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ECONOMIC IMPACT OF CORROSION AND SCALING PROBLEMS IN GEOTHERMAL ENERGY SYSTEMS

by

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SUMMARY

Corrosion and scaling problems have a significant impact on geothermal plant economics. A power plant must amortize the capital investment over a 20-year period and achieve satisfactory operating efficiency to achieve financial success.

Corrosion and scale incrustations have been encountered in all geothermal plants, and to various degrees, adversely affected plant life times and power output.

Using published data this report analyzes known geothermal corrosion and scaling phenomena for significant cost impacts on plant design and operation. It has been necessary to speculate about causes and mechanisms in order to estimate impacts on conceptual geothermal plants.

Silica is highly soluble in hot geothermal water and solubility decreases as water is cooled in a geothermal power plant. Calculations indicate as much as 30,000 tons/year could pass through a 100 MWe water cycle plant. The major cost impact will be on the reinjection well system where costs of 1 to 10 mills/kwhr of power produced could accrue to waste handling alone. On the other hand, steam cycle geothermal plants have a definite advantage in that significant silica problems will probably only occur in hot dry rock concepts, where steam above 250°C is produced. Calculation methods are given for estimating the required size and cost impact of a silica filtration plant and for sizing scrubbers.

The choice of materials is significantly affected by the pH of the geothermal water, temperature, chloride, and H_2S contents. Plant concepts which attempt to handle acid waters above 180°C will be forced to use

expensive corrosion resistant alloys or develop specialized materials. On the other hand, handling steam up to 500°C, and pH 9 water up to 180°C appears feasible using nominal cost steels, typical of today's geothermal plants.

A number of factors affecting plant or component availability have been identified. The most significant is a corrosion fatigue problem in geothermal turbines at the Geyser's geothermal plant which is presently reducing plant output by about 10%. This is equivalent to over $3 million per year in increased oil consumption to replace the power.

In the course of assessing the cost implications of corrosion and scaling problems, a number of areas of technological uncertainty were identified which should be considered in R&D planning in support of geothermal energy. Materials development with both laboratory and field testing will be necessary.

The economic analysis on which this report is based was done in support of an AEC Division of Applied Technology program to assess the factors affecting geothermal plant economics. The results of this report are to be used to develop computer models of overall plant economics, of which corrosion and scaling problems are only a part.

The translation of the economic analysis to the report which appears here, was done on AEC Special Studies Funds.

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INTRODUCTION

During the past three years awareness of an energy shortage has been growing; the crisis is now obvious. Studies of the energy demand vs. energy supply equation have repeatedly pointed out that the United States is still becoming less self-sufficient in energy and more dependent on imports of energy (even with population control and conservation). Recognition of the political and economic implications of this energy dependency has led to greatly expanded interest in developing U.S. energy sources. This interest is reflected in the need for increased research and development in a number of energy alternatives. Geothermal energy is one of these options.

Studies (Hickel 1972) already completed have shown geothermal energy has the potential to supply 132,000 MW of electrical power by 1985 and 395,000 MW by the year 2000. But if this is true, why is the utilization of geothermal energy in the U.S. presently limited to the Geysers field in California and a few uses of geothermal process heat? We believe part of the answer lies in the truism that a new technology will only displace an older technology if it can prove a superior benefit (not just equal benefit). Stated simply, no utility executive is going to invest millions of dollars in an unproved geothermal power plant, when he can buy electrical generating capacity by a proven technology from responsible vendors who will guarantee their product.

The beginnings of nuclear power are a clear example of this principle. It took government R&D support amounting to billions of dollars and years of deficits by major reactor vendors to penetrate a market dominated by proven fossil fuel plants. Today with prices of fossil fuels soaring (or even unavailable at any price), the lower fuel costs of nuclear plants are looking more and more attractive in spite of somewhat higher capital costs.

Geothermal plants are also capital intensive. The cost of a geothermal plant is primarily the capital and maintenance since the heat is free once you are equipped to make electricity from it. Up to now the less expensive fuel cost of fossil fuels, together with an unfamiliar geothermal technology, has inhibited use of hydrothermal steam and water.

We must emphasize the magnitude of the power generation problem in the United States in order to put the magnitude of the geothermal scaling and corrosion problem in perspective.

In late 1973 *Electric World* (Olmstedt 1973) in their 24th annual forecast of the electical industry listed the 1972 U.S. generating capability at 383,000 MW. They forecast this capacity will have to grow by 40,000 MW every year for the next few years, increasing to 62,000 MW/year by 1990 when total capacity will reach over 1,200,000 MW. In other words in the next 18 years we must build over twice as much generating capacity as we have in our total history. In considering where this capacity is to come from, *Electric World* did not even mention geothermal power as a source of this future generating capacity.

The Geysers geothermal plant has now become the world's largest geothermal system. It is expected to approach 400 MWe of capacity in 1974 and will grow at perhaps 100 MWe a year until the reservoir capacity is reached. Since Geysers is the only proven geothermal field in the U.S., and its growth represents only 0.25% of the required growth of the electric system, one begins to appreciate why *Electric World* didn't mention it. On must remember that today, utilities are routinely building fossil-fueled and nuclear power plants in the 1000 to 1200 MWe size range.

Even if the U.S. electrical growth pattern slows substantially it is still obvious that large scale generating plants are involved. Thus if geothermal power is to become a significant source of even 5% of the growing electrical market, one must consider new plant construction and operation of 20 "Geysers size" geothermal power plants of 100 MWe size or larger each year.

It has been shown (White, 1973) that steam geothermal fields like Geysers in California are very rare indeed. This combination of high temperature, water source, and rock permeability occurs so seldom that this type of geothermal power has no hope of making a significant impact. One must turn to utilization of hot water or hot dry rock resources (which are abundant), if the promise of geothermal power is to be realized.

Once we conclude it is necessary to develop the technology to exploit the heat in hot rock and hot water geothermal resources, we encounter a serious gap in our technology base. There is very limited experience with electricity generation using geothermal hot water and none using hot dry rock. These systems are also recognized to have the most serious scaling and corrosion problems. Just about every survey article on utilization of geothermal system acknowledges the problems of scaling and corrosion. A sampling of a few specific references to real geothermal power plants illustrates some of the problem areas:

- At Otake, Japan, plugging of a 14 inch line 2.5 miles long with silica. Line was used to dispose of water from bores. (Yangase 1970)
- At Wairakei, New Zealand, bore water is discharged to open drains to a river, "...but on the way it deposits a very large amount of silica..." Maintenance costs $15,000 year. (Koenig 1973)
- At Niland, California, "Market conditions and problems of corrosion, scaling, and waste disposal prevented commercial development of either electricity or a major chemical recovery works. ...Average well life was 2 years." (Koenig 1973)
- At Otake, Japan, "Limited life is predicted for the present wells because of scaling and fluctuations in pressure ... calcium carbonate scale requiring acidizing has been found in one well." (Koenig 1973)
- At Geysers, California, "The Hydrogen sulfide (H_2S) in the plant atmosphere has caused some problems with electrical equipment because of its corrosivity to copper alloys and silver." (Finney 1973)
- In the Hungarian Basin, "Since the water contains calcium carbonate it must be allowed to stand and thus precipitate within tanks rather than within the heating system." (Koenig 1973)
- At Taiwan, "Fluid pH has usually been less than 5.0 and as low as 2.0 causing problems of corrosion and disposal of residual fluid." (Koenig 1973)

- At Tekke Hamman, Turkey, "The well, ... in fact is inoperable because of calcite incrustation. Installation of a 10-20 MW generator utilizing a closed system heat exchanger is being considered ... reservoir fluid would be produced, utilized and reinjected under pressure, thus avoiding the separation of calcium carbonate from the fluid." (Koenig 1973)

A power plant must amortize the capital investment over a 20 to 30 year period. To achieve satisfactory operations costs the plant must generate electricity 60 to 80% of the time. Technical problems like those listed above jeopardize financial success. Investments of private capital will continue to be inhibited as long as plant life is not predictable.

Government sponsored research is needed to demonstrate that geothermal power using hot rock and hot water is feasible. This principle has been used before in synthetic rubber and nuclear power.

Today most of the practical geothermal power plant experience exists in foreign countries. For example, take the massive (1725 page) compendium of 198 papers to the "U.N. Symposium on Development and Utilization of Geothermal Resources" (Geothermics 1970). The United States contributed only about 8% of the pages to this symposium.

With most of the geothermal literature from foreign sources, compounded by long distance and language problems, the U.S. engineers can expect problems in getting needed data. This review is no exception. Little data has been published, and is often inconsistant. This review attempts to take that data published and analyze, and sometimes speculate, about the implications to future geothermal plant design.

CONCLUSIONS

This review focuses on some of the major scaling and corrosion problems in developing geothermal energy:

- Corrosion and Scaling

  Problems of scaling and corrosion are encountered in every geothermal power project and are a major cause of plant maintenance, repairs, and turbine downtime. Some geothermal ventures have had to be abandoned because of corrosion and/or scaling.

- Massive Silica Problem

  In a hot water type geothermal plant enormous quantities of silica will be brought to the surface; potentially 15,000 to 30,000 tons per year in a 100 MWe plant. If even a minor fraction deposits in the plant, plugging will occur. Fortunately, most goes out with the waste water, and most silica deposition occurs in the waste water system. Problems will be encountered in waste water reinjection.

- Turbine Scale

  Turbine scale has occurred in significant quantities whenever the steam contains moisture droplets with dissolved salts, or whenever the steam is significantly superheated. Use of water scrubbers is very effective in reducing scale formation, but this method degrades the energy recovery from superheated systems.

- Turbine Scale More Severe for High Temperature Systems.

  Silica carryover in steam is considerable and produces troublesome turbine scale in present geothermal plants. Silica transport increases with steam temperature and pressure. "Silica Separators" will be required for plants utilizing hot dry rock heat sources above 250°C. Calculations indicate over 80 tons of silica/year could be transported into the turbines in a 100 MWe plant at 300°C. The deposition rate is a small (but unknown) fraction of theoretical.

- Need to Control CO_2 Overpressure

  The strong dependence of calcite ($CaCO_3$) solubility on the carbon dioxide overpressure can cause geothermal bore plugging when boiling releases CO_2. Use of intermediate heat exchangers to avoid CO_2 gas loss may be necessary where calcite in the water is high.

- Need to Reinject Fluids

  Present geothermal plant practice of disposing of H_2S to the air and excess brines to rivers will be an untenable environmental problem. Successful reinjection of steam condensate at the Geysers geothermal plant in California does not mean disposal of high solid content brines by reinjection will be successful.

- Plugging of Reinjection Wells

  Suspended silica may plug reinjection wells. The retrograde solubility (decreasing solubility with increased temperature) of $CaCO_3$ and $CaSO_4$ will be of concern. Bicarbonate (HCO_3^-) and carbonate (CO_3^{--}) can be picked up from CO_2 in the air, and sulfate (SO_4^{--}) is the product of oxidation of H_2S by O_2. Use of cooling or retention ponds could lead to reinjection well plugging as fluids are reheated during reinjection.

- Wastewater Treatment and Reinjection May be Expensive

  It cannot be assumed that water recirculation in hot rock systems, or reinjection of waste brines will be economically feasible. Based on cost of reinjecting waste oil field brines, costs of 1 to 10 mills per kW-hr could accrue in waste handling alone in some geothermal electrical generating plants.

- Need for R&D on Rate of Scaling and Corrosion

  There is almost a complete lack of short time data on the rate that deposition problems will occur in real geothermal plants. Fluids will move through geothermal plants in minutes. However, most of the geochemical literature is oriented in geological time towards explanations of ore body formation.

- General Corrosion by H_2S

  Hydrogen sulfide has been a general corrosion and environmental problem. H_2S attacks copper and silver electrical equipment. Preventing H_2S release for environmental reasons will reduce this corrosion problem. Potential for hydrogen embrittlement due to H_2S must be considered in materials selection. Corrosion fatigue of turbine components continues to be a problem.

- Importance of Fluid pH on Corrosion

  The corrosion of iron-base alloys in geothermal waters is controlled by H^+ reduction, except where O_2 accidently leaks into the system. This means steels have acceptable corrosion rates in dry geothermal steam. However, carryover of 0.5 to 1% moisture in the steam and condensation can create very acid and corrosive conditions. For water handling parts of the plant, the fluid pH and temperature will be major factors in materials selection.

- Pitting and Stress Corrosion Cracking of Austenitic Stainless Steel

  The 300 Series stainless steels have been successfully used in condensate systems below 120°C where chlorides are low. Pitting failures and stress corrosion cracking are rapid where austenitic stainless steels have been tried in geothermal fluids containing chlorides.

