.4

Scraper pigs are used to remove scales formed in pipelines by running them through the lines at regular time intervals; these are inserted and removed at inlet and outlet traps. The scrapers frequently used in salt-water gathering systems are variously called steel-balls, chained rubber-balls, plugs and wire-brushes, go-devils, and spiral-brush pigs. A disadvantage of scrapers is the possibility of damage to any plastic lining of the pipes.

Application of waterjets to remove scale may be a potential method for geothermal systems. Cavitation descaling employs pulsating high pressure jets of water which are directed against the scale surfaces. If due to flow irregularities the condition of the water velocity are such that repetitive low- and high-pressure areas are developed, bubbles form and collapse at the solid-liquid interface. The collapse of these bubbles or cavities results in shock pressures reaching several hundred atmospheres in localized areas. The resultant impact tears out sections of porous or brittle material adhering to pipes.

Application of cavitation descaling to geothermal heat exchanger tubing and pipes is currently being investigated by studying the cleaning rates of various scale-filled pipes as a function of nozzle and jet parameters.4 In conducted tests, a 2 inch inside diameter pipe which had been reduced to 1-1/4 inches by an iron-rich silica scale was completely cleaned out by a cavitation hydrojet. Hydroblasting was used to clean approximately 1200 feet of the reinjection line and brine drain lines at the Niland Geothermal Test Facility. The hydroblasting was followed by a water flush. The best cleaning efficiency was achieved with a low number of orifices, moderately high pressure (5000 psig), high pump flow rates, and an impingement angle of 30° from the pipe center line.5

In summary, scale is removed by physical or chemical methods. An advantage of physical methods is that most scales can be removed. Disadvantages of physical methods include the following: (1) removal of scale from wellbores requires a drill rig and can be expensive; (2) the well or piping system must be shut down prior to reaming; (3) in a well, only the bore itself is cleaned so that any deposits in the formation are untouched; (4) drill cuttings may be squeezed into any pipe perforations, causing an impermeable layer to form and hot water production to fall off; (5) mechanical removal from a plugged slotted liner is very difficult; (6) plastic pipe lining may be damaged. Because of these factors, chemical methods are preferred in the oilfield industry.

Depending on scale composition, chemical treatment such as acidizing is generally economical and effective in removing scale from boreholes. A disadvantage of chemical treatment is the possible "eating a hole" through the scale, thereby leaking the chemical into the formation without dissolving scale.

Although the current methods of geothermal scale cleanup described above are satisfactory in some respects, they have at least four significant drawbacks: (1) The well must be taken out of service to perform cleanout; (2) Frequency of cleanout for some wells may be prohibitively high; (3) Scale buildup
A SURVEY OF TREATMENT METHODS FOR GEOTHERMAL FLUIDS

causes gradual reduction of pressure and flow with time during the interval between cleaning, and (4) Chemical or physical methods of cleaning may damage well casings and piping.

DEVELOPING METHODS

Included here are methods being investigated for controlling scale formation in geothermal hot water systems. These methods are and large are empirically-based, have not been extensively studied, and have been applied usually at only one location. (See Table 3.) Generally, the deposited scale is a mixture of sulfide, silica, carbonate, and metals.

A. Fresh Fluid Treatment

The term fresh fluid as used here refers to the hot water from the producing wells which is used in the power generation cycle.

1. Silica Treatment Methods

The solubility of silica in water depends on a number of parameters including form, pH, temperature, and time. For example, the solubility increases with temperature over the range of 0°C to about 300°C, then falls off for both quartz and chalcedony forms. The solubility increases at pH 8.5 and higher where soluble ions (silicates) form. Silica is less soluble in NaCl solutions than in pure water: an increase in salinity decreases the activity of water (3120) which in turn lowers silica solubility.

A brine treatment method for controlling silica scaling based on the injection of ammonia was investigated, the idea being to alter the nature of the precipitate so that it would not adhere to surfaces. Results of laboratory experiments on ammonia injection indicate that silica precipitation cannot be prevented, but that it may be possible to control where precipitation will occur. However, increasing the pH can cause precipitation of heavy metal hydroxides (e.g., Fe(OH)3, Mn(OH)2), carbonates, and sulfides at pH 6–9 thereby requiring pre-utilization removal of the precipitates to control erosion. A disadvantage associated with addition of base is the buffering action of the brine which would require increased quantities of added base and hence increased cost of the brine treatment.

