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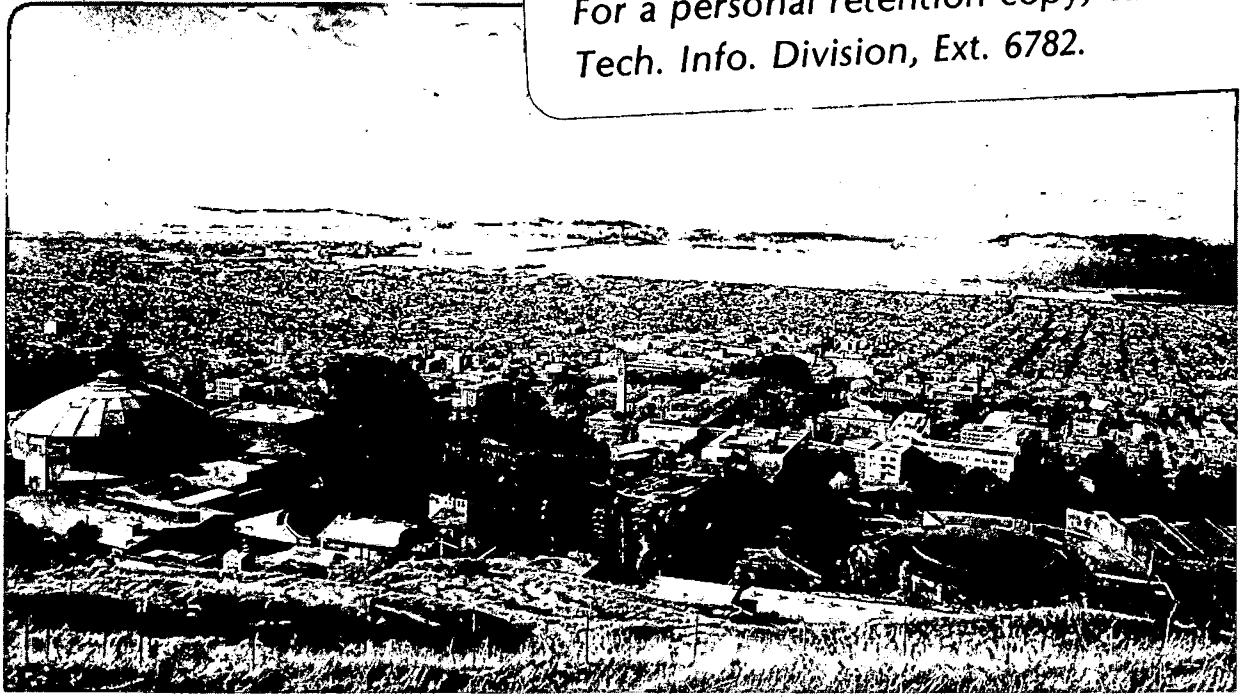
O. Weres

December 1984



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ENVIRONMENTAL PROTECTION AND THE CHEMISTRY OF GEOTHERMAL FLUIDS

A chapter in:

Geothermal energy technology,
J.C. Bresee and P.A. Witherspoon, *eds.,*
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1. Introduction

Geothermal heat is dispersed through a very large volume of hot rock and subterranean water. Utilization of geothermal heat requires the extraction of large volumes of water or steam from the reservoir. The chemical impurities in these fluids present a risk of environmental contamination. Much of the technical evolution of geothermal-electric technology has been motivated by the need to control the release of these impurities to the environment. In the United States, this is a practical imperative; experience at The Geysers has demonstrated that geothermal facilities would be unable to receive construction and operating licenses without strict environmental controls. The regulatory climate in Japan is similar.

The very large natural steam producing systems at Lardarello (Italy) and The Geysers (California) have supported the most extensive commercial development. In these areas only hot, high pressure steam is produced. Most of the steam condensate is consumed as cooling water. Air pollution with hydrogen sulfide is the major environmental problem associated with these developments. The problem of controlling H_2S emissions has dominated technical development at The Geysers.

Most geothermal reservoirs produce hot brine, rather than steam. These include the major developed fields at Wairakei (New Zealand), Cerro Prieto (Mexico), Tongonan (Phillipines), Ahuachapán (El Salvador), and Otake (Japan). Several hot brine fields probably will be developed soon in the United States, including Niland, Brawley, East Mesa and Heber (all in southern California). At all the developed fields, steam is produced by depressurizing the brine, and separating steam from residual brine. The generation of electric power using this steam is the same as with native steam at Lardarello and The Geysers, and so are the emissions from the powerplants proper.

No more than one-third of the brine is converted to steam; the remaining brine must be disposed of. At several Japanese fields and Ahuachapán it is disposed of by reinjection into the reservoir. Given American requirements for environmental protection, reinjection will certainly be required at all such developments in the U.S. Reinjected brine would cause no environmental problems, provided that leakage into shallow aquifers is prevented. Successful reinjection frequently requires the brine be treated to remove suspended solids, etc. Reinjection and associated brine treatment commonly present the major technical challenge in utilizing hot brines.

Ellis (1978), Weres (1980), and Crittenden (1981) surveyed the environmental impacts of geothermal development in general. Reed and Campbell (1976), and Weres *et al.* (1977) surveyed environmental impacts at The Geysers, and the means used to control them. Vollintine *et al.* (1977) described the population and economy of Lake County, California, and predicted the socioeconomic impacts of geothermal development there. Axtmann (1975) reviewed the environmental impacts of the Wairakei development. The environmental and socioeconomic impacts of geothermal development in Imperial County, California were predicted by Anspaugh *et al.* (1980), Armantrout *et al.* (1980), and Layton (1980).

2. Flows of water and heat

Approximate water flows and heat rejection rates in several geothermal powerplant cycles are summarized in Table 1. Heat rejection by wet cooling towers is assumed for all cases, with use of steam condensate for cooling

Table 1

Flows of heat and water in typical geothermal power cycles

	Actual efficiency[a]	Actual efficiency/ ideal efficiency[b]	Fluid produced[c,d]	Fluid reinjected[c]	Cooling water consumed[c,e]	Heat rejected[f]
Steam at 185°C[g] (Geysers)	0.15	0.65	8.9(0.78)	0.7(0.06)[h]	8.3(0.72)	5.5
Water at 160°C[i] (Heber)						
Binary[j]	0.09	0.58	78(6.8)	78(6.8)	15.0(1.31)	10.0
Water at 210°C[i] (East Mesa)						
Binary[j]	0.10	0.47	50(4.4)	50(4.4)	13.7(1.20)	9.1
Single flash[k]	0.07	0.32	72(6.3)	65(5.7)	6.9(0.61)	4.6
Double flash[k,l]	0.11	0.52	45(3.9)	36(3.2)	8.7(0.76)	5.8
Water at 300°C[i] (Brawley)						
Double flash[k,l]	0.16	0.55	19(1.7)	13(1.1)	6.8(0.60)	4.6

Table adapted from Weres (1980).

[a] Actual efficiency is defined as the ratio of the energy output (electrical) to the energy input (heat content in excess of that in 40°C water).

[b] The "ideal efficiency" is that of an hypothetical, isoentropic process operating between the same inlet and heat rejection temperatures as the actual process.

[c] Units are kg/kWhr. Values in parentheses are in units of 1,000 hectare-meters/ 100 MW-years. One hectare-meter = 10,000 cubic meters = 8.11 acre-feet.

[d] Fluid production rates for all cycles taken or derived from the graphs presented by Nathenson (1975). Other data were calculated assuming that the thermodynamic properties of the brine approximate those of pure water.

[e] Heat rejection by wet cooling towers assumed for all cycles. Binary cycle plants require an external supply of cooling water (use of dry towers would eliminate need for cooling water). Native- and flash- steam cycles use steam condensate for cooling water make-up.

[f] Units are kWhr(thermal)/kWhr(electrical).

[g] Temperature at powerplant inlet.

[h] Only cooling tower blowdown (i.e., residual condensate) is reinjected.

[i] Reservoir temperature.

[j] Downhole pumped production of brine assumed; thus, there is no flashing in the production wellbore, and the plant inlet temperature is approximately equal to the reservoir temperature.

[k] First stage separator pressure is 6 bar.

[l] Second stage separator pressure is 1 bar.

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water in all except the binary cycle. The realizable thermodynamic efficiencies are low, while the heat rejection rates and demands for cooling water are correspondingly high. (In comparison, the thermodynamic efficiency of a modern fossil fuel fired steam-electric plant is about 36%.) The brine production and reinjection rates in the hot-brine-based cycles are 2 to 10 times greater than the cooling water consumption rates. The flow of cooling water around the cooling tower circuit (not shown) is still greater - typically 250-330 kg/kWhr.

At all geothermal fields but Wairakei, heat is rejected with wet cooling towers, using steam condensate for cooling water make-up. No outside water supply is needed, and the cooling towers are relatively small and cheap. In most cases, this is practically the only means of heat rejection available. In principle, providing cooling water from without to a plant equipped with a surface condenser and wet tower could eliminate the need for using condensate, but usually this is impractical because of the large amount of water required.

Wairakei is located on a large river (the Waikato), and once-through cooling with jet-type contact condensers is practiced there. In most cases, this would be unacceptable because of the thermal and chemical pollution it causes.

Dry cooling towers don't need cooling water make-up, but have two major disadvantages: (1) they are very large and expensive, and (2) they cause the condensing temperature to be greater than the ambient dry bulb temperature. This reduces power output on hot summer days when demand is highest. Today there are no dry towers in electrical utility service outside of Europe. Their geothermal application probably will be limited to binary cycle powerplants located in arid areas.

3. Air pollution

Hydrogen sulfide is the air pollutant of major concern in geothermal development. The odor threshold for hydrogen sulfide in air is about 5 parts per billion by volume, and subtle physiological effects are detectable at slightly higher concentrations. Hydrogen sulfide above 30 ppb (the California ambient air quality standard) has an offensive smell, and toxic effects that

Table 2

Composition of geothermal steam[a]

	Geysers[b]	Lardarello[c]	Cerro Prieto[d]	Wairakei[e]
CO_2	3260	52300	9380	1467
H_2S	222	800	490	76
NH_3	194		80	7.6
N_2	52	250	110	4.7
H_2	56	50	10	
CH_4	194	240	150	4.4
Total gases	3980	53600	10200	1560
As	0.019			
B	16			0.06
Hg	0.005			

[a] All concentrations in parts per million by weight.

[b] Native steam. Average of concentrations in steam from 61 producing wells sampled 1972-74. Reported by Griffin, Dean, and McCluer (1974).

[c] Lardarello well 38, sampled February 1977. Analysis recalculated from D'Amore and Truesdell (1984).

[d] Cerro Prieto well M-11, sampled in 1982. Analysis recalculated from Nehring and D'Amore (1984).

[e] Steam separated from the brine. Reported by Axtmann (1975).

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increase in severity with concentration. In its physiological effects and toxicity hydrogen sulfide is similar to hydrogen cyanide (Weres *et al.* 1977, Chapter 9).

Steam compositions representative of four major geothermal fields are presented in Table 2. In all cases, carbon dioxide is the major noncondensible gas component. Hydrogen sulfide is the second or third noncondensible gas by weight. The steam composition varies widely among fields, and even among wells within a given field. At The Geysers the concentration of ammonia is comparable to the concentration of H_2S; at most other fields there is much less ammonia than H_2S.

Table 3 summarizes my best estimates of H_2S emissions from four major geothermal fields. The substantial reduction of H_2S emissions from The Geysers between 1974 and 1984, despite increased generating capacity, reflects the introduction of air pollution abatement technology. Hydrogen sulfide emissions from the other three fields are not abated. Aside from this, the different emissions per kWhr reflect differences in steam composition. Without abatement, the specific emissions of sulfur generally are comparable to those from coal-fired powerplants. Coal-fired powerplants and sulfide ore smelters emit weakly toxic sulfur dioxide, which transforms to more toxic sulfate particulates and sulfuric acid in the atmosphere. Geothermal plants release highly toxic and malodorous hydrogen sulfide, which likewise is ultimately converted to sulfate particulates and sulfuric acid. Thus, geothermal air pollution has immediate local impacts as well as delayed regional ones.