- Other Materials

  Corrosion of aluminum, copper, nickel, titanium, and zirconium and their alloys are discussed. All have some promise. Where pitting can be controlled aluminum has been successfully used, especially in acid condensates and plant structural applications. Copper alloys have often failued due to susceptibility to H_2S and occasionall air leaks. The other alloys have seen little geothermal service.

- Lack of Geothermal Materials Data

  The available published corrosion literature is sparse. Based on general corrosion experience, major materials problems and unknowns exist for plant designs using geothermal water (not steam) above 300°F especially as the pH becomes more acid than pH 7. Considerable materials evaluation work and field tests will be needed.

Potential for Silica Deposition in a Geothermal Plant Using Hot Water Sources

Silica (SiO_2) is highly soluble in both water and pressurized steam. The solubility increases with temperature. There are several forms of silica (e.g., quartz, cristobalite, tridymite, amorphous (opal), and solubilities vary with form. (Holland 1967, Alexander et al.1954, Morey 1962).

A simple calculation illustrates why geothermal plants have silica problems:

Given: 100 MWe Geothermal Plant
Thermodynamic Efficiency - 10 kg steam/kW-hr
Reservoir Temperature - 250°C
20% of fluid flashed to steam at 140°C (50 psi)
Assume water in reservoir saturated with quartz
(which is the least soluble form of SiO_2)

Question:
What is the potential deposition rate of silica in the plant?

Steam production - 100,000 kW x 10 kg/kWhr = 10^6kg/hr = 2.2×10^6 lb/hr

Total water production = $\frac{10^6 \text{ kg/hr}}{0.2} = 5 \times 10^6$ kg/hr = 1.1×10^7 lb/hr

Total silica (quartz) removed from reservoir = $(1.1 \times 10^7)(5.5 \times 10^{-4}) = 6.05 \times 10^3$ lb/hr = 3 tons/hr

(Solubility at 250°C = 0.055%)

Silica (amorphous) soluble in flash water = $(1.1 \times 10^7)(0.8)(5.5 \times 10^{-4}) = 4.8 \times 10^3$ lb/hr
(80% flash water)
(Solubility at 140°C = 0.055%)

Precipitation Potential at flash Tank = $6.05 \times 10^3 - 4.8 \times 10^3$
= 1.25×10^3 = 0.6 tons/hr

Silica (amorphous) soluble in
wastewater if it cools to 100°C = $(1.1 \times 10^7)(0.8)(4.0 \times 10^{-4})$
(Solubility at 100°C = 0.04%) = 3.5×10^3 lb/hr

Precipitation Potential in Waste Line = $6.05 \times 10^3 - 3.5 \times 10^3$
= 2.6×10^3 lb/hr = 1.3 tons/hr

Amorphous silica is the most soluble, but metastable phase of SiO_2. If the above calculation is done for quartz deposition, the numbers rise to a precipitation potential of over 2 tons/hr.

The real plant situation must consider the rate processes affecting deposition of amorphous silica and the growth of crystalline forms of silica. Most of the silica remains in the wastewater. What the designer of a plant needs to know is:

> "Where will silica deposit and at what rate?"
>
> "What parameters of temperature, temperature drop, velocity, Reynolds number, deposition surface/fluid ratio, time, fluid chemistry, etc., increase or decrease the rate and by how much?"

If he knows this before designing the plant he can design around the problem or at least make provisions for silica removal.

The Japanese (Yangase 1970) found the first hour was critical and installed stirred tanks to allow precipitation to occur in order to prevent deposition in the exit pipe. There is almost no engineering data available on the rates of silica deposition. We reviewed several original papers on silica solubility to see what data on rate processes are available. Usually the existing data were taken in small (few hundred ml size) bombs. Equilibrium is generally obtained in a few hours at 200 to 300°C, but may take months or longer at room temperature.

Silica Solubility During Water Injection Into Granite

The above discussion concentrated on SiO_2 solubility in natural water reservoirs that had thousands of years to form. The injection of fresh water into fractured rock introduces additional complexities.

The freshly injected water will leach impurities from this freshly fractured rock as the water is heated. Since heat transfer through the rock to the water is slow, it is clear this newly injected water will remain in the ground for a few days (or weeks) before reappearing as steam. The impurities present in the pressurized steam will be largely determined by the impurity content in the water phase, and the steam/water distribution ratios. But what are these compositions? Clearly, the impurity compositions in the water could be quite different from natural geothermal reservoirs that have undergone hydrothermal alteration for thousands of years. It is obvious that the impurity composition will depend on rock composition. In Figure 1 the major mineral content of extrusive (upper row) and intrusive (lower row) rocks is diagrammed. On the basis that most western U.S. hot rock plutons are expected to be granite, we would expect granite to affect the composition of the steam and water.

From Figure 1 it can be seen that feldspars are the major mineral in granite followed by silica, and various ferromagnesian minerals. Thus we should expect the composition of the water and steam phases to be determined largely by the hydrothermal alteration of freshly exposed feldspar and quartz plus any highly leachable materials present. Ellis and Mahon (1964) found chlorides and boric acid were highly leached by hot water in their leaching studies of igeneous rock done in static bombs. Helgeson (1971) and Hemley and Jones (1964) have discussed many of the theoretical aspects of hydrothermal alterations of feldspar, illustrated by the hydrolysis of K-Feldspar:

K-Feldspar K mica

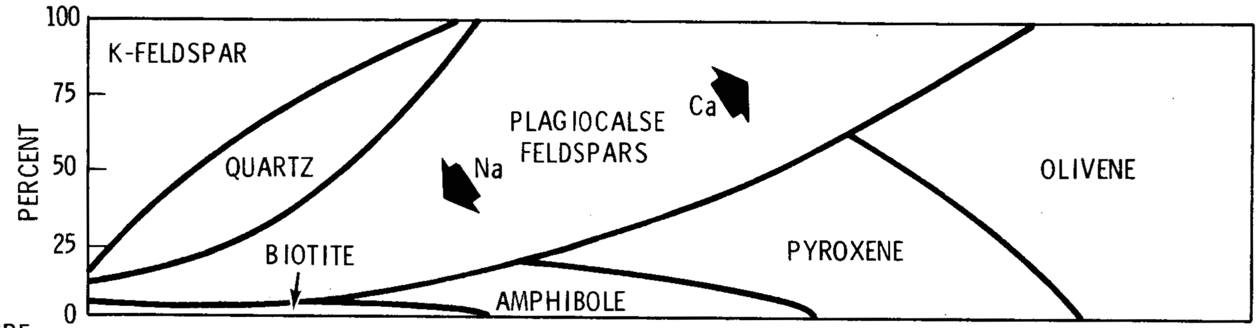
$$1.5\ \mathrm{K\,Al\,Si_3O_8} + \mathrm{H^+} \rightleftarrows 0.5\ \mathrm{K\,Al_3Si_3O_{10}(OH)_2} + 3\mathrm{SiO_2(aq)} + \mathrm{K^+} \quad (1)$$

K mica Kaolinite

$$\mathrm{K\,Al_3Si_3O_{10}(OH)_2} + 1.5\ \mathrm{H_2O} + \mathrm{H^+} \rightleftarrows 1.5\ \mathrm{Al_2Si_2O_5(OH)_4} + \mathrm{K^+} \quad (2)$$

Kaolinite Boehmite

$$\mathrm{Al_2Si_2O_5(OH)_4} \rightleftarrows 2\ \mathrm{AlO\ (OH)} + 2\mathrm{SiO_2(aq)} + \mathrm{H_2)} \quad (3)$$



ORIGIN	TEXTURE				
EXTRUSIVE	APHANITIC	RHYOLITE	ANDESITE	BASALT	DUNITE
INTRUSIVE	PHANERITIC	GRANITE	DIORITE	GABBRO	PERIDOTITE

FIGURE 1. Classification of Igneous Rocks

Similar reactions can be written for all potassium, sodium and calcium feldspars. The products of hydrolysis of granite will include K^+, Na^+, Ca^{++}, and SiO_2 (as $Si(OH)_4$). Both Hemley and Jones (1964) and Helgeson (1971) discuss the ratio of the cations K^+, Na^+, Ca^{++} to H^+, e.g., $\frac{a_{m^+}}{a_{H^+}}$ is critical to determining which mineral phase is stable and controlling a major source of SiO_2. Note also these reactions are pH dependent.

A second source of SiO_2 is direct solution from the quartz phase in granite:

$$\begin{tikzcd}
 & & \mathrm{SiO_2}\text{ (amorphous)} \\
\mathrm{SiO_2}\text{ (solid quartz)} \arrow[r] & \mathrm{SiO_2}\text{ (aq)} \arrow[ur] \arrow[r] \arrow[dr] & \mathrm{SiO_2}\text{ (cristobalite)} \\
 & & \mathrm{SiO_2}\text{ (quartz)}
\end{tikzcd}$$

The solubility of SiO_2 varies with its equilibrium solid phase. SiO_2 can remain supersaturated with respect to quartz for very long times. Ellis and Mahon (1964) found the SiO_2 concentration in their solutions was in between the solubility values for quartz and amorphous silica.

When hot water contacts granite, the water can pick up SiO_2 substantially in excess of equilibrium solubility because of inadequate time for equilibrium to occur in the redeposition step. If this water is moving, as in a geothermal plant, the deposition will take place some distance away from the original source. This has been observed in natural hydrothermal alteration of granite where veins "... are virtually glutted with Sio_2." (Holland 1967)

Helgeson (1971) discussed some of the kinetics of these processes. It is a very significant comment on the present state-of-the-art that he had only two experimental studies to draw actual data from; Wollast (1967) who worked at room temperature and one high temperature study (LaGache-1967) in a French journal. All the existing experimental data are at constant temperature and pressure. It is clear that a typical geothermal power plant, where wide temperature changes in short times occur, is a different system than has ever been studied before. We cannot assume SiO_2 in this power plant system will be in equilibrium with quartz. If the water is supersaturated with silica, we can expect the pressurized steam produced from the bores may contain more silica than would otherwise be predicted.

The SiO_2 content of the effluent steam can vary with temperature, pressure, and the $\frac{a_{m^+}}{a_{H^+}}$ ratio in the water. Fluorides, sulfides, chlorides and boric acid will be present depending on leaching rate and the ionization constants of HF, H_2S, HCl, and HBO_2, which also vary with temperature and pressure.

Control of Impurities in Effluent Steam by Controlling Injection Water Chemistry

The interrelationships of $\frac{a_{m^+}}{a_{H^+}}$, mineral stability, and silica content in the water, offer an interesting possibility of control of steam impurities by control of injected water chemistry. Note in the equation:

$$\text{Feldspar} + H^+ \rightleftarrows \text{Mica} + SiO_2 + K^+$$

that increasing K^+ or decreasing H^+ (more basic solution) should stabilize feldspar and reduce SiO_2 in solution. Experiments will have to investigate how effective this chemistry control is in reducing piping system deposits by reducing the impurity source rate in the steam.

Silica Deposition and Scaling in Turbines

Silica deposition on turbine blades is potentially very serious, because small deposits alter the vibration frequency of the blades leading to fatigue failures. More extensive scaling can change turbine efficiency.

Yoshida, et al. (1968) report operational experience on a 20 MW turbine at the Matsukawa geothermal station where turbine deposits, "... affected output rating seriously." The deposits were first noted when the turbine was overhauled after 50 days[!!] of operation. Approximately 40% of the scale was SiO_2 with $CaSO_4$, Na_2SO_4, Al_2O_3, MgO, $FeSO_4$, and FeS making up the remainder. They felt much of this material (especially water soluble compounds) was transported via the 1% moisture droplets in the steam.

They were working on better steam-water separators. Water droplets in the steam are also a major source of erosion. The water soluble salts can be washed off; however, insoluble deposits are more serious. They felt the SiO_2 was transported as dust particles.

It is well known SiO_2 is soluble in high temperature steam. Normal steam boiler practice is to carefully control silica in boiler feedwater. This control is much more difficult in a geothermal system where the feedwater is saturated with silica. Krikorian (1972) discusses silica transport relative to Plowshare nuclear geothermal power plants and concludes scrubbing the steam will be essential. The approximate equilibrium silica content (from Krikorian 1972) in the steam phase is:

T°C	$\sim SiO_2$ (ppm)
150	0.08
200	0.4
250	1
300	9
350	70

Using the previous data on a 100 MWe geothermal power plant, and 210-230 psi steam (200°C) typical of high pressure bores at Wairakei, New Zealand:

Steam production = 10^6 kg/hr

Silica in steam = $10^6 \text{ kg/hr} \times \frac{0.4}{10^6} = 0.4 \text{ kg/hr} = 0.9 \text{ lb/hr}$

In the utilization of hot dry rock this would rise to about 20 lb/hr for a 300°C system or about 175,000 lb/yr into the turbines (assuming 90% on-line time). Note that silica transport is a factor of 20 worse with a 100°C temperature rise.

