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REVIEW AND PROBLEM DEFINITION OF WATER/ROCK REACTIONS ASSOCIATED WITH
INJECTION OF SPENT GEOTHERMAL FLUIDS FROM A GEOTHERMAL PLANT INTO AQUIFERS

by

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ABSTRACT

Among the technical problems faced by the burgeoning geothermal industry is the disposal of spent fluids from power plants. Except in unusual circumstances the normal practice, especially in the U.S.A., is to pump these spent fluids into injection wells to prevent contamination of surface waters, and possibly in some cases, to reduce pressure drawdown in the producing aquifers. This report is a survey of experience in geothermal injection, emphasizing geochemical problems, and a discussion of approaches to their possible mitigation.

The extraction of enthalpy from geothermal fluid in power plants may cause solutions to be strongly supersaturated in various dissolved components such as silica, carbonates, sulfates, and sulfides. Injection of such supersaturated solutions into disposal wells has the potential to cause scaling in the well bores and plugging of the aquifers, leading to loss of injectivity. Various aspects of the geochemistry of geothermal brines and their potential for mineral formation are discussed, drawing upon a literature survey. Experience of brine treatment and handling, and the economics of mineral extraction are also addressed in this report. Finally suggestions are made on future needs for possible experimental, field and theoretical studies to avoid or control mineral scaling. The overall conclusion that, in principle, undesirable water/rock reactions between geothermal effluents and the wall rocks penetrated by injection wells can be prevented by various techniques. It is the practical application and economics of these various methods which require further development.

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1.0 INTRODUCTION

1.1 SCOPE OF AND SOURCES FOR THIS REPORT

This report was written in response to Dr. M. W. Molloy of the U.S. Department of Energy, San Francisco, who requested a "white paper on problem definition of water/rock reactions associated with reinjection¹ [sic] of spent brines from geothermal plants into aquifers." It is based upon a survey of worldwide literature rather than upon mathematical modeling or upon experimental or field work. The literature surveyed included textbooks, journals, conference proceedings, and various special reports of more limited distribution. A useful bibliography on geothermal injection technology is to be found in Darnell and Eichelberger (1982) and a convenient compilation of abstracts of publications on injection has appeared recently (Stone, 1985).

1.2 BACKGROUND OF THE PROBLEM

Compared with the petroleum industry the geothermal industry must handle relatively larger volumes of fluid for each kilojoule or kilowatt-hour of energy produced. This is because the energy density of geothermal fluids is much less than that of hydrocarbon fuels, such as petroleum or natural gas. The rate of fluid production necessary to operate a 100 MWe geothermal electric plant in a dry steam field is about 10^7 tonnes/year, while for a plant of similar size in a hot water field the rate is greater by a factor ranging from about 3 to 10, depending on the aquifer temperatures (Ellis and Mahon, 1977, p. 310).

¹In this report the term "injection" is preferred over the frequently used, but incorrect, term "reinjection."

Commonly these geothermal fluids contain undesirable dissolved components, such as high concentrations of salts, or more modest, but still undesirable, concentrations of arsenic, boron, and fluoride, which cannot be allowed to affect animal or plant life. In a vapor-dominated field, the steam condensate may contain high concentrations of boric acid, ammonia, sulfide and other undesirable constituents. For this reason, the usual practice is to inject spent geothermal fluids into aquifers adjacent to the zones of production. In certain circumstances this could have the added advantage of helping to maintain pressures in the production zone. This would be desirable both to enhance the longevity of a geothermal reservoir and also to reduce the potential for surface subsidence due to compaction accompanying mass withdrawal. However, there are other potential problems with injection. It can result in a thermal breakthrough from the injection wells to the production wells leading a premature reduction in power output. Furthermore there is some potential for increasing seismicity by injection. These potential advantages and problems are beyond the scope of this report and will not be considered further.

Extraction of useful work from geothermal fluids requires cooling, usually accompanied by boiling and loss of dissolved gases. These processes commonly lead to saturation of the hydrothermal solutions in one or more dissolved components. Injection of supersaturated solutions in addition to causing aquifer contamination can potentially lead to formation of mineral scales in well bores or in the injected aquifer. Similarly reactions between the cooled saturated fluid and the reservoir rocks encountered can lead to mineral formation. In

either case the result could be plugging of the aquifer and the loss of injectivity.²

1.3 POTENTIAL SCOPE OF THE PROBLEM

A roster of countries with geothermal power plants installed as of 1985 indicates that at year's end 188 electric plants will be operational, with a total installed capacity of 4,764 MWe (DiPippo, 1985, Table 20). Of this 1,792 MWe will be installed at the Geysers, California, U.S.A. (DiPippo, 1985, Table 5). Since 1979, when the world's installed geothermal electric power capacity was only 1,759 MWe, the annual percentage growth rate has been about 16.5%, which implies a doubling time of only five years (DiPippo, 1985, p. 11).

Using the average flow rates suggested by Ellis and Mahon (1977), the 1,792 MWe of installed capacity at the vapor-dominated Geysers Steam Field, California, uses fluid at the rate of about 180×10^6 tonnes/year. Flow rates necessary for the rest of the world's installed capacity 2,972 MWe, which is largely from water-dominated resources, depend upon local conditions, but should lie in the range of 900 to $3,000 \times 10^6$ tonnes/year. All of this fluid potentially could require disposal in injection boreholes.

In spite of these large numbers, they ignore a potentially even larger segment of the geothermal energy industry, i.e., non-electric or direct use geothermal power (Anderson and Lund, 1979). This involves extraction of beneficial heat from geothermal water for district heating and cooling systems, horti-

²"injectivity" - the ability of a borehole to accept injected fluid.

cultural, and aquacultural applications, drying and dehydration, and uses such as industrial evaporation, refrigeration, and washing. According to Gudmundsson (1985), at the end of 1984, the installed capacity of all geothermal direct use projects in the world was about 7,072 MW thermal. This corresponded to a thermal energy production of 23,957 GWh in 1984. Considering useful thermal power above 35 to 40°C, with an average load factor of 39%, this energy use required a flow rate of 57,803 kg/s (Gudmundsson 1985). This corresponds to $1,825 \times 10^6$ tonnes/year. Taking this together with the estimated flow rate necessary for electric power production, we see that the amount of geothermal fluid potentially requiring disposal is currently between 3 to 5×10^9 tonnes/year. Furthermore this amount may double in five years.

The costs of fluid disposal are a significant part of the costs of geothermal development. In general, the costs of drilling an injection well are the same as the costs of drilling a production well. For example, in 1975 Einarsson et al. estimated that approximately 10% of the total plant installation and generating costs from a 100 MWe power station at Ahuachapán, El Salvador, would be spent to inject the effluents. These numbers may be typical for a water-dominated field with a relatively "benign" water chemistry, which requires no special treatment before injection, and using a single flash steam generation system. Costs would be higher if the fluid chemistry is unfavorable or in the case of power production from lower temperature systems which require a higher fluid flow rate per MW. No up to date and comprehensive review of the costs of injection of spent fluids from geothermal power plants is readily available. However an earlier projection by Defferding and Walter (1978) estimated that the

cost of fluid disposal at a 50 MWe geothermal plant, using the binary fluid cycle energy conversion process, was expected to be about 19% of the total cost of the power. These costs may be relatively less for a flashed steam plant where the enthalpy is higher and thus conversion efficiency greater.

The capital costs of injection include drilling, logging, casing and completing the injection wells, and installing well head equipment, including pumps and piping (and brine treatment facilities, if necessary). Operating costs consist mainly of the energy cost of pumping, and maintenance costs. These latter may vary from negligible to prohibitive, depending upon the amount of wear, corrosion, scaling, or well plugging experienced. Hartley (1980, p. 850) quoted costs of \$400,000 to \$1,000,000 for a disposal well (in 1980 U.S. dollars). According to this author (Hartley, 1980, Table 9.13) to dispose of 350,000 lpm of fluid would require 44 wells each accepting 8,000 lpm. I have chosen the figure 350,000 lpm from Hartley's data because it corresponds approximately to the 180×10^6 tonnes/yr of fluid flow necessary to supply the 1,792 MWe of installed capacity at the Geysers, California. Assuming an 80% availability factor (i.e., each well is needed only 80% of the time), an amortization period of 30 years, and a low interest rate of 8%, Hartley (1980, p. 851) quoted an annualized cost, in 1980 U.S. dollars, of \$0.0133 to dispose of 1,000 liters of fluid, given a flow rate of 350,000 lpm. Using Hartley's cost estimates (Hartley, 1980) disposal of this flow rate would cost only $\$2.5 \times 10^6$ a year for 30 years (in 1980 U.S. dollars). Furthermore disposal of the up to $3,000 \times 10^6$ tonnes/year of fluid which supplies the remaining 2,972 MWe installed elsewhere would cost only $\$42 \times 10^6$ a year, using Hartley's method of

cost estimation.

These figures seem low, even allowing for inflation. However it is clear that costs will vary over a wide range according to local circumstances. Costs of drilling vary according to both geographical and geological factors. Similarly the injectivity depends both upon the lithology of the aquifer and the nature of the brine. Thus if loss of injectivity due to mineral formation in and around injection wells were to occur, there could be significant cost impacts.

1.4 CHEMISTRY OF GEOTHERMAL EFFLUENTS

1.4.1 Introduction

Although an extensive literature exists on the chemistry of fluids discharged from geothermal wells the world over, in most cases these reports discuss data only from individual geothermal wells or fields. However some idea of the wide range of chemical compositions of geothermal fluids can be gained from Figure 1.4 (Hartley, 1980). The upper limits of the ranges shown in the figure are considerably biased by the analyses from the Salton Sea Geothermal Field, Imperial Valley, California. Wells in this field produce fluids of more than 25% weight percent total dissolved solids, one of the highest concentrations known in natural hydrothermal systems.

1.4.2 Representative Analyses

A few compilations of geochemical data from high temperature geothermal systems have already appeared (Ellis and Mahon, 1977, Table 3.2; Fournier, 1981,

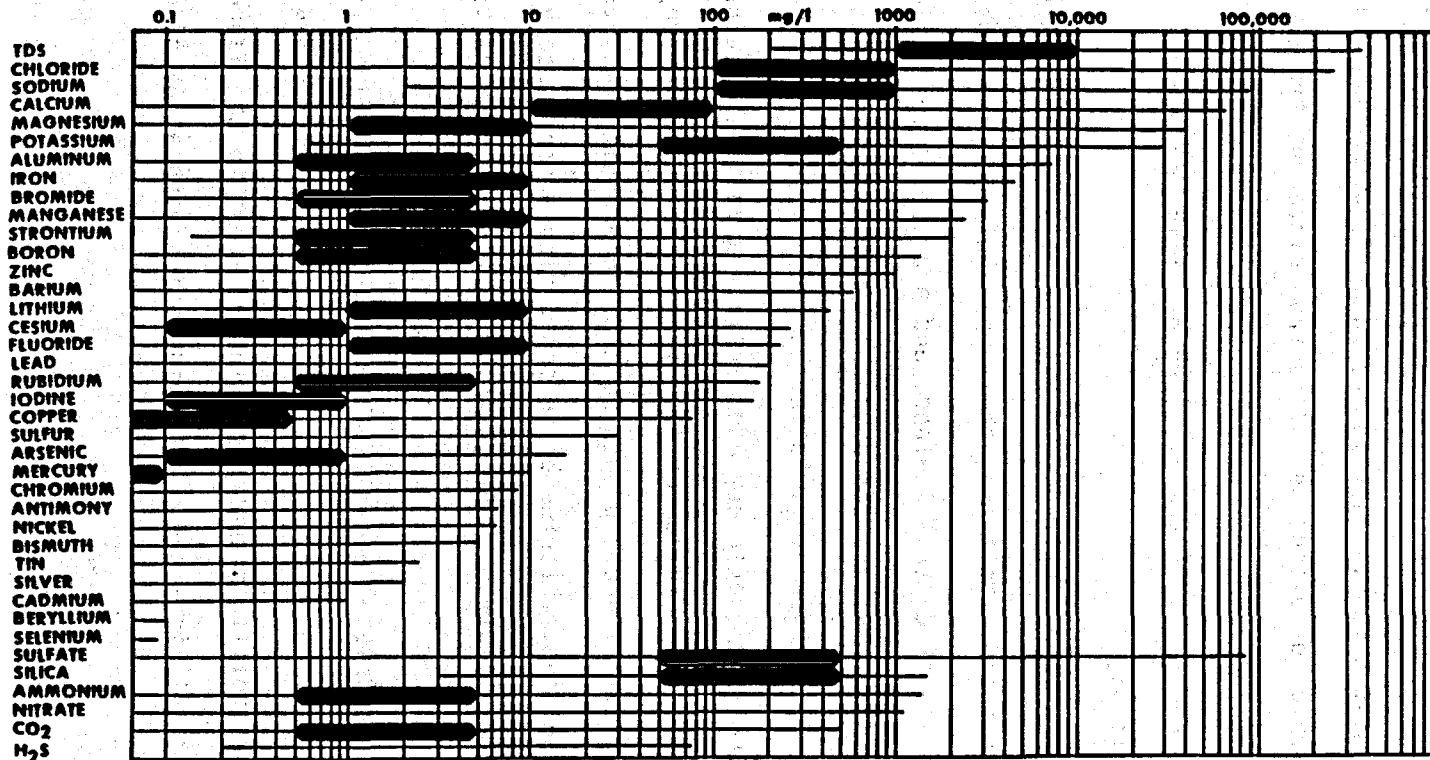


Figure 1.4 The wide range of chemical compositions of discharges from geothermal wells (mg/l). (From Hartley, 1980)

Table 4.2; and Hartley and Ellis, 1983, Table 1). These data indicate that total dissolved solids concentrations in geothermal fluids range from about 0.05% to 30%, but most commonly fall in the range 0.1-2%. Table 1.4 illustrates several typical samples of discharge waters from different types of geothermal fields, shown here to represent a broad spectrum of different geothermal brines. The table is based upon earlier compilations of Ellis and Mahon (1977) and Henley and Ellis (1983).

The first three sets of analyses are all relatively dilute waters from systems in volcanic rocks. Of these, the Hveragerdi geothermal system occurs in the Quaternary basalts of central Iceland, and produces a very dilute sodium, potassium mixed chloride-sulfate-bicarbonate brine, with less than 1,000 mg/kg TDS³. The Broadlands geothermal field in the Taupo Volcanic Zone of New Zealand is developed primarily in Quaternary and Tertiary Rhyolites. It produces a fairly dilute sodium, potassium chloride brine with about 3,800 mg/kg TDS. The Ahuachapán field in El Salvador, producing from an andesite reservoir is a sodium, potassium calcium, chloride brine containing approximately 19,000 mg/kg TDS, a value which is fairly typical of brines from hydrothermal systems in volcanic terrains.

The Ngawha, Cerro Prieto, and Salton Sea systems all produce fluids from sedimentary reservoirs. The Ngawha system produces from siltstones and sandstones underlain by argillites and gregwackes adjacent to the Taupo Volcanic Zone of New Zealand. It is a sodium chloride brine with a TDS of only 4,480

³TDS - Total Dissolved Solids.

TABLE 1.4

Compositions of geothermal well waters: Concentrations in mg/kg collected at atmospheric pressure from the discharge of geothermal wells.

| Well/Location | Depth | Temp. °C | pH | Li | Na | K | Rb | Ca | Mg | Cu | Mn | Fe | F | Cl | Br | SO ₄ | As | B | SiO ₂ | NH ₃ | HCO ₃ | H ₂ S |
|--------------------------------|--------|----------|-----|------|--------|--------|------|-------|------|--------|-------|-------|------|---------|------|-----------------|------|-------|------------------|-----------------|------------------|------------------|
| G3; Hveragerdi, Iceland | 650m | 216 | 9.6 | 0.3 | 212 | 27 | 0.04 | <0.02 | -- | 1.5 | -- | 0.1 | 1.9 | 197 | 0.45 | 61 | -- | 0.6 | 480 | 0.1 | 55 | 7.3 |
| Br 13; Broadlands, New Zealand | 1,000m | 260 | 8.6 | 12.6 | 900 | 200 | 2.2 | 1.3 | 0.02 | 2.4 | -- | -- | 4.5 | 1,668 | 5.3 | 6.5 | 3.2 | 48 | 750 | 1.9 | 117 | -- |
| 20; Ahuechapan, El Salvador | 550m | 225 | -- | 18.5 | 6,000 | 1,040 | 7.9 | 6.0 | 0.07 | 450 | -- | -- | 1.6 | 10,900 | 46 | 30 | 12 | 155 | 956 | -- | 23 | -- |
| Mg1, Ngawha, New Zealand | 505m | 230 | 7.4 | 12.2 | 950 | 80 | 0.8 | 0.4 | -- | 28 | 0.02 | 0.1 | 0.8 | 1,825 | -- | 17 | -- | 1,200 | 460 | 46 | 61 | <1 |
| M5; Cerro Prieto, Mexico | 1,205m | 340 | 7.7 | 38 | 9,062 | 2,287 | -- | -- | 1 | 520 | -- | 0.3 | 2 | 16,045 | 31 | 6 | 0.5 | 14 | 460 | 46 | 61 | -- |
| 11D #1; Salton Sea, USA | 1,600m | 340 | 4.7 | 215 | 50,408 | 17,500 | 135 | 14 | 94 | 28,000 | 1,400 | 2,290 | 15 | 155,000 | 120 | 5 | 12 | 390 | 1,260 | 21 | 56 | 16 |
| M8; Reykjanes, Iceland | 1,750m | 275 | 7.1 | 6.6 | 12,730 | 1,990 | 5.2 | -- | 9.8 | 2,249 | 2.6 | -- | 0.14 | 25,054 | 87 | 2.4 | 0.15 | 11.3 | 943 | 2.0 | -- | 5 |
| E-205; Matsuo, Taiwan | 1,500m | 245 | 2.4 | 26 | 3,490 | 900 | 12 | 9.6 | 131 | 1,470 | 40 | 220 | 7.0 | 13,400 | -- | 350 | 3.6 | 106 | 639 | 36 | 2 | -- |
| Well 1; Cesano Italy | 1,435m | 250 | 6.5 | 380 | 76,950 | 48,350 | 450 | 80 | 17 | 106 | 0.1 | 0.7 | 100 | 42,850 | -- | 163,290 | 8.3 | 2,650 | -- | 82 | 5,850 | -- |
| 1A; Kizildere, Turkey | 430m | 200 | 9.0 | 4.5 | 1,280 | 135 | -- | 0.33 | 0.2 | 2.5 | 0.2 | 0.09 | 0.0 | 117 | 1.2 | 770 | -- | 26.2 | 325 | 2.6 | 1,860 | -- |

Source: Kizildere - Ellis and Mahon, 1977; Others - Henley and Ellis, 1983;

HCO₃ is the total of CO₃²⁻ and HCO₃SiO₂ is the total of SiO₂ + silicate

mg/kg, similar to the Broadlands water except for its considerable enrichment in boron and depletion in potassium relative to the Broadlands fluid.