Addition of dilution water was successful in reducing silica scaling at Namafjall, Iceland. Before dilution, scale was deposited from 95°C hot water as loose, leaf-like flakes which grew to 15 to 30 mm inside a 20.3 cm (8 inch) pipe. The scaling was reduced by mixing unflashed fluid from the drillhole with cold water to a 35% dilution at atmospheric pressure. Addition of dilution water lowered the silica content of the fluid from 347 ppm to 188 ppm.

Addition of dilution water to unflashed fluid to reduce silica precipitation should be approached with caution: the diluant must be chemically compatible with the brine. Otherwise undesirable reactions (e.g., pH change) can occur. Other disadvantages of dilution water include the possible reduction in enthalpy of the geothermal brine and the quantity of clean water that may be required. For example, for a well flow rate of 1.8 x 10⁵ kg/hr at the Salton Sea Geothermal Field 35% dilution would require about 6.3 x 10⁴ kg/hr of water.

In treatment of boiler water for use in cooling, heating, and steam generation, the addition of magnesium salts (e.g., dolomite) during hot-lime softening reduces the silica content of the water. The reaction produces insoluble magnesium silicate:

\[ \text{H}_2\text{O} + 2\text{Mg}^{2+} + \text{SiO}_3^{2-} + \text{Mg}_2\text{SiO}_4 + 2\text{H}^+ \]

Optimum separation efficiency of silica is achieved at a pH >9, with about 15 minutes required for efficient silica removal. The method may have merit for fresh geothermal brines; however, the requirement of elevated pH can cause precipitation of insoluble metal oxides. Furthermore, retaining the fluids for required treatment time may result in reduction of fluid enthalpy, and removal of Mg₂SiO₄ may be required to control erosion effects.

2. Sulfide Treatment Methods

Methods to control sulfide scale center around removal of sulfide by either lowering the fluid pH to form gaseous hydrogen sulfide, or oxidizing sulfide to, for example, sulfur or sulfate. A disadvantage of acid addition is any fluid buffering action of soluble metal oxides which would require additional acid.

Oxidation of sulfide to sulfur or sulfate could be used as a means of controlling sulfide scale deposition. However, a possible problem here may be the formation of insoluble metal sulfates (e.g., CaSO₄), as well as elemental sulfur which could erode piping and cause plugging of injection systems. Addition of a dispersing agent to prevent the solids from settling out, or filtration would be required to remove the solids.
In water quality treatment, diffused-air aerators are used to remove gases such as H₂S and CO₂. The method utilizes injection of compressed air through a perforated pipe or similar system to produce fine air bubbles wherein the H₂S gas is exchanged from the water phase to the air phase. An advantage of aeration for H₂S removal from fresh geothermal fluid is the low cost of air used in aeration. However, aeration may cause formation of sulfate and subsequent deposition of insoluble metal sulfates.

3. Calcite Treatment Methods

Calcite (CaCO₃) is a common scaling problem associated with water intended for cooling, heating, and steam generation purposes. The solubility of CaCO₃ in water and geothermal fluids depends on a number of parameters including the following: CO₂ gas partial pressure, temperature, pH, and the chemical composition of the brines. Methods for preventing CaCO₃ precipitation are based on the suitable control of one or more of these parameters.

Calcium bicarbonate exists in solution primarily as calcium ions (Ca⁺⁺) and bicarbonate ions (HCO₃⁻). As the brine flows in a geothermal well from the reservoir, it depressurizes and CO₂ is released as a result of the fluid boiling. This release of CO₂ favors formation of insoluble calcite according to the following reaction:

\[ \text{Ca}^{++} + 2\text{HCO}_3^- \rightarrow \text{Ca} (\text{HCO}_3)_2 \]

\[ \text{Ca} (\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]

Thus, maintaining a CO₂ pressure should minimize calcite precipitation. However, a disadvantage of maintaining a high back pressure on the well is reduced flow rate.