Thus we encounter a trade-off. The thermodynamic efficiency of a geothermal plant rises dramatically with steam pressure, but so does silica carryover.

Water is very effective in scrubbing silica from steam as seen from the following distribution coefficients:

$$K_{\substack{\text{amorphous} \\ SiO_2}} = \frac{\text{ppm } SiO_2 \text{ in } H_2O}{\text{ppm } SiO_2 \text{ in steam}}$$

T°C	K
150	7500
200	2000
250	1000

For example, the 100 MWe plant above had 0.4 ppm SiO_2 in the steam at 200°C and would normally transport 0.4 kg/hr into the turbines. It is interesting to calculate how much scrub water is needed to remove this silica to a value of 0.01 ppm in the steam:

ppm SiO_2 in scrub water = (0.01)(2000) = 20 ppm

$$\frac{20}{10^6} = \frac{0.4 \text{ kg/hr}}{H_2O}$$

$$H_2O = 2 \times 10^4 \text{ kg/hr} = 4.4 \times 10^4 \text{ lb/hr}$$

$$\text{\% of total steam condensate used as scrub water} = \frac{4.4 \times 10^4 \text{ kg/hr} \times 100}{2.2 \times 10^6} = 2\%$$

This shows that when a system is running with saturated steam the normal condensate in the steam lines is a good scrubber. At Wairakei (Haldane 1962) they found "a moderate amount of pipeline condensation is beneficial; ...The pipeline in effect acts as an efficient scrubber." However, if the steam system is normally superheated as could be the case for hot dry rock, there would be a thermodynamic penalty for water scrubbing. Without scrubbing, silica transport to the turbine could increase dramatically.

Calcite Transport and Deposition

In contrast to silica, calcite ($CaCO_3$) and also gypsum ($CaSO_4 \cdot 2H_2O$) have retrograde solubilities--namely solubility decreases with increasing temperature. (Holland 1967, Ellis 1963) This means that as geothermal water cools, calcite and gypsum normally increase in solubility rather than decrease like silica. If so, why does calcite deposition show up so often in geothermal plants and bores? The answer is the solubility of $CaCO_3$ is strongly dependent on the CO_2 gas content of the water. (CO_2 is the major noncondensable gas in geothermal systems):

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca^{++} + 2HCO_3^-$$

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

The calcium ion concentration is related to the CO_2 overpressure by (Holland 1967):

$$M_{Ca^{++}} = \frac{K_1' \, K_{cal} B f_{CO_2}}{4K_2 \, \gamma^3_{\pm Ca(HCO_3)_2}}$$

where:

K_1' = first ionization constant of carbonic acid

K_2 = second ionization constant of carbonic acid

K_{cal} = solubility product of calcite

B = inverse Henry's Law constant for CO_2 in water; moles CO_2/liter of solution per atmosphere pressure

f_{CO_2} = fugacity of CO_2

$\gamma_{\pm Ca(HCO_3)_2}$ = mean activity coefficient of $Ca(HCO_3)_2$ in solution

Studies of the interactions of temperature and CO_2 over pressure with calcium solutions show:

- Calcite cannot deposit by simply cooling the solution.
- At any temperature calcite can be deposited by CO_2 release.

- Calcite can deposit if the solution boils and releases CO_2. Boiling can, and usually does, occur when water depressurizes as it comes up a geothermal bore.
- Calcite deposition is more likely to occur in production from lower temperature reservoirs with high CO_2 gas content where $CaCO_3$ is more soluble. For example: complete release of 70 atm CO_2 pressure from a 150°C solution would deposit 450 mg $CaCO_3$/kg solution, whereas the same release from a 300°C solution is only 60 mg/kg (Holland 1967).

The presence of NaCl in solution increases calcite solubility. Holland estimated that at any temperature up to 300°C, boiling could easily deposit at least 100 mg $CaCO_3$/kg solution.

Going back to the 100 MWe geothermal plant, the steam production rate was 10^6 kg/hr. $CaCO_3$ deposition = 10^{-4} kg CO_3/kg x 10^6 kg/hr = 100 kg/hr = 220 lb/hr. Thus it is not surprising that bores have plugged with calcite in cases where high calcium waters are encountered. It is also clear that maintaining CO_2 overpressures can inhibit calcite deposition which favors pressurized water heat exchangers vs. flash steam type systems.

We have not found any data on calcite deposition rates as a function of engineering plant design variables. The indications are that rates are much more rapid than the silica deposition.

Scale Formation Due To Water Soluble Salts

Not all scale formed in geothermal plants is caused by compounds with low water solubility such as silica and calcite. Turbine scale at Matsukawa (Ozawa 1970) had a measurable content of $FeSO_4$ and Na_2SO_4. This was thought to be dissolved in small moisture droplets carried in the steam. When the Matsukawa bores began delivering superheated dry steam (Ozawa 1970) the scale deposition rate "remarkably decreased". Formation of sulfate turbine scale is consistent with the work of Staub (1946) who classified turbine scale deposits in two types (1) water soluble such as sulfates, chlorides, and hydroxides, and (2) water insoluble such as silica. Staub found the least soluble compounds deposit first, and most turbine scale contained sulfate as the first depositions species. This is consistent with what is seen in geothermal turbines. He recommended control of moisture droplet carryover. For insoluble silica deposits, Staub recommended reductions in silica in feedwater, or if this was not possible, to use water scrubbers. His advice is still valid today for geothermal plants.

Some iron oxide and iron sulfide scales are occasionally seen as turbine scale, especially on startup, due to transport of iron corrosion products from the bore liners and pipelines.

At Larderello (Allegrini 1970) rapid silica scale buildup has been observed when "dragged water" gets into the steam lines. Considering how high the silica solubility in water is, this is not surprising.

Chlorides are a continuous corrosion problem. At Larderello (Allegrini 1970) a number of piping corrosion failures occurred due to chlorides. In some cases they have had to resort to injection of alkaline solutions into the pipelines to minimize chloride carryover into the turbines and condenser system.

Where very high concentrations of brine are encountered such as Salton Sea hydrothermal fluids, the process of boiling can exceed the solubility of salts. Alternatively water droplets carrying a high dissolved salt content can be carried with the steam, evaporate and deposit their salt content as scale.

The control of these water soluble scale formers depends primarily on good steam separator efficiency and the use of scrubbers. Fortunately even where water soluble scale builds up, they can usually be removed by water washing. Obviously, with higher total dissolved solids in the feedwater, carryover of water soluble scale becomes more serious. Conventional boiler practice is to hold total dissolved solids to below 4000 ppm. Since geothermal waters commonly are commonly 10,000 to 30,000 ppm and can range up to 350,000 ppm, problems with scaling are to be expected if direct flash steam generation is attempted on high saline brines.

REINJECTION OF GEOTHERMAL FLUIDS INTO THE RESERVOIR

Injecting water into the reservoir is often assumed as a necessary technology to:

- Dispose of excess brine wastes
- Maintain reservoir pressure
- Artificially create an aquifer in hot dry rock
- Conserve water in an arid region

There is considerable experience in reinjecting waste brines from oil fields, and limited experience in reinjecting steam condensate at the Geysers geothermal plant.

The Office of Saline Water (OSW) has extensively examined the technical feasibility and costs of deep well brine injection. An inland desalinization plant produces large volumes of waste brine similar to a geothermal plant. OSW surveyed oil field experience and costs (OSW R&D reports 432, 456, 555, 587, 650). They concluded waste brine disposal could be a major expense, varying over the range of $0.10 per 1000 gal where no pretreatment and low injection pressures are encountered, to over $1.00 per gal where pretreatment and/or high injection pressure are encountered. Based on oil field experience one study (OSW 432) indicated a range of costs to be expected was $0.25 to $0.70 per 1000 gal.

We have calculated in Table 1 the cost impact on geothermal power of waste treatment costs in the range of $0.10 to $1.00 per 1000 gal. The cost advantage of a Geysers type system where only 25% of the steam condensate remains to be injected is obvious. It is clear any geothermal system which works on a liquid phase water cycle will be at a cost disadvantage on waste handling. In a water system, up to five times more fluid must be handled, and because of higher impurity solubilities more extensive waste treatment will be required. Since dumping waste in a river costs under $0.01 per 1000 gal, it is easy to see why today's geothermal plants dispose of wastewater to the nearest river or lake (Wairakei New Zealand; Larderello, Italy; Otake, Japan; Cerro Prieto, Mexico).

TABLE 1. Water Treatment and Injection Costs

Cost of Treating & Injecting Water $/1000 gal	SYSTEM TYPE			
	Natural Steam(1) Inject Steam Condensate	Natural Hot Water (Binary Cycle)(2) Inject All Waste Water	Hot Rock(3) Inject Water Produce Steam	Hot Rock(4) Inject Water Produce Hot Water
$0.05	0.03 mils/kW-hr	0.6 mils/kW-hr	0.1 mils/kW-hr	0.5 mils/kW-hr
0.10	0.06	1	0.2	1
0.50	0.3	6	1	5
1.00	0.6	12	2	10

BASES:

(1) 18 lb steam/kW-hr required - 25% of steam condensate reinjected (Barton, 1970).

(2) 100 lb H_2O/kW-hr required - 100% reinjected - 380°F well temperature, 100°F condenser temperature (Anderson, 1973).

(3) 18 lb steam/kW-hr required - 100% of water injected.

(4) 17 lb steam/kW-hr required - 80 lb/kW-hr water, 100% reinjected. Calculations based on Wairakei performance data - 21% flashed to steam (Bolton, 1970).

Density of injected water assumed 8 lb/gal @ 100°C.

Since fossil fuel and nuclear power plants are producing electricity below 15 mils/kW-hr, some of the geothermal systems in Table 1 are not competitive.

Deep well injection usually requires pretreatment (OSW R&D Report 432, 1969):

1) Removal of suspended solids,
2) Removal of iron and manganese which form gelatinous precipitates in neutral pH waters,
3) Biocide treatments to prevent growths (may not be applicable to hot geothermal water).

In addition to pretreatment, costs of deep well disposal are strongly dependent on the volume to be injected and the required pressure head. Figure 2 (OSW R&D Report 456, 1969) shows the dramatic effect of well head pressure on costs. Well head pressure in turn depends on formation permeability and the volume of water injected per well. It is interesting to note that in Figure 3 (OSW R&D Report 456) most of the western U.S. considered unsuitable for deep well disposal of brines. This is because of the low permeability of igneous rocks which led to very high pressures and costs. This may not be a valid assumption if an extensive crack structure can be artificially induced, but does point out the importance of achieving and maintaining high underground permeability.

Since a geothermal plant produces large volumes of water that probably will have a large impurity burden, we must examine the specific problems.