Both the Cerro Prieto and Salton Sea systems are developed in the Quaternary and Tertiary deltaic sediments of the Colorado River, at the north end of the Gulf of California. Both produce sodium, potassium, calcium chloride brines, poor in sulfate and carbonate. However the Cerro Prieto brine contains 28,600 mg/kg TDS whereas that from the Salton Sea system is almost ten times more concentrated (258,000 mg/kg TDS). The Cerro Prieto brine is formed by reaction of partially evaporated river water with the sediments. It is believed that the source of the high salinity at Salton Sea field is due to dissolution of non-marine evaporites in the sedimentary section (Elders and Cohen, 1983). The Cerro Prieto fluid is therefore more typical of systems in sedimentary basins.

The analyses represented from the Reyjanes system in southern Iceland and from the Matsao system of Japan represent extremes in the chemistry of systems in volcanic terrains. The Reyjanes brine containing 43,000 mg/kg TDS is recharged by seawater mixed with rainwater flowing through basalt. It produces a nearly neutral sodium, potassium, calcium chloride brine. The Matsao system of Japan is developed in an andesite-sandstone sequence of rocks. Its fluid chemistry is highly acidic, a chloride-sulfate brine containing 73,000 mg/kg TDS (Henley and Ellis, 1983). Such acid chloride-sulfate brines may originate by mixing of neutral chloride waters with acid sulfate waters which in turn may be formed by steam condensates hydrolyzing sulfur to sulfuric acid (Ellis and Mahon, 1977, p. 61).

The Cesano system, located some 20 km north-northwest of Rome, Italy, produ-

ces one of the most concentrated hot brines found so far in the world, featuring 360,000 mg/kg TDS. It consists essentially of two-thirds sodium and potassium sulfate and one-third sodium and potassium chloride. Its ratio of potassium to sodium (0.6) is unusually high for a geothermal brine. Other unusual features include low contents of iron and manganese and high contents of boron. The geological section penetrated by this well is a series of Tertiary volcanics, including pyroclastics and explosion breccias, which overlie a Triassic flysch complex of brecciated limestones and marls. It is believed that this alkali sulfate-chloride water at Cesano originated when a more normal alkaline-bicarbonate-chloride brine, which had reacted with the potassic volcanics, encountered Triassic evaporitic formations containing abundant calcium sulfates and then formed a brine of mixed sulfate chloride type (Calamai, et al, 1975).

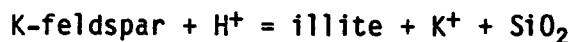
The Kizildere geothermal field in the Denizli Province of western Turkey produces water of a sodium bicarbonate type, high in sulfate, fluoride and boron, but low in chloride, and a TDS of 4,500 mg/kg. This field is developed in the Büyük Menderes graben in which a crystalline basement of augen gneiss, schist, quartzite and marble is overlain by Pliocene to Miocene sediments, containing conglomerates, sandstones, limestones, marls and siltstones (Şimşek, 1985).

1.4.3 Origin of the Dissolved Components

As illustrated by the data of Table 1.4 most high-temperature geothermal waters contain high concentrations of Na, K, Li, Rb, Cs as well as SiO₂, B, As, F, and NH₃. Except for relatively uncommon situations where fluids of low pH

occur, Fe and Mg are of low concentration and, except for the somewhat unique circumstances at Cesano, the ratio of chloride to sulfate is high.

A considerable body of literature (summarized in Fournier, 1981; Ellis and Mahon, 1977; and Henley and Ellis, 1983) leads to the interpretation that the source of the common solutes in geothermal fluids is mineral-fluid equilibria within the reservoirs. This concept is supported both by the study of active hydrothermal systems and by extensive experimental data (Ellis and Mahon, 1977, p. 83). The common solutes found in geothermal fluids can be divided into two main classes: (a) components of common rock-forming minerals, such as Si, Al, Na, K, Ca, Mg, Fe and Mn; and (b) soluble components, not forming abundant rock-forming minerals, such as Cl, Br, BO_3 , As and Cs. The members of the first group of components are strongly partitioned into the rock side of rock-water interactions. Their release into geothermal waters is usually governed by reactions such as:



The second group of components in most cases occurs as minor constituents of rocks, especially volcanic rocks, but are readily leached from mineral surface and fractures. For example, Ellis and Mahon (1977, p. 82) suggest that the outflow from the Wairakei geothermal system of New Zealand produces 20×10^6 tonnes of chloride and 1×10^6 tonnes of boron each year. As the volcanic rocks underlying this system contain between 200 to 1,000 mg/kg of Cl and 10 to 25 mg/kg of B, the solute output is equivalent to leaching only 0.01 to 0.05

km³/year of rhyolite or andesite. Obviously the very high chloride concentration in the Salton Sea brine and sulfate in the Cesano brine (Table 1.4) require enrichment by different processes involving evaporation of sea or lake waters, precipitation of salts, and dissolution of evaporites.

1.4.4 Rate of Chemical Discharges

It is evident that flowing geothermal wells bring large amounts of dissolved solid and gaseous components to the surface. Ellis and Mahon (1977, p. 310) have calculated the approximate mass discharge of chemicals from various fields, assuming flow rates necessary to supply a 100 MWe geothermal power plant. Table 1.4.4 shows a selection of their data with the addition of an estimate for the Salton Sea system, assuming that a (yet to be constructed) 100 MWe power plant there would have the same thermal efficiency and steam fraction as Ellis and Mahon's assumed 100 MWe plant at Cerro Prieto.

The first two examples in Table 1.4.4 the Geysers and Laderello, are vapor dominated fields producing essentially dry steam. A 100 MWe plant there should require a steam flow each year producing between 10⁴ to 10⁵ tonnes of carbon dioxide and several thousand tonnes of hydrogen sulfide, as well as significant amounts of ammonia and boron. While these numbers may seem alarming, Ellis and Mahon (1977, p. 311) point out that a 100 MWe coal-fired electric plant could emit 7 x 10⁵ tonnes of CO₂ and 6,000 tons of SO₂ a year.

The next three examples are from water-dominated geothermal fields where each tonne of steam produced requires disposal of several tonnes of saline water. The examples are chosen to span a wide range from about 4,000 mg/kg to

TABLE 1.4.4
 Potential Chemical Discharge from 100 MWe Power Plants at Five Sites
 (Quantity Discharged in tonnes/year)

| Constituent | The Geysers | Laderello | Broadlands | Cerro Prieto | Salton Sea |
|------------------|---------------------|---------------------|---------------------|-----------------------|-----------------------|
| Li | -- | -- | 300 | 320 | 1,800 |
| Na | -- | -- | 3 x 10 ⁴ | 1 x 10 ⁵ | 6 x 10 ⁵ |
| K | -- | -- | 5,000 | 4 x 10 ⁴ | 3 x 10 ⁵ |
| Ca | -- | -- | 80 | 1 x 10 ⁴ | 5 x 10 ⁵ |
| F | -- | -- | 200 | 40 | 300 |
| Cl | -- | -- | 5 x 10 ⁴ | 3 x 10 ⁵ | 3 x 10 ⁶ |
| Br | -- | -- | 150 | 500 | 1,900 |
| SO ₄ | -- | -- | 200 | 170 | 140 |
| NH ₄ | 1,700 | 1,300 | 500 | 800 | 400 |
| B | 200 | 200 | 1,100 | 400 | 1 x 10 ⁴ |
| SiO ₂ | -- | -- | 2 x 10 ⁴ | 4 x 10 ⁴ | 1 x 10 ⁵ |
| As | -- | -- | 100 | 30 | 700 |
| Hg | 0.04 | -- | 0.035 | -- | -- |
| CO ₂ | 3 x 10 ⁴ | 4 x 10 ⁵ | 4 x 10 ⁵ | 1.5 x 10 ⁵ | 1.5 x 10 ⁵ |
| H ₂ S | 2,000 | 5,000 | 6,000 | 4,000 | 4,000 |

(Modified from Ellis and Mahon, 1977, Table 8.10 with additions)

260,000 mg/kg TDS. Although these three cases illustrate a wide range they would share an equally acute disposal problem if only one constituent, e.g. As, exceeded the standards of water quality for industrial effluents.

1.5 WATER QUALITY STANDARDS

A thorough discussion of potential environmental effects of discharges from geothermal power plants is beyond the scope of this paper. However, in order to complete this brief introduction to the chemistry of geothermal effluents, some mention of the acceptable limits for deleterious components in waters used for different purposes is in order. Although some geothermal fields may produce fluids, which after dilution, are of a quality sufficient for subsequent use, this is not generally true. Potential uses of water downstream of a geothermal power plant which may be impacted include domestic use, support of aquatic life, watering stock, irrigation, and industrial purposes.

Criteria for water quality for different purposes are determined by various international, federal and state agencies (e.g. World Health Organization, 1971; Environmental Protection Agency, 1976A, B, and National Academy of Sciences, 1973). Some examples are illustrated in Tables 1.5A, 1.5B and 1.5C. It must be emphasized that the omission of a component such as Br, Li, I, Sb, or Bi, which occur in geothermal brines, from the criteria for drinking water or fresh-water fish does not mean that they do not have significance for pollution, but rather that are not common enough yet in surface waters to require establishing limits for their safe concentration (Hartley, 1980, p. 810).

Comparison of the data of Tables 1.4, 1.5A, 1.5B and 1.5C dramatizes the

TABLE 1.5A
Water Quality Standards

| Constituent | Drinking Water* Standard mg/L | Freshwater** Fish Criteria mg/L |
|------------------|----------------------------------|------------------------------------|
| Ammonia | 0.5 | 0.02 |
| Arsenic | 0.05 | 1.0 |
| Beryllium | 1.0 | 0.11 |
| Boron | 1.0 | 50 |
| Cadmium | 0.01 | 0.004 |
| Chromium | 0.05 | 0.01 |
| Iron | 0.3 | 1.0 |
| Lead | 1.4 | ? |
| Manganese | 0.05 | 0.1 |
| Mercury | 0.002 | 0.0005 |
| Selenium | 0.01 | 2.5 |
| Zinc | 5.0 | ? |
| SO ₄ | 250 | ? |
| H ₂ S | 0.05 | 0.3 |
| TDS | 500 | ? |

(*Compiled from Environmental Protection Agency 1976A; **Compiled from Environmental Protection Agency 1976B)

TABLE 1.5B

Trace-element tolerances for irrigation waters. (From U.S. National Technical Advisory Committee on Water Quality Criteria, 1968)

| | For water used continuously on all soils | For short-term use on fine-textured soils only |
|------------|--|--|
| | mg/L | mg/L |
| Aluminum | 1.0 | 20.0 |
| Arsenic | 1.0 | 10.0 |
| Beryllium | 0.5 | 1.0 |
| Boron | 0.75 | 2.0 |
| Cadmium | 0.005 | 0.05 |
| Chromium | 5.0 | 20.0 |
| Cobalt | 0.2 | 10.0 |
| Copper | 0.2 | 5.0 |
| Fluorine | 1 | 1 |
| Iron | 1 | 1 |
| Lead | 5.0 | 20.0 |
| Lithium | 5.0 | 5.0 |
| Manganese | 2.0 | 20.0 |
| Molybdenum | 0.005 | 0.05 |
| Nickel | 0.5 | 2.0 |
| Selenium | 0.05 | 0.05 |
| Tin | 1 | 1 |
| Tungsten | 1 | 1 |
| Vanadium | 10.0 | 10.0 |
| Zinc | 5.0 | 10.0 |

¹Tolerance not determined.

TABLE 1.5C

Maximum Total Dissolved Solid Concentrations of Surface Waters
Used in Different Industrial Applications.

| <u>Industry/Use</u> | <u>Maximum Concentration mg/L</u> |
|---------------------|-----------------------------------|
| Textiles | 150 |
| Pulp and Paper | 1,080 |
| Primary Metals | 1,500 |
| Copper Mining | 2,100 |
| Chemical | 2,500 |
| Boiler Make-up | 35,000 |

(Source National Academy of Sciences, 1973; cited in Hartley, 1980, Table 9.6)

problem of geothermal effluent disposal. The case of arsenic is illustrative of the magnitude of the problem. The As contents of the geothermal fluids shown in Table 1.4 range between 0.5 to 12 mg/kg: to bring them to the drinking water quality standard of 0.05 mg/kg would require dilution by a factor of 100 to 250. In some instances a specific element presents a problem. For example, to use water from Ahuachapán in wood pulp and paper processing might require dilution by a factor of 20. However to use it for irrigation in the adjacent coffee plantations, which are particularly sensitive to boron, would require dilution by a factor of 200 or more.

2.0 GEOTHERMAL EFFLUENT DISPOSAL PRACTICES

2.1 SURVEY OF OPTIONS AVAILABLE

Among the various options currently being used or developed to dispose of large quantities of geothermal effluents are: (1) direct discharge into surface waters, (2) ponding and surface evaporation, (3) treatment and surface discharge, (4) secondary use of effluents, (5) injection, (6) injection with pretreatment, and (7) injection after extraction of valuable mineral products. These strategies of disposal are compared in Table 2-1 (modified after Table 1 of Defferding and Walter, 1978).

2.2 SURFACE DISCHARGE

Except in favorable geographic situations, and benign water chemistry, disposal of geothermal effluents for crop irrigation or into bodies of surface water is environmentally unacceptable (Brockway, et al., 1984). These criteria are unlikely to be met for the effluent from many geothermal power plants.

2.2.1 Wairakei, New Zealand

An exception occurs in the case of the Wairakei plant in New Zealand which, as the forerunner of all power plants exploiting water-dominated geothermal fields, commenced power production in 1959. This plant currently has an installed capacity of 157 MWe and produces 4,000 tonnes/hour of effluent (Thain, 1985). These liquid wastes, averaging 4,400 mg/l TDS (similar to Broadlands, see Table 1.4) have been discharged to the Waikato River, since the beginning of

TABLE 2-1

OPTIONS AVAILABLE FOR GEOTHERMAL DISPOSAL
(Modified from Defferding and Walter, 1978)

| <u>METHOD</u> | <u>RELATIVE COSTS</u> | <u>STATUS OF TECHNOLOGY</u> | <u>ENVIRONMENTAL STATUS</u> | <u>LEGAL ASPECTS</u> |
|--------------------------------------|---|--|--|---|
| 1. Direct Surface Discharge | Low | Existing technology | Unacceptable for most geothermal sites; exceptions are low temperature fluids for direct use | Most effluents cannot meet water quality standards |
| 2. Ponding | Highly variable, mainly dependent upon liner and land costs | Reliable liners that are low in cost require development | Past experience of poor performance; break-through of wastes can pollute ground waters | Closely controlled by environmental standards |
| 3. Treatment and Surface Disposal | Treatment costs high for large flow volumes | Development of less expensive treatment technology necessary | Reliability of treatment systems to prevent inadvertent release of pollutants important; subsidence potential high at liquid-dominated sites | Acceptable if systems are reliable and subsidence is controlled |
| 4. Secondary Use of Effluents | With relatively clean effluents, revenues may be realized | Development of less expensive treatment technology necessary | Determination of toxic effects of low level contamination on environment needed | Acceptable if environmental constraints met |
| 5. Injection | Costs may be 10 to 20% of power rate; highly dependent upon injection well capacity | Additional reservoir characterization needed; plugging may be a major problem of sites | Considered to be environmentally most acceptable of all disposal options | Acceptable; some legal restrictions possible from Safe Drinking Water Act |
| 6. Injection with Pretreatment | Expensive; treatment costs are high | Development of less expensive treatment technology needed | Acceptable | Acceptable |
| 7. Injection with Mineral Extraction | Expensive; treatment costs offset by sale of products; revenues could be realized | Development of cost effective technologies and markets for products | Acceptable | Acceptable |

power production. The power plant discharges 50×10^6 tonnes of effluent into the river each year. As a result the river water normally contains less than 0.05 mg/kg of arsenic and about 0.3 mg/kg of boron and 0.15 mg/kg lithium (Rothbaum, 1985). This has led to a reduction in fish populations, an increase in aquatic plant growth, and contamination of some plants with arsenic (Axtmann, 1975) (See section 2.4.1).

Withdrawal of fluid from the reservoir which supplies the Wairakei field has caused subsidence of the ground surface of up to 5 m. This, together with the environmental effects on the Waikato River, has led to the initiation of injection tests during the last few years (Thain, 1985; Allis, 1980).

2.2.2 Ahuachapán, El Salvador

Since most rivers are used extensively for domestic purposes and for irrigation, pollutants potentially harmful to animals and plants, such as arsenic and boron, must be kept below strict limits. In the Ahuachapán geothermal field, it was found that conforming to these limits meant that the nearby Rio La Paz could only accommodate effluent, averaging 20,000 mg/l TDS (see Table 1.4), from a 30 MWe power station (Einarsson, et al., 1975). Currently the installed capacity is 95 MWe. Therefore the waste from the first 30 MWe plant was discharged to the river only at the beginning of plant operations in 1975. A reinjection program was then initiated and construction of a 75 km long covered canal was begun to conduct the waste to the Pacific Ocean (Cuéllar et al., 1981). From 1975 until 1984, 167.4×10^6 tonnes of fluid have been produced and 37.6×10^6 tonnes (or 22.5%) have been reinjected (DiPippo, 1985). The experience of injection at this field is further discussed in section 4.3.1.

2.2.3 Kizildere, Turkey

Another example of surface discharge is the Demizli-Kizildere Geothermal Plant in Turkey. There the effluent of a 20 MWe plant is discharged to the Büyük Menderes River at the rate of 1,500 tonnes/hour. By mixing with the river water the concentration of boron is reduced from 30 mg/kg to less than 1 mg/kg (see Table 1.4). However further development of this field must await installation of an injection system (Şimşek, 1985). The case for injection is discussed in section 4.3.3 of this report.

2.3 PONDING AND SURFACE EVAPORATION

2.3.1 Cerro Prieto, Mexico

This is an option only exercisable where there is an appropriate combination of land costs and climate. The pre-eminent example of this circumstance occurs at Cerro Prieto, in Baja California, Mexico, where the installed capacity is currently 400 MWe with another 220 MWe about to come on line. The total production of fluid at Cerro Prieto up to 1983 was 298.4×10^6 tonnes of brine, averaging 18,000 mg/kg TDS before flashing to steam (see Table 1.4) (Alonzo, 1985a). Surface disposal is to an evaporation pond of about 8 km² area. A 36 km long canal carries the overflow to a dry lake, Laguna Salada. At Cerro Prieto injection of geothermal effluent is also under consideration (Tsang, et al., 1980), and a plant for brine treatment is under construction (see section 2.5).