In 1974-1978, The Geysers was one of the largest fixed sources of sulfur air pollution in California. There were frequent complaints about the odor, headaches, etc., from people in the communities immediately downwind of the project, even though the H_2S concentration there rarely exceeded 30 ppb. State and local air pollution control agencies mandated that emissions of H_2S from The Geysers be reduced. The Pacific Gas and Electric Company, The Union Oil Company of California, and others involved in The Geysers developed the technology needed to reduce H_2S emissions, and emissions have been reduced despite continuing expansion of generating capacity.

Perforce, most geothermal H_2S abatement technology has been developed at The Geysers, or borrowed from other industries and demonstrated there first. Because all steam cycle geothermal power plants are basically similar, air pollution control technology developed at The Geysers is universally applicable, where needed. There is no distinction between native steam fields and hot brine fields in this regard.

Important contributions to the technology of geothermal air pollution control were made by: chemists G.A. Allen, S.G. Sharp, M.A. Yancey, G. Dorighi, H.M. Castrantas, O. Weres, and W.W. Harvey, mechanical engineers H.K. McCluer, J.P. Finney, J. Laszlo, and G.E. Coury, condenser designers L.L. Forster and H.W. Braun, technical managers C.J. Weinberg, R.F. Cayot, and R.P. Wischow, petroleum engineer T. Turner, and others. Air pollution officers M.W. Tolmasoff, F. Tucker and G. Taylor contributed indirectly.

3.1. Preplant emissions of hydrogen sulfide

Two categories of H_2S emissions from geothermal developments may be distinguished: (1) "preplant emissions", associated with the escape of raw steam to the atmosphere during drilling, well testing, and powerplant outages, and (2) emissions from the powerplants associated with routine operation.

The emissions associated with powerplant outages are the largest of the preplant emissions. Turning a geothermal well on or off is a major operation,

Table 3

Hydrogen sulfide emissions from geothermal fields

	Year	Rated power (MW)	Grams per kWhr	Metric tons per 100 MW-years	Metric tons per day
Lardarello[a]	1977	365	7.6	6,700	67
Cerro Prieto[b]	1984	180	4.5	3,900	19
PG&E Geysers[c]	1974	396	2.3	2,000	22
PG&E Geysers[d]	1984	1190	0.2	200	6
Wairakei[e]	1975	192	0.5	500	2

[a] Assumes 8.9 kg/kWhr steam rate, 1.2 kg/kWhr vented preplant, and 752 ppmw H_2S in the steam, estimated by averaging steam compositions presented by D'Amore and Truesdell (1984).

[b] Cerro Prieto Units 1 to 4 take high pressure steam from the first stage steam separators, and generate 150 MW. For Units 1 to 4, I have assumed a steam rate of 9.4 kg/kWhr, 1.0 kg/kWhr vented preplant, and 514ppmw H_2S in the steam, estimated by averaging 1982 steam compositions presented by Nehring and D'Amore (1984). Unit 5 generates 30 MW using low pressure steam from the second stage steam separators which contains very little H_2S.

[c] Assumes no emission abatement, 231ppm H_2S in the steam, 3% natural oxidation, a steam rate of 8.9 kg/kWhr, and 1.2 kg/kWhr vented preplant.

[d] Emissions from the powerplants amount to 62% of total emissions; estimates of powerplant emissions provided by G. Dorighi of the Department of Engineering Research, Pacific Gas and Electric Company. Preplant emissions estimated assuming 5.6% of total steam production is vented preplant, and that only 7% of this steam is treated to remove H_2S. Preplant emission rate calculated for Union Oil's part of The Geysers field by W.A. Smith of Union Oil's Geothermal Division.

[e] Recalculated from data presented by Axtmann (1975a). Axtmann's values appear not to include preplant emissions.

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and risks damaging the wellbore and surface equipment. There is a strong incentive not to interrupt the production of steam during a powerplant outage. At The Geysers, the thermal excursions associated with shutting in and restarting a well loosen rocks in the wellbore. When the well is restarted, fragments of rock come up with the steam. For a few hours following the resumption of steam production the well must be vented directly to the atmosphere to prevent serious damage to the steam gathering system. If the outage is expected to last only a few hours, the wells are not shut in at all, but allowed to discharge steam to the atmosphere instead. The wells at Cerro Prieto are also rarely shut in and production of steam and brine continues during powerplant outages.

About 5.6% of the steam produced in Union Oil's area of The Geysers was vented preplant in 1984*, down from about 12% in 1976. Before powerplant emissions were abated (starting in 1975), the preplant emissions represented 12% of total emissions. With improving abatement of powerplant emissions, the relative importance of preplant emissions has increased steadily. Preplant emissions now represent nearly 40% of the total H_2S emissions at The Geysers.

The most effective, and potentially cheapest means of abating preplant emissions is to reduce the amount of steam vented. Increasing powerplant reliability has this effect. The need to vent wells has also been reduced by interconnecting the steam transmission lines that supply the different Units at The Geysers; when one Unit goes out, part of its steam supply is diverted to another Unit, and its wells continue to produce steam at a reduced rate without atmospheric venting. Installation of steam valves that may be operated by remote control at The Geysers has made it possible to shut in wells more quickly and conveniently, further reducing preplant emissions.

At the Sacramento Municipal Utility District's and Occidental Petroleum's powerplants at The Geysers, the full steam flow can be routed directly to the condenser without going through the turbine. This procedure allows the condenser and Stretford Unit to remain in operation during most powerplant outages, with continued full H_2S emission abatement.

Hydrogen sulfide emissions during air drilling are abated by injecting hydrogen peroxide and sodium hydroxide into the pipe through which drilling air and steam are vented to the atmosphere (Castrantas *et al.* 1976; Turner and Rex, 1978; Woertz, 1979).

In principle, hydrogen peroxide may also be used to remove the H_2S from steam vented during powerplant outages, but this would be expensive.

3.2. Emission of hydrogen sulfide from powerplants

Hydrogen sulfide is emitted from a steam-cycle geothermal powerplant by two routes: with the condenser vent-gas, which is vented to the atmosphere, and from the cooling tower. The volume of vent-gas is small, and the concentration of H_2S in it is fairly large (ca. 1% by weight at The Geysers). Removing H_2S from the vent-gas is relatively straightforward, and technology developed in other contexts may be applied (Section 3.5). The emission of H_2S from the cooling tower is caused by the use of steam condensate for cooling water makeup; the condensate contains some of the H_2S that was originally in the steam. The concentration of H_2S in the condensate and cooling water is low, and the water flow is very large; removing the H_2S from this water is difficult.

In principle, the hard-to-control emissions of H_2S from the cooling tower could be avoided by not using condensate for cooling water makeup.

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* Estimate provided by W.A. Smith of Union Oil's Geothermal Division in Santa Rosa.

Then, all of the condensate could be reinjected, along with the H_2S dissolved in it. In most cases, there is no practical alternative to using condensate for cooling water makeup (Section 2).

The greater the fraction of H_2S that ends up in the condenser vent-gas, the better. This is a matter of condenser design. Most geothermal powerplants, including Units 1 to 12 at The Geysers, are equipped with contact condensers. In contact condensers, the condensing steam comes into contact with the cooling water and mixes with it. The ratio of condensing steam to cooling water typically is 1 to 25. This small vapor to liquid ratio causes a large fraction of the H_2S in the steam to dissolve in the cooling water. A simplified schematic of The Geysers Unit 6 - a typical Unit of this kind - is presented in Figure 1.

Surface-type condensers contain heat exchange tubes through which the cooling water flows. The steam condenses on the outer surface of the tubes, and never comes into contact with the cooling water. The ratio of condensing steam to condensate is one, and this low vapor to liquid ratio causes a smaller fraction of H_2S to dissolve in the condensate. Using this condensate for cooling water makeup results in smaller H_2S emissions. This is why Units 13 and beyond at The Geysers are equipped with surface condensers. Figure 2 is a simplified schematic of Unit 13.

3.3. The effect of steam composition on gas partitioning

The ammonia in The Geysers' steam increases the solubility of H_2S by reacting with it as a base:

$$H_2S + NH_3 \rightarrow HS^- + NH_4^+$$

Essentially, the ammonia makes hydrogen sulfide go into solution as HS^- as well as H_2S. At The Geysers, there is enough ammonia present to increase the solubility of the H_2S by between five- and fifty-fold.

Carbon dioxide is an acid gas and, in principle, it ought to reduce the solubility of hydrogen sulfide by decreasing the pH of the condensate. Carbon dioxide dissolved in the condensate may lower the pH by reacting with water to produce carbonic acid which then releases a proton:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 \rightarrow HCO_3^- + H^+$$

or CO_2 may react with hydroxide ion to give bicarbonate directly:

$$CO_2 + OH^- \rightarrow HCO_3^-$$

The effect of carbon dioxide is limited by the slow rates of these reactions. In a surface condenser, most of the CO_2 remains in the vapor phase, and the concentration of CO_2 dissolved in the condensate and available for reaction is small. The pH of surface condenser condensate is determined by the ammonia and H_2S in it, while the CO_2 and boric acid (a very weak acid) have little effect.

Much data on the partitioning of H_2S in geothermal plant condensers has been gathered at The Geysers. This data has been analyzed and extrapolated to different condenser designs, and different steam compositions by computer modeling studies (Weres 1983, 1984 and 1984a; early work

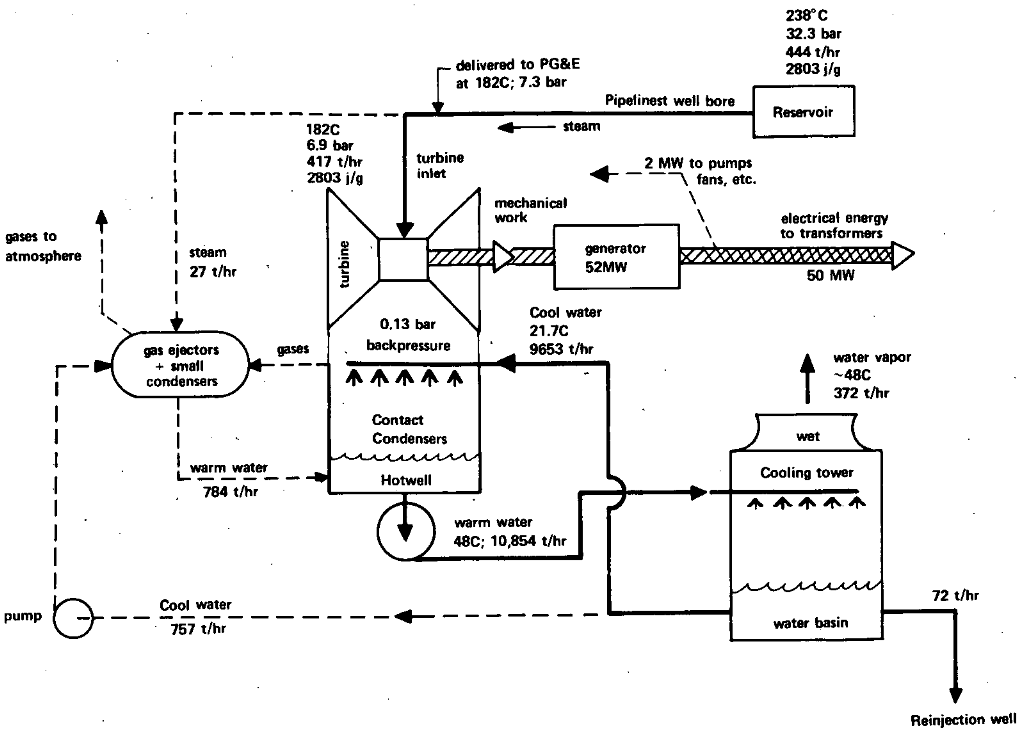

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Figure 1. A simplified schematic of Geysers Unit 6 - a typical geothermal Unit equipped with a contact condenser. Reproduced from Weres *et al.* (1977).