Steam Condensate

If a hot dry rock system is operated to produce only steam up the bores, the amount of silica brought to the surface will rise exponentially with steam pressure and temperature. Early in bore life, when rock temperatures are high, silica could be a reinjection problem. As caluclated above a 100 MWe plant operating with 300°C steam will bring about 79,000 lb/yr of silica dissolved in the steam to the surface. To prevent plant and turbine

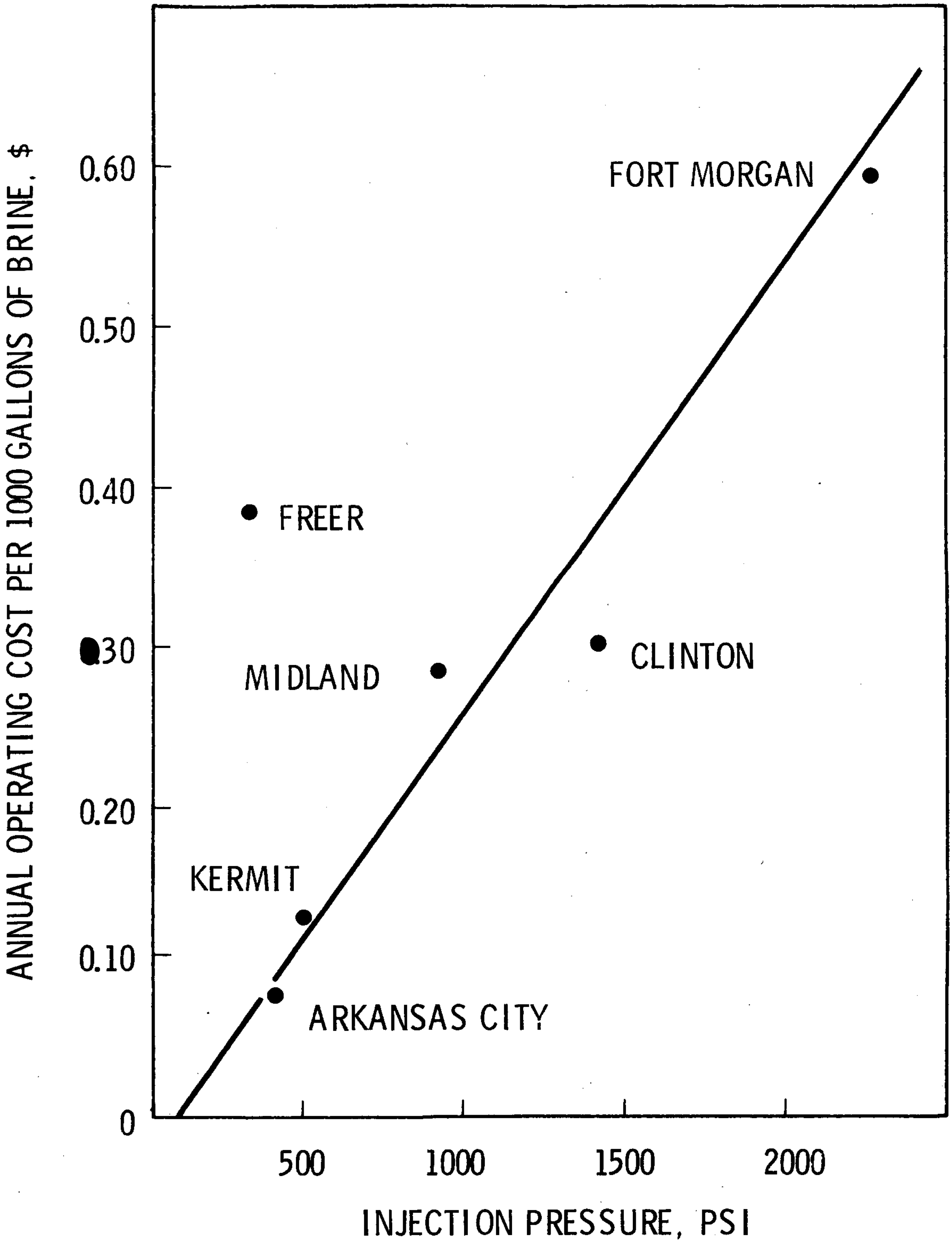


FIGURE 2. Operating Cost as a Function of Injection Pressure (from OSW-456)

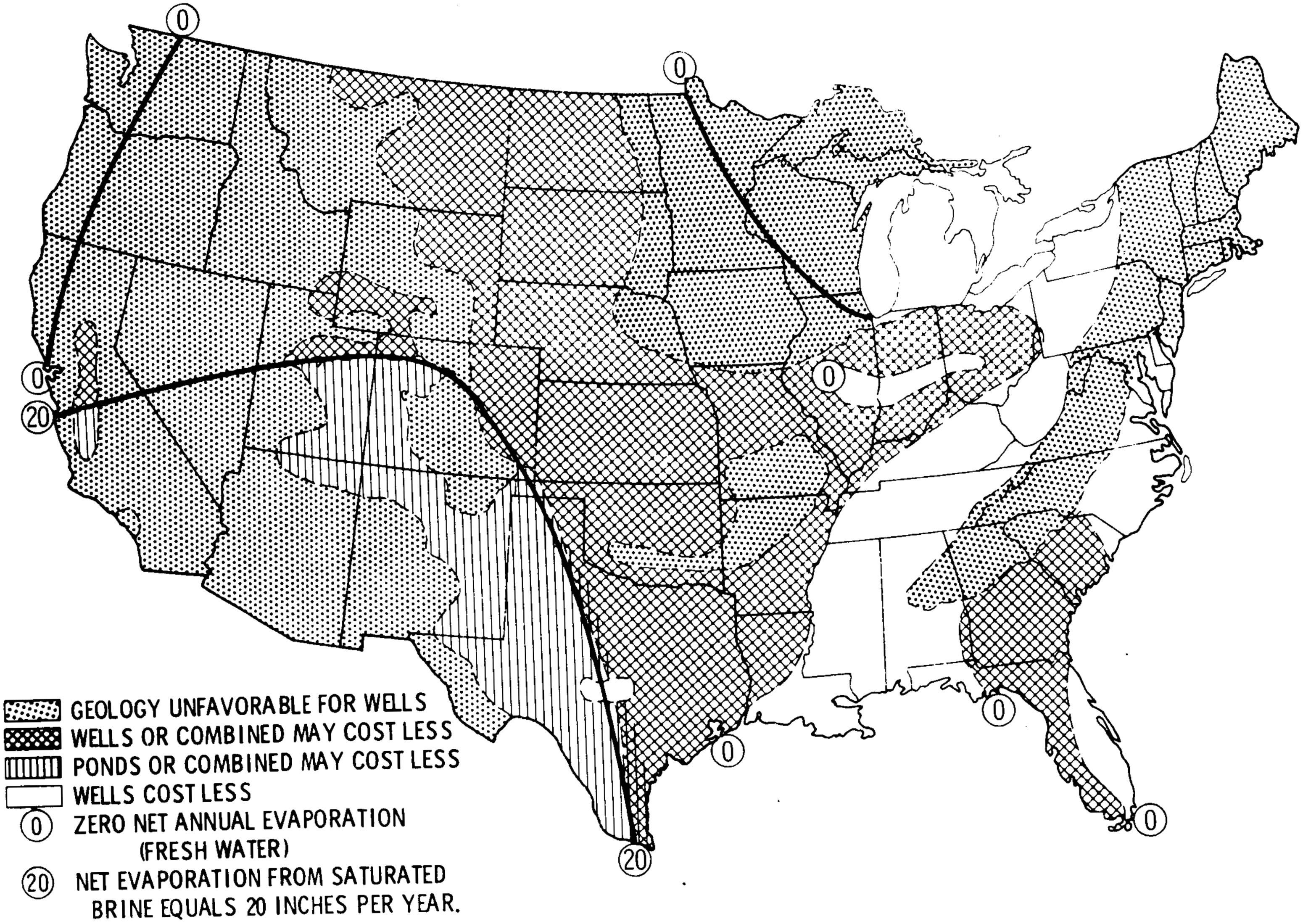


FIGURE 3. Geographical Suitability for Waste Disposal Wells (from OSW-456)

deposition, most of this silica should remain in the return condensate either as a supersaturated solution, or probably as a gel in suspension. Plugging of a formation could occur if this material is injected into a fine pore structure before the temperature rises to increase the silica solubility.

Waste Water from Flash System

The large volumes of waste water from a flash steam system would be a more serious case because much more silica will be brought to the surface--17,000 tons/year for the MWe plant example. This was the cause of the wastewater line plugging observed by the Japanese (Yangase 1970). Obviously any scheme to reinject such large quantities of silica should be looked at carefully. It may be necessary to have a settling basin and filtration to remove the silica before reinjecting the water.

Calcium and Gypsum

The retrograde solubilities of calcite and gypsum could cause a reinjection problem. Normally water produced from high temperature reservoirs is low in $CaCO_3$ and $CaSO_4$ because of the low solubility of these materials at high temperature. Thus the Salton Sea brines (>300°C) have only 10 ppm sulfate, but 40,000 ppm calcium (as chloride). If such waters are exposed to oxygen or carbon dioxide while cooling above ground appreciable quantities of soluble bicarbonate, carbonate and sulfate could form as indicated in these equations:

(Oxidation of hydrogen sulfide) $H_2S + SO_2 \rightleftarrows SO_4^{--} + 2H^+$

(pH dependent solubility of CO_2) $CO_2 + H_2O \rightleftarrows HCO_3^- + H^+$

$HCO_3^- \rightleftarrows CO_3^{--} + H^+$

When reheated during reinjection, the SO_4^{--} and CO_3^{--} would become insoluble in the presence of the excess calcium and precipitates would form:

$$\mathrm{Ca^{++} + SO_4^{--} \rightleftarrows CaSO_4 \downarrow}$$

Low Temperature High Temperature

$$\mathrm{Ca^{++} + CO_3^{--} \rightleftarrows CaCO_3 \downarrow}$$

An open air settling pond to remove silica could lead to calcite or gypsum deposits in the reinjection well. This suggests a settling pond may require an inert cover gas or remain pressurized and oxygen free.

Hot rock geothermal systems using injected water will need make up water. Natural waters usually contain calcium and magnesium together with carbonates, bicarbonates, and sulfates e.g., "hardness". When such waters are heated scale is formed; scale which could plug an injection well or rock formation. The principle is exactly the same as heating water for boiler use, and the same boiler feedwater technology could control the problem; however at a cost.

It is possible this scaling mechanism could be an advantage to a hot rock reservoir, if properly managed. By letting scale slowly build up in rock cracks, flow will be restricted at the same time the heat is withdrawn. Thus old areas of the formation could be "sealed off" as they cool, forcing the water to follow new cracks into freshly fractured hot rock.

Ferrous/Ferric Ions

Geothermal fluids often contain ferrous ion, Fe^{++}, which is soluble as chloride. When exposed to air the Fe^{++} is oxidized to Fe^{+++} which hydrolizes to increase the acidity:

$$\mathrm{4\ Fe^{++} + O_2 + 2H_2O \rightarrow 4Fe^{+++} + 4OH^-}$$

$$\mathrm{Fe^{+++} + H_2O \rightleftarrows FeOH^{++} + H^+}$$

When such an acidic solution is neutralized by reinjection into rock, precipitation of ferric hydroxide can occur. Under the buffering conditions typical of some hydrothermal solutions, insoluble iron hydroxide can form in the cooling pond.

Conclusions on Reinjection

The above discussion is indicative of some of the complexities. It is clear we should <u>not</u> assume reinjection will be successful without careful control of pH, and the chemical species and solids present in the fluid and compatibility with underground formations.

CORROSION OF MATERIALS FOR GEOTHERMAL ENERGY SYSTEMS

State-of-the-Art in Geothermal Corrosion

The selection of materials for a geothermal plant is a trade-off between initial cost *vs* life time and replacement cost (including cost of lost production during downtime). All power plants are under constraints to minimize capital costs; the plant capital cost amortization visibly affects the cost of electricity. Thus, the plant design engineer must have accurate knowledge of corrosion of various materials in the geothermal fluids to be used. Lack of this knowledge will affect the plant design. Either capital cost will be unnecessarily increased by excessive use of corrosion resistant materials, or operating costs will be increased by downtime and replacement costs of components with inadequate corrosion resistance. In Figure 4, a vivid example of retrofitting a desalting plant with more corrosion resistant materials was recently discussed (Morin, 1974). Excessive corrosion of various components caused plant availability to drop from 70% to 41% in four years while product water costs doubled.

This review has resulted in several conclusions about the present state-of-the-art in geothermal corrosion:

- Very little geothermal corrosion data have been published.
- Those corrosion data available are reported for one specific set of conditions at one site. Extrapolation to other types of plants is difficult.
- Corrosion data are nonexistent for hot dry rock geothermal plants and hot water binary cycle plants.

Some relevant information is available from desalting plant technology, although usually only up to about 110°C temperatures, and often corrosion data are in oxygenated systems, which are irrelevant to geothermal fluids. There is considerable literature on corrosion and sulfide cracking of "sour brine" encountered in petroleum technology, but at lower temperatures than geothermal applications. It is clear more geothermal corrosion work is needed.