2.4 TREATMENT AND SURFACE DISCHARGE

In sections 1.4 and 1.5 we saw that geothermal effluents may contain deleterious trace elements, notably boron, arsenic, and mercury. For example, Anderson (1975) notes that steam condensate from typical wells in the Geysers Geothermal Field contain 0.01-5.0 mg/l of boron. Although the safe limit for drinking water is as high as 1.0 mg/l, certain crops have maximum safe limits of only 0.75 mg/l for irrigation water (Table 1.5). One obvious strategy is to reduce the concentration of such trace elements to safe values before discharge of effluent into surface water.

2.4.1 Pilot Study at Wairakei, New Zealand

This option does not appear to have been used yet on a full commercial operational scale. However there have been several pilot studies along this line. For example, Rothbaum and Anderton (1975) described a pilot project to remove arsenic from the effluent at Wairakei, which contains 500 to 1,000 mg/kg of silica and 3 to 5 mg/kg of arsenic. They proposed removing the As by preoxidizing it to the pentavalent state and coprecipitating it with SiO_2 by dosing the "aged" effluent with 700 mg/kg of slaked lime. The resultant gel could then be dried to a low-density calcium silicate powder which could have a market as an insulant. A preliminary study of the feasibility of using this process at Ahuachapán suggested that the estimated costs of 3.2 mills/kw-hr would be prohibitive (Defferding and Walter, 1978). Shannon et al. (1982) described an improved pilot plant in which the discharge water was continuously dosed with ferric sulfate, a flocculant and surfactant. The resulting iron floc, with co-

precipitated arsenic, could be separated by dissolved air flotation very readily. More recently, therefore, a commercial organization has obtained permission to reexamine the economics of extracting chemicals of commercial purity from the waste water at Wairakei (Thain, 1985, p. 150).

2.5 SECONDARY USE OF EFFLUENTS

The feasibility of this option is closely tied to that of the case just discussed. Except for low- to moderate-enthalpy resources used for direct geothermal applications, geothermal fluids usually have total dissolved solids concentrations too high to be used for potable water or irrigation. This can be seen by comparison of Table 1.4 and Figure 1.4 with Table 1.5. Many geothermal effluents exceed these limits for some of these components. Any additional uses of high enthalpy resources for industrial processes such as paper making, drying and dehydration are still subject to the problem of effluent disposal.

2.5.1 Kawerau, New Zealand

A case in point is Kawerau, New Zealand, where four wells supply steam to a pulp and paper company plant which generates 10 MWe of electric power and uses 122 MW thermal, above 100°C condensate, as process heat (Freeston, 1985). Most of the latter use of geothermal steam is in shell-and-tube boilers where clean steam is generated for use in paper-making equipment. Between 600 and 700 tonnes/hour of geothermal effluent containing up to 3,000 ppm TDS is discharged to the Tarawera River. Further development of this resource is limited by a water right which limits dissolved H₂S discharge to 1.5 g/sec and heat discharge

to 75.4 MWt above 0°C (Berry, et al., 1985). For this reason experiments on injection are underway.

2.5.2 Cerro Prieto, Mexico

A second interesting case of secondary use of effluents is incidental to the extraction of useful minerals from a geothermal brine. At Cerro Prieto, Mexico, a plant is under construction to produce 200,000 tonnes/year of potassium chloride for fertilizer. (See section 2.3.1 for more details of this field). This amounts to 85% of the annual domestic demand in the Republic of Mexico (Alonzo, 1985b). The system will use solar heat to evaporate brine in a series of five holding ponds covering an area of 16 km², using progressive fractional crystallization. Mixtures of solid KCl and NaCl are then to be separated by flotation. The cost per tonne of potash is expected to be lower than that of the imported product. Similarly markets for sodium, calcium and lithium salts are being explored (Mercado, et al., 1979). Other experiments at Cerro Prieto involve the use of steam condensate to irrigate greenhouse cultivation, where its content of potassium chloride and ammonium nitrate is used to advantage (Alonzo, 1985b).

Before similar schemes are developed at other sites, an unusual combination of criteria must be satisfied. In addition to having a market for KCl, Cerro Prieto has: (a) a market for electricity, (b) a large available geothermal reservoir, (c) low land costs, (d) an arid climate (evaporation 2,500 mm/yr), (e) an absence of sensitive environmental factors, and (f) a government agency willing to make the necessary investment in an uncommon technological applica-

tion. Although this site may be unique in these respects, other geothermal developers will watch with interest the technical and economic program of this ambitious secondary use of geothermal effluents.

2.6 INJECTION

2.6.1 Introduction

Currently disposal of geothermal effluents in injection wells is the normal practice in most situations. In most cases although injection may appear more costly than direct surface disposal in the short term, it may prove more cost effective in the long term also. Experience at toxic waste disposal sites suggests that prevention of environmental degradation is an economically sounder practice than remedial action after the fact. Thus injection is usually performed for environmental reasons.

However various authors have also alluded to the advantages of injection of effluents from high temperature geothermal systems to increase reservoir life. Various authors mention returning fluids and residual heat to the producing formations to maintain reservoir pressures, to delay cooling of the reservoir, and to inhibit subsidence (Defferding and Walter, 1978; Einarsson, et al., 1975).

Because this method of disposal of effluents from geothermal power plants is widely used but has a number of problems associated with it, the literature on injection is extensive. Possibly because injection of low enthalpy effluents in direct use applications presents fewer problems, the literature on this aspect is much less profuse (see, for example, TenDam, 1984).

The extensive literature can be categorized as follows:

(a) Case studies, e.g. Arnold 1984; Horne 1982a, b; Dobbie and Maunder, 1982; Grant, et al., 1982; (see section 4.0);

(b) monitoring of injection behavior and use of tracers, e.g. Wilt, et al., 1983; Benson and Bodvarsson, 1982; Vetter and Zinnrow, 1981; Wright, 1985;

(c) modeling of injection behavior, e.g. Gringarten and Sauty, 1975; Bodvarsson and Tsang, 1982; Preuss and Bodvarsson, 1984;

(d) treatment of effluents before injection (see section 2.7);

(e) minerals recovery (see section 2.8).

2.6.2 Vapor-dominated Systems

Vapor-dominated fields, in general, have fewer problems with injection as a disposal method than in the case of water-dominated fields. Firstly, there is relatively less water requiring disposal. Only about 20-40% of the mass of the produced geothermal fluid remains as excess condensate from the cooling tower basins. Secondly, the condensate is relatively free of dissolved solids, compared to fluids from water-dominated fields. Thirdly, because vapor-dominated reservoirs are underpressured, actual injection is done by gravity feed and injectivity may actually increase through time (Chasteen, 1975). Some representative examples are discussed in section 4.2.

2.6.3 Water-dominated Systems

Injection of effluents from power plants exploiting water-dominated systems takes place in a much more diverse range of conditions than those just discussed. Consequently problems encountered range from those having negligible impact, to those still awaiting effective and commercially viable solutions.

Horne (1982a) among others, has commented that, in the case of fractured geothermal reservoirs, there have been both positive and negative experiences from injection. In principle, injection should help support reservoir pressures and hence promote more efficient thermal energy recovery. However, up to the present, injection has been used primarily for waste water disposal.

Consideration of reservoir maintenance has been largely restricted to avoiding detrimental effects (Horne, 1982a). Care must be taken to prevent premature return of the injected water into production wells through high permeability fractures, leading to reduction of discharge enthalpy and hence of useful energy output. For this reason most of the literature on the topic injection concerns experiments and field tests, tracer returns, and modeling of the thermal and hydraulic influences of injection on bore fields (Darnell and Eichelberger, 1982; Horne, 1982a)

Injection of power plant discharges in water-dominated geothermal fields is currently practiced on a commercial production scale in the following countries: El Salvador, Japan, Philippines and U.S.A. In section 4.3 some representative examples of these experiences are discussed, highlighting problems and their solution.

2.7 INJECTION WITH PRETREATMENT

2.7.1 Introduction

Because of the expense involved, pretreatment of geothermal effluent before injection is avoided where possible. However there are various systems where, out of necessity, this kind of treatment is part of commercial scale geothermal

power plant cycles. Similarly, because of problems encountered, elsewhere there have been numerous laboratory and field tests of various schemes for pretreatment. The rather voluminous literature on this topic has recently been summarized by Weres and Apps (1982), and Kindle, et al. (1984).

The problem arises when, during production and use of geothermal fluids from water dominated systems, the solutions become supersaturated in various dissolved components. Many hot geothermal aquifers (those with temperatures exceeding 200°) contain waters in equilibrium with quartz. The fluids produced from them are therefore saturated with silica. Other geothermal waters contain appreciable quantities of carbon dioxide (> 0.2% wt) and are therefore saturated with calcite. Similarly some geothermal waters are close to saturation with calcium sulfate (Table 1.4). Some representative examples are described in section 4.0. Although silica and calcium carbonate and sulfate are the main likely precipitates from geothermal brines, in some cases heavy metal sulfides, sulfates, oxides and carbonates form. Occasionally minerals such as strontium carbonate, barium sulfate and ammonium carbonate may also be formed (see section 3.0).

2.7.2 Problems Caused by Mineral Precipitation

Experience at geothermal power plants in various countries indicates that the most common mineral scales which cause problems are amorphous silica, calcium carbonate (calcite and aragonite), calcium sulfate (anhydrite or gypsum) and barium sulfate. Other scales usually occur in too small amounts to cause practical problems (Weres and Apps, 1982, p. 409). One exception is the Salton

Sea geothermal field of California, U.S.A., when the brines contain substantial amounts of iron, zinc, lead and other heavy metals. Thus sphalerite, galena, pyrrhotite and pyrite form in this system, in addition to amorphous silica (see Table 1.4 and section 4.3.7).

Scaling can occur in every part of the system in contact with the geothermal fluid, including the production well bores, surface piping, flash tanks, heat exchangers, pumps, valves, and in the injection well bores. Furthermore, addition of suspended particulate matter and reactions between the injected fluid and the aquifer rocks may lead to plugging of the formation surrounding the borehole. Such plugging can lead to loss of injectivity in the injection well. This problem increases both the constructional and operational costs of geothermal power plant systems. In some of the more serious cases the operation of the geothermal field may be stopped because of scaling e.g., Tekkehaman and Kizildere, Turkey (see section 4.3.3).

2.7.3 Control of Scaling

The type of treatment necessary depends upon the nature of the scale, which in turn depends upon the temperature and chemistry of the geothermal fluid produced. Scaling can be controlled either by selecting a specific power cycle which minimizes precipitation of scales or by treating the geothermal process fluid, either upstream or downstream of the power plant, to control precipitation and minimize its effects. These two approaches are discussed in more detail in section 3.8 and so will only be referred to briefly here.

Avoiding precipitation can be achieved by manipulating process parameters

such as pressure and temperature, or by the use of various scale inhibitors, or other additives, to manipulate the chemistry of precipitation or its kinetics. Scale inhibitors have proved particularly effective in avoiding carbonate and sulfate scales (Kindle, et al., 1984, p. 513).

Controlling precipitation is the preferred option when it is uneconomic to prevent precipitation. In this case scale formation is induced in a form and at a location where it can be handled and removed in the most economical manner. The strategies employed include both chemical and mechanical approaches to use the kinetics of precipitation to advantage. Use is made of crystallizers, crystallizer-separators, reactor clarifiers, carbon dioxide injection, pH control and aging of the brine in a tank or pond (Kindle, et al., 1984, p. 518). Various examples of these approaches are further discussed in section 4.0.

2.7.4 Costs of Pretreatment

Because of the diversity of different geothermal brines, geothermal fields, and geothermal power plants, it is difficult to generalize the relative costs of brine treatment systems. One useful approach is to compare the life-cycle cost of treatment in the most hostile treatment/injection location versus the life-cycle costs of no fluid treatment prior to injection in the same environment. Kindle, et al. (1984, p. 7.1) have done this based on data from the Salton Sea geothermal field of California (see section 4.3.7). These authors compared the costs of using a crystallization/clarification system versus the base case of no fluid treatment prior to injection (see section 3.8.8). The base case assumption included the costs of cleaning injection wells when plugging occurs and the

need to switch to spare injection wells during the cleaning cycle. They assumed that for a hypothetical plant, 10 injection wells each with a capacity of 3,785 lpm (1000 gal/m) would be needed. 5 spare injection wells would be needed for use while the injection wells were being cleaned by backflushing and acid treatment. As a baseline it was assumed that the injection wells would need to be cleaned once a month, a conservative estimate.

According to Kindle, et al. (1984, p. 7.3) the life-cycle unit cost of handling brine disposal without pretreatment would be $\$1.08/10^3$ ($\$4.11/10^3$ gal.) whereas the cost using a crystallizer/clarifier system would be $\$0.65/10^3$ ($\$2.45/10^3$ gal.). For a geothermal plant which required a flow rate of 2.27×10^6 l/h (6×10^5 gal/h) from the production wells the savings for the crystallizer/clarifier system over the no treatment system were calculated to be $\$6.9 \times 10^6$ a year (Kindle, et al., 1984, p. 7.5). If, in the no treatment case, the wells were cleaned every three months this would save $\$2.6 \times 10^6$ a year. This reduces the net savings for the case using the crystallizer-clarifier system to only $\$7.3 \times 10^6$ a year (Kindle, et al., 1984, p. 7.5). However in both cases pretreatment is more economic than no treatment.

Unfortunately, most of the relevant operating experience from operating power plants using hypersaline brines in the U.S.A. is held proprietary. However, even in the absence of the operational costs figures, we can infer that the analysis of Kindle, et al. (1984) is at least correct in principal. In the Imperial Valley of California there are two hydrothermal systems with hypersaline brines which have operational power plants. These are the North Brawley field and the Salton Sea field. The North Brawley Plant of 10 MWe was designed

to rely on brine handling techniques requiring maintaining solids in solution. It required extensive workovers of the injection wells. In contrast the Salton Sea plant, also of 10 MWe, relied on a crystallization/clarification system. After several years of operation the Brawley plant has been decommissioned and the wells plugged. However, the operator of the steam gathering and brine disposal system at both sites now intends to build a 50 MWe plant at the Salton Sea field using the crystallization/clarification technology (personal communication C. Otte, Unocal Geothermal Co., 1986). These systems are further discussed in section 4.3.7.

2.8 INJECTION AFTER MINERAL RECOVERY

An obvious point is that, if valuable chemical components can be extracted from geothermal brines before injection and sold at a profit, then the economics of brine treatment might be considerably improved. It well known that small quantities of base and precious metals, locally of ore grade concentration, are depositing in active geothermal systems throughout the world (Browne, 1984). For example, in the New Zealand geothermal fields, even with their low salinity of 3,000 mg/kg, base-metal sulfides, native silver and traces of gold, are being precipitated from near neutral alkali chloride fluids.

However the occurrences which have occasioned the greatest interest are the highly saline brines of the Salton Trough (White, 1981). Fairly abundant ore minerals especially galena, sphalerite, and chalcopyrite occur in this system (McKibben and Elders, 1985) and scales formed from the brine may contain abundant zinc, lead, copper and up to 6% of silver (Skinner, et al., 1967). However

although the concept of commercial extraction of minerals from geothermal fluids is not a novelty, there appear to be no current commercial activities, apart from the potassium chloride system at Cerro Prieto, mentioned in section 2.5.2 above (Crane, 1982).

The high concentrations of potentially valuable constituents in the hypersaline brines of the Salton Trough have attracted considerable interest. For example, Maimoni (1982) estimated that the potential revenues from minerals recovery from a combined geothermal power and mineral recovery plant in the Salton Sea geothermal field could exceed those from sales of electricity. This author estimated that a 1,000 MWe plant selling electricity at 6 cents/kWh would earn $\$394 \times 10^6$ /year. Assuming that 90% of the mineral values in the brine could be recovered and sold, the market value of the minerals produced would be between $\$500$ to $\$1,500 \times 10^6$ /year in 1986 \$. Such a plant could supply between 14 to 31% of the U.S. demand for manganese, a strategic metal. However, in spite of the large amounts of metals which would pass in solution through a power plant in this field, it is by no means clear that the techniques available to produce them would be economic, at present.

There has been considerable theoretical and experimental study of the mineral values in the Salton Sea geothermal field brines (Arthur, 1983; Harrar and Raber, 1984; Schultze and Bauer, 1982; Schultze, 1984; Michels, 1985; Byeseda and Hunter, 1985). Table 2.8 shows some of the potential mineral recovery values from a hypersaline brine passing through a hypothetical 50 MWe plant in the Salton Sea geothermal field. It is important to consider the market demand as well as the technological aspects of such estimates. Based on such

TABLE 2.8

Potential Mineral Recovery Rates from Hypersaline Brine in the
Salton Sea Geothermal Field from the Fluid Supply of a 50 MWe Power Plant
(After Michels, 1985)

| Product | Concn mg/kg | Industrial Form | Recovery Efficiency | Tonnes/Year Recoverable | \$/ton | Gross/value \$ millions/yr |
|-------------|-------------|---------------------------------|---------------------|-------------------------|---------|----------------------------|
| Na | 57,100 | NaCl | 0.9 | 2,618,180 | 50 | 144 (e) |
| Ca | 25,700 | CaCl ₂ (a) | 0.8 | 3,000,000 | 32 | 106 (e) |
| K | 14,700 | KCl (b) | 0.8 | 449,090 | 60 | 30 (e) |
| Fe | 1,770 | Fe(OH)3.2 H ₂ O | 0.9 | 71,818 | 120 | 9.5 (e) |
| Mn | 1,230 | MnO ₂ | 0.8 | 31,180 | 175 | 6. (f) |
| Zn | 715 | Zn | 0.8 | 11,450 | 450 | 5.7 |
| Sr | 620 | SrSO ₄ (c) | 0.4 | 10,545 | 640 | 7.4 (e) |
| Ba | 550 | BaSO ₄ | 0.9 | 9,909 | 100 | 1.1 |
| B | 365 | H ₃ BO ₃ | 0.05 | 2,090 | 550 | 1.3 (e) |
| Li | 283 | Li ₂ CO ₃ | 0.6 | 364 | 2,800 | 1.12 |
| Pb | 114 | Pb | 0.95 | 2,182 | 300 | 0.72 |
| Br | 29 | Br ₂ | 0.1 | 58 | 600 | 0.038 |
| Cu | 2.4 | Cu | 0.5 | 24 | 1,300 | 0.034 |
| Ag | 0.09 | Ag | 0.5 | 9 | 250,000 | 2.5 |
| Electricity | -- | -- | 0.8 | (g) | | 21 |

- (a) 38% liquid
 (b) fertilizer grade
 (c) requires conversion to SrCO₃
 (d) \$9 per Troy ounce
 (e) inadequate market
 (f) unknown marketability
 (g) \$0.06/kWh

considerations Wei, (1982) considered that the following components might be profitably recovered from the hypersaline brines of the Imperial Valley: Li, B, Mn, Zn, Sr, I₂, Fe, Pb, Br₂, CO₂, NH₃, Cu, Ni.