Addition of acid favors removal of carbonate by formation of CO₂:

\[ \text{CO}_2(\text{gas}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \]

\[ \text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \]

\[ \text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-} \]

Removal of carbonate prevents formation of calcite. A disadvantage is the quantity of acid required due to any buffering action by the geothermal fluid.

In steam generating systems, calcium is precipitated in the form of a sludge by addition of alkaline phosphate:

\[ 10\text{Ca}^{++} + 6\text{PO}_4^{3-} + 20\text{OH}^- \rightarrow 3\text{Ca}_3(\text{PO}_4)_2\text{Ca} (\text{OH})_2 \ 	ext{(sludge)} \]

The sludge formed is less likely to scale than CaCO₃ because it is relatively nonadherent to boiler metals and is easily removed by manual blowdown. Sometimes a synthetic polymer is added to enhance flocculation, reduce its adherence, and maintain its dispersion. A disadvantage of this method is precipitation of insoluble substances (e.g., H₂S sulfides, hydroxides, carbonates) at the elevated pH required for phosphate precipitation.

Sulfate addition is the method of controlling scale in boiler water based on the hundredfold greater solubility of CaSO₄ as compared to CaCO₃. A disadvantage in application to geothermal brines is the precipitation of other insoluble sulfates (e.g., BaSO₄) which may form scales, and plugging of injection systems by the formed CaSO₄.

4. Mixed Scales

As used here, the term mixed scales refers to geothermal scales composed of a mixture of metal (e.g., Fe, Ag) sulfides, carbonates, and silicates. The treatment methods for fresh geothermal fluids are largely empirical, and in early developmental stages. For example, at Miland, California, Lawrence Livermore Laboratory found beneficial in controlling scaling (copper sulfide, native silver, and iron-rich amorphous silica) from unmodified brine (pH = 5.5-5.8) which had resulted in closure of up to 10% of the cross-sectional areas of nozzle throats. However, when brine was acidified to pH 1.5, 2.3, and 4.0, scaling in nozzles was eliminated and substantially reduced on carbide clad, acidified brine effluents remained clear several hours after collection, while unmodified brine was slightly turbid when collected, with precipitates forming a few minutes after samples were taken.

In tests conducted at the East Mesa KGRA on brine from Well 6-1, a thermal shock method was used to remove scale from a test probe in a simulated vertical tube evaporator. An electrically heated probe was placed inside a test section of pyrex pipe through which geothermal brine was flowing at a constant rate. Buildup of scale on the probe was monitored by measuring the change in heat transfer due to scale buildup. The scaled system was subjected to a thermal shock by closing the liquid flow to the test section, thus causing the temperature on the probe to rise. During this temperature rise, boiling of the liquid caused slugs of vapor to move up the test section and the liquid to flow down. Differential expansion of the metal probe and scale along with the rapid vaporization of moisture in the scale next to the heated probe was thought to be partly responsible for the effectiveness of thermal shock in scale
removal. About 30 to 40% of this scale fell free leaving the probe clear and wet.

The injection of heavy diesel oils was used to aid in scale removal from turbine blades at Larderello, Italy. The spaced injection of heavy diesel oils into the turbine made the scales softer and easy to remove. The scale was composed of iron sulfide, clay, ammonium, calcium, and alkaline metal salts of borate, sulfuric, hydrochloric and carbonic acid.1

Experiments at Lawrence Livermore Laboratory on brine from a flowing geothermal well studied the influence of electrical potential on scale deposition. Experiments were run by flowing fluid through a 6" nozzle with 5 volts, -5 volts, and +30 volts applied potentials. It was found that more scale formed on negative than on either positive or neutral electrodes. The method may have merit for the control or prevention of scale formation on selected portions of geothermal piping or heat exchangers.