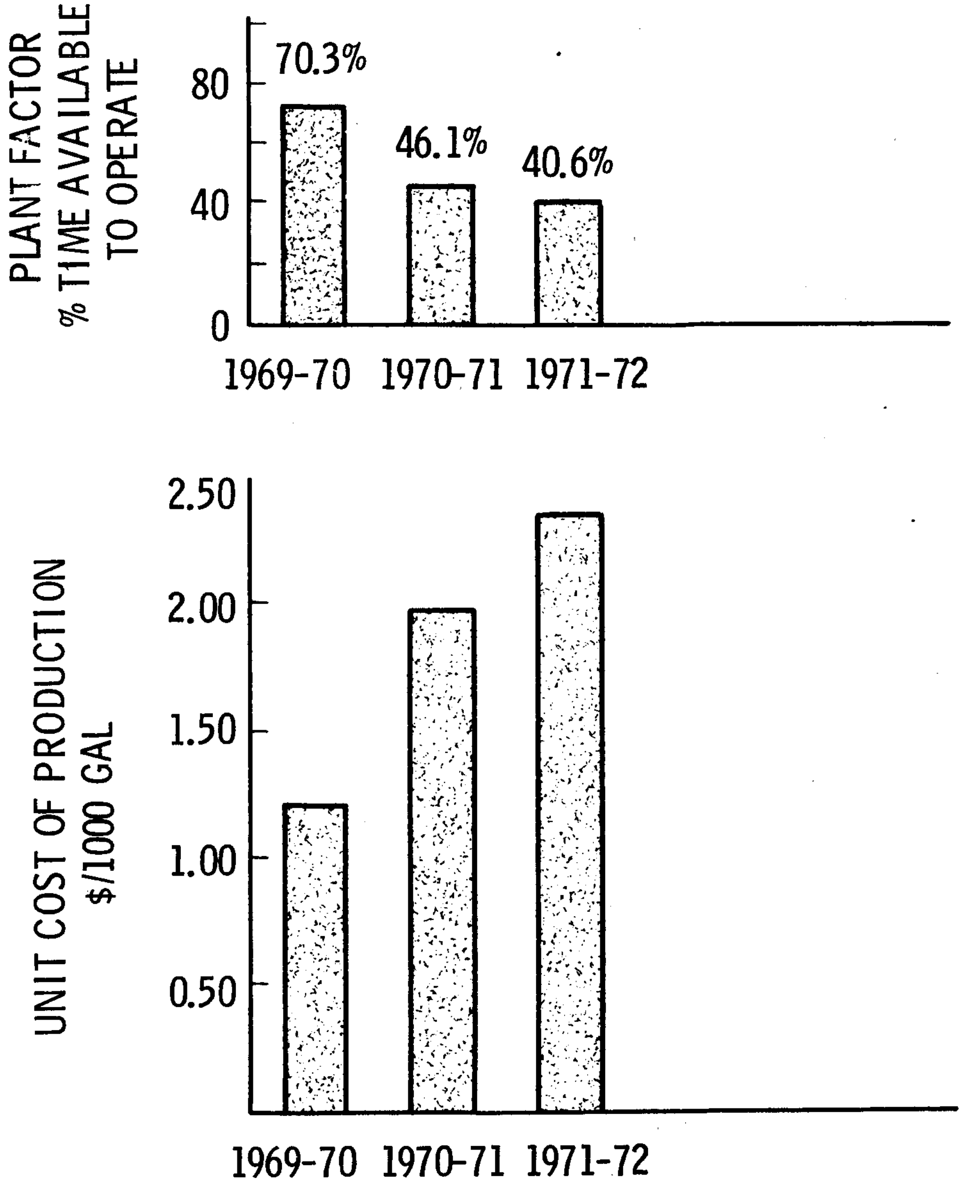


FIGURE 4. Impact of Corrosion Failures and Design Changes on Key West, Florida, Desalting Plant Performance (Morin, 1974)

With so few geothermal corrosion data available, extrapolation to new geothermal concepts becomes risky and speculative.

This report attempts to interpret what has been observed in the light of general corrosion theory. Once some of the basic principles are understood, the usefulness of a single data point can be better judged when considering a new geothermal plant design.

Need for Specific Analysis and Corrosion Tests of Each Geothermal Site

Depending on whether the geothermal resource is steam, hot water, or hot brine, corrosion problems and material selection can vary.

It has been past practice to begin an experimental corrosion test program as soon as geothermal fluids are available at a site. Study of the specific chemicals present and the pH will suggest a series of materials for each part of the system. Specific corrosion test data will permit an economic trade-off between life and cost. Generally, one to two years is the minimum exposure time needed to measure corrosion rates; thus such corrosion test work needs to begin well in advance of detailed plant design. The corrosion monitoring program should continue into the first years of plant operation to verify proper materials performance and identify any problem areas.

TYPES OF CORROSION IN GEOTHERMAL PLANTS

Corrosion is a general word for a number of material degradation processes. While the plant manager may lump all such failures together as "corrosion," the engineer seeking a materials selection must consider all the diverse types of corrosion before selecting a remedy.

Geothermal plants are afflicted with so many different types of corrosion that a complete discussion would fill a textbook (such a book needs to be written). As an introduction to this discussion the following comments on types of corrosion may be of assistance:

Uniform Corrosion - Uniform corrosion is a general loss of metal and wall thinning. Failure occurs when remaining metal cannot support mechanical stresses. Formation of passive protective films reduces reduces uniform corrosion of many metals. The objective of alloying is often to generate passive corrosion product films to reduce corrosion.

Galvanic Corrosion - When two dissimilar metals are placed in electrical contact in a conducting brine, a galvanic cell (e.g., battery) is set up. Corrosion is accelerated in the less noble metal in proportion to the surface areas. Thus, iron rivets in copper sheet in sea water will fail rapidly. Iron is anodic to copper and the entire anodic current is concentrated on the iron rivets. It is interesting that such iron corrosion can be reduced by painting the noncorroding copper, thus reducing the effective cathode surface area and the total galvanic current. A better solution is to avoid such noncompatible couples.

Pitting and Crevice Corrosion - Many metals such as austenitic stainless steel, aluminim, and titanium depend upon a passive protective film for corrosion resistance. Under certain conditions localized breakdown of the protective film occurs, and localized galvanic cells are set up in the same piece of metal. The potential difference between the pit area (anodic) and the rest of the metal (cathodic) causes electrons to flow through the base metal and the corrosion becomes self-sustaining. Often pitting is associated with chemistry changes (such as oxygen gradients) between the bulk environment and the pit. Crevice corrosion is a special case where such chemical concentration differences between the crevice and the bulk solution can set up localized galvanic cells.

Fretting and Erosion Corrosion - When mechanical abrasion removes the protective passive film on a metal, rapid corrosion can occur since the protective film is lost as fast as it reforms.

Intergranular Corrosion - In some media, grain boundaries are less corrosion resistant than the rest of the grain and corrosion can proceed along these less resistant paths at a high rate.

Corrosion Fatigue - In the absence of a corrosive media, metals can be subjected to cyclic stress without fatigue failure. However, in the presence of a corrosive media and cyclic stress there no longer is a fatigue stress limit, and the fatigue strength decreases with time. Often corrosion pits are stress risers from which a corrosion fatigue crack will propagate at right angles to the stress. The crack will grow until the remaining metal section fails by mechanical fatigue.

Sulfide Corrosion/Hydrogen Embrittlement - H_2S enhances uptake of corrosion product hydrogen in steels. This nacent hydrogen in the metal can produce brittle fracture in high strength steels, especially steels with hardness above R_c22.

Stress Corrosion Cracking - Stress corrosion cracking generally occurs under conditions that produce little uniform corrosion. Sudden brittle fracture occurs as a result of intergranular or transgranular corrosion cracking. Some examples are cracking of 300 series austenitic steels and high strength aluminum alloys in chloride solutions, and copper alloys in ammonia.

High Temperature Oxidation - High temperature oxidation is a gas phase, direct chemical reaction between the metal and the corroding species.

CORROSION OF CARBON STEEL AND LOW ALLOY STEELS

Uniform Corrosion in Water

At the temperatures encountered in geothermal plants, the corrosion of steels is more severe in liquid environment. This uniform corrosion process is electrochemical:

$$Fe \rightarrow Fe^{++} + 2e^- \quad \text{(anode reaction)} \qquad (1)$$

In order for iron to dissolve, there must be a companion cathode reaction in order to conserve electrical neutrality. Two of the most common cathode reactions are:

$$2H^+ + 2e^- \rightarrow H_2\uparrow \qquad (2)$$

$$\text{(sometimes accelerated by } 1/2\,O_2 + 2H_2 \rightarrow H_2O)$$

and

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (3)$$

$$\text{(followed by } Fe^{++} + 2OH^- \rightarrow Fe(OH)_2)$$

Since geothermal fluids are normally oxygen free, the corrosion rate of steel is controlled primarily by the hydrogen evolution reaction (Eq. 2) (T. Marshall, 1957; Tskhvirashvili, 1970). This mechanism of hydrogen evolution cathodic control has three important implications:

- In 150°C dry geothermal steam corrosion of carbon steels will be low, since an aqueous phase is needed to complete the electrical circuit of the electrochemical cell.
- In steam condensate and in water dominated systems, the pH of the water will be of great importance in determining the corrosion rate.
- Introduction of significant oxygen levels will accelerate corrosion rates by the depolarizing reaction (Eq. 2), and adding a second cathode reactions (Eq. 3).

Effect of pH*

Extensive studies of the effects of pH on corrosion of steels in boilers has shown minimum corrosion of steel occurs between pH 10 and pH 11. This is why all boiler water treatment maintains alkaline conditions (see Figure 5). Since geothermal waters are rarely over pH 10, and more commonly pH 5 to 8, one can predict pH 4.9 brines from the Salton Sea (Ellis, 1970) will be substantially more corrosive than pH 8.7 to 9.4 waters from Iceland (Hermannson, 1970) or pH 7.8 to 8.3 waters at Wairakei, NZ (Ellis, 1970). In Figure 6 we have plotted corrosion data from several geothermal plants on a corrosion *vs* pH curve of corrosion by hot seawater (seawater data - Behrens, et al., 1970). Corrosion data from Russian geothermal springs *vs* pH is in Figure 7. These data show clearly that carbon steels become less satisfactory as the pH becomes lower. Assuming a 0.125 inch (1/8 in.) corrosion allowance on pipe, lifetimes of carbon steel pipe *vs* pH can be estimated from Figure 6 for 40°C - 50°C geothermal water as in Table 2.

TABLE 2. Estimated Life of Carbon Steel Pipe in Oxygen-Free Geothermal Water @ 40-50°C

pH	Yr
4 *	2
5 *	15
6 *	30
7	40
8	60
9	100

* Note at pH <6 pipe life can be strongly influenced by velocity effects and other anions present.

Note especially that below pH 6 the curve begins to rise steeply and other effects, such as velocity, can be pronounced.

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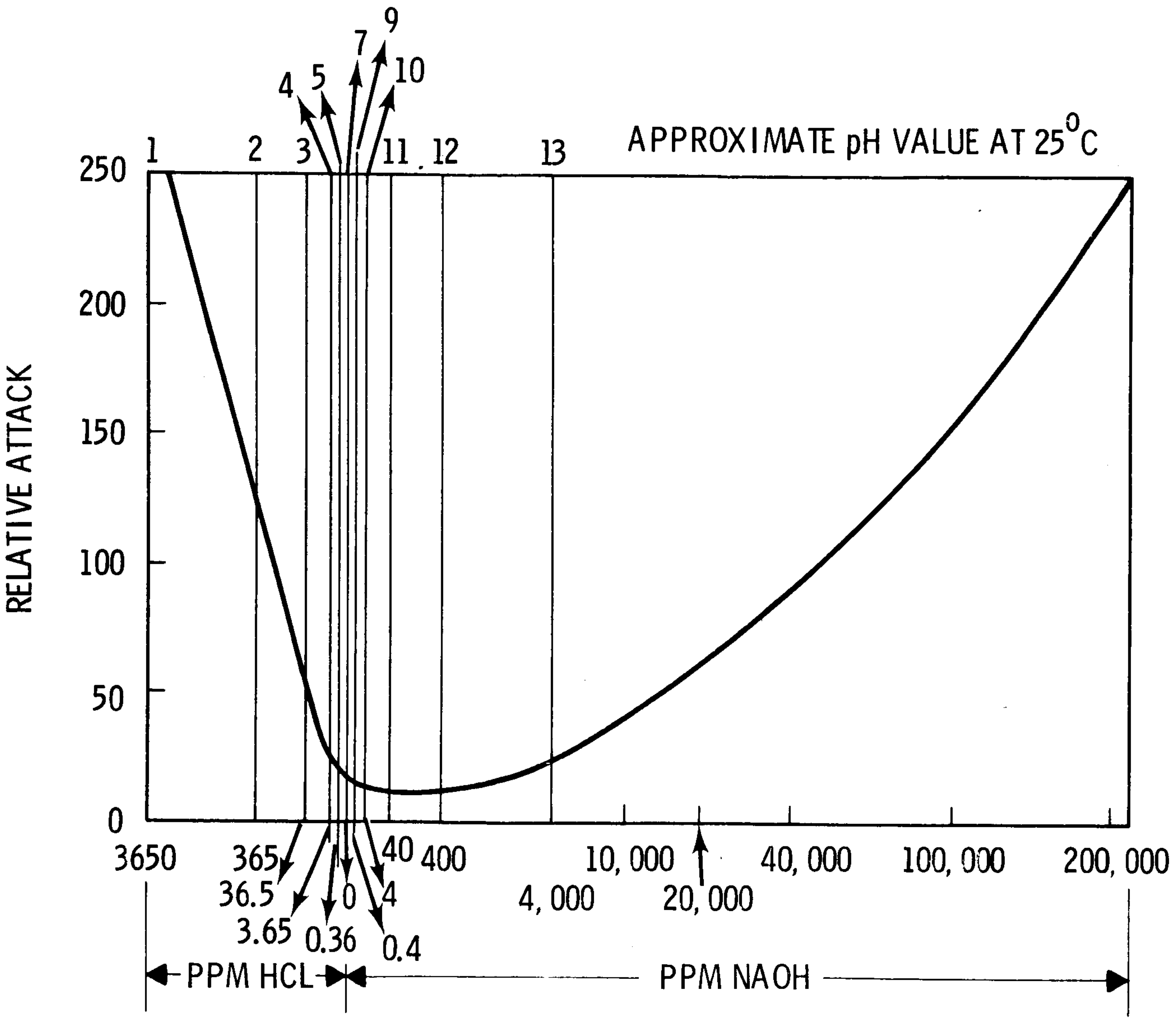
* pH values refer to room temperature pH measurements rather than pH at temperature.