Byeseda and Hunter (1985) after considering various process technologies such as (1) precipitation reactions, (2) electrolytic reduction, (3) biological concentration, (4) solid-bed ion exchange and (5) solvent extraction, and testing them on a laboratory bench scale and in a field trial concluded that solvent extraction of zinc is the probably the closest to being put into commercial production. Recovery rates of better than 80% were achieved for this metal.

In spite of the obvious potential for earning revenues by mineral extraction I know of no serious plans to implement such recovery schemes for these brines at present. However removing valuable minerals might also improve the injectability of the effluents involved.

3.0 CHEMICAL, MINERALOGICAL, AND PHYSICAL ASPECTS OF INJECTION

3.1 INTRODUCTION

The chemistry of geothermal fluids was discussed above in section 1.4 and the most important scaling or plugging agents were mentioned in section 2.7. Chemical problems of reinjection have recently been addressed by Weres and Apps (1982), Kindle et al. (1984), and Vetter and Crichlow (1979). Of the several hundred possible hydrothermal minerals known, only a half dozen present problems due to scaling or plugging in injection wells. According to Weres and Apps (1982, p. 408), it is difficult to confirm with certainty that even limited thermodynamic equilibrium has been achieved in reactions between brines and rock. Fortunately, the concentrations of major scaling components of a geothermal fluid can usually be reconciled with the assumption of thermodynamic equilibrium with respect to the more soluble minerals in the host rock (Weres and Apps, 1982, p. 408). In the following discussion of the solid phases which may form, in equilibrium or metastably, from spent fluids from a geothermal plant, we can use as a guide information from natural hydrothermal systems, as well as theoretical and experimental studies.

The literature on water/rock reactions in natural geothermal systems, both active and fossil, is extensive. Some excellent reviews of the mineralogy of these systems include Barnes (1979), Browne (1978), Ellis and Mahon (1977), Fournier (1981), Giggenbach (1981), Henley and Ellis (1983), Henley, et al. (1984) and White (1981). A great deal of useful information on the rock-forming minerals occurring in hydrothermal reservoirs is reviewed in this literature,

including data on the minerals responsible for scaling, cementation or plugging of injection wells. The chemistry of these phases is reviewed in the following sections. However as will be shown, study of equilibrium mineral phases is not sufficient for an understanding of the problem or its mitigation, as kinetic factors become very important, especially in process control.

3.2 WHY SCALES FORM

The sources of the dissolved components in geothermal waters have already been discussed (section 1.4.3). Power production from geothermal waters involves large temperature drops. Many dissolved components, notably SiO_2 , exhibit prograde solubility, i.e., over the temperature range of interest they become more soluble as temperatures rise. Thus adiabatic cooling is sufficient to induce precipitation. However other components, the most important of which are calcium carbonate and sulfate, exhibit retrograde solubility, i.e., they are more soluble in cold rather than in hot water. Nonetheless minerals with retrograde solubility may be precipitated by isoenthalpic processes during power production.

In most water dominated systems boiling is induced in the well bores to cause the geothermal fluid to flow to the surface without pumping. This causes concentration of the dissolved components in the residual hot water. According to Henry's law the solubility of dissolved gases in water under aquifer conditions is greater than that under the lower pressures of the boiling zone. Carbon dioxide and hydrogen sulfide fractionate into the steam. The resulting vapor phase enriched in CO_2 , H_2S , and H_2SO_4 becomes more acidic and the residual

liquid phase therefore becomes more basic. As a result of these physical and chemical changes induced by boiling, the solution may become unstable and precipitate certain components even as phases with retrograde solubility. Thus precipitation can occur by simple cooling, by CO_2 and H_2S loss, pH changes, or it may occur by mixing of incompatible waters.

It is worthwhile to summarize and restate these concepts, emphasizing the engineering conditions which affect the chemical conditions of scaling and plugging. This can be done conveniently in tabular form in Tables 3.2A and 3.2B. Discussions of the chemistry of the common scale types and methods of mitigation now follow.

3.3 SILICA

3.3.1 Silica Solubility

Experience has shown (see section 4.0) that the most widespread and acute form of scaling is due to silica. Quartz is the most stable and most common form of silica in geothermal reservoirs so that, above 150°C , the concentration of dissolved silica in geothermal fluids is governed by quartz solubility. However in geothermal brines silica is in a monomeric form (possibly H_4SiO_4 or $\text{Si}(\text{OH})_4$) (Ellis and Mahon, 1977). Cooling hot geothermal brines can lead to supersaturation with silica. However the precipitation of silica from aqueous solution is very slow and is governed by polymerization and precipitation as amorphous silica, which is more soluble than quartz, as is shown in Figure 3.3A. Dissolved salts cause a decreasing solubility for both amorphous silica and quartz with increasing NaCl molality, with the effect being greater in the case

TABLE 3.2A

Factors Affecting Mineral Scale Formation

- Brine Composition
- Gas composition and concentration (CO_2 , H_2S , NH_3 , HCl , H_2 , O_2)
- pH
- Temperature of produced fluid
- Single or two-phase fluid flow
- Degree of flashing and steam quality
- Partitioning of gases between liquid and vapor
- Pressure and Temperatures after steam separation
- Oxidation-reduction potential
- Residual brine concentration due to steam loss
- Nucleation-growth phenomena
- Deposition surface
- Velocity, Reynolds number, and other flow effects

(After Shannon, 1977)

TABLE 3.2B

Processes Causing Scale Formation

| | |
|-----------------------|---|
| Silica and Silicates | Temperature drop causes saturation, steam loss concentrates brine, boiling-induced pH increase affects kinetics. |
| Calcite and Aragonite | CO ₂ loss into steam increases pH of brine, steam loss concentrates brine. |
| Sulfates | Temperature and pressure changes decrease calcium sulfate solubility, and mixing different fluids e.g. make up water and spent geothermal brine cause barite scale. |
| Sulfides | Temperature drop decreases solubility and boiling increases pH. |
| Iron deposits | Corrosion causes Fe ⁺² precipitates on surfaces and in other scale deposits. |
| Other | Incomplete steam separation results in aerosol carry-over of salts. |

(After Shannon, 1977)

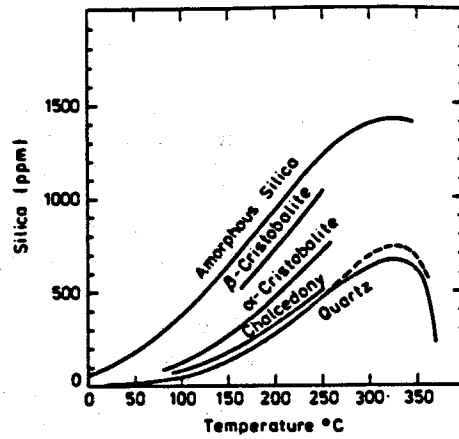


Figure 3.3A. The solubility of various forms of silica in water at saturated vapor pressures (from Fournier, 1973).

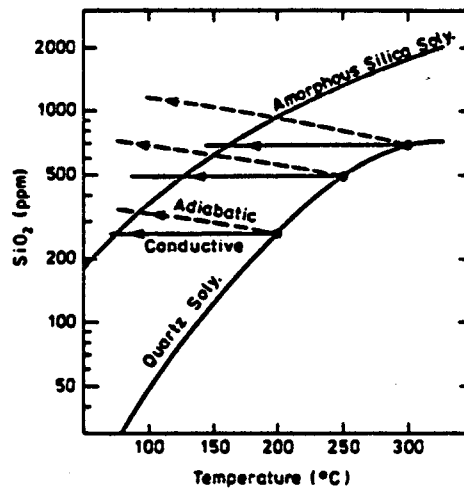


Figure 3.3B. Trends in silica concentrations during cooling of geothermal waters by steam loss and by heat exchange. Lines for quartz and amorphous silica solubility are shown (from Ellis and Mahon, 1977).

of amorphous silica (Kindle, *et al.*, 1984, Fig. 4.2).

Ellis and Mahon (1977) applied the data of Figure 3.3A to two different situations which occur in geothermal power plant engineering. Fluid produced from geothermal wells may be cooled in two broadly different ways. For example, in binary plants, such as the Magma Power Company plant at East Mesa, and at the Heber Binary Demonstration Plant, both in the Imperial Valley of California, U.S.A., hot brine is pumped to the surface and cooled in a heat exchanger without boiling. Figure 3.3B shows hot brine saturated with quartz at three different temperatures 200°, 250° and 300°C respectively. The dissolved silica in these three brines remains at constant concentration (along the conductive cooling lines in the figure) until the amorphous silica saturation curve is intersected at 75°, 125° and 160°C respectively (Ellis and Mahon, 1977, p. 305). Below these temperatures amorphous silica may be deposited, depending on kinetic factors.

If the fluid flashes partly to steam in the production well bore and then flashes again in steam separation tanks, the fluid would cool along adiabatic cooling lines (shown as dashed lines in Figure 3.3B). Furthermore the residual brines would be concentrated by steam losses. In this case the three hypothetical brines at 200°, 250° and 300°C would reach amorphous silica saturation at 95°, 150° and 200°C respectively. Below these temperatures polymerization of the excess silica is likely. In designing a process cycle, therefore, temperatures should not be allowed to go much below the temperatures at which the solubility of amorphous silica reaches saturation (Ellis and Mahon, 1977, p. 306). In practice the points at which scaling becomes troublesome are considerably lower due to the peculiarity of the polymerization process.

3.3.2 Silica Precipitation

In nature, the formation of the most thermodynamically stable phase, quartz is favored by relatively high temperatures of precipitation, slow rates of deposition and relatively low degrees of supersaturation. On the other hand, the effluent from geothermal power plants normally precipitates amorphous silica after supersaturation is attained relative to that phase. According to Weres and Apps (1982, p. 410), there are two basic pathways whereby amorphous silica precipitates, (a) by molecular deposition upon solid surfaces to give a dense, compact, silica glass, and (b) by homogeneous nucleation and growth of colloidal silica particles in the solution, which then coagulate and precipitate or adhere to solid surfaces (which may cause plugging in the pore spaces of rock formations). The kinetics of molecular deposition and homogeneous nucleation have been studied both experimentally and theoretically by Weres, et al. (1980), and is also discussed by Ellis and Mahon (1977), and Kindle, et al. (1984).

According to these authors, the rate of homogeneous nucleation is strongly dependent upon the saturation ratio, i.e., the ratio of silica concentration, under the given conditions, to the concentration at equilibrium solubility. When the saturation ratio exceeds two, homogeneous nucleation dominates and becomes very rapid when the ratio exceeds three. When the saturation ratio is less than two, or when flow velocity is high enough to inhibit homogeneous nucleation, then the molecular precipitation mechanism dominates (Weres and Apps, 1982, p. 410).

Amorphous silica precipitation is favored by high initial brine temperatures so that the brine contains sufficient silica to have a high saturation ratio

when cooled. In practice this means that silica precipitation is not likely to be a problem for geothermal reservoirs cooler than 240°C, but may be acute for hotter reservoirs.

3.3.3 Kinetics of Silica Scaling

In addition to the factors which control silica solubility, kinetic factors have a great influence on silica scaling. These aspects of the problem are also discussed by Weres and Apps (1982) and Kindle et al. (1984), among others. The rate at which silica comes out of solution depends upon saturation ratio, temperature, availability of nucleation sites and the presence of catalytic agencies. The presence of OH⁻ ions as well as Cl⁻, Br⁻ and F⁻ ions has a catalytic effect upon polymerization of silica in solution. Once the saturation ratio exceeds 2, silica precipitates rapidly, and the rate becomes maximum when brines are cooled 25 to 50°C below their saturation temperatures.

Weres et al. (1980) list the following stages in silica precipitation:

1. formation of silica polymers in solution;
2. nucleation of amorphous silica as colloidal particles;
3. growth of the colloidal particles to above a critical size by additions of amorphous silica;
4. coagulation of colloidal particles to form a precipitate or flocculation to a semisolid material;
5. cementation of these particles in the deposit by further additions of silica;
6. (more rarely) growth of a secondary phase in the interstices between particles of amorphous silica.

Solid surfaces in contact with supersaturated solutions of amorphous silica may be covered by a layer of amorphous silica and then further deposition may occur by step 3. Colloidal amorphous silica may also adhere to solid surfaces with further deposition occurring in steps 4 and 5. Nucleation of amorphous

silica on other scale particles, on Fe^{++} , or on silicates or carbonates may also occur (Weres et al., 1980).

The nucleation process usually involves a "lag time" during which concentrations of silica are constant. When nucleation begins, then the concentration declines. Kindle et al. (1984) offer two explanations this lag time or induction period. Firstly, they suggest that this is the time necessary for subcritical clusters of amorphous silica to reach critical size for rapid particle growth. Their second interpretation is that the induction time is simply the length of time necessary for enough particles to nucleate and grow to the point where the concentration of molecular silicic acid in the solution decreases.

Kindle et al. (1984) discuss other chemical controls over the kinetics of silica scale. Their review of silica deposition kinetics is summarized in Table 3.3.

3.3.4 Effects of Silica on Injectivity

Any injected geothermal effluent supersaturated with silica, or carrying floc of colloidal silica may damage the wellbore and the formation receiving it. According to Weres and Apps (1982), such brines will deposit vitreous silica on solid surfaces at rates determined by the concentration and temperature. In the case of moderate concentrations and temperatures this rate may be negligible. However, the definition of what constitutes a negligible rate depends not only on the properties of the solution but upon the physical properties of the receiving aquifer. These authors cite the following example, "20 $\mu\text{m}\cdot\text{y}^{-1}$ would be negligible when the injected fluid is going into a 4 mm fracture. It would

TABLE 3.3

Factors Affecting Kinetics of Silica Deposition

| <u>Factor</u> | <u>Impact</u> |
|-----------------------|---|
| pH | Lowering pH slows kinetics by a factor of 10 for each pH unit. |
| Supersaturation ratio | Precipitation becomes rapid as the ratio exceeds 2. |
| Temperature | Kinetics slows as temperatures decline counteracting the increase in supersaturation ratio. Maximum depositional rates occur at 25 to 50°C below saturation temperatures. |
| Salinity | Increased salinity increases the kinetics of deposition. |
| Catalysts | Catalysts such as fluoride ions speed up precipitation especially at low pH. |

(Modified after Kindle et al., 1984, Table 4.4)

be catastrophic if the rock has pore permeability only and an average pore size of 10 μm " (Weres and Apps, 1982, p. 411).

Flocculant precipitates will tend to accumulate in pores or small fractures in the formation, so that plugging will be most acute right at the wellbore, where it can do the most harm, most rapidly. In a fractured aquifer the floc may penetrate further into the formation so that injectivity does not decline (Weres and Apps, 1984). The situation is improved if the cooled brine is injected into a hotter formation so that silica redissolves as the brine heats.

Reaction of the brine with reservoir minerals, on the other, tends to destabilize colloids and accelerate deposition. Weres and Apps (1982, p. 411) state, "For example, injecting brine that is undersaturated with calcite into a calcite-bearing formation would cause the pH and the calcium content of the brine to increase, thereby destabilizing the (silica) colloid."

Nucleation of colloidal silica in the formation after brine injection could involve rapid cementation because there would be simultaneous substantial colloid loading and substantial silica supersaturation. Greater supersaturation would permit nucleation nearer the wellbore, and cause greater damage (Weres and Apps, 1982).

The subject of the kinetics of silica precipitation is difficult to assess quantitatively without field tests. For example, silica plugging is a minor problem in the Cerro Prieto geothermal system of Mexico, which has a TDS of about 28,000 ppm and a SiO_2 concentration of about 720 ppm. In contrast it is a major problem in the Salton Sea geothermal field in U.S.A. which has a TDS of about 250,000 ppm and a SiO_2 concentration of only about 460 ppm (Table 1.4).

Both these fields produce from similar deltaic sedimentary reservoirs at temperatures in the range of 300 to 350°C.

3.4 CARBONATES

3.4.1 Carbonate Solubility

The commonest carbonate is calcium carbonate which has three polymorphs, calcite, aragonite, and vaterite; however the latter is not a problem for geothermal fluid disposal. From the thermodynamic viewpoint, calcite is the stable form under the pressure/temperature conditions of geothermal systems. However aragonite frequently forms metastably due to kinetic factors. Other alkali earth metals such as Sr^{++} , Ba^{++} , and metallic ions such as Fe^{++} and Pb^{++} may also occur as carbonates in scales (Ellis and Mahon, 1977; Michels, 1981).

Calcite has retrograde solubility so that it does not precipitate from solution by cooling alone. However brines which were originally close to saturation with respect to calcite may reach supersaturation by decrease in pressure, boiling, loss of carbon dioxide, and the increase of pH which follows. This is due to speciation in the aqueous phase and can be described as follows (Ellis and Mahon, 1977; Michels, 1984):



Loss of carbon dioxide to the vapor causes dissociation of the bicarbonate ion:

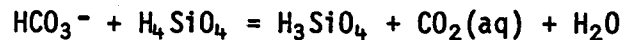
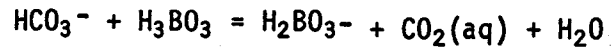


Under the influence of rising pH and CO_2 pressure, calcite becomes saturated:



The boric and silicic acids that are often present in some high-temperature

geothermal brines react with bicarbonate ions due to carbon dioxide loss and may reduce the pH again.



The effect of CO_2 loss on calcium carbonate precipitation has been directly evaluated by Arnórsson (1978) for eight geothermal wells from Iceland. His results verify that during one-stage adiabatic flashing of geothermal brine there is a decrease in total carbonate and increases in pH, activity of Ca^{++} and activity of CO_3^- .

3.4.2 Calcite Precipitation

The kinetics of calcite solution and precipitation are extremely rapid (Weres and Apps, 1982). Under flashing conditions in geothermal wells or flash tanks, due to the high degree of supersaturation and the high temperatures, precipitation of calcium carbonate is therefore very fast. Under injection conditions supersaturation may still occur due to the residual effects of flashing, and the effects of heating by the formation into which injection is occurring. Similarly supersaturation of residual brine after flashing may also be enhanced by addition of make-up water containing dissolved calcium and carbonate ions.

Although there have been numerous studies of calcium carbonate crystal growth and dissolution, the work so far accomplished is still insufficient to predict with any degree of certainty, the impact of carbonate precipitation when supersaturated spent brine is injected (Weres and Apps, 1982, p. 418). The induction time for nucleation and growth may be heavily dependent on the pre-

sence of small amounts of Mg^{++} , Sr^{++} and Ba^{++} . Similarly the possibility of aragonite precipitation needs to be further evaluated. Increasing magnesium ion concentration causes a progressive decrease in nucleation rates of both calcite and aragonite.