B. SPENT FLUID

Fluid production from a geothermal field for power generation will be in large volumes, e.g., 1.8 x 10^3 kg/hr/well in the Salton Sea. These hot fluids may contain silica, carbonates, chlorides of sodium, potassium, and calcium, and various undesirable elements, e.g., B, CO₂, H₂S, NH₃, As, Hg. Disposal of geothermal spent fluids poses a problem in the development of geothermal resources. Injection into wells may have advantages over other forms of disposal, for example elimination of thermal pollution of the environment and reduction of ground subsidence. In several geothermal fields, such as the Geysers steam field and Niland area of the Imperial Valley, Valles Caldera in New Mexico, Ahuachapan in El Salvador, and Nachmanot in Japan, disposal of effluents through injection has been or is being tried experimentally. However, there is a problem of scale formation in pipes and reservoir rocks.

In this section, we discuss existing geothermal and other methods (e.g., oilfield) used to treat spent brines prior to disposal. Currently, spent geothermal brines are not treated to a significant extent and little data is available on the effectiveness of the various chemical and physical steps. Thus, this section draws on oilfield and industrial wastewater techniques which appear appropriate for application to geothermal fluids, for example, the use of closed systems, coagulation, filtration, and sedimentation.

Spent geothermal fluids will have a lower temperature than fresh geothermal fluids; thus some oilfield treatment techniques, e.g., addition of decomposable sequestrants, may be applicable. In evaluating geothermal effluent treatment possibilities, however, one will have to consider a variety of parameters including chemical compatibility of the additive with brine, compatibility of the brine with receiving rock formations, mechanical requirements for removal of solids, and cost.

1. Silica Treatment Methods

This section covers mainly a discussion of methods that have been applied to spent geothermal hot waters to remove silica.

Sedimentation is a commonly used wastewater treatment practice in which suspended materials settle from the fluid under the influence of gravity. This settling process usually takes place in specially designed circular or rectangular basins with either horizontal or vertical fluid flow.

The precipitation of silica from supersaturated solution is a progressive process in which a colloidal silica is produced which gradually forms gel or precipitate. Several days or even weeks may be required to reach equilibrium, depending on the temperature. Because of the slowness of precipitation, geothermal brines which appear clear become cloudy after standing at ambient temperatures for a few hours. This cloudiness may turn into a heavy precipitate which subsequently settles.

A retention tank with a series of baffles was used at the Otake geothermal plant in Japan to control silica scale in hot water pipes. It was found that one hour retention was sufficient to reduce silica scale formation before discharging the brines to pipelines. This delay in time permitted the silica to change from the monomeric state to the amorphous settleable state, where it deposited on the walls of the concrete holding tank. Similar methods were used at Ahuachapan, El Salvador, to prevent silica deposition in a disposal culvert.

In coagulation, chemicals are added to the wastewater with the idea to gather all suspended particles (colloids), enhance settling, and prevent the small particles from passing through filters. The addition of a coagulant essentially enlarges the small particles by causing the aggregation of fine particles to produce a floc which settles rapidly, thus increasing the efficiency of the sedimentation process. Coagulation has the advantage in requiring smaller settling basins and lower initial cost than sedimentation.
Coagulation using slaked lime was applied to remove both silica and arsenic from cooled (90°C) geothermal discharge waters at Wairakei and Broadlands. The spent fluid (90°C) was aged to allow silica to polymerize; addition of slaked lime to the water then rapidly precipitated a flocculent, hydrated calcium silicate gel, which readily settled in settling tanks. Arsenic was coprecipitated in the pentavalent state.

2. Calcite Treatment Methods

Calcite can also be removed by sedimentation and coagulation processes, using methods similar to those discussed under silica treatment. In this section, other methods to prevent calcium carbonate scales in spent fluids are discussed.

Sequestration is the process of maintaining scale-forming cations (e.g., calcium, barium, iron) as soluble complex metallic ions by addition of chelating or sequestering agents to the wastewater. The most popular sequestering agents in water treatment are the inorganic polymetalophosphates. Care should be taken to avoid using acids along with polymetaphosphates since acids promote formation of orthophosphate ion which reacts with calcium in the water to form insoluble calcium phosphate. Scale formed on downhole oilwell tubing and pumps has been controlled by introducing phosphates. A dosage of 2 to 10 ppm of phosphate in the produced water is usually sufficient to prevent scale formation.