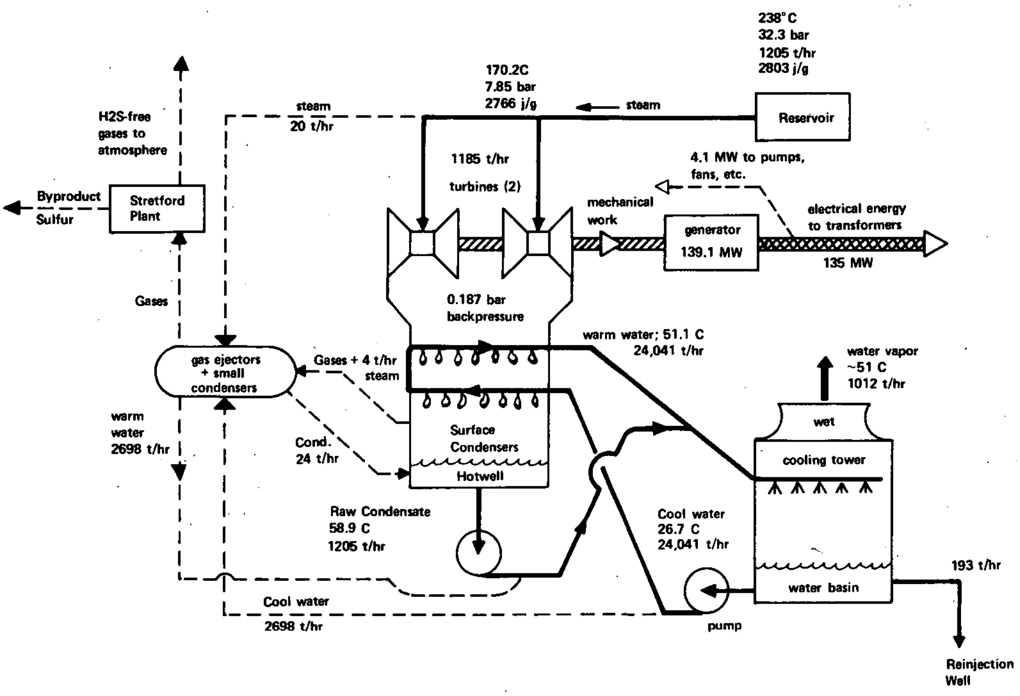

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Figure 2. A simplified schematic of Geysers Unit 13 - a typical geothermal Unit equipped with a surface condenser. Reproduced from Weres *et al.* (1977).

reviewed by Weres *et al.*, 1977). In the contact condenser Units, about 60% of the H_2S dissolves in the condensate; if not for the ammonia, this would be 25-30%. Surface condensers now in use or under construction at The Geysers put 8-20% of the H_2S into the condensate; if not for the ammonia, this would be 0.2% or less. Thus, the combination of surface condensers and Stretford Unit (Section 3.5) would provide practically complete abatement at fields with low ammonia steam.

3.4. Practical problems of condenser design

The concentration of noncondensible gases in geothermal steam is much greater than with other kinds of steam-electric powerplants. Despite large gas ejectors, this large gas concentration can degrade condenser performance and increase turbine back pressure. Three condenser designs used at The Geysers have this problem: the contact condenser common to Units 5 through 10, the contact condenser of Units 11 and 12, and the surface condenser of Units 13, 14, and 15. The case of Unit 5 is described by Forster and Pietruszkiewicz (1978).

Unit 15 was the first of the surface condenser equipped Units to go on line, and its disappointing condenser performance was evaluated in detail. Numerical modelling work suggested the cause of this condenser's mediocre H_2S partitioning performance (Weres, 1983). The gas ejectors were effectively removing noncondensible gases from one end of the condenser only; noncondensible gases accumulated throughout the rest of the condenser, causing poor H_2S partitioning and increased turbine backpressure. The condenser was physically modified to force uniform venting of noncondensibles throughout, and H_2S partitioning improved approximately as predicted. The contact condensers of Units 11 and 12 were modified analogously, improving their backpressure. Units 16 and beyond are equipped with a different surface condenser with provisions for uniform venting, and have not encountered problems of this kind.

The partitioning of H_2S can be improved by reducing condensate pH and further improving condenser design. Ammonia in the steam may be neutralized by adding acid. In practice, pH is best kept above 6 to limit corrosion. Computer modeling studies suggest that adding SO_2 to the surface condensers at The Geysers could reduce the H_2S in the condensate to less than 2% that of the incoming steam while maintaining acceptable pH (Weres 1983 and 1984).

An advanced, but still practical surface condenser design could reduce the condensate H_2S to about 5% with typical Geysers' steam. An advanced "hybrid" condenser, which combines a contact type main condenser with a much smaller surface type vent condenser, could achieve 10% condensate H_2S (Weres, 1984a). An advanced contact condenser capable of achieving 10% condensate H_2S with low ammonia steam has been pilot tested at Wairakei (Hart, 1980).

In all cases, properly designed geothermal condensers have explicit provisions to prevent gas blockage, and to steam strip the condensate within the condenser. The high performance types mentioned in the preceding paragraph condense the last, gasiest steam in a separate section or vent condenser, thereby keeping it from contacting the major part of the condensate.

3.5. Desulfurization of the condenser vent gas

Removing relatively concentrated H_2S from a gas stream is a common industrial problem, and technical means for this purpose are available. The Stretford Unit, originally developed for desulfurizing natural gas, is used at The Geysers Units 13 and beyond (Kirk-Othmer 1983). It converts H_2S to elemental sulfur by indirect, catalytic reaction with oxygen from the air. The net reaction is:

$$2\ H_2S + O_2 \rightarrow 2\ S^{(0)} + 2\ H_2O$$

The H_2S is absorbed from the vent-gas by a scrubber solution which contains sodium bicarbonate, sodium vanadate, and anthroquinone disulfonic acid. The latter two compounds catalyze the oxidation reaction. In a separate vessel, air is blown through the scrubber solution to aerate it and collect the colloidal sulfur as a froth. This froth is pumped out to other equipment which removes and concentrates the sulfur, ultimately producing pure sulfur in liquid form. This sulfur is of high purity, and may be sold.

The Stretford Unit removes more than 99% of the H_2S from the vent-gas. The only chemical cost is that of occasionally replenishing the catalytic scrubber solution. Operating costs are moderate, and the Stretford Units in service at The Geysers have been trouble-free.

A Stretford Unit costs several million dollars. Having several power-plants share a Stretford Unit could result in considerable savings.

Sulfur dioxide may be needed at the powerplant to lower condensate pH, or to surpress the formation of colloidal sulfur (Section 3.6). In principle, Stretford Unit sulfur may be burned to produce SO_2. In practice, direct oxidation of H_2S to SO_2 is much simpler and therefore preferred. Because it contains a considerable amount of methane and hydrogen, the vent-gas at The Geysers is weakly flammable when mixed with air. The Geysers Units 1, 2, 7 and 8 are equipped with gas incinerators which mix the vent-gas with air, burn it, and remove the SO_2 from the incinerator exhaust by washing the exhaust gas with cooling water. These gas incinerators are somewhat temperamental, because the low fuel value of the vent-gas makes it difficult to keep the flame going. When necessary, propane is added to invigorate the flame.

The Selectox process, developed by Union Oil, is a possible replacement for the vent-gas incinerator (Hansford and Hass, 1979). This is a flameless process that utilizes a catalyst to induce reaction between H_2S and atmospheric oxygen. The Selectox process has been successfully tested at The Geysers. Because it does not rely on the meager and unreliable fuel value of the vent gas, Selectox may be preferred in areas where the gas contains little hydrogen or methane.

3.6. Removal of hydrogen sulfide from the condensate

In principle, the H_2S in the condensate or cooling water may be stripped from it using air or other gas. The H_2S is then removed from the stripping gas as from the condenser vent gas, using the Stretford or equivalent process. At the Matsukawa Power Station, Japan, a pilot plant for air stripping part of the cooling water will be tested in 1984 (Project Sunshine, 1984, pp. 160-163). The practical problem with this approach is the very large volume of stripping gas that must be treated. At Matsukawa, the gas treatment plant is designed to handle 300 m^3/hr of condenser vent gas, plus

2,200 m^3/hr of air from the water stripping tower. Ammonia in the steam and cooling water would increase the solubility of H_2S, greatly increasing the volume of gas required. Stripping the condensate with desulfurized condenser vent gas has also been suggested (Domahidy, 1983). The CO_2 in the gas would neutralize part of the ammonia, thereby decreasing the solubility of H_2S and the volume of gas required.

In most cases, once H_2S is dissolved in the condensate, oxidation is practically the only way to prevent its emission to the atmosphere. At The Geysers Units 15 and 17, hydrogen peroxide is used to remove H_2S from surface condenser condensate before it is mixed with the cooling water (Sharp, 1982). About 1 ppm iron chelated by hydroxyacetate is added to catalyze the reaction. With a H_2O_2:H_2S mole ratio of about 2:1, essentially complete conversion to soluble compounds is achieved. Thiosulfate probably is the major reaction product.

Hydrogen peroxide is effective, but expensive. In bulk, 50% H_2O_2 costs about 0.71 dollars/kg. Applying H_2O_2 at a 2:1 mole ratio costs about 2.84 dollars/kg H_2S removed, and this does not include the cost of the other chemicals. A typical 55 MW Unit at The Geysers receives 100 kg/hr H_2S with its steam. Although reaction with H_2O_2 could be used as the primary means of H_2S emission abatement, the chemical cost makes this option unattractive.

The cooling water returns from the cooling tower saturated with atmospheric oxygen. Oxygen by itself is unreactive, but a suitable catalyst may be added to the cooling water to catalyze the reaction between oxygen and dissolved H_2S. Reaction with oxygen will reduce or eliminate the need for costly hydrogen peroxide.

For several years ferrous sulfate was added to the cooling water of The Geysers Units 11 and 12 to maintain 30 ppm iron in the water. The iron catalyzed a reaction with dissolved oxygen that removed over 90% of the H_2S from the cooling water before it could be emitted to the atmosphere. The condenser vent-gas was vented into the bottom of the cooling tower, and was stripped of H_2S by the iron-rich cooling water. However, the iron-rich cooling water was highly corrosive, necessitating frequent repairs. Iron hydroxide, iron sulfide, and colloidal sulfur formed a messy precipitate that was purged from the cooling tower basin, dewatered, and disposed of as toxic solid waste (it contained arsenic and mercury; see Section 6). An improved derivative of this process is still used at The Geysers Units 5, 6 and 12. The improved process requires less iron sulfate, the vent gas is stripped of H_2S by adding $NaOH$ to the aftercondenser's cooling water supply, and hydrogen peroxide is added to improve abatement and prevent formation of colloidal sulfur.

A modern, practical air oxidation process utilizes iron chelated with N-hydroxyethylenediaminetriacetate (*FeHEDTA*) as the catalyst (Dorighi and Henderson, 1984). Between 5 and 20 ppm of chelated iron in the cooling water allows 98+% overall abatement to be achieved. Caustic soda is added to maintain acceptable cooling water pH. Vent-gas H_2S is converted to SO_2 in a vent-gas incinerator. In the cooling water, the SO_2 is converted to sulfite ion, which reacts with elemental sulfur to produce thiosulfate:

$$SO_2 + H_2O \rightarrow SO_3^{=} + 2\,H^+$$

$$SO_3^{=} + S^{(0)} \rightarrow S_2O_3^{=}$$

These reactions prevent precipitation of colloidal sulfur. This process is presently used at The Geysers Units 1, 2, 7 and 8. Corrosion rates are acceptable (Weres *et al.* 1985). The major drawback of this process is the relatively high cost of the catalyst; the cost for catalyst alone is about 1.5 mils/ kWhr. PG&E buys about five million dollars worth of *FeHEDTA* per year.

The FeHEDTA catalyst is used without a vent-gas incinerator at Units 3, 4, 9, 10 and 11. At Units 3, 4 and 11 hydrogen peroxide is added to the cooling water to prevent the production of colloidal sulfur.

Other potential catalysts for this application have been evaluated (*Ibid.*; and Weres and Tsao, 1983). Iron citrate appears to be as effective as *FeHEDTA* but cheaper. Unchelated nickel is the most effective and cheapest of all. Laboratory studies suggest that 0.6 ppm of nickel in the cooling water may allow 99% abatement to be attained, at a negligible catalyst cost (<0.01 mils/kWhr). The occupational hazard posed by the nickel would be small because of the very small concentration required. The measures needed to protect powerplant workers from the arsenic in the cooling tower sludge would effectively mitigate the nickel hazard as well (Section 6). The mechanism, kinetics and stoichiometry of the $H_2S/O_2/SO_2/Ni$ reaction system are described in the references cited above.