3.5 SULFATES

3.5.1 Chemistry of Sulfates

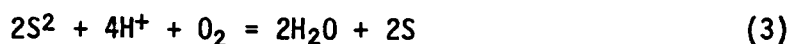
Sulfates are much less likely to present a problem in injection wells than silica or carbonates as they are usually much less abundant. However it is possible that such phases as gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$) or barite ($BaSO_4$) could form in an injection well or in the surrounding formation particularly if make-up water containing sulfate is mixed with the residual brines (Weres and Apps, 1982). Calcium and strontium sulfates have retrograde solubilities in water from about 30° to 300°C. The presence of NaCl increases their solubility but the solubility remains retrograde in this temperature range for $SrSO_4$ up to 2 m NaCl and for $CaSO_4$ up to 5 m NaCl (Kindle et al., 1984). The solubility of barite is prograde in water up to 100°C but the presence of NaCl in concentrations > 1 m can raise this to 300°C. Brine solutions containing > 1 m NaCl saturated with $BaSO_4$ at 300°C could precipitate barite as they cooled. Although sulfate scales commonly form in surface installations, only a few examples of loss of injectivity due to sulfates been reported in the literature (Cope et al., 1985). The kinetics of sulfate depositions are similar to those of the carbonates reported above in section 3.4.

3.6 SULFIDES AND OTHER SCALES

3.6.1 Chemistry of Sulfides

Precipitation of heavy metal sulfides is also effected by temperature reduction and loss of carbon dioxide. Both these effects increase the saturation of sulfides. Most sulfides have prograde solubility and are more soluble at low pH, while loss of CO₂ increases pH. At the pH values normal to geothermal brines (pH 4 to 9), most sulfur is present as H₂S or HS⁻. Loss of H₂S during boiling will reduce H⁺ concentrations and cause additional sulfide precipitation.

The precipitation of sulfides from geothermal plant fluids may be illustrated by the following reactions given for Cu₂S (Chalcocite) (Jackson and Hill, 1976):



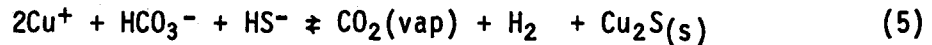
These are reactions by which the activity of S²⁻ can be reduced through conversion into other species, enhancing the solubility of Cu₂S.

The critical reaction for chalcocite is the precipitation equilibrium reaction:



However other processes affect the activities of Cu⁺ and S²⁻ and determine whether enough are present to exceed the ion product and precipitate sulfide scale in a silica matrix. These processes include CO₂ removal and chloride

complexing:



Reactions such as (5), where boiling or pressure release causes formation of CO_2 gas increasing the pH, could also encourage sulfide precipitation (Jackson and Hill, 1976). The presence of Cl^- ions in the brine may cause the formation of chloride complexes (6) and thus reduce the amount of Cu_2S that precipitates.

Although sulfide rich scales are known in surface installations in the Salton Sea geothermal field (Skinner, et al., 1967) plugging of injection wells by sulfides has not yet been reported as a problem. However it could be a contributory factor to silica cementation and plugging.

3.6.2 Other Possible Scaling Agents

Hydroxide, silicate, and fluoride precipitates are also possible from geothermal waters undergoing injection. Although these are of minor importance they are included here for completeness. An exception is iron hydroxide, a corrosion product, which has been observed when spent hydrothermal brines, contaminated with atmospheric oxygen, reacted with steel piping and casing, in the hypersaline brines of the Salton Sea geothermal field of California. It is not known if these products are a problem in injection wells, however corrosion of casings and liners is an acute problem in fields which produce hypersaline brines (Shannon, 1975).

3.7 COMPUTATIONAL APPROACHES

A widely used approach used in geochemistry to predict the outcome of water/rock reactions is theoretical modeling. This approach has had great success in predicting or explaining the stability (or non-stability) or mineral phases under wide ranges of pressure, temperature and fluid chemistry. Geochemical models use principles of thermodynamics to calculate the series of reactions which occur as a rock/water system proceeds to equilibrium. These computer codes can calculate the final composition of a solution after dissolution and precipitation of a series of minerals has run to completion, and calculate the final mineral assemblage in equilibrium at given conditions. Some of these codes also calculate reaction paths, as reactions proceed, by a detailed sequence of precipitations or dissolutions of solid phases. One of the most successful of these codes is EQ3/EQ6 (Wolery, 1979).

Using such codes we can calculate the masses of minerals which would be dissolved or precipitated if fluids of known composition are injected into aquifer under known conditions (Kindle et al., 1984; Henley et al., 1984; Miller et al., 1977). This kind of information may be useful in predicting potential plugging of injection wells, in that we can calculate what minerals will precipitate. However such geochemical modeling does not address the possible physical changes in the system, such as reduction in porosity and permeability due to mineral precipitation.

However recently mathematical models of plugging of porous media have been developed. For example, Itoi, et al., 1985 have developed a quantitative model

for silica deposition in a porous medium. The model takes into consideration equations of fluid flow, silica concentration and silica deposition, and obtained a reasonable match for calculated and observed flow rates.

An example of the computational approach to predicting scaling potential of calcite and anhydrite in wells in the Philippines has also recently appeared (Cope et al., 1985).

3.8 CONTROL OF SCALING AND PLUGGING

3.8.1 Introduction

As was indicated in section 2.7, above, the treatment of spent brine prior to disposal is by no means universally necessary. This may come about because of a particularly favorable brine chemistry or from the deliberate choice of a process system which minimizes the problem. However, in many cases, brine treatment before injection is essential to prevent blockage of the injection wells. Control of scaling and plugging is dealt with in review papers by Kindle et al. (1984); Kindle, (1984); Weres and Apps (1982); and Vetter and Crichlow, 1979.

Current and future possible practices of injection can be classified as follows (after Kindle, 1984, p. 9):

- a) immediate injection with no treatment;
- b) injection after aging the brine;
- c) maintaining temperature for silica control and CO₂ pressure for calcite control;
- d) inhibiting silica precipitation by acidifying;

- e) flocculating silica by raising the pH by adding lime;
- f) use of a calcite scale inhibitor and maintaining high temperature for silica control;
- g) using a recycled sludge to seed precipitation of silica.

Examples of these approaches are cited in section 4.0 of this report.

As can be seen from the above, these strategies can be further divided into (i) avoiding precipitation, (ii) controlling precipitation to minimize its effects, and (iii) separating out the particulates before injection.

3.8.2 Avoiding Precipitation

One frequently used strategy is to select a specific power cycle so that the precipitation of scales is reduced rather than aggravated. The effect of process parameters on scale formation is illustrated in Table 3.8A.

The simplest approach to avoiding silica precipitation is to design the plant so that silica concentration is kept below the saturation level for amorphous silica. In a binary plant this is achieved by controlling temperature drops, as at Heber, California. However this has the disadvantage of requiring a high injection temperature. In the case of a flashed steam plant, control over the degree of steam fractionation is required. Awerbuck et al. (1983) have proposed to dilute the residual brine after flashing by reheated steam condensate to avoid silica supersaturation. Dilution has yet to be tried on a commercial size plant. Some potential problems with adding make-up water include (1) its cost and availability, (2) possible inappropriate chemistry, e.g., presence of Ba^{++} , Ca^{++} or Sr^{++} sulfates and carbonates, (3) problems with

TABLE 3.8A

Effect of Process Parameters on Scale Formation

| Process Parameter | Effect on Potential Scale Species* | | | |
|--|------------------------------------|-------------------|----------|------------|
| | SiO ₂ | CaCO ₃ | Sulfides | Sulfates |
| Temperature Decrease (as in plant cycle) | + | - | + | -Ca +Ba |
| Temperature Increase (injection into hot aquifer) | - | + | - | +Ca -Ba |
| Boiling causing pH increase (CO ₂ fractionates into steam) | - (pH > 9) | + | + | + |
| Decrease pH (if acid is added) | - | - | - | - |
| Boiling causes salt concentration | + | - | - | - |

* + aggravates problem
 - alleviates problem

(After Kindle et al., 1984, Table 4.1)

the introduction of atmospheric oxygen leading to corrosion, (4) possible introduction of suspended solids, and (5) the disadvantage mixing causing cooling and supersaturation of silica and (6) the increased cooling may cause thermal break through within the injected aquifer from the injection zone to the production zone.

3.8.3 Aging the Brine

"Aging" of brine to convert dissolved silica to colloidal silica has been used in a number of cases (Weres and Apps, 1982). The desired goal is to reduce the rate of scaling in surface waste brine disposal systems, in cases where untreated brine caused cementation of hard scale in pipes and tanks. It was found that "aging" the brine in a retaining tank for one hour at Hatchobaru, Japan, allowed time for the conversion of dissolved silica into colloidal silica. This colloidal silica is a weakly cemented, floc-like scale which is easily removed before the brine is injected (see section 4.3.5).

3.8.4 Maintaining Pressure and Temperature

Carbonate scales can be controlled by keeping the pressure on solutions high enough so that CO_2 is kept in solution and CaCO_3 scale is avoided. Similarly silica scale can be avoided if the temperature is kept above that at which amorphous silica is saturated. This requires control of the lowest temperature prior to injection. This system is used, for example, in the Magma Power Co., binary geothermal plant, at East Mesa, in the Imperial Valley of California.

3.8.5 Acidifying the Brine

One way to slow down silica precipitation is to control the pH (Henley,

1983). Rates of silica polymerization decrease with decreasing pH. Acidification by hydrochloric acid addition has been attempted in the Salton Sea geothermal field on a pilot scale (Harrar et al., 1979). Grens and Owen (1977) reported that adding approximately 200 ppm of HCl to the brine could completely eliminate scaling at a cost of 1 to 2 mils/kwh (about 6% of the value of the electricity produced). However, tests with pumping this low pH fluid through sandstone cores lead to solution of calcite. The loosened matrix of the sandstone caused serious plugging. It would appear that after acidifying the pH would have to be increased once more. Evidently acidifying is an expensive and complicated technique (Weres and Apps, 1982).

3.8.6 Raising the pH by adding Lime

The addition of lime to geothermal effluent has been tested in several localities to remove silica and heavy metals such as arsenic (Kindle et al., 1984). Rothbaum and Anderton (1975) used this approach on a pilot scale at Wairakei, New Zealand, where their aim was to remove As (see section 2.4.1). The addition of 40 to 700 ppm of CaO to aged brine permitted the settling and removal of a flocculant precipitate of silica. However, this process is not yet used on a commercial scale.

3.8.7 Use of Scale Inhibitors, etc.

Scale inhibitors are used widely in industry to treat boiler water, etc.; inhibitors are substances added to the water, usually at the ppm level, to retard the growth of scale (Rosmalen, 1983). Coagulants and flocculants are substances that are added to the brine to remove precipitates or suspended

substances when formed. Table 3.8B (after Phillips, 1980) classifies additives used to control scales into (a) alterants, i.e., substances added to the brine to change its chemistry, e.g., HCl to lower pH; (b) inhibitors, i.e. substances added to the brine, usually at the ppm level, to retard growth of scale; and (c) coagulants and flocculants, i.e., substances that are added to the brine to remove precipitates or suspended solids.

The greatest success with inhibitors has been in the case of calcite for which inhibitors have proved effective at very low concentrations. Vetter and Campbell (1979), for example, performed CaCO_3 scale inhibition tests at a test facility of East Mesa, California, using Monsanto's Dequest 2060 Phosphonate inhibitor. They concluded that calcite scale could be prevented by addition of 1 μl of Dequest 2060 per liter of total flow at temperatures of 160°C . They noted that precise control of the concentrations of the inhibitor is necessary. At $< 1 \mu\text{l}$ per liter the inhibitor is not sufficiently active. At $> 7.5 \mu\text{l}$ per liter a pseudoscale of calcium phosphonate formed. These authors concluded that the inhibitor would add less than 0.3 mill/kWh to the cost of electricity, much more economical than acidification (see also Michels, 1983). Another highly successful use of calcite antiscalants has been applied at the Rotorua geothermal field in New Zealand (Brown and Gould, 1985).

Silica inhibitors have been tried at the Salton Sea field by Harrar (1982) at temperature ranges of from 90°C to 200°C . After testing a broad spectrum of inhibitors, no single chemical proved totally effective. Harrar (1982) recommends a mixture of acid to slow precipitation, an organic inhibitor for silica, and a carbonate scale inhibitor. It does not appear that silica, sulfide or sulfate inhibitors are yet used in commercial power plants.

TABLE 3.8B

Typical Treatment Methods to Prevent Scaling of Fresh and Spent
Geothermal and Other Brines.

| Treatment Method | Prevents or Controls |
|---|---|
| Inhibitors | |
| Lime slurry | calcite |
| Phosphonate + polymer | silica scale, mixed scales |
| Ethylene oxide polymer | silica, corrosion |
| Hydroxyethylcellulose | silica deposition, corrosion |
| Low molecular weight carboxylic acid | silica, corrosion |
| Amine | silica, corrosion |
| Sludge | silica, corrosion |
| Phosphoric acid | calcite |
| Polymeric carboxylic acid | calcite |
| Seeding with scale | calcite |
| EDTA | calcite |
| Polyacrylate | scales |
| Dispersant (highly carboxylated polymers) | calcite |
| Phosphate + sand | calcite, BaSO ₄ , CaSO ₄ |
| Solutions of amines, amides, carboxylic acids | scales, inhibits to 204.4°C (400°F) |
| Molybdate | scales |
| Alterants | |
| Hydrochloric acid | silica, calcite |
| Hydrogen peroxide, nitric acid | H ₂ S |
| Fresh water diluent | silica |
| Heavy diesel oil | silica, FeS, borate |
| CO ₂ pressure | calcite |
| Temperature | silica, calcite |
| Air, oxygen | H ₂ S, Mn ⁺⁺ , Fe ⁺⁺ |
| Chlorine | H ₂ S, biogrowth |
| Ion-exchange resin | dissolved metals, borate |
| Coagulants and Flocculants | |
| Anionic polyelectrolyte | flocculant |
| Slaked lime + hypochlorite | silica, arsenic |
| Aluminum sulfate, ferrous sulfate | suspended solids, colloids |
| Cellulose xanthate | heavy metals |
| Other | |
| Metallic core piping | scale, corrosion |
| Ultraviolet light | biogrowth |

(Phillips et al., 1980)

3.8.8 Crystallizers and Reactor Clarifiers

In this technology precipitation of scale is induced in a flash crystallizer/separator tank by adding a sludge containing seeds or crystal nuclei to promote crystallization and precipitation. Thus growth of solids is transferred from the walls of the tank and piping to the surface of the solid particles in the sludge. The mass of new sludge is removed from the bottom of the crystallizer, and steam is removed from the top, while the brine moves on to the next stage of flashing. The sludge passes to a reactor clarifier where sedimentation separates the solids from the liquids. The solids are disposed of in a solid waste dump. The liquids then go to an injection well. This technology has been used since July 1982 by Unocal, Inc. to supply steam to a 10 MWe plant in the Salton Sea geothermal field (Mass et al., 1983). Figure 3-8 is a schematic of the design of the 10 MWe flash-crystallizer and reactor-clarifier technology at the Salton Sea. These plants are discussed further in section 4.0.

3.9 SUMMARY OF BRINE TREATMENT

Kindle (1984) has conveniently summarized the brine treatment processes which could be used to protect injection systems. This summary is reproduced in Table 3-9. In 1986 this table can be brought up to date by (a) adding the Vulcan Plant to the roster of crystallizer-reactor clarifier technology (b) noting that the Brawley 10 MWe plant is decommissioned and the wells plugged, and (c) noting that the Heber Binary plant was completed in the fall of 1985.

Kindle (1984 p. 11-12) compares the particulate load for injection for two

SALTON SEA GEOTHERMAL PROJECT

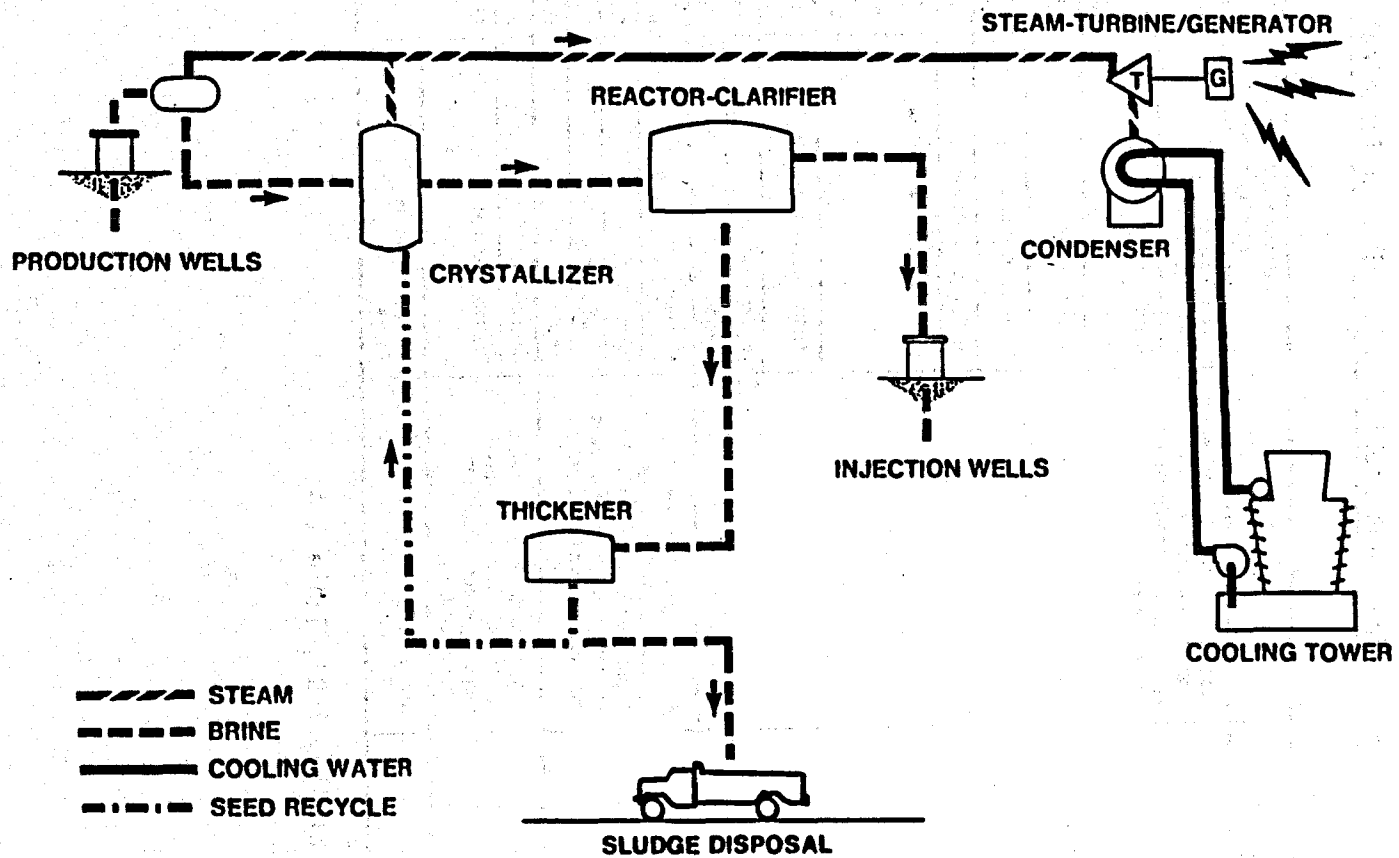


Figure 3.8. Brine handling at the Salton Sea 10 MWe pilot plant (courtesy Union Oil Geothermal Division).