Ethylene diaminetetraacetic acid (EDTA) and its sodium salts are used as scale inhibitors in boiler water treatment. EDTA forms stable soluble complexes with nearly all metallic ions, e.g., Mg++, Ca++, Sn++, Ba++, and has an advantage over polymetaphosphates in not hydrolyzing to form phosphate ions. The maximum complexing or chelating efficiency of EDTA for Ca is obtained at pH 6, and thereafter remains nearly constant.

BRINE TREATMENT FOR CORROSION CONTROL

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

Geothermal fluids may contain appreciable quantities of dissolved salts and gases that are generally more corrosive to materials of construction than other standard environments for the production of electrical power. In a geothermal power system corrosion may take place in well casings (downhole corrosion), surface lines, separators, turbines, heat exchangers, cooling towers, and discharge lines. Corrosion rates in geothermal plants are dependent primarily on fluid pH, mineral content, temperature, flow rate (velocity), partial pressure of CO₂, H₂S, NH₃, and H₂, and the oxygen content of the system. Because geothermal fluids vary in composition from one field to another, treatment to prevent corrosion may require extensive tests and analyses of brine data for each geothermal site.

Aeration is a process used in "open-type" systems involving a mass transfer between the water and gas phases. Aeration speeds up the rate of interchange between air and water by producing a larger contact surface area, and is effective in removing acidic gases such as H₂S and CO₂. However, over-aeration may cause additional corrosion due to introduction of excess dissolved oxygen. The excess oxygen can be removed by treatment with added chemicals. For example, sodium sulfite (10 ppm Na₂S₂O₃ per 1 ppm O₂) was added to the 86°C geothermal water in the Reykjavik Municipal Heating System, Iceland, to reduce oxygen and thereby control internal corrosion of metals in the heating system.

There is an active research and development effort centered on developing alloys with resistance to geothermal corrosion. Generally, the materials include carbon steels, and aluminum, titanium, and zirconium alloys. The reader is referred to Ref. 11 and 12 for a thorough review of corrosion resistance of metals in hot brines.

SUMMARY AND RECOMMENDATIONS

Present methods for controlling scale deposition and materials corrosion in the geothermal industry are mainly cleanup and replacement of pipes and other components on an as-required basis. Incrustations due to deposition of scales (e.g., silica, sulfide) from hot brines are usually removed from boreholes by acidizing or reaming; those in piping are mechanically removed by wire-brushing scrapers or hydroblasting. Materials rendered unserviceable by corrosion are replaced with new parts.

Research and development activities centered around geothermal scale and corrosion control by treatment of brines have been increasing within the past two years. A brine treatment program would include the following:
1. Characterization of brine chemistry and deposited scales in order to determine the causes and possible means of control. The scale and corrosion products reflect the variable brine composition for different geothermal areas. Brine treatment methods can then be devised for the particular production fluid and for the particular method of disposal under consideration.

2. Basic laboratory data are needed on the mechanisms and rates of scale formation due to corrosion or scale deposition. Basic data are transferable to all geothermal sites and will be needed to select, for example, additives and materials which would control scaling and corrosion.

3. Development of additives, inhibitors, sequestants, and instruments to monitor the important geothermal brine scale and corrosion parameters (e.g., silica, pH, E≡). The instrument sensors should be sufficiently rugged to monitor geothermal fresh fluids in a reliable manner.

4. Correlation of laboratory test results with actual tests in field conditions. In this way, feedback on the predictions based on laboratory results can be quickly verified and incorporated into brine treatment programs.

5. Development of laboratory screening methods for commercially available scale and corrosion inhibitors, with the idea to evaluate their effectiveness under geothermal conditions. The inhibitors should be effective at the elevated temperatures and pressures encountered in geothermal systems and should not react with brine constituents either to form harmful products or to reduce the effectiveness of the additive.