SOURCE: ULIG, 1948

FIGURE 5. Attack on Steel at 310°C (590°F) by Water of Varying Degrees of Acidity and Alkalinity

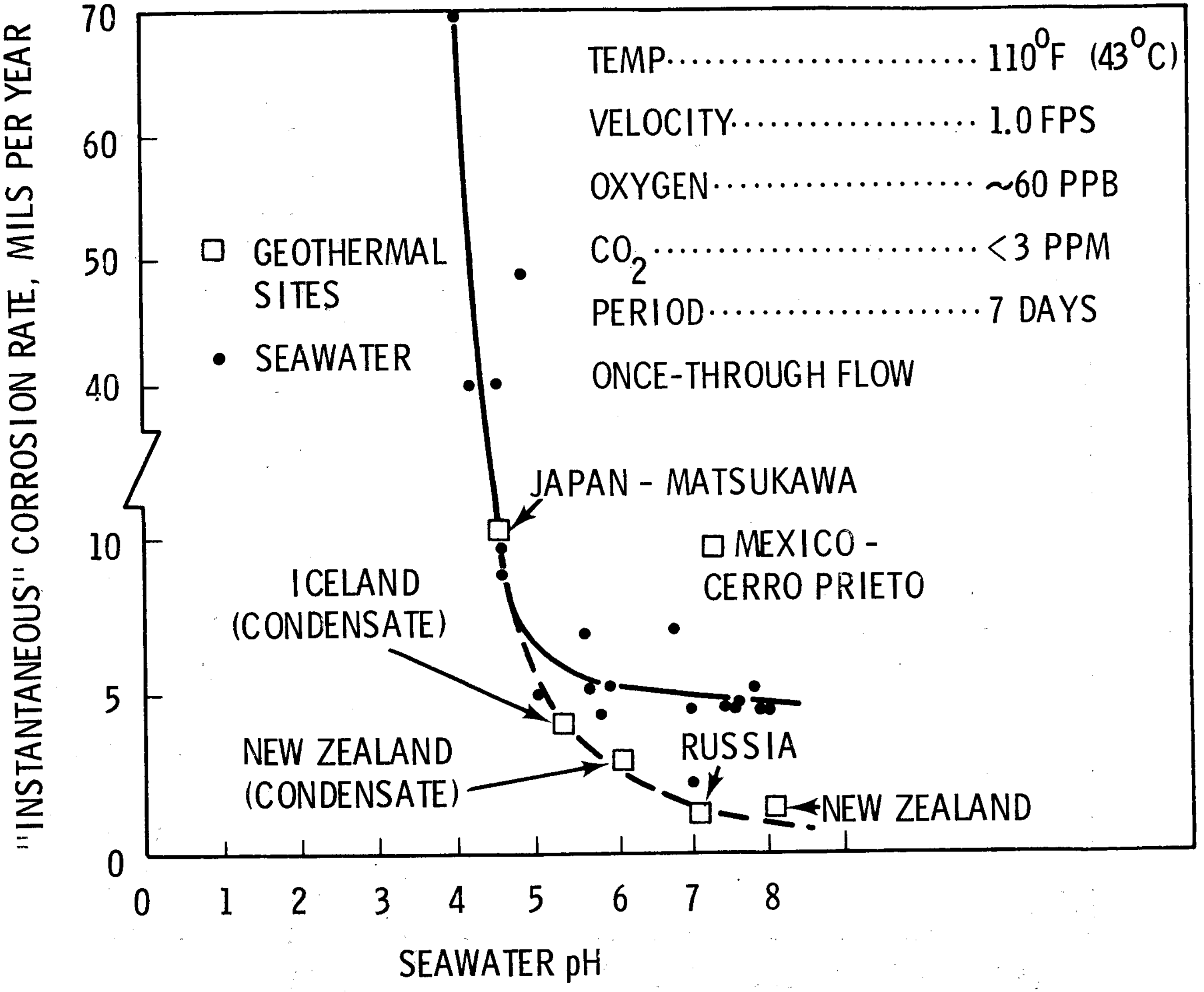
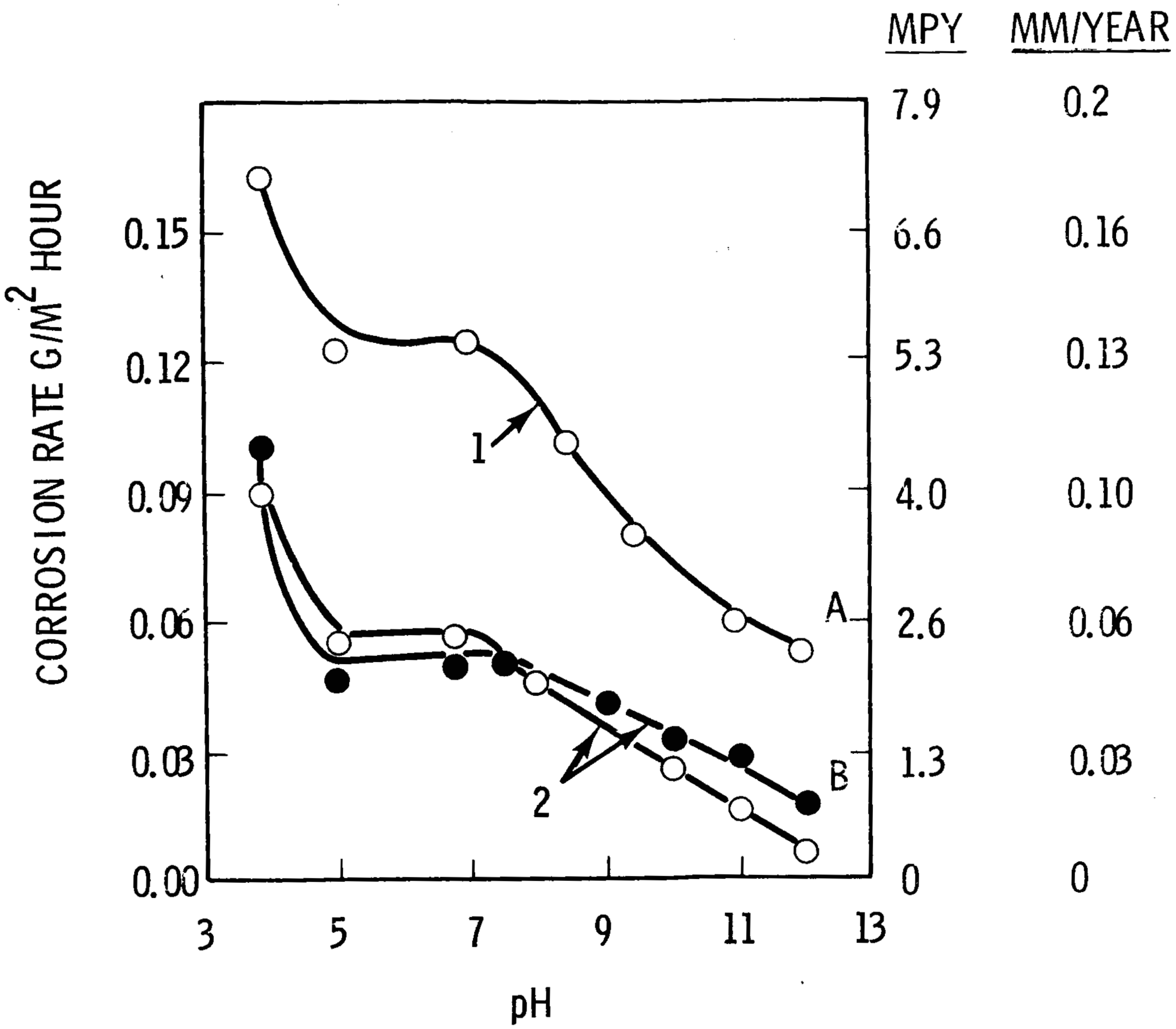


FIGURE 6. Effect of pH on the Corrosion Rate of 1010 Mild Steel



SOURCE: TSKHVIRSHVILI et al., 1972

FIGURE 7. Dependence of the Corrosion Rate of Carbon Steel on the pH of Thermal Waters of Zugdidi Spring No. 4 (1) and Zugdidi Spring No. 3 (2)

Unfortunately the corrosion rate is not a simple function of pH, since other anions can shift the hydrogen evolution point. Such hydrogen depolarization effects are what necessitates individual corrosion rate measurements in each geothermal fluid at each proposed site.

Effect of Oxygen

Comparison of the geothermal data plotted in Figure 6 versus the original seawater data shows at pH 8 that the geothermal corrosion rates are lower. This is probably due to the effect of oxygen depolarization of H_2 evolution in seawater (Eq. 2). (Note the seawater has 60 ppb O_2.)

A number of discussions of geothermal plants call attention to the severe corrosion that can occur if oxygen from the air enters the piping, turbine or condenser system (Marshall 1957, Haldane 1962, Tolivia 1970). In Table 3 corrosion data in oxygen free and aerated geothermal fluids illustrate the necessity of excluding oxygen and air inleakage.

TABLE 3. Effect of Oxygen on Corrosion of Steel in Geothermal Fluids

Marshall & Hugill (1957)	Gas free (140°F) Condensate	Aerated Steam (140°F) Condensate
Wairakei, NZ Carbon Steel	0.01 mm/yr (0.4 mil/yr)	0.8 mm/yr (30 mil/yr)
Tolivia (1970 CerroPrieto, Mexico	Separated Steam (147°C)	Aerated Separated Steam (70°C)*
ASTM 285	0.004 mm/yr (0.15 mils/yr)	0.4 mm/yr (17 mils/yr)

*Note: Rate is factor of 100 higher even with lower temperature.

Hermannson (1970) states that 1 to 2.6 ppm dissolved oxygen in municipal hot geothermal water (86°C) at Rekjavik, Iceland "caused severe internal corrosion of metals in the heating system of the town. Sodium sulfite additions were used to reduce O_2. Another water system with only 0.1 to 0.4 ppm O_2 "does not cause any appreciable corrosion."

In present day geothermal plants oxygen inleakage has been a relatively minor problem, but cases of "standby corrosion" due to air leaks have been reported (Haldane 1963).

New geothermal concepts, such as hot dry rock, which inject water into the reservoir could carry substantial amounts of dissolved oxygen into the reservoir if untreated, air saturated, makeup water, is used.

Until proven otherwise a proposed geothermal plant should provide for (and cost) equipment for deoxygenating <u>all</u> water to be injected underground. Deoxygenation of injected water in oil field flooding operations has proved necessary (Cubine 1973). Deoxygenation to below 0.05 ppm O_2 avoids catastrophic corrosion of the injection well pumps and casing, and possible chemical incompatibilities with underground formations. Various deoxygenation schemes are available including vacuum, gas scrubbing, and reaction with sodium sulfite. Sodium sulfite should be used with caution since the sulfate ion formed could result in plugging the injection well with $CaSO_4$ which becomes insoluble on heating. Substantial volumes of CO_2 and H_2S gases are usually pumped off the turbine condensers in a geothermal plant an it may be possible to use these gases to deoxygenate makeup water.