TABLE 3-9

Brine Treatment Problems and Selected Technical Options

| Problem | Occurrence | Possible Solution or Component | Geothermal Experience |
|----------|---|---|--|
| Silica | Japan, El Salvador, Mexico, New Zealand, Hawaii, and Imperial Valley; most common problem for injection disposal. | Crystallizer-reactor clarifier technology | GLEF, Salton Sea 10-MWe. |
| | | Acidification | Tested in New Zealand, Salton Sea; now used at Brawley 10-MWe. |
| | | Add base/lime | Tested in New Zealand, Cerro Prieto, Los Azufres. |
| | | Chemical inhibitors | Tested at Salton Sea and Cerro Prieto. |
| | | Air flotation separator | Tested at Wairakei. |
| | | Ponding/aging-sedimentation | Japan (Hatchobaru), Hawaii, and Cerro Prieto (no injection); unsuccessfully tested in New Zealand and at Brawley 10-MWe plant. |
| | | Maintenance temperature | El Salvador, East Mesa, Heber (under construction). |
| | | High-rate settler | Tested at Los Azufres. |
| | | Dilution | Tested in Iceland. |
| Calcite | Turkey, Azores, East Mesa Desert Peak, and Brady Hot Springs. Mainly a production problem, although calcite crystals may nucleate silica particles. | Maintain pressure | East Mesa, Brady Hot Springs, Heber (under construction). |
| | | Inject CO ₂ | Desert Peak test. |
| | | Acidification | East Mesa tests. |
| | | Inhibitors | Roosevelt Hot Springs. |
| Sulfides | Salton Sea, Brawley, East Mesa, Desert Peak, and New Zealand; frequently in conjunction with other precipitates. | Acidification | Brawley 10-MWe plant. |
| | | Crystallizer-clarifier | Salton Sea 10-MWe plant and GLEF. |
| Sulfates | Salton Sea | Avoid incompatible waters | |

(From Kindle, 1984, Table 1.4)

different reservoirs -- a binary plant where precipitation avoidance is practiced by maintaining temperature and pressure, and a controlled precipitation plant with crystallizer, reactor clarifier and media filter technology i.e. a Heber type and a Salton Sea type of operation. At the plant inlet of the Heber-type plant the particle concentration would be 0.7 mg/l and at the injection well this would rise to 1.1 mg/l (because of some iron sulfite scale). The brine flowing to the reactor clarifier system might be carrying up to 20,000-mg/l of particulates. After going through the treatment process, at the injection well heat it might be carrying 10 to 20 mg/l of particulates, an order of magnitude more than in the case of the binary system. As both plants are running we are now in a position to get operational experience of the effects that these suspended loads will have on injectivity. It is possible that work over of the injection wells by back flushing or acid treatment will be necessary in the future in either case.

4.0 CASE HISTORIES OF INJECTION

4.1 INTRODUCTION

In this chapter a review is presented, of examples on a world-wide basis, of experience with injection of geothermal effluents. The aim is to highlight both the successes and the problems encountered. Tables 4.2 and 4.3 list the cases discussed drawing on the data of DiPippo (1985) and other sources cited in the text. Both to vapor-dominated systems, where most of the successes are to be found, and water-dominated systems, where most of the problems remain, will be treated.

4.2 VAPOR-DOMINATED SYSTEMS

4.2.1 The Geysers Geothermal Field, U.S.A.

The Geysers Geothermal Field in California, U.S.A., may be regarded as the prime representative of this type, although, as it has the largest installed capacity of any of the world's geothermal fields, it can scarcely be said to be typical. The principal contaminants in the condensate are ammonia and boron, both of which have concentrations exceeding the limits of the Regional Water Quality Board for surface discharge (Chasteen, 1975). From 1960 until 1969, while the installed capacity rose from 11 to 78 MWe, excess condensate was disposed of by surface discharge into a river, Big Sulfur Creek. Now the excess condensate from the 1,792 MWe installed electric capacity is all injected into the producing reservoir. For each additional 110 MWe unit, an additional 3,400

TABLE 4-2

Examples of Injection in Vapor-dominated Systems

| <u>Field Name</u> | <u>Location</u> | <u>Field Type</u> | <u>Installed Capacity</u> | <u>Remarks</u> | <u>Problems</u> |
|----------------------------|--------------------------------|---|---|---|--|
| 1 Geysers | Northern California, U.S.A. | Reservoir occurs in fractured greywacke. | 1,792 MWe with more than 200 wells supplying steam at ~180°C. | Injection has been standard since 1969, using gravity feed. Currently 20 x 10 ⁶ tonnes/yr. | Minor: Solids removal necessary to prevent plugging and deaera- tion to prevent corrosion. |
| 2 Larderello | Tuscany, Italy | Main reservoir in dolomite overlying a fractured metamorphic basement. | 384.7 MWe; 200 producing wells, out of 578 drilled, supply steam at 130 to 260°C, with ~ 5% CO ₂ . | Injection of 5.25 x 10 ⁶ tonnes/yr of excess condensate. Injection has been standard since 1981 using gravity feed. | See above |
| 3 Travale- Radiocondoli | Tuscany, Italy | Reservoir similar to Larderello | 48 MWe; 14 wells produce steam out of the 59 wells drilled to date. | Injection has been used since 1979 and was 10 ⁶ tonnes in 1984. | Injection may be re- ducing pressure drop, but break-through of cold water could occur. |

TABLE 4.3A

Examples of Injection in Water-dominated Systems

| <u>Field Name</u> | <u>Location</u> | <u>Field Type</u> | <u>Installed Capacity</u> | <u>Remarks</u> | <u>Problems</u> |
|-------------------|--------------------------------|--|---|---|--|
| Ahuachapán | Rio La Paz El Salvador | Reservoir in andesites and other volcanic rocks, average temperature 230°C Effluent salinity 20,000 ppm TDS | 95 MWe supplied by 17 wells with a flow rate of 17.4×10^6 tonnes/yr | Injection occurs for environmental reasons and for pressure maintenance. Up to 1983 22.5% of the total flow was injected i.e., 37.6×10^6 tonnes | Has partially mitigated pressure declines but unsuitable well citing caused cooling of some adjacent production wells. No chemical problems observed. New injection wells are planned. |
| Svartsengi | Rekjanes Peninsula, Iceland | Reservoir in Quaternary basalts, average temperatures 240°C and salinity 23,000 ppm TDS. | 8 MWe and 125 MW thermal for space heating, supplied by 12 wells. A total of 30×10^6 tonnes has been produced. | Injection is being attempted, after brine treatment by mixing with steam condensate. Current disposal is in a surface pond. | Silica plugging in the formation severely reduced injectivity of a disposal well. Acidification or other processing will be necessary. |
| Denizli-Kizildere | Western Anatolia, Turkey | An upper reservoir occurs in fractured limestones and a lower one in marbles, quartzites and schists. A sodium bicarbonate brine with 4,000 ppm TDS. | 20.6 MWe supplied from 6 wells out of 16 drilled. Flow rate 14×10^6 tonnes/yr | Currently waste fluid is sent to a river. Injection was attempted and but abandoned. It will be tried again. Should use scale inhibitors or try acidifying injection wells. | High boron content of the surface discharge. Carbonate scaling in production wells and surface installations. Loss of injectivity and low permeability of injection wells. |

TABLE 4.3A (continued)

Examples of Injection in Water-dominated Systems

| <u>Field Name</u> | <u>Location</u> | <u>Field Type</u> | <u>Installed Capacity</u> | <u>Remarks</u> | <u>Problems</u> |
|----------------------|-------------------------|--|--|--|---|
| Kakkonda | Iwate Prefecture, Japan | Reservoir produces from Miocene tuffs and sandstones overlain by late Tertiary and Quaternary andesites and pyroclastics. The brine is a chloride type with moderate salinity. | 50 MWe, supplied by 17 wells and using 19 injection wells disposing of a brine flow of 2.8 tonnes/yr. | Injection occurs at high pressure (540 kPa) and temperature (~140°C). This avoids scale build up. Production and injection wells are as close as 150 m. | Avoidance of loss of injectivity has been successful. Some cooling of the production zones is occurring. |
| Otake and Hatchobaru | Oita Prefecture, Japan | Production is from Tertiary tuffs and andesites, overlain by Quaternary andesites. The fluid is a low salinity (< 4,000 ppm) chloride brine. | Otake has 12.5 MWe with 14 production and 17 injection wells. Hatchobaru has 55 MWe with 20 production and 17 injection wells. | The two plants are 2 km apart and excess brine from Hatchobaru is injected at Otake. Control of scaling has been attempted by aging, acidification, and other strategies. Hydrofracture of plugged wells also seems promising. | Silica plugging causes loss of injectivity, averaging 20% a year. Some wells have been lost. Interferences with production zones are acute in some cases. |

TABLE 4.3A (continued)

Examples of Injection in Water-dominated Systems

| <u>Field Name</u> | <u>Location</u> | <u>Field Type</u> | <u>Installed Capacity</u> | <u>Remarks</u> | <u>Problems</u> |
|-------------------|------------------------------------|---|---|--|--|
| North Brawley | Imperial Valley, California U.S.A. | Reservoir is in late Tertiary deltaic sediments with temperatures exceeding 300°C. Hypersaline brine with 200,000 ppm TDS. | 10 MWe but decommissioned after 6 years of pilot plant operation. | The design was intended to keep silica in solution using high temperature of injection > 100°C. Injection wells needed workover and acid treatment. | Loss of injectivity of injection wells was a recurring problem. Other problems of corrosion and loss of production occurred. |
| Salton Sea | Imperial Valley, California U.S.A. | Reservoir is in late Tertiary deltaic sediments with temperatures reaching up to 365° at 2 km. Hypersaline brine with up to 250,000 ppm TDS | A 10 MWe plant has operated for four years with four or more production wells supplying 5.6 x 10 ⁶ tonnes/yr of fluid and injecting into two disposal wells. A 39 MWe plant began operation in 1985 and has available 12 production and 6 injection wells. | These two plants are the first commercial scale systems to use flash-crystallizer and reactor-clarifier technology to remove silica scale before injection. They appear to be successful and more plants of the same type are to be built. | There appear to have been no problems as yet with loss of injectivity due to plugging. However much of the data on operational experience is not freely available. |

m³/day must be injected (Kestin, 1980). Thus for the current 1,792 MWe capacity 55,400 m³/day of effluent are injected (approximately 20 x 10⁶ tonnes/year).

This long history of large scale injection has apparently been without major problems. However during the early history of injection some cooling of adjacent production wells was observed, due to intercommunication in the fractured greywacke reservoir. Therefore injection wells are now completed as far as possible from the production wells and where possible at greater depth (Chasteen, 1975; Schroeder, 1982).

Pretreatment of the condensate before injection is simple. The excess from the cooling tower basins is piped to ponds where solids are allowed to settle out to minimize plugging of the injection wells. Similarly deaerating vessels are installed on the injection lines to limit oxidation and corrosion of the pipelines and casing. As well as being deleterious to the plumbing, corrosion can also add to the load of suspended solids and so decrease the injectability⁴ of the effluent. High injection rates of 76 l/sec in wells from 720 to 2,500 m deep are sustainable with no back pressure at the well head. A minor problem of loss of injectivity due to plugging of the fractures in a well bore by elemental sulfur is easily overcome by shutting in the well and allowing it to heat up to above 114°C, the melting point of sulfur (Chasteen, 1975).

4.2.2 Larderello Geothermal Field, Italy

At the Larderello Geothermal Field, in the southwest part of the province of Tuscany, Italy, power production began 80 years ago. This dry-steam field now

⁴"injectability" - the ability of a fluid to be injected in a borehole.

has an explored area of 250 km² (Ferrara, et al., 1985). Because of this long history, more than 578 wells have been drilled there, of which only 200 are currently producing dry steam (at temperatures of 130-260°C) from a reservoir consisting of (i) an upper zone of marine shales and marls 100-300 m deep, with temperature of 120-170°C, (ii) a main production zone of dolomitic limestone 400-1,500 m deep, with temperatures of 200-270°C, and (iii) a basement of schist and phyllite more than 2,500 m deep, with temperatures of 300-400°C. The current installed electricity production of 384.7 MWe requires a production of 2,800 tonnes/hour.

Prior to 1981, surface discharge of the excess condensate was the standard practice. Since then all of the condensate from the power plants has been injected into the main reservoir at a rate of 600 m³/hr or 5.25 x 10⁶ tonnes/year (Ferrara, et al., 1985).

In addition to waste disposal, an important aim of this injection activity is an experiment to limit the strong decreases in pressure in the more exploited areas of the reservoir, where pressure now averages only 0.5-0.7 MPa. However temperature remains at about 250°C, so that injection into this zone could improve heat recovery (Bertrami, et al., 1985). During the period 1979-1982 injection rates as high as 10-50 kg/s were maintained in individual wells, into fractured zones at 400 to 600 m depth. More than 85% of the injected water was recovered but no thermal breakthrough occurred, nor was there any decrease in well head temperature in neighboring wells only 150 m away from the injection site. Because of this success, a large-scale injection program is planned using both deep and shallow wells, with the objective of increasing energy recovery (Bertrami, et al., 1985).

4.2.3 Travale-Radiocondoli Geothermal Field, Italy

The Travale-Radiocondoli Geothermal Field, 15 km southeast of Laderello, is also developed in Mesozoic carbonates of the Tuscan Series, overlying a basement of Paleozoic metasediments (DiFilippo, et al., 1985). Here an installed capacity of 48 MWe is serviced by 14 dry steam wells. Seven deeper wells required to supply steam to an additional 80 MWe are planned for 1985-95 (Ferrara, et al., 1985).

Exploitation began in 1952 in the southwest part of the field. However incursions of cold shallow waters from permeable rocks which crop out to the southwest, caused industrial exploitation to be abandoned in 1962. Power production from the newer field, to the northeast, began in 1972, using surface disposal of the excess condensate. ReInjection of excess condensate began in 1979 at a rate of 10^5 tonnes/year, increasing to 10^6 tonnes/year in 1984; it now amounts to 40% of the fluid extracted. According to DiFilippo et al., (1985) pressures in the exploited reservoir have decreased by about 4 MPa in the central part of the field, and ground subsidence of the order of 20-25 cm has been observed. The subsidence curves, based upon repeated leveling since 1973, suggest that in the northeastern part of the field reInjection of condensate has partly offset the pressure drop (DiFilippo, et al., 1985). However construction of a pipeline 40 km long to connect this area to Laderello is planned. Its installation will permit transport of all, or part, of the excess condensate waters from the Travale power plants for injection into disposal wells at Laderello (Ferrara, et al., 1985). Presumably there is concern that, in this permeable reservoir, a larger scale of injection could lead to break-through of the condensate to the production well.

4.3 WATER-DOMINATED SYSTEMS

4.3.1 The Ahuachapán Geothermal Field, El Salvador

The Ahuachapán Geothermal Field is in El Salvador, 15 km east of the La Paz River which forms the international border with Guatemala to the west. Although this site has already been discussed in connection with surface disposal (see section 2.2.2 above), there are three reasons for also discussing it here as an example of injection in a water-dominated geothermal system. Firstly, its geology, which consists of fractured andesites and other volcanic rocks, is typical of numerous geothermal fields throughout the world, particularly around the Pacific rim. Secondly, although most of the effluent is disposed of by a canal running to the ocean, the experience of injection gained there is more extensive than that at any other water-dominated field (Cuéllar, *et al.*, 1981; Campos, 1985). Furthermore, this experience has not been without problems. Thirdly, it is a prime example of minimizing problems by precipitation avoidance.

The Ahuachapán Geothermal Field lies within the south flank of the central Salvadorean median trough, and is associated with the northwest sector of the Cerro Languna Verde volcanic group, an extrusive complex which developed during Quaternary time. The field is developed beneath a faulted sequence of Pleistocene tuffs and lavas and volcanic agglomerates forming an essentially impermeable caprock. The reservoir formation consists of Ahuachapán andesite lavas with intercalations of pyroclastics forming a Pliocene-Pleistocene sequence up to 300 m thick. Permeability is fracture dominated, consisting

partly of columnar jointing and formation contacts, but largely of tectonic fractures (Cuéllar, et al., 1981). The permeability is therefore extremely variable and anisotropic. The reservoir brines are of sodium chloride type averaging 14,000 ppm TDS before flashing, and temperatures in the production zones typically average 230°C (see Table 1.4 for the brine chemistry).

The installed capacity of the field is 95 MWe (in three units rated 30, 30 and 35 MW, respectively) (DiPippo, 1985). These generating plants are supplied from 17 deep production wells in an area of only 0.71 km². These wells produce 1.45 x 10⁶ tonnes each month of geothermal fluid, or 17.4 x 10⁶ tonnes/year. When exploitation of the reservoir started in 1975, a total of 40 x 10⁶ tonnes of mass had been extracted. By the end of 1984 the total mass extracted was 167.4 x 10⁶ tonnes, out of which 37.6 x 10⁶ tonnes (22.5%) had been injected, by gravity drive, with the rest being disposed of by surface discharge. Injectivity in the disposal wells is maintained by keeping the temperature of the disposed fluid above 150°C to minimize polymerization of silica.

According to Vides-Ramos (1985) it is evident that the field has been over-exploited. A pressure drop from 34 kg/cm² in 1975 to 21.6 kg/cm² in 1984 has been experienced in the center of the field (3.47 MPa to 2.2 MPa). During the period September 1976 to August 1977 approximately 39% of the mass extracted was injected, from September 1977 until October 1978, 44% was injected and between October 1978 until September 1980 the fraction of the produced mass injected exceeded 30% (Vides-Ramos, 1985). The cumulative effect was to stabilize the reservoir pressure at about 28 kg/cm². The onset of operation of the third power unit of 35 MWe, in November 1980, required an increase in mass extraction

of 23%. This resulted in destabilizing the reservoir as the pressure decline rate of the reservoir increased from 1.37 kg/cm² per year to 2.91 kg/cm². The temperature of the waste water is approximately 150°C i.e. 70 to 80°C less than the mean reservoir temperature. From 1975 until 1984 the reduction of pressure in the reservoir has caused a vaporization of the liquid phase in the production zone. This has been accompanied by a temperature drop, which is related to pressure by the saturated vapor pressure curve, from 20 to 25°C in the production zone (Vides-Ramos, 1985).

Although injection has generally produced positive results as regards reservoir engineering, the two injection wells were badly situated with respect to the producing wells, which caused additional cooling of the reservoir. Consequently injection was stopped in 1983. It is now planned that a new injection program will begin to increase reservoir pressure with more efficient siting of the injection wells. During the injection of 37.6 x 10⁶ tonnes of effluent, without brine treatment, no change in the injectivity of the wells is reported (Vides-Ramos, 1985). Thus the problems of injection at Ahuachapán have been physical rather than chemical, provided injection temperatures are kept high.