All chemical reactions that convert H_2S to water soluble sulfur compounds release protons. For example:

$$2\ H_2S + 2\ O_2 \rightarrow S_2O_3^{=} + H_2O + 2\ H^+$$

Base must be provided to maintain acceptable cooling water pH. At The Geysers, the ammonia present in the steam neutralizes most of the acid produced. With low ammonia steam, the full requirement for base would have to be supplied from without; caustic soda is most convenient, but soda ash (sodium carbonate) is cheaper. Lime cannot be used because it would produce calcium sulfate scale. The need to neutralize the acid produced may restrict application of liquid-phase oxidation processes (including use of hydrogen peroxide) to The Geysers and other areas with ammonia-rich steam.

In areas with ammonia-rich steam, the advanced air-oxidation processes offer a practical alternative to the surface condenser/Stretford Unit/hydrogen peroxide approach, and are superior to it in retrofit applications.

3.7. Upstream abatement processes

Removing the H_2S from the steam before it reaches the powerplant would allow one system to stop emissions during powerplant outages as well as normal operation. An "upstream" abatement process would be well suited to retrofitting existing powerplants that do not have provisions for air pollution abatement. Two such processes have been pilot tested at The Geysers. Treating the steam before it reaches the turbine inevitably reduces temperature and pressure to some extent, but practical experience suggests that these losses can be reduced to tolerable levels.

The copper sulfate process. In the copper sulfate process H_2S is scrubbed from the steam by reaction with a copper sulfate solution to produce copper sulfide (Harvey and Makrides, 1980). The copper sulfide is reacted with oxygen or air at high pressure to regenerate copper ion and sulfuric acid. At The Geysers, part of the sulfuric acid is neutralized by the ammonia in the steam. Externally supplied ammonia must be added to neutralize the rest. Copper is recovered from the ammonium sulfate purge stream by ion exchange.

The copper sulfate process has been successfully pilot tested on a 5 MW scale. Removal of 95-99.9% of the H_2S has been demonstrated. About 75% of the boron, 50% of the arsenic, and 80% of the ammonia were also removed (EIC and PG&E, 1980).

The copper sulfate process is complicated, and would require large capital investment. The scrubber solution must be maintained at the steam temperature and pressure, and it is strongly acidic (pH about 1.3). This necessitates the use of expensive titanium vessels and piping in the scrubber part of the system.

The steam converter. The heart of the steam converter is a tube-and-shell heat exchanger. The incoming steam condenses outside the tubes. The part of the steam not condensed (the vapor purge) is removed from the system. It contains most of the noncondensible gases, including H_2S. The condensate is re-evaporated inside the tubes to make clean steam. The source of heat for this is the steam condensing outside the tubes. Because one pass is insufficient to re-evaporate the condensate completely, it is recirculated through the tubes. Dust, boric acid, and some arsenic accumulate in the condensate loop. They are removed from the system with the liquid purge. Removing the noncondensibles reduces the load on the gas ejectors; fifty years ago, steam converters were widely used at Lardarello for this purpose (Villa, 1976).

A modern steam converter has been tested at The Geysers on pilot scale and achieved 90% H_2S removal (Coury 1981 and 1982). With no ammonia in the steam, 99+% H_2S removal should readily be attainable.

A steam converter removes the H_2S from the steam, but does not destroy the H_2S. A Stretford Unit or equivalent device would destroy the H_2S. Clearly, the capital investment for air pollution abatement using a steam converter plus Stretford Unit would exceed that for abatement using a surface condenser plus Stretford Unit. However, this cost may be justified in retrofit applications.

Steam converters may find application in removing the H_2S from steam that is vented preplant. The regenerated, clean steam would be vented to the atmosphere. A relatively small, uninsulated heat exchanger might suffice in this application. The H_2S would be removed from the vapor purge by the Stretford Unit of the given unit or one of its neighbors.

3.8. Other atmospheric emissions

Hydrogen sulfide is the only geothermal air pollutant of consequence. The emissions of ammonia are small. The amount of CO_2 emitted per kWhr is typically 1/30-th that emitted from coal-fired powerplants (Axtmann 1975a). Geothermal steam also contains boric acid and trace amounts of mercury, arsenic, and radon (Table 2). Estimated rates of emission from The Geysers Units 1 to 11 in 1976 are summarized in Table 4. At that time, only Unit 11 was provided with means for H_2S emission abatement. Therefore, data for 1976 allows the effect of air pollution abatement to be conveniently illustrated.

Table 4

Atmospheric emissions from The Geysers in 1976

	Units 1 to 11					Venting steam supply of 106 MW Unit (kg/hr)
		g/kWhr		Actual Average Amounts (kg/hr)		
	From normal operation	Preplant releases	Total	From normal operation	Total	
H_2S	1.6	0.3	1.9	790	970	210
NH_3	1.7	0.2	2.0	870	980	180
CO_2	29	4	33	$15\text{x}10^3$	$17\text{x}10^3$	$3.1\text{x}10^3$
B	0.013	0.019	0.033	6.7	16	15
As	$6\text{x}10^{-6}$	$23\text{x}10^{-6}$	$29\text{x}10^{-6}$	$3.1\text{x}10^{-3}$	$15\text{x}10^{-3}$	$18\text{x}10^{-3}$
Hg	$28\text{x}10^{-6}$	$8\text{x}10^{-6}$	$37\text{x}10^{-6}$	$14\text{x}10^{-3}$	$18\text{x}10^{-3}$	$6.6\text{x}10^{-3}$
^{222}Rn*	$1.8\text{x}10^{-7}$	$0.2\text{x}10^{-7}$	$2.1\text{x}10^{-7}$	0.093	0.11	0.02

*Radon values in Curies/kWhr and Curies as appropriate.

Table adapted from Weres *et al.* (1977), Table 10.2. Estimates are based on data and calculations of Griffin *et al.* (1974), Serpa *et al.* (1974), and Robertson *et al.* (1977).

All the radon in the steam is released to the atmosphere with the condenser vent-gas. At The Geysers, this radon is rapidly diluted to background levels (Anspaugh and Phelps, 1975). Seventy to eighty percent of the mercury in The Geysers' steam is in elemental form; 40-60% of the total incoming mercury is emitted to the atmosphere, and the rest probably accumulates in the cooling tower sludge (Robertson *et al.* 1977).

Most of the arsenic that enters the power plants at The Geysers and Cerro Prieto with the steam is retained in the cooling water and cooling tower sludge (Crecelius *et al.*, 1976; Robertson *et al.*, 1978). Likewise, the volatility of boric acid is so low that most of it remains in the cooling water. At Cerro Prieto most of the arsenic and boric acid in the brine are retained by the brine when the steam is separated from it (*Ibid.*). Under normal operating conditions, the only atmospheric emissions of arsenic and boric acid are those associated with cooling tower drift; i.e., minute droplets of cooling water entrained by the cooling tower air flow. Boric acid is a potent phytotoxin. Localized vegetation damage has been observed near some of the older Units at The Geysers; probably, this was caused by the cooling tower drift.

Most of the arsenic and boric acid emitted to the atmosphere are associated with pre-plant steam releases. This is illustrated in Table 4.

4. Subsidence and reinjection

The weight of the earth above a reservoir of groundwater, petroleum or geothermal brine is carried in part by the mineral skeleton of the reservoir rock, and in part by the pore fluids. As the fluids are removed and the pore pressure is reduced, there is a tendency for the earth to subside, the movement sometimes occurring horizontally as well as vertically. For example, subsidence by several meters has occurred in the Long Beach oil field and in the San Joaquin Valley in California (Poland, 1973; Poland and Davis, 1969). Subsidence in the San Joaquin Valley was caused by pumping of ground water for agriculture.

The scale of geothermal brine extraction is comparable to large agricultural ground water withdrawals (Table 1). A serious potential for subsidence is associated with geothermal development. Up to 4.5 meters subsidence occurred between 1964 and 1974 at the Wairakei geothermal field, where the brine is not reinjected (Stilwell *et al.*, 1976). The subsidence was greater where the underlying breccia was thicker. This illustrates the effect of local geology on subsidence.

In high temperature geothermal reservoirs like Cerro Prieto the rock is thermally metamorphosed to some extent and harder than the sedimentary rock in moderate temperature reservoirs. Less subsidence is to be expected with harder reservoir rock; in fact, at Cerro Prieto subsidence is measured in centimeters (Garcia, 1979). At The Geysers the reservoir is in hard metamorphic rock (Franciscan graywacke, metachert, and blueschist), the mass of steam withdrawn is small, and subsidence is negligible.

The practical impacts of subsidence will vary with location. The extensive subsidence at Wairakei has had little impact, because there is little in the area that is sensitive to subsidence. A few meters of subsidence in the Imperial Valley could disrupt the irrigation system there. Also vulnerable are the geothermal wells themselves: subsidence in the San Joaquin Valley irreparably damaged many of the deep irrigation wells there.

Where subsidence is likely and the environment is sensitive to it, prudently planned reinjection of the residual brine is essential. In most cases, reinjection is also desirable to help maintain reservoir pressure, extract additional heat from the rock, and prolong the useful life of the resource.

Subterranean water injection may induce seismic activity by reducing effective stresses, loosening tight vertical faults, and causing the release of tectonic stress accumulated along them. This was demonstrated at the Rangely oil field in Colorado, where high pressure water injection produced small earthquakes (Raleigh *et al.*, 1975). Prudent field development practices effectively mitigate the hazard of induced seismicity; normally, the injection pressure is not high enough to induce seismicity.

In principle, the production and reinjection of geothermal brines may affect shallow fresh-water aquifers. There is geochemical evidence that fresh water is entering the top of the geothermal system at Cerro Prieto (Grant *et al.*, 1984) and the edges of the system at Larderello (Celati, *et al.*, 1973; D'Amore, *et al.*, 1977) in response to the pressure drop caused by the extraction of geothermal fluids. Improper reinjection could contaminate shallow aquifiers. These hazards deserve careful consideration in water short areas.

5. Liquid effluents

Most high temperature geothermal waters are saline, and most contain toxic trace contaminants. Boron, arsenic, and mercury are ubiquitous. Highly saline waters contain much toxic lead, and also iron and manganese which produce acidity when they oxidize and precipitate as oxides. Table 5 shows chemical compositions of typical geothermal fluids. Cosner and Apps (1978) have compiled many other analyses.

The arsenic, mercury and other toxic elements in geothermal brines are discussed by Bowman *et al.* (1974), Sabadell and Axtmann (1975), Siegel and Siegel (1975), Weissberg and Zobel (1973), and Weissberg (1969). White and Roberson (1962) discuss the association of mercury with hot springs.

5.1. Surface disposal of geothermal brines

Practical experience with surface disposal of geothermal brines illustrates why this practice is forbidden in the United States.

At Wairakei, most of the spent brine is dumped into the Waikato River. The environmental impacts of this practice have been surveyed by Axtmann (1975). At the river's minimum flow rate of 14 cubic meters per second, 0.32 ppm of arsenic is added to the river water, enough to render it unfit to drink[*]. The water temperature is increased by 6°C. Downstream, a hydroelectric reservoir is clogged with algae whose growth is stimulated by the heat and CO_2 added to the water, and unusual concentrations of mercury are found in fish and water plants. Within the field itself, massive silica deposits frequently must be cleaned from the spent brine drains.

Wairakei is a geothermal development of moderate size, the geothermal brine there is relatively innocuous, and the Waikato is a large river. All this reduces the impacts of dumping the brine in the river; this practice would have much worse impacts in most other areas.

At Cerro Prieto, the residual brine is dumped into an evaporation pond with an area of 8 km^2 (Figure 3). There, evaporation concentrates it several-fold. A canal carries this concentrated brine to the Rio Hardy, which flows into the Gulf of California (Mercado, 1976). A process for extracting valuable potassium chloride from the brine by fractional crystallization has been successfully demonstrated on pilot-plant scale (Mercado *et al.*, 1979). This process produces concentrated residual brines and solid wastes which must be disposed of.