Effect of H_2S, CO_2 and NH_3 on pH

The gases H_2S, CO_2 and NH_3 occur in geothermal fluids and can produce significant pH effects. In aqueous solution, H_2S and CO_2 are weak acids:

$$H_2S \rightleftarrows H^+ + HS^-$$

$$CO_2 + H_2O \rightleftarrows H^+ + HCO_3^-$$

NH_3 is a weak base:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

In the absence of other species in the water, H_2S and CO_2 combine to create acidic conditions which corrode carbon steel and low alloy steels. These effects are especially pronounced in steam condensate systems since H_2S and CO_2 are gases carried with the steam phase through the turbine into the condensor. Thus a geothermal water which is alkaline can produce acidic steam condensate since the alkaline species (except NH_3) are non-volatile and remain with the water during flash boiling. Such acidic condensate can be highly corrosive (Figure 6).

In the design of strippers to remove H_2S from low pH refinery waste waters (Hildebrand, 1974), describes a test at 82°F) where the only resistant materials were tantalum, titanium, Hastelloy B & C, and aluminum. However, in spite of high corrosion rates, carbon steels are used with a 1/8 to 1/4 inch (3.2 to 6.4 mm) corrosion allowance.

It has been known for many years that corrosion in partially dissociated acids in the pH range of 4 to 7 is highly dependent on the H^+ activity at the metal surface (Ulig, 1948). Because of this fact corrosion becomes highly dependent on hydrogen overvoltages on the metal (e.g., alloy effects), H^+ activity in solution (e.g., degree of dissociation of weak acids and bases), and velocity since turbulent mixing at the metal surface enhances H^+ transfer across the boundary layer. The effect of temperature on corrosion rates above 100°C is highly uncertain since little work has been done in pressurized aqueous solutions in the 100 - 300°C range. Since weak acids change in dissociation by orders of magnitude in this temperature range, the net effect of changing reaction kinetics in a multiparameter system is highly uncertain.

Sometimes NH_3 is present in sufficient quantity (such as at the Geysers Geothermal Plant) to neutralize the H_2S and CO_2 in the steam condensate making it much less corrosive to cooling tower and reinjection pumps and wells. Caution should be exercised in extrapolating Geysers plant materials data to other systems containing <u>less</u> NH_3.

Effect of Elemental Sulfur on pH

Elemental sulfur is sometimes encountered in geothermal and volcanic regions. Hot water reacts with sulfur (Ellis, 1970):

$$4H_2O + 4S \rightarrow 3H_2S + H_2SO_4$$

Such effects can produce water of pH 3 or over, such as in the Tatus area on Taiwain, and some shallow New Zealand areas. Obviously such a situation produces low pH water so corrosive as to make carbon steel components unacceptable.

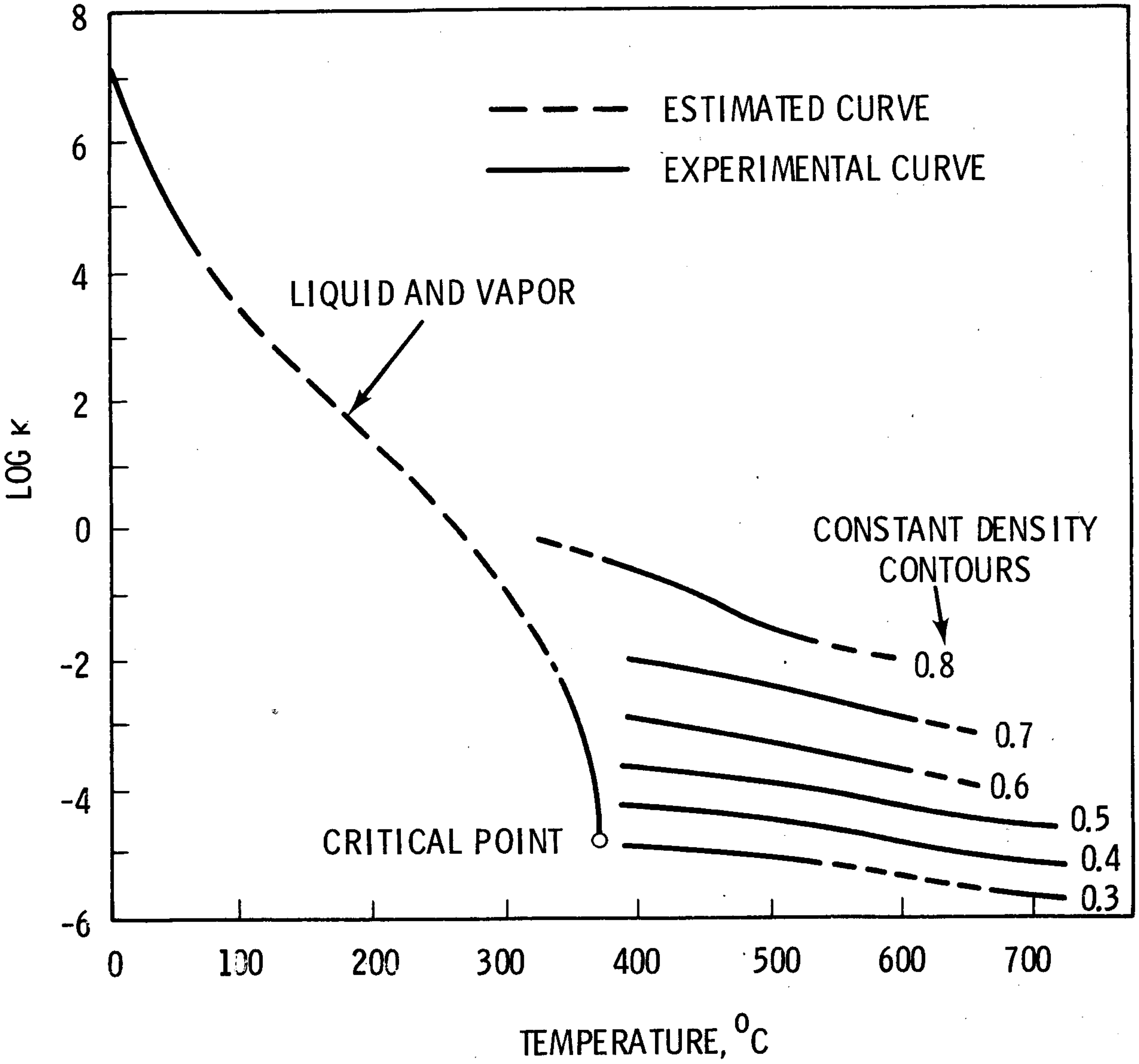
Effect of Salt Content of Geothermal Brine

There is a tendency to consider high salinity brines as more corrosive than low salinity brines. While this may be true for most actual field cases, it is erroneous to ascribe the increasing corrosiveness to increases in NaCl, KCl, and $CaCl_2$ concentrations, per se. Certainly increasing the ionic strength of the salt solution can accelerate electron conductance in galvanic cells, but this is a second order effect since all geothermal waters are highly conductive. A number of studies (Foley, 1970) have shown that chlorides and other anions can profoundly affect the character of the protective films on iron alloys (Foley lists 81 references). However, unless there is O_2 or H^+ to provide the cathode reaction, iron alloys corrode very little in quite high concentrations of neutral pH, O_2-free, salt solutions.

Since geothermal fluids are O_2-free (excluding design and operating mistakes), the effect of salt content on pH, and the effect of salt content anions on the hydrogen evolution reaction produce the major effects seen in geothermal fluids. One such effect is the dissociation of hydrochloric acid:

$$HCl \rightleftarrows H^+ + Cl^-$$

Normally we think of HCl as a highly dissociated strong acid that is very corrosive to iron alloys. However, at high temperatures typical of underground geothermal systems, HCl is predominately in molecular form, Figure 8.



SOURCE: BARNES, 1967

FIGURE 8. The Ionization Constant of HCl, $K_{HCl} = \frac{[a_{H^+}]\,[a_{Cl^-}]}{[a_{HCl}]}$,
As A Function of Temperature
and Density.

Substantial amounts of undissociated HCl can form at the expense of H_2S and HS^- (Helgeson, 1964) in the concentrations of chloride at temperatures and pressures encountered in the geothermal reservoir. When such fluids are rapidly produced up a well, the molecular HCl can dissociate and produce highly acidic solution at the surface. Whether this happens or not depends on the combinations of <u>other</u> species present to react with the H^+ released as HCl dissociates <u>and</u> the kinetics of that reaction. When other species which consume the H^+ are <u>not</u> present, the high chloride brines will be acid and highly corrosive to carbon steels. A typical example is probably the Salton Sea brines that are below pH 5.

A second effect of salinity (pointed out by Ellis, 1970) is the equilibrium of the hot water in the reservoir with the surrounding rocks:

$$1/2\text{K Mica} + 3\text{ Quartz} + K^+ \rightleftarrows 3/2\text{ K-Feldspar} + H^+$$

$$2\text{ Na Montmorillonite} + 10\text{ Quartz} + 6\text{ Na}^+ \rightleftarrows 7\text{ Albite} + 6\text{ H}^+$$

As the amount of K^+ and Na^+ in solution goes up, reaction with the rocks will make the equilibrium solution more acid.

Thus in the general case we can conclude as salinity increases we would expect the solutions to become more acid and more corrosive to steels unless alkaline species are also present to offset these effects.

<u>Effects of Cations More Noble Than H^+ in The Cathode Reactions</u>

Geothermal fluids contain traces of a number of cations more electrochemically noble than H^+ and capable of absorbing electrons in a cathode reaction. Examples of some such reactions occur in Salton Sea brines:

<u>Concentration in Salton Sea Brine</u> (Werner 1970)		Cathode Reaction
Cu^+	10 ppm	$Cu^+ + e^- \rightarrow Cu$
As^{+++}	15 ppm	$As^{+++} + 3e^- \rightarrow As$
Ag^+	1 ppm	$Ag^+ + e^- \rightarrow Ag$
Not Reported		$Hg^+ + e^- \rightarrow Hg$
Not Reported		$Sb^{+++} + 3e^- \rightarrow Sb$

While the concentrations are small, and the total effect on corrosion may be small compared with H^+ reduction, these species could play a role in localized corrosion. It is to be noted that Werner (1970) reports copper and silver as over 1% concentration in the scale formed on steel pipe pumping Salton Sea brine. Antimony (Sb) and arsenic were also found. Scanning electron microscope studies of a fractured turbine blade from the Geysers revealed the presence of arsenic on the fracture surface (Shannon, 1974).

An assessment of the impact of these cations on corrosion in geothermal brines and the effect of deposits of these metals on steel and the resulting impact on galvanic cells has yet not been studied.

Corrosion by Geothermal Steam at 140°C - 150°C

In the absence of a water phase, or O_2, the gas phase reactions produce corrosion of less than 1 mil/year in geothermal steam:

$$Fe + H_2S \rightarrow FeS + H_2$$

$$FeS + H_2S \rightarrow FeS_2 + H_2$$

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Hildebrand (1974) discusses design of units to strip H_2S from water by distillation at 212°F and says, "The overhead vapor line is made of carbon steel. If there is little or no condensation in this line, there is little corrosive attack on the metal."

However, in practice in a geothermal plant, some water almost always accompanies the steam either as entrained water droplets from incomplete steam separation (usually 0.5 to 1% moisture) or from condensation during steam transport. Galvanic cells can be set up when liquid is present. Thus in real life, geothermal steam is measurably corrosive to carbon steel. The corrosion rates listed in Table 4 are low enough to be acceptable provided a small corrosion allowance is made in the piping design.

TABLE 4. Corrosion of Carbon Steel in Geothermal Steam

	Japan* Matsukawa (Nakanishi, et al-1970)	Mexico Cerro Prieto (Nakanishi, et al-1970)	New Zealand Wairakei (Marshall 1957)
Steam Temp.	140°C	147°C	140°C
Corrosion Rate mils/yr	11	2-5	6
mm/yr	0.28	0.04 - 0.13	0.15

---

*Matsukawa has a very acid (pH 4-5) water accompanying the steam which causes higher corrosion rates.

Corrosion in a Hot Dry Rock Geothermal Plant by High Temperature Geothermal Steam Above 150°C

Discussions of hot dry rock geothermal plants often discuss the thermodynamic advantages of the super heated steam of up to 500°C (932°F) that might be generated. No corrosion data have yet been developed specifically for such a system. Carbon steel could be completely acceptable in deoxygenated dry steam at these temperatures since a protective magnetite (Fe_3O_4) film forms which reduces corrosion rates to acceptable levels. Small additions of chromium increase corrosion resistance significantly in the region above 400°C by formation of a Fe-Cr spinel protective film.