4.3.2 Svartsengi, Iceland

In Iceland, up to 1984, 637 geothermal wells had been drilled for direct use purposes and 76 wells had been drilled for electrical and combined use. However out of a total of 713 wells, only one is listed as a disposal well in a compilation published in 1985 (Pálmason, 1985, Table 4). This is at Svartsengi, a

geothermal field in the Reykjanes Peninsula, at the southwest tip of Iceland. Although the volume of fluid injected is, as yet, not great, it exemplifies the problems encountered with injection in a high temperature, water-dominated, field with moderately high salinity, developed in basaltic terrain.

The Reykjanes Peninsula is a direct landward continuation of the Mid-Atlantic Ridge, and consists of Pleistocene and Holocene basalt flows and subglacial Pleistocene hyaloclastites, with very high permeability. The groundwater of the Peninsula consists of seawater under a thin lens of fresh water. The chloride content of geothermal reservoirs changes from that of seawater (analysis H8 in Table 1.4) in the Reykjanes geothermal field, to 70% of seawater at the Svartsengi field 15 km northeast. The fluid chemistry and petrology of the Svartsengi system has recently been discussed by Ragnarsdóttir et al. (1984). The reservoir temperatures are in the range 235° to 240°C and the produced fluids are of a composition equivalent to a mixture of 70% seawater and 30% rainwater, which has reacted with basalts. Potassium, calcium, boron, iron, silica, CO₂ and H₂S are enriched in the reservoir fluid relative to a simple groundwater/seawater mixture and sodium, magnesium, aluminum, fluoride and sulfate are depleted. That the sources and sinks of these elements are the basaltic rocks of the reservoir is shown by highly altered nature of the rocks in which zeolite and greenschist metamorphic facies minerals are abundant (Ragnarsdóttir et al., 1984).

Two single stage flash power plants of one MWe each were installed in 1978 and 1979, and a third of 6 MWe was added in 1980. These are supplied by 12 production wells ranging in depth from 239 m to 1,734 m which penetrate the

basaltic reservoir, in which rather uniform temperatures of 235° to 240°C are encountered in the production zones between 400-600 m depth. In addition to the 8 MWe of installed electrical capacity, the field also produces 125 MW of thermal power for district heating. The brine is used at a rate of 456 kg/S down to a base temperature of 35° to 45°C by a district heating company (Gudmundsson and Hauksson, 1985). Fluid production at Svartsengi has resulted in a drawdown of 100 m after a fluid production of 30×10^6 tonnes of fluid since inception of the plant. This rapid drawdown led to the development of a steam zone in the reservoir, consequently, tests of injection systems were initiated in 1982 (Gudmundsson and Hauksson, 1985).

Two phase flow from the production wells entering the power plant is separated at 5.5 bar-g pressure in a high pressure system and then passes to a low pressure barometric system where it flashed down to 75°C. The steam passes through the turbines driving the electrical generators and condenses on to plate heat exchangers to heat water for the district heating system. The brine passes to a disposal pond and percolates into the groundwater system.

This residual brine after steam fractionation contains 630 mg/l of SiO_2 and is highly supersaturated with silica which rapidly polymerizes and deposits in the surface equipment and pond. This brine must be treated before injection. The obvious approach is to lower the pH of the brine stream to slow down the polymerization and deposition reactions. Bench-scale experiments indicated that it needed to be lowered to pH 5.5 to prevent significant silica deposition (Gudmundsson and Hauksson, 1985). The approach taken is to combine the brine with the low pH steam condensate from the power plant.

In a test of this scheme in 1984 the condensate was mixed with the brine and injected into a disposal well at 50 kg/S for 77 days, by which time 1.86×10^5 tonnes of fluid had been injected. The geothermal brine produced from the production wells contains 440 mg/l of SiO_2 . After steam separation this rises to 630 mg/l and the pH rises to 7.8. The mixture of condensate and brine was injected at 80°C and had a SiO_2 concentration of 490 mg/l and a pH of 6.7. Experiments showed that the silica concentration of this mixture remained constant for longer than the one hour, more than enough time for the mixture to move from the mixing tank to the reservoir (Gudmundsson and Hauksson, 1985).

During the test, the water level in the disposal well rose from 300 m to 180 m depth and there was a marked loss of injectivity. A caliper survey indicated no measurable deposition in the bore of the disposal well so that the loss of injectivity appears to have occurred due to silica deposition in the formation. When silica-free water was injected, most of the lost injectivity was regained. It is concluded therefore that use of condensate from the turbines by itself is inadequate to preserve injectivity and that some acid will have to be added (Gudmundsson and Hauksson, 1985). Another strategy might be to use coagulants to leave the silica behind in the holding pond. However this approach has the disadvantage of a lower injection temperature. The economics of flash-crystallizers and reactor-clarifiers might also be investigated.

4.3.3 Denizli-Kizildere, Turkey

Practices at this geothermal field have already been discussed under the heading of "surface discharge" (see section 2.2.3). To discuss it again as a

"Case History of Injection" may seem inappropriate as injection is not currently practiced there. However it is included here as an example of a case where injection is clearly desirable but is prevented from being implemented by chemical problems. It represents a class of water-dominated geothermal fields developed in calcareous sediments, where carbonate scaling is acute.

The Kizildere geothermal field is in the Denizli Province of south-western Turkey, north of the Menderes River. It lies in the Büyük Menderes graben, an active orogenic belt dominated by block faulting. A major fault across the northern part of the field separates crystalline basement to the north from Miocene-Pliocene sedimentary strata to the south. These sediments are broken into a series of horsts and grabens by block faulting. The geology of the field consists of a basement of gneisses, schists and metasediments overlain by Pliocene sediments of sandstones, conglomerates, claystones, overlain by limestones, marls and siltstones, which in turn are overlain by poorly consolidated conglomerates, sandstones and claystones. The stratigraphy and structure is reminiscent of the Laderello field discussed above, (section 4.2.2) but lacks volcanic rocks. However the field is water-dominated, apart from shallow fumarolic activity at high elevations (Şimşek, 1985).

The installed capacity is currently 20.6 MWe which is supplied with 1,600 tonnes/hr of geothermal fluid from 6 of the 16 wells drilled to depths of between 370 and 1,241 m deep, which produce from two reservoirs. The shallower reservoir is developed in fractured limestones at a depth of 500 to 600 m, where temperatures of 170° to 200°C are encountered. The deeper reservoir has been penetrated in wells 660 to 1,241 m deep and produces from marbles, quartzites

and schists of the Menderes metamorphic group. These latter have high secondary porosity and permeability. The temperatures in this reservoir vary from 170° to 212°C. The brine in the Kizildere system is of sodium bicarbonate type with 4,000 to 5,000 ppm TDS, high in sulfate, low in chloride, and containing relatively high fluoride, boron and ammonia (Table 1.4). The two reservoirs produce fluids which are chemically similar, indicating a common origin. They are characterized by unusually high carbon dioxide content, up to 1.6% of the total well discharges (Şimşek, 1985; Ellis and Mahon, 1977).

There are two problems which result from the peculiarities of this chemistry. The problem of wastewater disposal of water containing 30 ppm of boron has already been referred to above (section 2.3.3). The high gas content of this system presents a second set of problems. The noncondensable gases comprise about 10 to 22% by weight of the steam at the separator pressure of 4 kg cm⁻²g. These gases consist of 96 to 99% CO₂ and 100 to 200 ppm of H₂S. The high CO₂ content causes precipitation of calcite, magnesite, and strontianite in the boiling zone of the production wells and in the surface installations. Scaling in the production facilities has been minimized by keeping the well head pressures above 15 kg cm⁻²g and by mechanical cleaning. The production wells are worked over every six months. Experiments are going on to use inhibitors or to reduce scale by injecting carbon dioxide below the bubbling point in the production wells (Şimşek, 1985).

As long ago as 1977, injection of the geothermal effluent was attempted. The aim was to maintain pressure in the reservoir and to limit contamination of the Büyük Menderes River. However these attempts were abandoned because of low

capacity and loss of injectivity in the upper reservoir. A new round of injection experiments is now planned (Şimşek, 1985). This would appear to be a good candidate for experiments with calcite scale inhibitors and acidification and backflushing of injection wells

4.3.4 Japan's Injection Experience

Of the countries with major investments in geothermal power Japan's injection experience is the most diverse if not the most extensive (Horne, 1982b). In January 1985 there was a total of 215 MWe of installed geothermal electric power, representing installations in nine different geothermal fields. A compilation of wells drilled to support this power production lists a total of 86 production wells and 73 injection wells. Surface disposal is used in only three fields, at Matsukawa (22 MWe), Suginoi (3 MWe) and Kirishima Kakusai (0.1 MWe) (Mori, 1985). In the remaining 6 plants the injection experience has had mixed results.

Injection is apparently working successfully in Mori (50 MWe, 6 production and 11 injection wells) but there is evidence for thermal interference at Otake (12.5 MWe, 14 production and 16 injection wells), Hatchobaru (55 MWe, 20 production and 17 injection wells), Onuma (10 MWe, 5 production and 6 injection wells), and Kakkonda (50 MWe, 17 production and 19 injection wells). In many cases injected fluids move through highly permeable fractures in the reservoir, which could lead to enthalpy declines from the production zones. On the other hand, such hydraulic interference can be beneficial in providing pressure support (Horne, 1982b).

Loss of injection capability is a problem at Otake and Hatchobaru, but has been avoided or minimized, by the choice of a high pressure injection system at Kakkonda. These three sites will be discussed therefore as illustrative of methods of dealing with chemical problems of injection.

4.3.5 Kakkonda, Japan

The Kakkonda geothermal power plant is situated in Takinoue geothermal field, Iwate Prefecture, in the vicinity of the Hatchimontai National Park, Hokkaido. A 50 MWe power station has been operating there since 1978 in an environmentally sensitive setting. The plant is supplied from 17 production wells 887 to 1,600 m deep and discharges waste to 19 injection wells 521 to 1,600 m deep. A second power plant is under development (Mori, 1985). Injection wells and production wells are interspersed, with injection generally occurring at shallower levels than production (Horne, 1982b).

The injection program at Kakkonda is unusual in that the effluent is injected at separator pressure (539 kPa) rather than at atmospheric pressure and injection occurs at very large flow rates (3,160 tonnes/hr of brine disposal for 636 tonnes/hr of steam production). This represents a "worst case" in terms of hydraulic break-through as injection wells are close to production wells, injection pressure is high and very large volumes of fluid are injected. The result has been a decline in enthalpy leading to a reduction in output to 40 MWe by August 1980 (Horne, 1982b).

However this extensive injection program has not led to loss of injectivity in the disposal wells. Certainly precipitation of silica is minimized by the

high injection pressure (~ 540 kPa) and temperature ($\sim 100^\circ\text{C}$). Thus the strategy of exploitation at Kakkonda has avoided scaling problems by process design, albeit with a penalty in overall thermal efficiency.

4.3.6 Otake and Hatchobaru, Japan

The Otake power station of 12.5 MWe has operated since 1967 and is located in Kokonoecho, Oita Prefecture, Kyshu Island. It lies 2 km north of the adjacent Hatchobaru field, which has an installed capacity of 55 MWe and has operated since 1977. These geothermal fields are situated at the southern margin of the east-west trending Aso-Beppu depression. In both fields the geological sequence consist of a basement of granitic and metamorphic rocks overlain by Tertiary tuffs and volcanic agglomerates, pyroxene andesites and tuff breccias and Quaternary hornblende andesites (Yoshida *et al.*, 1985; Inoue and Shimada, 1985). The reservoir is primarily developed in the pyroxene andesites and there is no production from the crystalline basement. The geothermal brine is primarily produced from a shallow reservoir between 250 and 500 m at Otake, with temperatures about 200°C and is a typical sodium chloride brine with 3,500 ppm TDS and 668 ppm of SiO_2 .

When the Otake plant started operations in 1967 surface discharge was used for disposal in a pond 4 km away. A year later silica scale 30-40 mm thick had accumulated in the 35 cm diameter pipeline used. Because of the clogging in these surface installations the production was scaled back temporarily to 8.5 MWe in 1968 and a system of aging in holding ponds was resorted to. In 1972

because of environmental concerns with arsenic, injection was initiated (Inoue and Shimada, 1985).

The Hatchobaru plant taps a deeper reservoir at up to 1,000 m depth, with temperatures of 230°C. The brine produced is also a sodium chloride brine with up to 9,000 ppm TDS and 890 ppm SiO₂. It was the first double flash geothermal plant in the world and began operations in 1977, with an output of 23 MWe which rose to 55 MWe only in 1980. Injection wells and production wells were arranged side by side at similar depths as no other suitable permeable horizon was available.

Interferences between injection and production wells were noted in both the Otake and Hatchobaru. At Otake injection initially caused a rise in productivity until 1975 when thermal break-through occurred sufficient to cause one production well to fail. In 1979-80 new wells had to be drilled. These problems were even more acute at Hatchobaru so that it was necessary to export 175 tonnes/hr out of the 645 tonnes/hr produced to Otake for injection (Horne, 1982b).

The declining enthalpy of the production zones has also been accompanied by chemical changes in these reservoirs due to injection. Total dissolved solids have in some cases increased markedly and there are many indications of chemical interference (Inoue and Shimada, 1985).

Another observable change has been a large reduction in injectivity of the disposal wells. For example, the well HR18 at Hatchobaru had its injectivity decline from 350 tonnes/hr in 1982 to 200 tonnes/hr in 1984. A typical loss of injectivity approaches 20% per year. When injection is halted and then resumed

the injection capacity is not restored. Blockage of the surface plumbing by silica scale is also a serious problem. It is concluded therefore that loss of injectivity is due to silica scaling (Inoue and Shimada, 1985).

Remedial measures in these fields have only been partly successful. New injection wells have been sited in locations to minimize hydraulic interference with production wells but this strategy is limited by the hydrology of the system. In both fields various methods to prevent or remove silica deposits have been attempted with limited success. These include: (i) Use of a retaining tank to age the brine for one hour. The effectiveness of this approach depends upon the temperature, pH and SiO_2 of the brine involved. (ii) It was found that exposure to air accelerated silica scaling and so the surface installations were redesigned to exclude air. (iii) Another approach was to site injection wells to inject into parts of the system with acid altered rocks or acidic groundwater. In practice, injectivity of a well in such a location did not sensibly decline in use. (iv) The strategy of injecting at high temperatures was abandoned because of the penalty of reduced steam flow. In both Otake and Hatchobaru injection occurs at 95°C and atmospheric pressure. (v) pH control by adding mineral acid was abandoned because of corrosion of surface installations and casings and possible environmental concerns (Inoue and Shimada, 1985).

Studies are underway to find acceptable solutions to this problem. They fall into two classes, chemical and mechanical. Nishiyama et al. (1985) have carried out basic studies of rock/water interaction using Hatchobaru and Otake brines in batch-type autoclaves, and in simulated injection tests. Possible

countermeasures suggested by these authors include: (1) siting injection wells in fracture zones, (2) injection into high temperature zones, (3) choosing a process cycle which keeps injection temperatures as high as possible, and (4) acidifying the brine, or injecting into acidic alteration zones. A possible method of lowering the pH is to utilize the exhaust gases of the Hatchobaru plant, where the steam contains up to 0.6% of non-condensate gases. A change in the process cycle to use a non-flashing or binary cycle would be an expensive option (Nishiyama et al., 1985).

Mechanical approaches to the problem have also been attempted. Simple hydraulic fracturing without proppants has been used to restore injectivity in the wells HR13 and HR14 at Hatchobaru. The wells were pressurized at 20 to 30 kg cm⁻² by pumping, which induced hydrofractures. In the case of well HR13 the injection capacity increased from 5.6 tonnes/hr to over 100 tonnes/hr after fracturing and continued at 40 tonnes/hr for 4 months. Capacity of well HR14 increased from 4 tonnes/hr to 65 tonnes/hr after fracturing, but then declined to 16 tonnes/hr over the next 3 months (Inoue and Shimada, 1985). The experiments of Nishiyama et al. (1985) indicated that in a flow-through experiment using five cylinders packed with rock fragments in series, using Hatchobaru brine with a high saturation ratio, silica scale was concentrated in the upper part of the first cylinder, regardless of the grain size of the packing materials. If this experience is applicable to the reservoir, it would imply that most scaling occurs at the rock/water interface immediately adjacent to the well bore. This kind of "skin damage" would be amenable to treatment by hydrofracturing using a proppant to hold open the fractures. This would permit

the silica saturated brine to penetrate deeper into the reservoir and encounter progressively larger volumes of hot rock.

4.3.7 Hypersaline Fields in California, U.S.A.

The hypersaline geothermal fields of the Imperial Valley of California, U.S.A. present a special challenge in the area of brine handling and injection. However there are currently two power plants operating in the Salton Sea field, the Southern California Edison plant of 10 MWe, and the Magma Power Co., Vulcan Plant of 34.5 MWe. A third plant of 10 MWe recently ceased operations in the North Brawley field.

The Imperial Valley comprises the northern part of the Salton Trough, a structural depression forming the landward continuation of the Gulf of California. This basin is bordered by granitic and crystalline metamorphic rocks of Mesozoic age, and is partially filled with late Tertiary to Quaternary deltaic sediments deposited by the Colorado River. Quaternary volcanoes have been emplaced into these sediments at Cerro Prieto, in Mexico, and at the southern end of the Salton Sea in California. These locations are also the sites of high temperature geothermal fields (Elders et al., 1972, Elders and Cohen, 1984). However, within the trough, other high temperature geothermal fields, such as the North Brawley field, are not associated with surface manifestations. The North Brawley field and the Salton Sea field have in common: (i) temperatures exceeding 300° at only 2 km depth and reaching 350° at 3 km, and (ii) extremely high salinities, in the 20 to 25% by weight range of total dissolved solids (Table 1.4).

Development of the geothermal resources of the Salton Sea field was attempted in the 1960's but abandoned due to the problems of scaling and corrosion. By the mid 1970's some twenty production wells with depths of from 1 to 2 km had been drilled and a test facility was operated in order to gain experience of brine handling and injection using flash-crystallizer and reactor-clarifier technology (San Diego Gas and Electric, Co., 1980; Quong, 1976).

Meanwhile the Southern California Edison Co., constructed a simpler system on the North Brawley field with the steam gathering system operated by Unocal Geothermal Co., using six production wells and three injection wells.