5.2. Geothermal brine chemistry

Chemical treatment of spent brine to prevent damage to the injection wells and reservoir is a major consideration in geothermal reinjection, and pre-injection treatment is the major practical application of geothermal brine chemistry. Scaling within the production well-bore or surface equipment is a related problem, dealt with by similar methods. In principle, corrosion can be a problem, but it is easily mitigated by keeping the brine out of contact with air, and not reducing brine pH too much by adding acid.

Undisturbed brines in a geothermal reservoir are in chemical equilibrium with the reservoir rock. The large temperature drop and steam loss the brine undergoes during production and energy extraction may cause various solids to precipitate from it. The initial characteristics of the brine and the nature

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[*] This arsenic can be removed from the water by ordinary municipal water treatment.

(text is continued on page 21)

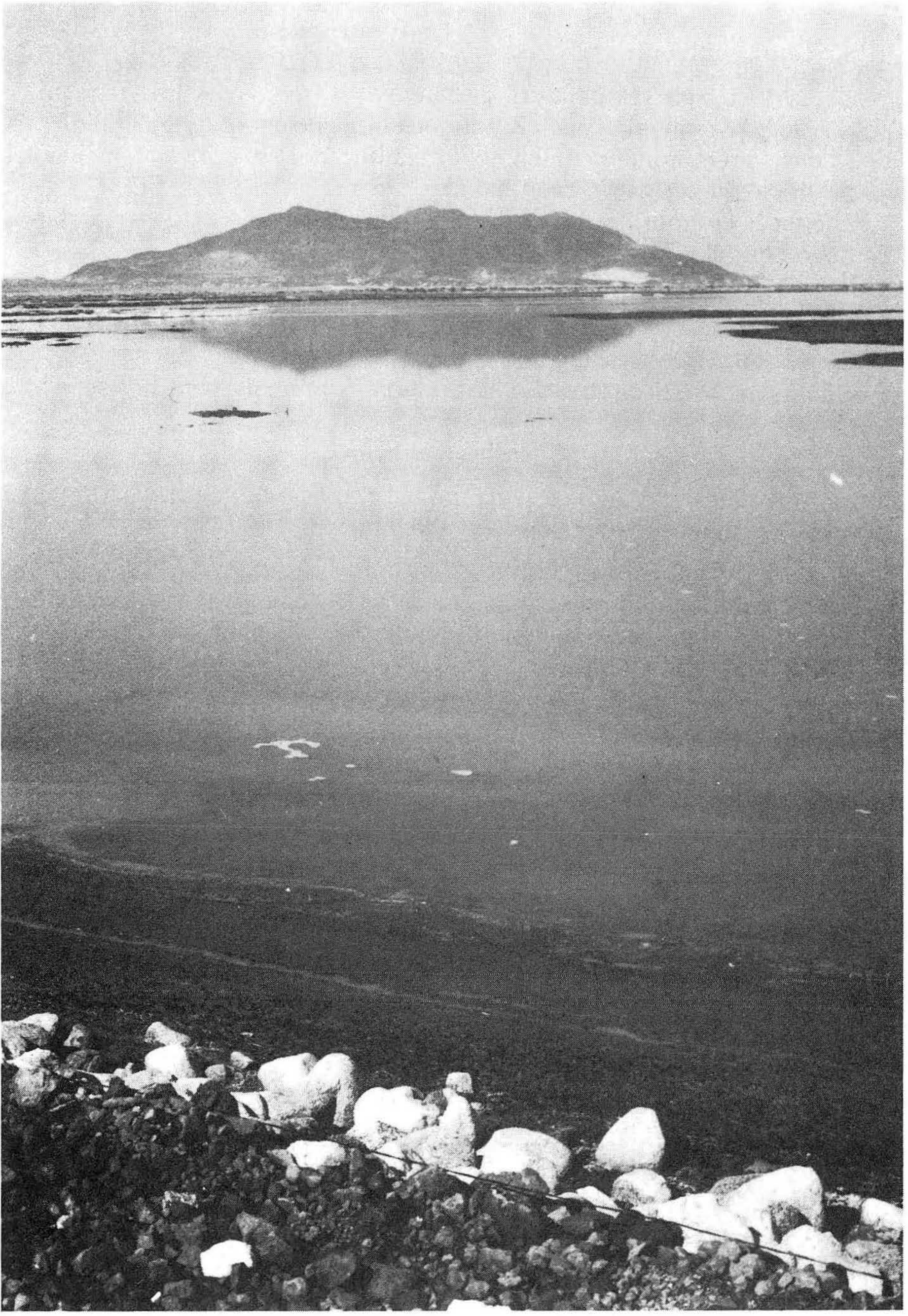

Figure 3. The brine evaporation pond at Cerro Prieto (LBL file photo). The area of the pond is 8 km^3. The hill behind it is the volcano Cerro Prieto.

Table 5. Chemical composition of geothermal fluids[a].

	Geysers steam condensate[b]	Geysers reservoir water[c]	Bank Mine[d] (hot spring)	Long Valley[e]	Wairakei[f]	Broadlands[g]	Cerro Prieto[h]	Salton Sea[i]
Li	<0.01		4.4	2.8	12	12	17.7	215
Na	<0.5	400	1,190	390	1,235	1,050	7,079	50,400
K	<0.5	37	23	45	197	224	1,439	17,500
Rb		0.3		0.48				137
Cs				0.6				16
Mg	0.04	<0.1	55	0.1			0.61	54
Ca	<0.1	10	20	0.9			445	28,000
Sr		0.6	2.2	0.14				609
Ba				nd				235
Mn			0.1	<0.02				1,560
Fe			0.0	0.05				2,090
Cu				<0.03				8
Ag				<0.04				0.8
Zn				0.10				790
Hg				10^{-4}				0.006
Tl								1.5
Pb				<0.1				84
As			0.0	2.2		8	1.5	12
Sb				0.2				0.4
F	<0.1		1.0	12	9	7.3	2.38	15
Cl	10	504	644	280	2,180	1,743	13,113	155,000
Br			1.6	1.1		5.7	17.5	120

I			3.2	0.4		0.8	0.59	18
B	1.2	27	620	15	30	49	18.38	390
CO_2	34	340	2,370	346	(44)	(748)	36	>108
SiO_2	4.3	353	42	340	620	805	960	400
NH_3	9	50	438	0.4		2.1		386
H_2S	35	4.3	12	10	(3.5)	(120)		17-29
$SO_4^=$	7.3	<11	598	130	34	8	11.	5.4
pH	5.7	6.2	6.8	9.2			8.05	

Table adapted from Weres *et al.* (1977), Table 12.2.

[a] All values in parts per million by weight. nd = not detected. Blanks signify not reported, rather than zero. All samples have lost gases during collection and handling. Thus, concentrations of CO_2 and H_2S reported are substantially lower than exist in the reservoir. Most CO_2 reported is present as HCO_3^-; ammonia is present as NH_4^+. Steam separation from brine may increase solute concentrations. Except for Cerro Prieto, all analyses corrected for water loss, or else samples taken with little water loss. In all cases, part or all of sulfate reported probably formed by oxidation of H_2S after sample collection.

[b] Steam condensate from a well in the Castle Rock Springs area in Lake County. Sample 2 reported by Truesdell *et al.* (1981). Mg, Ca, Fe, and part of SiO_2 reported are from dust entrained by the steam. *Cl* and *Na* are from entrained reservoir water.

[c] First brine sample ever collected downhole at The Geysers. Sample collected in the Aminoil USA area of The Geysers, March 1981, by the Lawrence Berkeley Laboratory and Aminoil (Michel *et al.*, 1982, Appendix D). Reservoir temperature about 260°C.

[d] Water from a hot spring in the Sulfur Bank mercury mine near Clearlake Park, Lake County, California. "Analysis number 5" reported by White and Roberson (1962).

[e] Well Magma-Ritchie 5 in Long Valley, Mono County, California, reported by Willey, O'Neil, and Rapp (1974). Downhole temperature 200°-240°C.

[f] Wairakei Bore 71, reported by Weissberg (1969). Analysis corrected for water loss; values in parentheses corrected for gas loss. Maximum temperature measured was 239°C.

[g] Broadlands Drill Hole 2, reported by Weissberg (1969). Corrected for water

loss; values in parentheses corrected for gas loss. Maximum measured temperature was 294°C.

[h] Cerro Prieto Well M-14, sampled September 23, 1976. Mañón *et al.* (1977), p. 67. Analysis not corrected for steam separation.

[i] Sample from Well No. 1-IID in the Niland area. Analysis corrected for water loss and reported by Skinner *et al.* (1967).

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and operating parameters of the energy conversion processes determine what precipitates, in what quantity, and where.

There can be large variations in chemical behavior from well to well in a single field; extrapolation from field to field is more hazardous still. Perforce, geothermal brine treatment processes tend to be site-specific, and their development relies heavily on site-specific bench- and field testing.

In most cases, calcium carbonate or colloidal amorphous silica is the major precipitate. Massive carbonate precipitation is more typical of moderate temperature brines (e.g. East Mesa), and massive amorphous silica precipitation is limited to hotter brines (Niland, Cerro Prieto, Wairakei). The same correlation is observed for hot spring deposits. Up to several hundred grams of silica may precipitate from a ton of brine.

Smaller amounts of other materials like amorphous iron silicate, iron sulfide, lead sulfide, or iron carbonate are also encountered. In general, the importance of these "exotic" precipitates increases with increasing salinity and initial temperature. Except for extreme cases (e.g. Niland) they amount to only a few grams per ton of brine. At Niland and similar areas with very hot, very saline brine, the scale within the production wellbore consists mostly of galena (PbS) and/or amorphous iron silicate. Beyond the steam separator, galena and iron silicate precipitate together with silica, and do not present a separate problem. Arnørsson (1981) discusses the determinants of scale type, with application to Iceland; Harrar *et al.* (1979) describe scaling at Niland.

Binary cycle power plants are very sensitive to scale build-up on their heat exchange surfaces; less than a millimeter of scale there would force the unit to be taken down for cleaning. Even slow deposition of "exotic" scale may render a binary plant uneconomical. Fortunately, scaling tends to be slow in binary systems.

Flash cycle systems, which often encounter severe scaling, are much less vulnerable. The power-plant is unaffected by scaling, and the steam separators and brine conduits need to be cleaned only when scale build-up interferes with fluid flow or valve operation. Usually, only calcium carbonate and amorphous silica scale have practical significance in a flash steam system; other kinds of scale build up too slowly to matter.

5.3. Precipitation of carbonates and sulfates

Michels (1980, 1980a) studied the precipitation of calcium carbonate from East Mesa brines. Michels (1981) presented a general model of calcium carborate precipitation. Plummer *et al.* (1979) and Weres and Apps (1982) have reviewed the kinetics of calcium carbonate deposition in general.

Calcium carbonate normally precipitates from the brine in response to steam separation; separating the steam removes CO_2 from the brine, and causes its pH to increase. Steam separation occurs in the production wellbore and in the steam separators, and these are the usual locations of calcium carbonate scale. Places in the wellbore where the flow is constricted are particularly prone to scale accumulation. Calcium carbonate precipitation may be reduced by controlling the pressure drop within the wellbore, and by injecting hydrochloric acid or threshold-type scale inhibitors before the point of scaling (Vetter, 1979). The use of scale inhibitors for this purpose is very site-specific and must be considered experimental; therefore, HCl is practically the additive of choice. The cost of the HCl will depend on the concentration of bicarbonate in the brine, and may be high. Sulfuric acid is much cheaper, but precipitation of calcium, strontium or barium sulfate usually precludes its use.

The precipitation of calcium carbonate (or other carbonate or sulfate minerals) can be caused by mixing "incompatible" brines; e.g. mixing a brine rich in bicarbonate or sulfate with one rich in calcium. If a well produces brine from two or more horizons, this can happen within the production wellbore. It can also happen in the surface equipment or injection wells, where brine from different wells is mixed.

Lime and other additives that increase brine pH can cause serious calcium carbonate scaling. If there were no bicarbonate present in the brine, this could not occur. Adding enough acid to the brine fully to convert the bicarbonate to CO_2 before the final steam separation step would prevent this problem (see Section 5.6).