REFERENCES


<table>
<thead>
<tr>
<th>Scale and Incrustation</th>
<th>Materials Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid phase (steam or water)</td>
<td>Stress levels in materials and especially cyclic stresses</td>
</tr>
<tr>
<td>Brine composition</td>
<td>Crevices</td>
</tr>
<tr>
<td>Temperature and temperature changes</td>
<td>Presence of scale deposits</td>
</tr>
<tr>
<td>Pressure changes, including partial pressure change in CO₂, H₂S, NH₃</td>
<td>Passive or active state of metal protective films</td>
</tr>
<tr>
<td>Residence time in each part of plant</td>
<td>Velocity of fluid</td>
</tr>
<tr>
<td>Surface effects and surface to volume ratio effects</td>
<td>Suspended solids content</td>
</tr>
<tr>
<td>Geometry of power plant components</td>
<td>Ionic strength of water</td>
</tr>
<tr>
<td>Salt carryover in steam phase</td>
<td>Galvanic coupling of dissimilar metals</td>
</tr>
</tbody>
</table>

**TABLE 1 - IMPORTANT PARAMETERS AFFECTING SCALING AND CORROSION IN GEOTHERMAL PLANTS**
<table>
<thead>
<tr>
<th>Scale Type</th>
<th>Treatment Method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CURRENT METHODS:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃ (calcite) in borehole</td>
<td>Pump inhibited HCl into the well</td>
<td>Acidizing used at East Mesa Well 5-1 and Otake, Japan</td>
</tr>
<tr>
<td>Calcite in well casings</td>
<td>Wash with inhibited HCl</td>
<td>Used in Hungary and Kawerau, New Zealand</td>
</tr>
<tr>
<td>Silica in flow control equipment and heat exchangers</td>
<td>Wash with ammonium bifluoride</td>
<td>Acidizing, used at Hveragerdi, Iceland</td>
</tr>
<tr>
<td>Silica in borehole</td>
<td>Pump NaOH solution into the well</td>
<td>Used at Matsukawa, Japan</td>
</tr>
<tr>
<td>Calcite in borehole</td>
<td>Reaming or redrilling</td>
<td>Used in New Zealand, Hungary, and Mexico</td>
</tr>
<tr>
<td>Mixed scales in turbine components</td>
<td>Spaced injection of heavy diesel oils</td>
<td>Used at Larderello, Italy</td>
</tr>
<tr>
<td>Mixed scales in injection and brine drain lines</td>
<td>Hydroblasting followed by water flush</td>
<td>Used at Niland Geothermal Test Facility, California</td>
</tr>
<tr>
<td><strong>DEVELOPING METHODS:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed scales in heat exchanger tubing and piping</td>
<td>Cavitation descaling</td>
<td>Laboratory experiments</td>
</tr>
<tr>
<td>Calcite scale (test probe)</td>
<td>Application of thermal shock</td>
<td>&quot; &quot;</td>
</tr>
</tbody>
</table>
### TABLE 3 - TYPICAL TREATMENT METHODS TO CONTROL SCALE FORMATION

<table>
<thead>
<tr>
<th>Scale Type</th>
<th>Treatment Method</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>pH adjustment (acid injection)</td>
<td>Tested at Magmamax No. 1 well, Niland, California</td>
</tr>
<tr>
<td>Silica</td>
<td>Injection of base (NH₃ or NaOH)</td>
<td>Sinclair wells, California</td>
</tr>
<tr>
<td>Silica</td>
<td>Dilution of the unflashed geothermal fluid</td>
<td>Namafjall, Iceland</td>
</tr>
<tr>
<td>Mixed (?)</td>
<td>Application of electrical potential</td>
<td>Sinclair Well No. 4, California</td>
</tr>
</tbody>
</table>

### TREATMENT METHODS FOR SPENT FLUID DISPOSAL

<table>
<thead>
<tr>
<th>Scale Type and arsenic</th>
<th>Treatment Method</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica and arsenic</td>
<td>Sedimentation and coagulation (addition of slaked lime, hypochlorite, and flocculant)</td>
<td>Used at Wairakei and Broadlands, New Zealand</td>
</tr>
<tr>
<td>Silica</td>
<td>Plain sedimentation; retention tank</td>
<td>Used at Otake, Japan, and Ahuachapan, El Salvador</td>
</tr>
</tbody>
</table>
This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.