This 10 MWe single-flash plant at North Brawley ran from 1980 until early 1986 when it was decommissioned. This plant was not entirely satisfactory from an operational viewpoint as it had an overall capacity factor of only 35% (DiPippo, 1985). This system relied on brine handling techniques requiring maintaining dissolved solids in solution. The brine chemistry of this field is similar to that of the Salton Sea field (Table 1.4), being only slightly less saline. Disposal of SiO_2 saturated brines into injection wells in this field caused loss of injection capability. It was concluded that most of this occurred not in the borehole itself, but by particle invasion and subsequent plugging of the sand matrix along with precipitation of SiO_2 within the matrix. Significant damage occurred within 5 cm and 60 cm of the well bore due to plugging and precipitation. Acid stimulation was resorted to in order to restore injectivity (Kindle, *et al.*, 1984, p. 8.7).

In contrast considerably better performance was experienced in the Salton Sea geothermal field where a two stage flash plant of 10 MWe has been operated

by the same two organizations since July 1982 (Figure 3.8). The plant has a lifetime on-line factor of about 85% and a capacity factor of about 75% (DiPippo, 1985). Utilizing lessons learned at Brawley, an elaborate brine handling facility was installed (Elders, 1984). Mixtures of brine and steam from the production wells are allowed to flash in a high pressure separator (Figure 3.8). The steam goes to the high pressure side of the turbine after passing through a scrubber and demister. The brine from the separator is super-saturated with silica, carbonates and sulfides. To control scaling the brine flows to flash-crystallizer where it flashes to steam a second time and is injected with seed crystals of scale and agitated so that the precipitate remains in suspension. From there it passes to a reactor-clarifier where the solids are removed as sludge and the clarifier brines go to the injection wells. After thickening the sludge, the solid waste is disposed of in a solid waste facility, apart from about 1% which is returned to the crystallizer for use as nucleants (Moss et al., 1982). Since December 1985 the Vulcan Power Plant, also in the Salton Sea field, has been producing 34.5 MWe net using the same technology for which the operator, Magma Power Company, holds patents. It operates from 12 production and six injection wells averaging 1.5 km deep. Unocal Geothermal Division, which supplies steam to the plant illustrated in Figure 3.8 now intends to develop a 50 MWe plant in the same part of the field using similar technology (personal communication, C. Otte, 1986). As yet information on the injectivity performance of the disposal wells in these systems has not been released, much of it is yet to be acquired.

5.0 EXECUTIVE SUMMARY

5.1 INTRODUCTION

The purpose of this report is to attempt problem definition of water/rock reactions associated with injection of spent brines from geothermal plants into aquifers. It is based primarily upon a literature survey rather than upon new laboratory or field investigations.

Geothermal plants require very high fluid rates of flow, for example, a 100 MWe power plant requires between 3 to 10×10^7 tonnes of steam/brine mixture each year. Injection of the liquid effluent from these plants is usually necessary either for environmental reasons or in order to maintain pressures in the reservoir. Flashing of brine to steam and cooling frequently cause the solutions to become saturated with various components, which can lead to formation of mineral scales in well bores and in the injected aquifers.

It is estimated on a world-wide basis, at the end of 1985 there were 188 geothermal electric plants operational, which required a combined flow of up to 3×10^9 tonnes a year of geothermal fluid, a large portion of which requires injection. Given the current growth rate of the industry, the installed capacity could double in five to eight years. It is estimated that approximately 10 to 20% of the total costs of installation and operation of a typical geothermal power station and bore field are consumed in disposal of the effluents.

5.2 CHEMISTRY OF GEOTHERMAL EFFLUENTS

Geothermal reservoirs contain an enormous diversity of chemical compositions, ranging from 1,000 ppm to 300,000 ppm of total dissolved solids, but

most commonly having less than 20,000 ppm TDS. Common types include sodium chloride brines, and mixed chloride-sulfate-bicarbonate brines, both usually with neutral to slightly acid pH. The common dissolved components are derived almost entirely by reactions between the fluids and common rock-forming minerals in subterranean aquifers, or by leaching of highly soluble components, such as evaporitic minerals.

A typical geothermal plant requires the disposal of several tonnes of saline water for each tonne of steam consumed. Many of the dissolved components are environmentally undesirable. These include elements such as arsenic and boron which can render water unfit for drinking or irrigation at concentrations as low as 0.05 mg/l and 0.75 mg/l respectively.

5.3 GEOTHERMAL EFFLUENT DISPOSAL PRACTICES

The strategies available for disposal of the effluents from geothermal power plants include: (1) direct discharge into surface waters, (2) ponding and surface evaporation, (3) treatment and surface discharge, (4) secondary use of effluents, (5) injection, (6) injection with pretreatment, and (7) injection after extraction of valuable mineral products. With few exceptions, the trend in various countries is to use injection as the method of disposal, primarily for environmental reasons. Only in situations of particularly benign water chemistry and a favorable environment, surface disposal possible. Thus injection is usually performed with reservoir engineering purposes as only a secondary aim.

Because of problems encountered with loss of injectivity in disposal wells in several geothermal fields, it is becoming increasingly common to pretreat the brine before injection. On the other hand, in many instances, deliberate choices are made to use processes which avoid scale formation rather than remedy it. An option which has been much discussed, but for which we have yet to gain operational experience, is extraction of valuable minerals before injection. Potentially valuable components include L, B, Mn, Zn, Sr, I₂, Fe, Pb, Br₂, CO₂, NH₃, Cu, Ni, etc. It has been suggested by some authors that potential earnings from dissolved minerals in geothermal brines could, in certain circumstances, exceed the earnings from power sales.

5.4 CHEMICAL AND PHYSICAL ASPECTS OF PLUGGING

5.4.1 Introduction

Although almost the whole periodic table of elements might be found in a geothermal brine, relatively few of the dissolved components cause problems with injection. The chief culprits forming precipitates are: (a) silica, (b) calcite and aragonite, (c) sulfates, (d) sulfides, and (e) iron hydroxides, etc. Other possible phases which might be formed from geothermal brines are either too soluble or have unsuitable kinetics to be a problem in the environment of injection. Equilibrium considerations can tell us what minerals are potentially able to form. Kinetic considerations explain which ones actually do form. However only field trials can tell us what effects the formation of these minerals will have on injectivity.

Many dissolved phases, notably silica, are less soluble at low temperatures than at high temperatures. Thus cooling is sufficient to cause solutions to become saturated with these minerals. However other phases, especially calcium carbonate and sulfate, are more soluble in hot water than in cold. In spite of this, they can be induced to precipitate by boiling. When boiling occurs CO_2 , H_2S , and H_2SO_4 , if present, fractionate from brine into the steam, which therefore becomes more acidic. The residual brine becomes more concentrated but also more basic and can become saturated in carbonate and sulfate. Thus even minerals with retrograde solubility may be induced to precipitate by boiling and loss of gases.

5.4.2 Silica Precipitation

In geothermal brines silica occurs as a monomer H_4SiO_4 (or $\text{Si}(\text{OH})_4$). If the brine becomes supersaturated with SiO_2 , due to cooling or boiling, the brine does not precipitate the stable form quartz but instead forms amorphous silica (which is more soluble than quartz at equilibrium). The kinetics of precipitation of SiO_2 are quite slow, being governed by polymerization/nucleation/growth phenomena. The rate of homogeneous nucleation of amorphous silica is strongly dependent on the saturation ratio, i.e. the ratio of silica concentration to the equilibrium concentration of amorphous silica. Silica is precipitated very easily when the brine is 25 to 50°C below the temperature of saturation of amorphous silica for a given concentration. Silica precipitation is most acute for fluids produced from reservoirs with a formation temperature greater than

240°C, which easily attain saturation ratios of two or more, if boiled and cooled.

Because precipitation of silica involves polymerization, nucleation and growth, there is a lag time or induction period between attaining supersaturation and precipitation. This lag time may be hours. Brines supersaturated with silica are often responsible for declines in injectivity of disposal wells. Flocculant precipitates tend to accumulate in pore spaces and small fractures. Plugging tends to be most acute right at the wellbore/rock interface.

5.4.3 Calcite Precipitation

Brines which were originally close to saturation with carbonates may reach supersaturation by decreases in pressure, boiling, CO₂ loss, etc., and begin to precipitate calcite. The rate of calcite precipitation after nucleation is essentially instantaneous.

5.4.4 Sulfate Precipitation

Phases such as anhydrite (CaSO₄) and barite (BaSO₄) are known to be sometimes responsible for declines in injectivity of disposal wells. Calcium sulfates have retrograde solubility like the carbonates. They may also be induced to precipitate by the destabilizing effect of boiling on brines.

5.4.5 Other Precipitates

Most sulfides have prograde solubility. Loss of H₂S during boiling will favor precipitation of sulfides just as in the case of the calcite. Other pre-

cipitates, such as hydroxides, silicates, and fluorides, are known in nature and may, in certain instances, be at least partly responsible for plugging of injection wells.

5.4.6 Computational Approaches

There are a number of computer codes available which can predict which minerals are stable in equilibrium at a given reservoir conditions and reservoir chemistry. Some of these codes have been developed to model plugging of porous media by mineral scales. Application of equilibrium thermodynamic models alone has proven to be inadequate to characterize plugging of injection wells, as kinetic factors, and reservoir parameters such as porosity and fracture apertures seem to be more important than the mineralogy of the reservoir per se.

5.5 CONTROL OF SCALING AND PLUGGING

Strategies for control fall naturally into two categories, avoidance of mineral precipitation, and remedial action when precipitation occurs. Avoiding precipitation can be achieved by selecting process parameters such as pressure and temperature, or by the use of various scale inhibitors, additives which retard precipitation. Scale inhibitors have proved particularly successful in controlling calcite scaling. As an example of controlling process parameters, we can cite the advantages of binary cycles where boiling is not necessary, so that CO_2 is kept in solution and hence CaCO_3 does not precipitate. The choice of process parameters however must also optimize the efficiency of power production. Whereas a higher injection temperature helps keep silica in solution, it

reduces power output. In the same vein, it is obviously advantageous to keep minerals with prograde solubility in solution by injecting into the hottest part of the reservoir. However this strategy may extract a penalty by reducing the enthalpy of the production zones. Silica precipitation can also be kept in check by reducing the pH of the injectate, by adding acid, or steam condensate and non-condensable gases. In some cases it is even possible to choose injection locations with acid alteration zones and acid groundwater.

Controlling precipitation is the preferred option where avoidance is uneconomic. For example, simple aging of brine in a holding tank may permit silica floc to settle out before injecting. A very promising technology, currently used in the Salton Sea geothermal field of California, is the use of crystallizer-separators and reactor-clarifiers to remove silica before injection. In this technology a sludge of silica nuclei is introduced into flash tanks where steam is separated for use in turbines. The sludge induces precipitation of silica which is kept in suspension until it can be removed in a reactor-clarifier and disposed of in a solid waste dump. The clarified brine is then injected. Cost comparisons show that, in favorable cases, this strategy is more economical than accepting the cost of working over plugged injection wells. Without question, as operating experience is gained, this technique will be refined and applied more widely.

5.6 CASE HISTORIES OF INJECTION

5.6.1 Vapor-dominated Systems

Vapor-dominated systems have many fewer problems associated with disposal

than in the case of water-dominated systems. Only about 20-40% of the mass of the produced geothermal steam remains as excess condensate and requires injection. Actual injection can be done by gravity feed. Furthermore the condensate is relatively free of dissolved solids which could cause plugging. Thus the story of injection in vapor-dominated fields is one of success as far as plugging is concerned. At the Geysers in California, U.S.A., approximately 20×10^6 tonnes/yr of condensate is injected without problems. At Laderello and at Travale-Radiocondoli in southwest Tuscany, Italy, apart from environmental considerations, an important reason for injection is pressure maintenance in the production zone and control of subsidence.

5.6.2 Water-dominated Systems

Injection of effluents from water-dominated systems takes place in a much more diverse range of conditions than those just discussed. Consequently problems encountered range from negligible to insurmountable. Injection goes on on a commercial scale in El Salvador, Japan, Philippines, and U.S.A., but there has been a myriad of field test and experiments in many locations.

To date, experience with injection for pressure maintenance has not been always worthwhile. Great care must be exercised to prevent premature thermal and chemical break-through. However there are many locations where, for various reasons, optimal siting of production and injection wells has not occurred. Usually this occurs because optimum locations were determined after the fact of drilling.

The field with the most extensive experience is Ahuachapán, El Salvador. By

the end of 1984 a total of 167.4×10^6 tonnes of fluid had been produced, most of which was discharged by canal to the ocean. However 37.6×10^6 tonnes (27.5%) had been injected. This is a prime example of using process parameters to avoid chemical problems of injection. Injectivity of the disposal wells is maintained by keeping the temperature of the disposed fluid above 150°C to minimize polymerization and precipitation of silica. Thus problems with injection at Ahuachapán have been physical (cooling of the reservoir) rather than chemical.

A much smaller scale operation at Svartsengi, Iceland, is offered as an example of plugging control by brine treatment. The Svartsengi plant is a combined electrical and direct use system currently using surface disposal of geothermal effluent. Because of pressure drops in the reservoir and environmental considerations, injection experiments are being performed. It was found necessary to lower the pH of the injected brine to prevent silica plugging of disposal wells. The approach taken was to mix the brine with steam condensate from the power plant. This was only partially successful.

The Kizildere power plant in western Anatolia, Turkey, represents a case where injection is highly desirable but has proved impossible, so far, because of the difficult brine chemistry. The brine in this reservoir is of the sodium bicarbonate type and has a high CO_2 content (1.6% of the total flow). The non-condensable gases comprise 10 to 22% of the steam fraction. Precipitation of carbonates in the production wells and surface installations is a pervasive problem. Scaling has been reduced by keeping wellhead pressures up to $15 \text{ kg cm}^{-2}\text{g}$ but it is still necessary to workover the wells every six months.

Injection has been a failure due to loss of injectivity by carbonate scaling.

In Japan injection has been routine in six different geothermal fields for some time. Three examples with different problems and different solutions are cited. At Kakkonda, in Iwate Prefecture, injectivity problems are solved by process control. Injection of 3,160 tonnes/hr of brine occurs at separator pressure and temperature, i.e. at ~ 540 kPa and ~ 100°C. This has avoided scaling problems, albeit with a penalty in overall thermal efficiency.

The Otake and Hatchobaru power plants are 2 km apart in Kokonoecho, Oita Prefecture. Both have had extensive injection experience with mixed results. There has been a history of declining enthalpy due to thermal break-through from injection to production wells. Large reductions in injectivity of the disposal wells, typically approaching 20% a year, have been experienced. This appears to be entirely due to silica scaling.

In contrast to the Kakkonda field injection occurs at atmospheric pressure, and 95°C so there is little help from process control. Mitigation of the problems has been attempted by: (1) aging the brine (impractical), (2) deaeration of the brine (necessary), (3) injection into acid-altered parts of the reservoir (only locally possible), (4) attempting higher temperatures for injection (impractical), (5) pH control by adding acids (impractical), (6) utilizing non-condensable gases to lower pH (pilot scale only), (7) hydrofracture of the plugged wells (seems promising). These two geothermal installations appear to be a wonderful large-scale laboratory to test of methods to control silica scale.

The hypersaline geothermal fields of the Imperial Valley of California,

U.S.A. represent a special challenge because of their high temperature, (> 300°C) and unusual chemistry (25% wt TDS). A 10 MWe pilot plant at North Brawley was designed to attempt to keep silica in solution by high temperature injection. However repeated workovers and acid stimulation of the injection wells were found necessary. This plant was abandoned after six years of operation during which it had only a capacity factor of only 35%, due to various problems, including loss of injectivity.

Currently two plants are utilizing similar brines in the Salton Sea geothermal field, employing the flash-crystallizer/reactor-clarifier technology. In these plants silica is precipitated in a controlled way and the solids removed before injection. This scheme seems to hold great promise although, as yet, long-term operational experience is still being acquired.

5.7 TOWARDS A PROBLEM DEFINITION

Compared to the complexity of water/rock reactions which occur in natural geothermal systems in the undisturbed state, only a handful of reactions are of importance in reducing injectivity of disposal wells. Although geothermal brines are diverse in their concentration and content, the most ubiquitous problem occurs from silica polymerization when brine is cooled or concentrated and destabilized by flashing to steam. Once formed in an injection system it is difficult to remove, even by acidification and backflushing.

Except in the special case of sodium bicarbonate brines, etc., calcite is more of a problem in production wells and surface installations than in injection wells. The same seems to be largely true for sulfates, sulfides and other

phases which can form mineral scales. Thus, reduced to simple terms, the definition of the problem reduces to understanding the behavior of injected silica-saturated brine, reacting with aquifer rocks. In this quite extensive survey of the literature, there seems to be hardly any significance attached to the actual mineralogy or chemistry of the injected formation. One small (and special) exception is at Hatchobaru where it was found to be advantageous to inject into zones containing acid alteration zones or acidic groundwater. Thus, reduced to even simpler terms, the definition of the problem of "water/rock reactions associated with (re)injection of spent brines from geothermal plants into aquifers," devolves into the realm of physics rather than chemistry. A large fracture aperture can offset an unfavorable chemistry; hydraulic fracturing can reopen blocked pathways to injection; and so on. Thus it is clear, that although we need to understand the chemistry better, we ignore the physics at our peril.

5.8 TOWARDS A DEFINITION OF SOLUTIONS

Avoidance of injectivity problems first requires recognition that there is a problem to avoid. During the development stage of a geothermal field it is therefore necessary that the team of power engineers and reservoir engineers interacts with a team of geochemists and chemical engineers to assess the potential for mineral scaling for different power production and borefield strategies. Along with the usual production and injection tests, there should be tests performed specifically on scaling and loss of injectivity. It should then be possible to select a process to optimize the economics of power production and effluent disposal jointly, by appropriate choices of well head temperatures

and pressures of disposal wells and their locations relative to the production wells. A wide range of choices is possible, ranging from binary cycles to flash-crystallizer/reactor-clarifiers. Do not wait to call in the geochemist until after the engineering is designed, constructed, and in trouble.

Meanwhile there is work for the geochemists. Bench scale experiments need to be carried out on the effect of precipitation of silica, carbonates, and sulfates on a variety of rock types, in order to relate progressive stages of precipitation with reductions in porosity and permeability. These data are needed to set up quantitative models of the process of injectivity reduction. These models in turn need to be tested and refined against actual field trials. When developed and validated the models can be used predictively, and to design and improve operational practices. One promising field method is the "injection-backflow" technique of testing geothermal wells, in which alternate injection and pumping out of injectate can test the effects of water/rock interactions on injection wells (see, for example, Wright, 1985).

Further work is necessary on scale inhibitors, especially for silica, for we have, as yet, not experienced with silica the success seen with carbonate scale inhibition. As well as laboratory studies, it is crucially important to have field trials of these scale inhibitors to acquire data to assess their practicality and economics. Consideration should also be given to simplifying and optimizing the promising crystallizer-clarifier technology and adapting it for use in other situations than the hypersaline systems to which it is being applied currently. Finally, it is crucially important to continue to monitor

injection practices on a worldwide scale, to collect engineering and economic data, and to benefit mutually from these collective experiences of success and failure.

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