The mixing of alkaline drilling mud or mud filtrate with brines that are rich in both calcium and CO_2 can also cause the precipitation of calcium carbonate.

Once formed, calcium carbonate scale may be removed either mechanically or with acid. Sulfate scales must be removed mechanically.

5.4. The chemistry of silica in geothermal brines

Geothermal brines initially hotter than about 240°C contain enough dissolved silica to enable the formation of abundant colloidal silica after the steam is separated from them. Usually, the removal of colloidal silica is the primary purpose of preinjection brine treatment. In extreme cases like Niland and Cerro Prieto, rapid silica scaling may occur in the steam separators and associated piping. Consequently, the chemistry of silica is the most important facet of geothermal brine chemistry, and has received the most attention.

The chemistry of silica in geothermal brines is reviewed by Weres *et al.* (1980a). The kinetics of polymerization of dissolved silica were studied by Weres *et al.* (1980a, 1981, 1982). Similar studies were reported by Baumann (1959), Makrides *et al.* (1980), Rothbaum and Rohde (1979), Bohlmann *et al.* (1980), and Crerar *et al.* (1981). The chemistry, colloidal properties, and uses of silica were surveyed by Iler (1979).

Sections 5.4 through 5.7 draw on the reviews by Weres *et al.* (1980a) and Weres and Apps (1982).

Quartz is the common and most stable form of silica in nature. The initial concentration of silica in a geothermal brine usually corresponds to the solubility of quartz under the given reservoir conditions. The predominant form of dissolved silica is monosilicic acid, $Si(OH)_4$.

When the brine is cooled in the course of production and energy extraction, it becomes supersaturated relative to quartz. The rate of deposition of quartz and the other crystalline forms of silica from the brine is negligibly small. Usually, the precipitation of silica from the brine becomes noticeable only after supersaturation relative to amorphous silica is attained, and the usual product is amorphous silica.

The polymerization of monosilicic acid and formation of silica scale are depicted in Figure 4. Normally, the dissolved silica first polymerizes to colloidal silica particles that nucleate in the brine.

The rate of homogeneous nucleation depends very strongly upon the saturation ratio; i.e., the ratio of silica concentration to solubility under the given conditions. Roughly, polymerization is very slow when the saturation ratio is below two, and very fast when the saturation ratio is above three.

When the saturation ratio is too small for rapid homogeneous nucleation to occur, heterogeneous nucleation and molecular deposition on solid surfaces dominate. In areas with very hot brine, like Cerro Prieto, glassy silica scale formed by molecular deposition alone is sometimes observed in the high temperature part of the system. In most cases molecular deposition onto solid surfaces is too slow to be noticed. Colloidal silica particles grow by molecular deposition, and this is the main practical significance of the process.

In heterogeneous nucleation a preexisting particle serves as the substrate for molecular deposition. This relatively slow process resembles homogeneous nucleation and replaces it at low supersaturation.

Colloidal silica particles may be coagulated by cations in the brine; calcium and iron are particularly effective in this regard. The same electrostatic forces cause colloidal silica particles to adhere to solid surfaces. Because it releases iron ions, corrosion accelerates the deposition of silica scale on steel.

Once attached to a solid surface, colloidal silica is converted to solid scale by molecular deposition of dissolved silica between the particles. Solid deposits may form at a moderate rate (centimeters per year) where both colloidal silica and substantially supersaturated dissolved silica are present. Sometimes cementation proceeds to the point of producing a glasslike material.

Figure 5 illustrates the effects of pH on molecular deposition, nucleation, and coagulation. At low pH, molecular deposition and nucleation are catalyzed by traces of hydrogen fluoride. Above pH 4, the rate of molecular deposition is proportional to the negative surface charge on amorphous silica. The rates of nucleation and coagulation also increase with surface charge. Increasing salinity also increases surface charge, and accelerates all three processes.

At constant supersaturation, the rates of molecular deposition and nucleation steadily increase with pH. Above pH 7 monosilicic acid begins to dissociate:

$$Si(OH)_4 \rightarrow Si(OH)_3O^- + H^+$$

This increases the solubility of silica. At fixed concentration of dissolved silica, the saturation ratio decreases with increasing pH. This retards molecular deposition and nucleation, and finally stops them altogether.

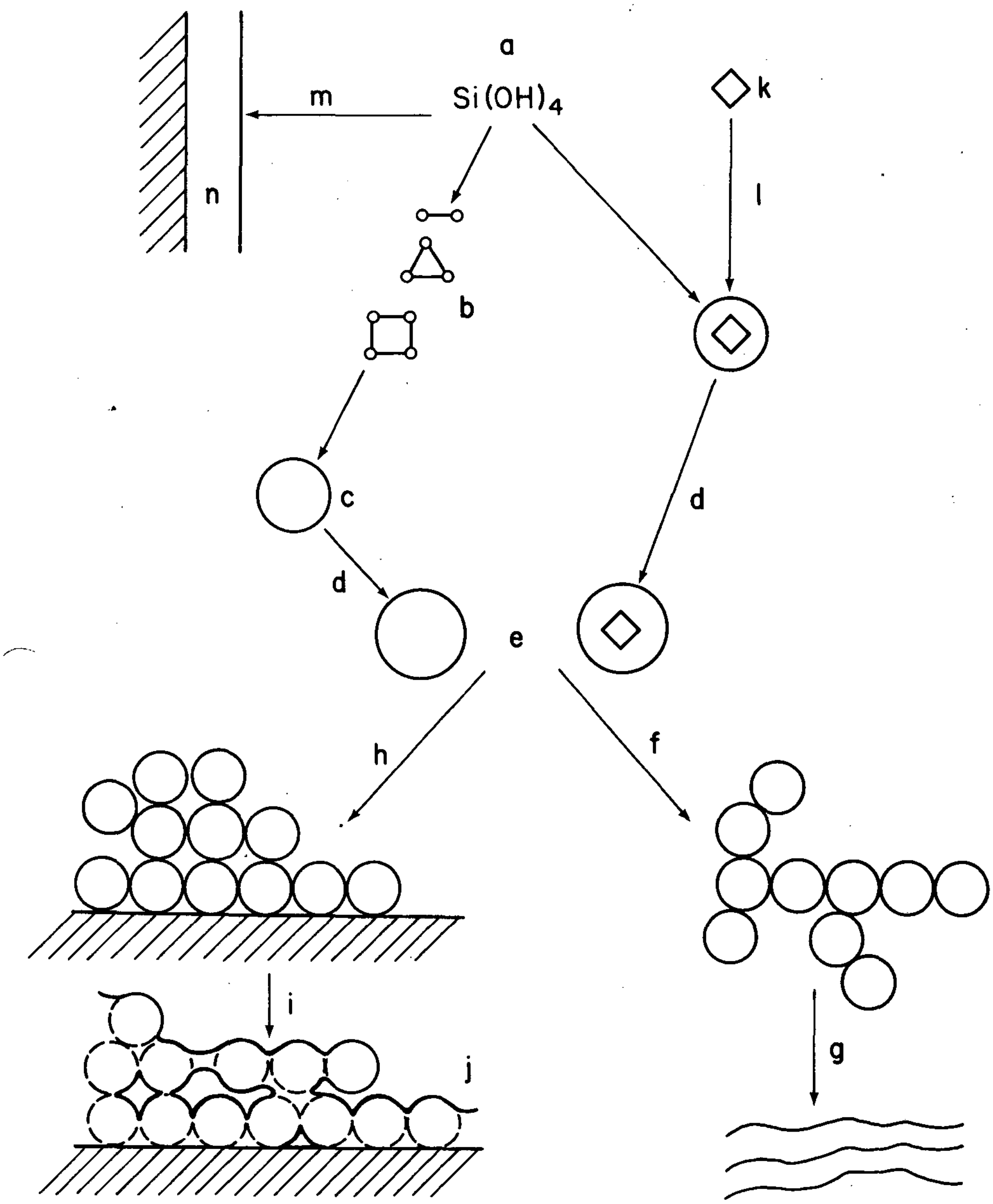

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Figure 4. Silica deposition mechanisms. (a) Dissolved silica (mostly monosilicic acid, $Si(OH)_4$). (b) Formation of small silicic acid polymers (dimer, trimer, etc.). (c) A few polymers grow to critical nucleus size, typically about 1 nm in diameter. (d) Particles grow by molecular deposition of dissolved silica on them. (Not to scale.) (e) "Mature" colloidal silica particles, 10-100 nm in diameter. (f) Colloidal particles coagulate in the brine. (g) Coagulated colloidal silica deposited from the brine by gravitational settling. (h) Colloidal silica particles adhere to solid substrate. (i) Particles are cemented together by molecular deposition of dissolved silica between them. (j) "Common" amorphous silica scale; deposition rate up to 1mm/day at 100°C. (k) Heteronucleus; typically an aluminosilicate or ferrosilicate polymer. (l) Heterogeneous nucleation. (m) Molecular deposition directly on to a solid substrate. (n) Hard, glassy silica scale; typical deposition rate 1mm/year at 160°C.

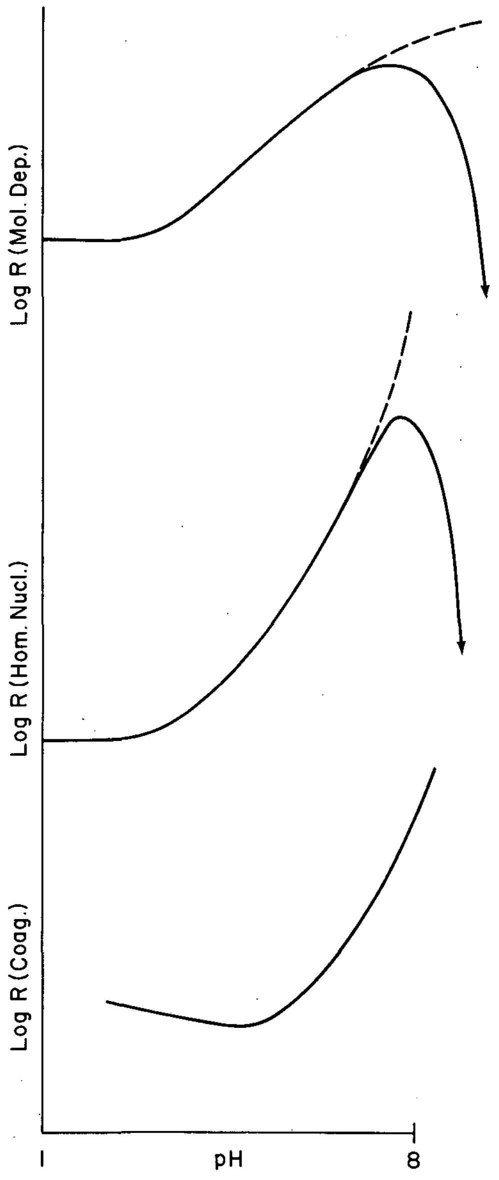

Figure 5. Schematic effect of pH upon rates of molecular deposition, homogeneous nucleation, and coagulation of silica. Solid lines: rate at constant total dissolved silica concentration (i.e., including silicate ions). Dashed lines: rate at constant concentration of monosilicic acid. Coagulation rate depends on the concentration of colloidal silica, but is independent of concentration of dissolved silica.

Reinjecting brine that contains colloidal silica or supersaturated dissolved silica risks formation damage. Coagulated colloidal silica will accumulate in pores and fractures in the formation. If supersaturated dissolved silica is also present, it will cement these deposits; this is the worst situation. If the brine is hot and contains enough dissolved silica for rapid molecular deposition to occur (e.g. 0.5 mm/year), molecular deposition alone may seal pores and fine fractures in the receiving formation, damaging it.

Reinjected brine may react with the reservoir matrix. For example, an acidified brine will dissolve calcite, its pH and calcium content will increase, and this may coagulate colloidal silica and hasten its deposition.

5.5. Means of controlling silica scale

If the brine is maintained and reinjected at a temperature so high that the dissolved silica in it remains undersaturated with amorphous silica, the silica will not polymerize. This is the practice at Ahuachapán (see Section 5.7).

At Broadlands (New Zealand) the pH of the flashed brine is high enough (>8) for the solubility of silica to be enhanced. There, proper steam separator operation maximizes brine pH, supersaturation is avoided, and silica deposition is surpressed (Henley, 1983; Henley and Singers, 1982). Methods to calculate the solubility of silica over a wide range of conditions are described by Fleming and Crerar (1982).

Acidifying the brine will retard the nucleation, growth, and coagulation of colloidal silica particles. The pH may also be kept down by not flashing the brine, as in a binary cycle with downhole pumped brine production. Reducing pH may also prevent the precipitation of calcium carbonate and sulfide minerals.

Lowering the pH of brine at Wairakei and Broadlands to 4 or 5 reduces the rate of scale deposition a hundred-fold (Rothbaum *et al.*, 1979). Adding enough *HCl* to Niland brine to reduce its pH to 3 or less completely stops scale deposition (Grens and Owen, 1977). Unfortunately, this acidified brine is corrosive, and may react with reservoir rock, damaging its permeability (Piwinskii and Netherton, 1977). Decreasing the pH of Cerro Prieto brine by one unit would decrease the rate of scale deposition severalfold (Weres *et al.* 1980; Weres and Tsao, 1981). This moderate acid treatment is practical, and may suffice in some applications.

"Aging" the flashed brine in a suitable holding tank converts the dissolved silica to colloidal silica, reducing supersaturation. This prevents the cementation of weakly adherent deposits and their conversion to solid scale. This treatment has been demonstrated at Otake (Yanagase, *et al.*, 1970) and Ahuachapán (Cuéllar, 1976). In both cases, the untreated brine deposited hard silica scale in conduits, while deposits from the aged brine were small, soft and easy to remove. In New Zealand, brine aging changed scale morphology, but little effected scaling rate (Rothbaum and Anderton, 1976; Rothbaum *et al.*, 1979).

Sludge separated from the flashed brine may be recirculated to the steam separators. The particles in the sludge provide a very large surface area for dissolved silica to deposit on, and this prevents large supersaturation and scale deposition. The reaction between freshly flashed brine and sludge is completed in a so-called "flash crystallizer", immediately downstream of the separators. In principle, this method should inhibit the deposition of all kinds of scale in the surface equipment.

Threshold-type scale inhibitors do not stop silica scale because the silica is amorphous. Harrar *et al.* (1980, 1980a) found several proprietary products capable of somewhat retarding the precipitation of colloidal silica and deposition of scale from flashed brine at Niland. Apparently, these act by stabilizing colloidal silica, preventing its deposition as scale.

Midkiff and Foyt (1976, 1977) reported deposition of silica scale cemented with calcium carbonate from saline cooling tower water. Chelating agents like EDTA inhibit deposition of this scale by chelating calcium, and partially dissolve scale already formed.

5.6. Removing colloidal silica from the brine

Colloidal silica and dissolved silica in excess of saturation should be removed from the brine before reinjection. Much of the technology for this has been borrowed from other applications of water treatment.

A typical brine treatment system is illustrated in Figure 6. This particular system was developed for use at Cerro Prieto, but is typical of the lot. The process it embodies was proposed and tested on bench scale by Weres and Tsao (1981). They recommended a field test, using the pilot-plant in Figure 6. This pilot-plant was actually built and operated by Hurtado *et al.* (1981), with results that closely corresponded to the predictions of Weres and Tsao.

The fresh brine is aged for 10-20 minutes to polymerize the silica and reduce supersaturation. Then about 30ppm of lime ($Ca(OH)_2$) is added.

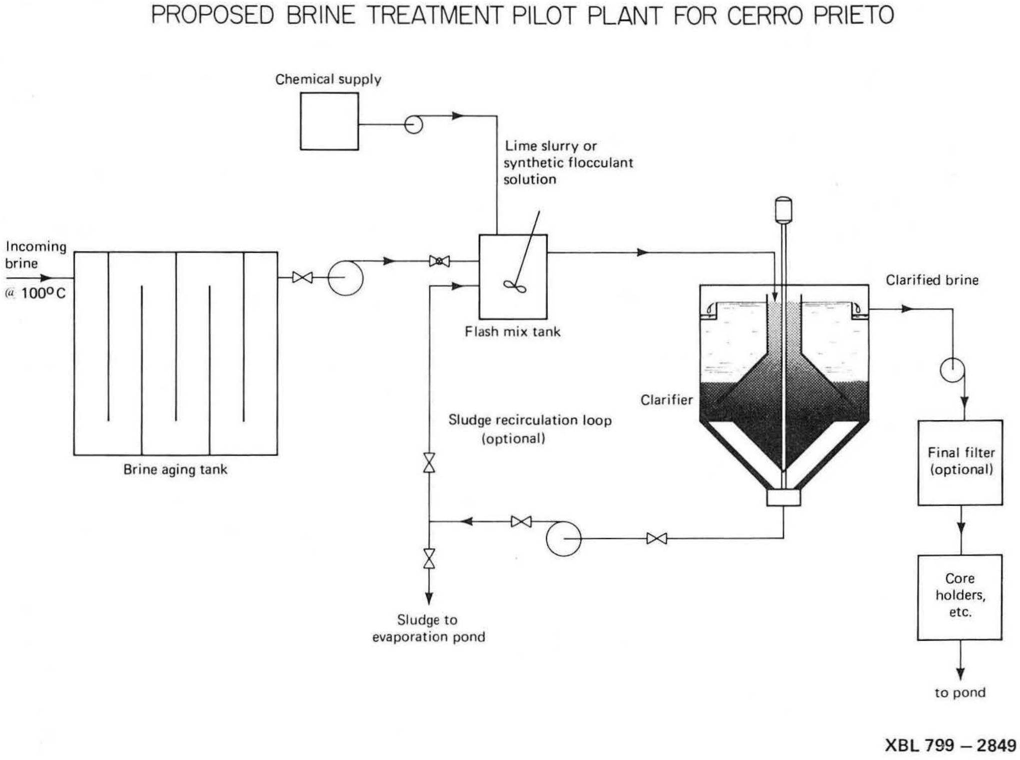

Figure 6. Proposed preinjection brine treatment process for Cerro Prieto. Reproduced from Weres *et al.* (1980).

Adding lime increases the pH of the brine by 0.5 unit to about 7.8, which induces strong coagulation of the colloidal silica. The coagulated silica settles at about 1 mm/s, and is separated from the brine in the clarifier. The final concentration of colloidal silica in the brine is about 3ppm without filtration. The sludge is dumped into the existing evaporation pond. The overall cost of this process on commercial scale has been estimated as 1.3 mils/kwhr (*Ibid.*).

The coagulated silica sludge provides a very large area for the molecular deposition of dissolved silica, and recirculation of sludge to the reaction zone enables silica supersaturation to be quickly reduced. Because silica polymerization is rapid at Cerro Prieto, sludge recirculation is not needed there.

Severe scaling occurs in the atmospheric pressure separator (not shown). Two solutions to this problem were evaluated. Recirculating part of the sludge to the separator may reduce supersaturation so quickly that the aging tank will no longer be needed, and cemented silica scale will not form (essentially, the flash crystallizer approach). Adding 50ppm of sulfuric acid upstream of the separator would lower the pH of the flashed brine to about 6.3, and reduce the rate of scale deposition several-fold (Weres and Tsao, 1981; Weres *et al.*, 1980). Adding acid would also remove the bicarbonate from the brine, eliminating any possibility that calcium carbonate will precipitate after lime is added (Weres *et al.* 1980; Iglesias and Weres, 1981). Adding acid for this purpose *would not* increase the need for lime, because the acidity would be steam stripped from the brine as CO_2. The concentrations of calcium, strontium, and barium in Cerro Prieto brine are so low that sulfuric acid may be used without the risk of sulfate scale deposition (*Ibid.*).

A similar process has been tested successfully at Niland by Quong *et al.* (1978). In their process, the functions of the mixing tank, clarifier, and sludge recirculation loop are combined in a single unit, the *reactor-clarifier,* and an aging tank is not needed. Flashed Niland brine is exceptionally saline and contains much calcium, but the pH is only about 5.5. At this low pH silica polymerization is slow, and the coagulation of the colloidal silica formed is incomplete. Sludge recirculation (within the reactor-clarifier) is essential to remove supersaturation. The brine is strongly buffered by bicarbonate, and this increases the cost of changing brine pH. Raising the pH accelerates polymerization and coagulation, but causes the supernatant to cloud with ferric hydroxide, and introduces the danger of calcium carbonate precipitation. Instead, 5ppm of an anionic polymer is used to enhance coagulation. The "clarified" brine still contains about 40ppm of colloidal silica, which is reduced to an acceptable 2ppm by finally filtering the brine. The sludge is converted to solid "cake" by mechanical dewatering.

The brine treatment processes developed for Cerro Prieto and Niland are closely related, but each is tailored to the given brine. This illustrates how an "off-the-shelf" approach is not appropriate to geothermal brine treatment.

It is hard to induce coagulation of colloidal silica in low salinity brines like those in New Zealand. Rothbaum and Anderton (1976) developed a process for removing silica and arsenic from the spent brine at Wairakei, to reduce scaling in the brine drains and reduce pollution of the Waikato River. The brine is aged for 150 minutes to convert much of the dissolved silica to colloidal form. Then 400 to 700 ppm of unslaked lime (calcium oxide) and 10 ppm of sodium hypochlorite are added. The brine reacts with the silica to produce amorphous calcium silicate, which precipitates. The hypochlorite oxidises the the arsenic to arsenite, which precipitates with the silica. This process is fundamentally different from that developed for the Cerro Prieto field, in that the silica is removed by chemical reaction, and much more lime is required.

This process was tested on large scale at Broadlands, and the treated brine was reinjected (Bixley, 1978). The increased pH caused calcium carbonate scale mixed with calcium silicate to deposit in the injection wellbore. The rate of wellbore scale deposition was ten times greater with treated brine than untreated.

Shannon *et al.* (1982) described another treatment that removes arsenic and inhibits deposition of silica from New Zealand brines. The brine is dosed with ferric sulfate, a flocculant, and a surfactant. The ferric iron hydrolyzes forming a ferric hydroxide floc, and lowers the pH of the brine to about 4 in doing so. The floc is separated from the brine by dissolved air flotation, and carries most of the arsenic in the water with it. Adding 17ppm iron allows 98% of the arsenic to be removed. The low final pH inhibits the deposition of silica scale.

In Japan, a process to remove colloidal silica from low salinity brine by air flotation is being tested (Project Sunshine, 1984, pp. 71-81).

5.7. Silica and reinjection: practical experience

Routine reinjection at separator pressure is practiced at Ahuachapán (Cuéllar *et al.*, 1981; Einarsson *et al.*, 1976; Cuéllar, 1976) and Kakkonda (Horne, 1981). The high injection temperature allows supersaturation with dissolved silica to be avoided, and injection at both fields has been trouble free. The same approach has been tested successfully at Tongonan (Studt, 1980).

Untreated brine is injected at atmospheric pressure at Otake and Hatchobaru (Kubota and Aosaki, 1976; Horne, 1981). In both cases, the injectivity of the wells drops rapidly, and new injection wells must frequently be drilled. Apparently, this is caused by silica scaling. However, untreated brine is reinjected at atmospheric pressure at Onikobe and Onuma, without any problems attributable to scaling or plugging (Horne, 1981).

The injectability of the flashed brine at Niland has been studied on bench scale, and by actual injection experiments (Netherton and Owen, 1978; Owen *et al.* 1977). It was concluded that colloidal silica must be removed from the brine before reinjection. In an injection test, the untreated brine quickly destroyed the pore permeability of the receiving formation. However, injection continued because a large fracture zone continued to take the brine.

5.8. Miscellaneous liquid wastes

In addition to the spent brine effluent of routine power generation, some waste brine will also be produced during drilling, well testing, powerplant upsets, and reinjection system upsets. Waste brine from these sources will be erratically produced in relatively small volumes, and is likely to be cooled down, aerated or otherwise contaminated. Small volumes of powerplant condensate, drilling waste, etc., will also be produced. These miscellaneous liquid wastes will normally require preinjection treatment different from that which the "routine" spent brine receives. In some cases (e.g. during exploratory drilling) it may not be possible to reinject the liquid waste at all.

In some cases, geothermal fluids are so toxic that even small releases to the environment must be carefully avoided or decontaminated. For example, the brine at Tongonan contains 27ppm arsenic and 300ppm boron (Studt, 1980). Six to 315ppm arsenic and 129-236ppm boron have been reported in samples of power-plant cooling water at The Geysers (Weres *et al.* 1977, p. X-7). There have been numerous small spills of cooling water at The Geysers, and these have killed fish and contaminated soil. Some Imperial Valley brines are so saline that they could severely contaminate surface water and soil if spilled (Table 5).

In most cases, these fluids will need to be deoxygenated before they are reinjected, and solids will need to be flocculated or filtered out. The pH may need to be adjusted and, if surface disposal is contemplated, toxic trace contaminants may need to be removed. The trend seems to be toward separate, auxiliary brine conduits and brine treatment processes to handle these fluids. In this context, brine decontamination processes, like those developed in New Zealand, may find application in the U.S.

At The Geysers, the excess condensate (i.e., cooling water) has been routinely reinjected with few problems since the inception of the project. A short settling period to remove solid particles is the only treatment it receives. This is an exceptional case, because the amount of fluid is relatively small, and it is low in dissolved and suspended solids.

6. Solid waste

Colloidal silica is removed from flashed brine as a watery sludge that must be dewatered and disposed of. A future 50MW flash-cycle powerplant at Niland would produce about 10 tons/hr of sludge containing 5% solids. If this were dewatered to 50% moisture, 24 tons/day of this cake would have to be disposed of. Because of the lead, zinc, etc., in it, it would have to be handled and disposed as hazardous solid waste. At Cerro Prieto, nearly pure amorphous silica precipitates from the spent brine. This material is relatively innocuous, but there is a lot of it; I estimate that about 50,000 tons of it had accumulated in the evaporation pond by 1979.

Ideally, some use should be found for this solid waste. In the case of Niland, it may be possible profitably to remove the valuable (and toxic) metals from it. At Cerro Prieto, the relatively clean silica might find use as a component of cement or drilling mud. Rothbaum and Anderton (1976) have suggested using the calcium silicate precipitated from New Zealand brines as an additive to cement or other building materials.

Cooling tower sludge in geothermal powerplants is particularly hazardous because of the arsenic and mercury in it. Handling and disposing of this material has proved a chronic nuisance at The Geysers. Arsenic is considered an occupational carcinogen, and workers at The Geysers are required to take appropriate precautions. Before entering an area where they may come into contact with cooling tower sludge or cooling water, they don high efficiency particulate respirators and rubber coveralls, boots, and gloves. "Arsenic contaminated" areas are designated, and workers leaving these areas must shower and change.

Geothermal drilling produces waste mud, drilling chips, and similar waste. These relatively innocuous materials are disposed of as in the petroleum industry, by filling up and sealing the sump.

7. Impacts of drilling and development

Geothermal field development and powerplant construction are large scale engineering projects, and have the corresponding environmental impacts. These include noise, the disruption of land surface and ecosystems, increased erosion, dust generation, etc. The severity of these impacts will depend on the scale of the project, its location, and the mitigating measures that are taken. These impacts have been reviewed by Reed and Campbell (1976), Weres *et al.* (1977, Chapter V), and Crittenden (1981).

Geothermal heat has the major advantage over other energy sources that all activities - extraction, conversion, and waste disposal - are located in one place. Geothermal heat is so diffuse that the individual power plants are of necessity small. This makes geothermal developments relatively small, and allows local impacts to be minimized. In major fields like The Geysers, building one power plant at a time results in step-wise field development activity which is prolonged, but limited in spatial extent at any given time. This is good for the labor force and the communities they live in, because it makes possible semipermanent employment.

The Geysers Unit 11 is typical of The Geysers. Unit 11 and its 15 associated wells occupy about 200 hectares, of which 32 hectares have actually been built on or otherwise disrupted. The disrupted area includes the actual plant site, the well pads, access roads, and steam pipe corridors.

A hot brine based development would require substantial additional area for brine treatment facilities, secondary waste brine sumps and conduits, and injection wells. Slant drilling several wells from a single pad allows the disrupted area to be reduced, but at some additional cost.

At Cerro Prieto the evaporation pond occupies 8 km ^{2}, and nearly the whole area of the field has been disrupted by brine ditches and construction activity. At the opposite extreme, the impacts at the Japanese brine fields are smaller than at The Geysers, due to extensive slant drilling from pads adjacent to the powerplants. (Some of these developments are within National Parks.)

Geothermal brine wells usually are drilled with mud. In the production zone, fluid loss and formation damage caused by chemical interactions between mud and brine are common. Despite progress with sepiolite-based and other high temperature muds, the art needs improvement.

The steam wells at The Geysers are started with mud but completed with air, which allows much faster penetration and eliminates fluid loss problems. However, air drilling is much noisier and much dustier than mud drilling (Table 6). After the production zone is reached, drilling is completed under conditions of "controlled blowout". Because the air column is nearly weightless, air drilling entails a much greater blowout risk than does drilling with mud. The steam wells at Lardarello are drilled with water, which represents a practical compromise between air and mud.

Because they are associated with vulcanism and tectonism, geothermal resources tend to be located in geologically treacherous terrain. For example, 91 of the 168 wells completed at The Geysers by 1975 were on inactive landslides (Bacon, 1976). Two catastrophic blowouts have occurred there. One well blew out when the dormant landslide it was located on moved following heavy rains (*Ibid.*). The other blowout, caused by careless drilling early in the development of the field, has remained practically uncontrolled

Table 6

Noise levels at The Geysers

Activity	Maximum noise level at 15.2 m (50 ft)	Noise levels with attenuation from wave divergence at 800 m (2600 ft)
Drill Pad Construction	90 dBA	56 dBA
Mud Drilling	90 dBA	56 dBA
Compressed Air Drilling		
No Muffler	100 dBA	66 dBA
Cyclonic Muffler	90 dBA	56 dBA
Well Cleanout and Testing		
No Muffler	120 dBA	86 dBA
Cyclonic Muffler	95 dBA	61 dBA
Shut-In Well Bleed	75 dBA	41 dBA

From Weres *et al.* (1977; p. V-19).

since 1957.

Geothermal blowouts do not present the danger of conflagration, but the mass flow is potentially enormous - up to several hundred tons per hour in the case of hot brine. Drilling mishaps much smaller than this can quickly overwhelm the capacity of the drilling mud sump, and cause a major spill of brine.

Noise levels associated with various activities at The Geysers in 1976 are summarized in Table 6. The noise levels at the other fields probably are comparable, except for the absence of air drilling. Noise levels at The Geysers have since been reduced by two technical innovations. During powerplant outages, steam is vented through a muffler consisting of a large box filled with basalt cinder (Figure 7). Lead-vinyl blankets are hung up around drilling pads to muffle drilling noise.

8. Summary

Experience has demonstrated that the environmental impacts of geothermal development can be severe if not mitigated.

Air pollution by hydrogen sulfide has been greatly reduced at The Geysers, but efforts to reduce cost and improve reliability continue. The combination of surface condenser and Stretford Unit is not completely effective because the steam contains ammonia as well as H_2S. Hydrogen peroxide is used to eliminate the H_2S that dissolves in the condensate. Emissions of H_2S from the older Units equipped with contact condensers can be

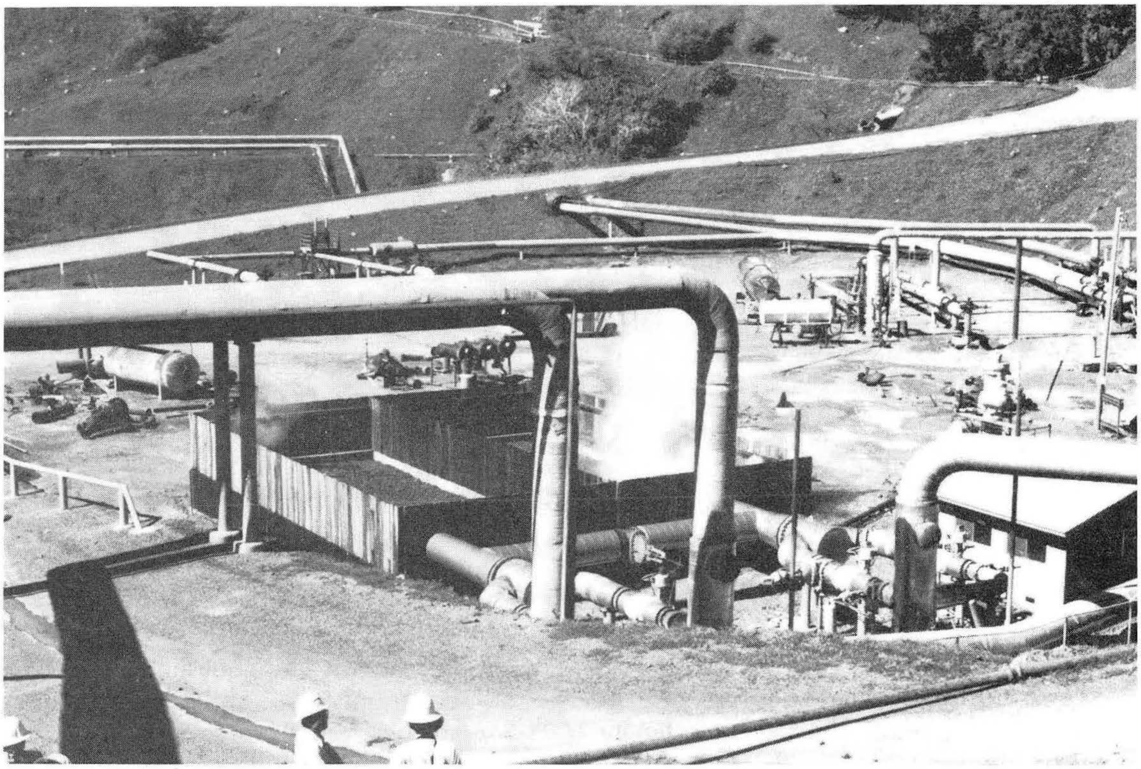

Figure 7. Muffler used to reduce noise from venting of steam during powerplant outages at The Geysers (photo by author). It consists of a large wood box filled with basaltic cinders. The steam is released through a perforated distributor pipe at the bottom of the box.

reduced by using iron HEDTA or nickel sulfate to catalyze reaction with air, plus a vent gas incinerator to remove H_2S from the condenser vent-gas and produce the SO_2 needed to prevent formation of colloidal sulfur.

Much of the air pollution control technology developed at The Geysers can be transferred to other geothermal areas, allowing for differences in steam composition. In areas where the steam contains less ammonia, the combination of surface condenser and Stretford Unit will be fully effective in stopping H_2S emissions. Advanced contact or hybrid condensers may compete with surface condensers in this application.

Reinjection into the geothermal reservoir is usually the only acceptable means to dispose of spent geothermal brines. Plugging of injection wells and the receiving formations by silica poses the greatest practical problem in reinjection. Trouble-free, large scale reinjection of spent brine has been demonstrated in several areas. Pre-reinjection brine treatments needed to remove silica have been demonstrated on the pilot scale at Cerro Prieto and Niland.

The physics and economics of geothermal power generation dictate that very large volumes of water must be treated very cheaply and without deleterious side effects. Brute-force chemical treatment methods are either impractical or expensive because of the large mass flows involved. Proprietary chemical additives (e.g. flocculating agents) are unpredictably site-specific in their effects. This places a great premium on careful forethought, based on a sound analysis of the chemistry involved. Often, a subtle but effective solution to the problem can be discovered in this way.

Experience at The Geysers and in Japan shows that the environmental impacts of drilling and construction activities may be effectively mitigated. It is likely that reinjection will allow subsidence to be adequately controlled in most cases.

Means to mitigate most impacts associated with geothermal development have been demonstrated, at least in particular cases. Work continues on applying available technology to specific sites, and developing improved methods. The degree of mitigation actually achieved will in large measure be determined by the regulatory climate. Problems related to environmental protection and fluid chemistry need not delay geothermal development, if they are anticipated.

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