However, for geothermal applications we may, or may not, have sufficiently oxidizing conditions to form the protective film such as occurs in pure steam. As temperatures rise above 150°C one must consider gas phase reactions such as:

$$Fe + 2H_2S \rightarrow FeS_2 + 2H_2$$

Thermodynamic stability calculations indicate geothermal steam typical of the Geysers plant has sufficient H_2 and H_2S to reduce the oxygen chemical activity (fugacity-fo_2) to below $fo_2 = 10^{-46}$ atm. The calculated oxygen and sulfur fugacities for a geothermal steam typical of the Geyser's plant (H_2 = 0.0018 - 0.019%; H_2S = 0.0005 - 0.16%) is plotted on an iron phase diagram (from Helgeson 1969) Figure 9. It is interesting to note either magnetite (Fe_3O_4) or Pyrite (FeS_2) may be stable. Subject to the usual reservations about the accuracy of such calculations, one can estimate that at higher H_2S concentrations iron sulfides may be more stable than the more protective oxide in geothermal steam.

In Figure 10 we examine the reduction of magnetite by hydrogen sulfide:

$$\underset{\text{magnetite}}{Fe_3O_4} + 6H_2S \rightleftarrows \underset{\text{pyrite}}{FeS_2} + 4H_2O + 2H_2$$

When the free energy change (ΔF) of this reaction is negative pyrite tends to form. When ΔF is positive the reverse reaction goes to form magnetite. In Figure 7 we have calculated ΔF for a number of cases using the relationships:

$$\Delta F = \Delta F^\circ_T + RT \ln \frac{(PH_2O)^4 (PH_2)^2}{(PH_2S)^6}$$

$$\Delta F^\circ_T = \Delta \overset{o}{H} - T\Delta S^\circ$$

Free energy data were used from tables in Garrels and Christ (1965) and Krauskopf (1967). The equilibrium point, ΔF = 0, is in the range of H_2S levels found in real geothermal systems. This indicates a system could fluctuate from forming protective Fe_3O_4 to nonprotective Fe_2S and back again. If H_2S is low enough (note, Wairakei, NZ), corrosion rates of carbon steels should be lower.

We have examined in Case 5 in Figure 10 a hot dry rock system producing steam at 54.4 atm (800 psi) and 345°C (650°F). The higher steam pressure tends to stabilize Fe_3O_4 to quite high H_2S levels. Since hot dry rock systems may be relatively low in H_2S, it appears carbon steel or Fe-Cr steels could be used to at least 500°C. Where H_2S is low enough for magnetite to be stable, corrosion rates of Fe-Cr steels should be less than 5 mils/year.

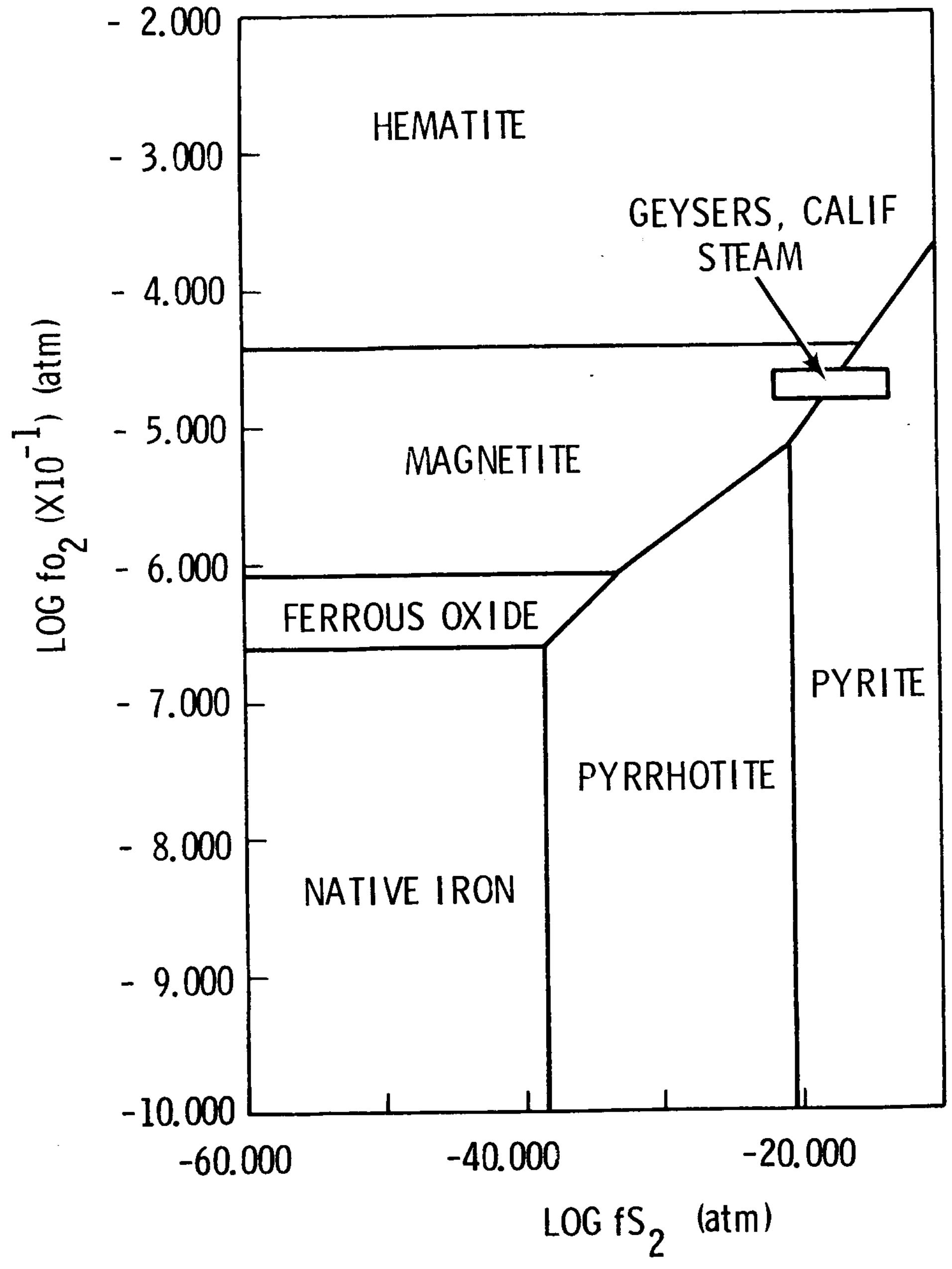


FIGURE 9. Fugacity Diagram - The System $HCl-H_2O-FeS-H_2S-H_2SO_4$ at 150°C

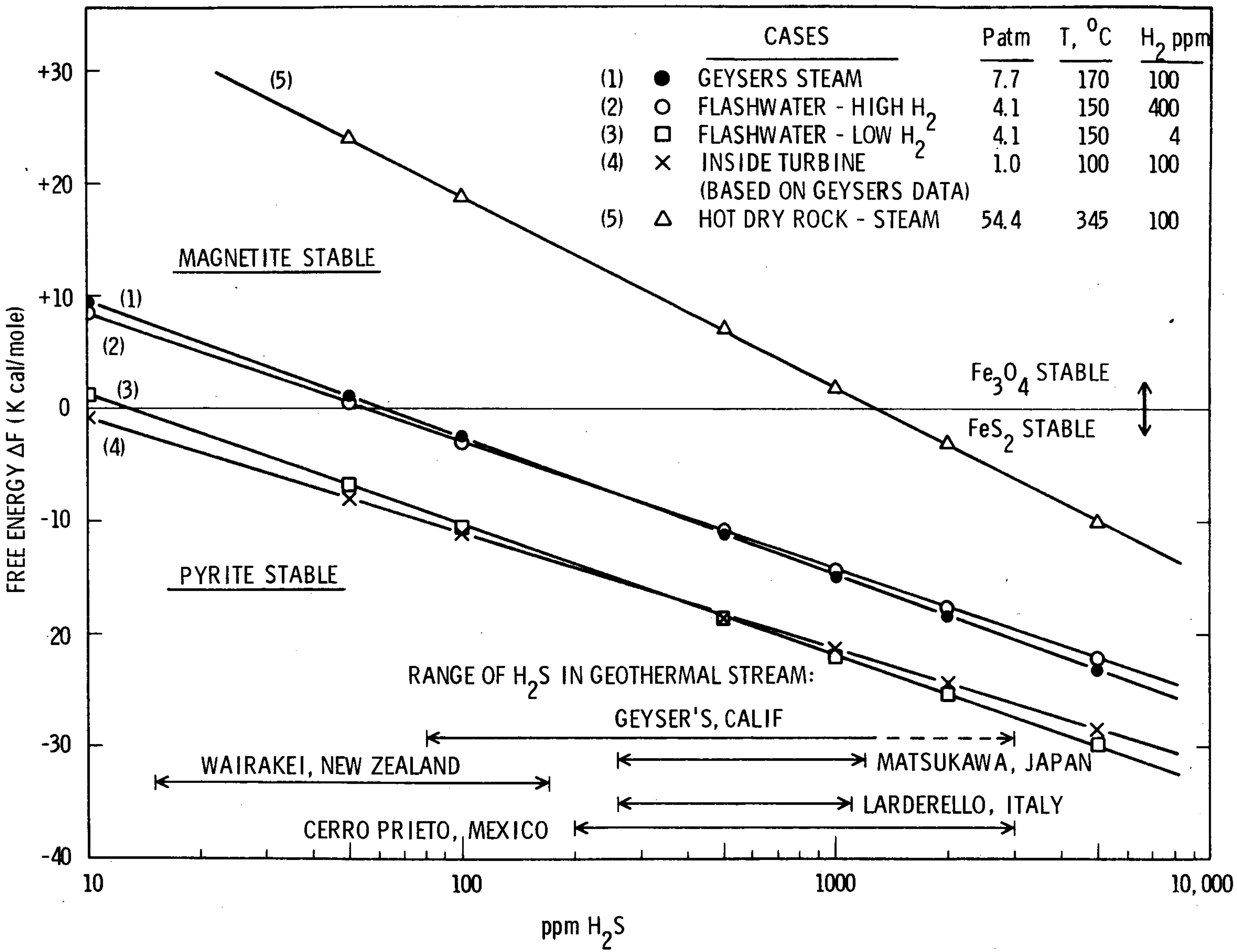


FIGURE 10. Free Energy of Reaction $Fe_3O_4 + 6H_2S \rightleftarrows 3FeS_2 + 4H_2O + 2H_2$

However, if direct reaction of H_2S with iron at these temperatures is probable (in preference to oxide formation) then some estimate of the H_2S corrosion rates on steels can be obtained from the oil refinery data in Figures 11 and 12 (McCoy 1974). If we assume an H_2S concentration of 0.025 to 0.05%, the expected corrosion rates for carbon steels are in the 20 to 30 mils/yr range at 400°C (750°F). Chromium additions only reduce the rates slightly. Figure 13 shows the corrosion rate rises rapidly in the low H_2S partial pressure range of interest to geothermal plants. Scanning electron microscope studies by McCoy showed the existence of an inner protective scale, primarily of composition $FeCr_2S_4$. One of the most interesting findings in McCoy's study was the pronounced reduction in corrosion rates achieved by aluminizing chrome-moly alloy steels, "which were almost completely resistant to H_2S attack in these tests at temperatures below 900°F. For example, at 900°F the corrosion rate of 9 Cr - 1 Mo alloy was 335.8 mils/year versus 2.1 mils/year for aluminimized coupons prepared by a diffusion technique. Such aluminizing should be investigated for geothermal applications where high temperature gas phase corrosion by H_2S may be encountered.

Corrosion Fatigue and Geothermal Turbine Blade Failures

Corrosion fatigue has caused innumerable failures in iron base alloys for many years and geothermal applications are no exception. Evans (1960) provides an entire chapter on corrosion fatigue in his book and discusses the principles involved. A recent review (McEvily & Staehle, 1971) discusses corrosion fatigue in depth. In the absence of corrosion effects, materials may be stress-cycled below their fatigue limit. However, in a corrosive environment the concept of a fatigue limit is no longer valid, and fatigue strength decreases with time, ultimately causing a fatigue fracture, Figure 14.

Corrosion fatigue is often associated with families of pits which start as pure pitting attack. The pit begins to grow preferentially at right angles to the applied stress and a corrosion crack begins to form in the base of the pits. Eventually the metal section is weakened where the final fracture occurs by pure mechanical fatigue.

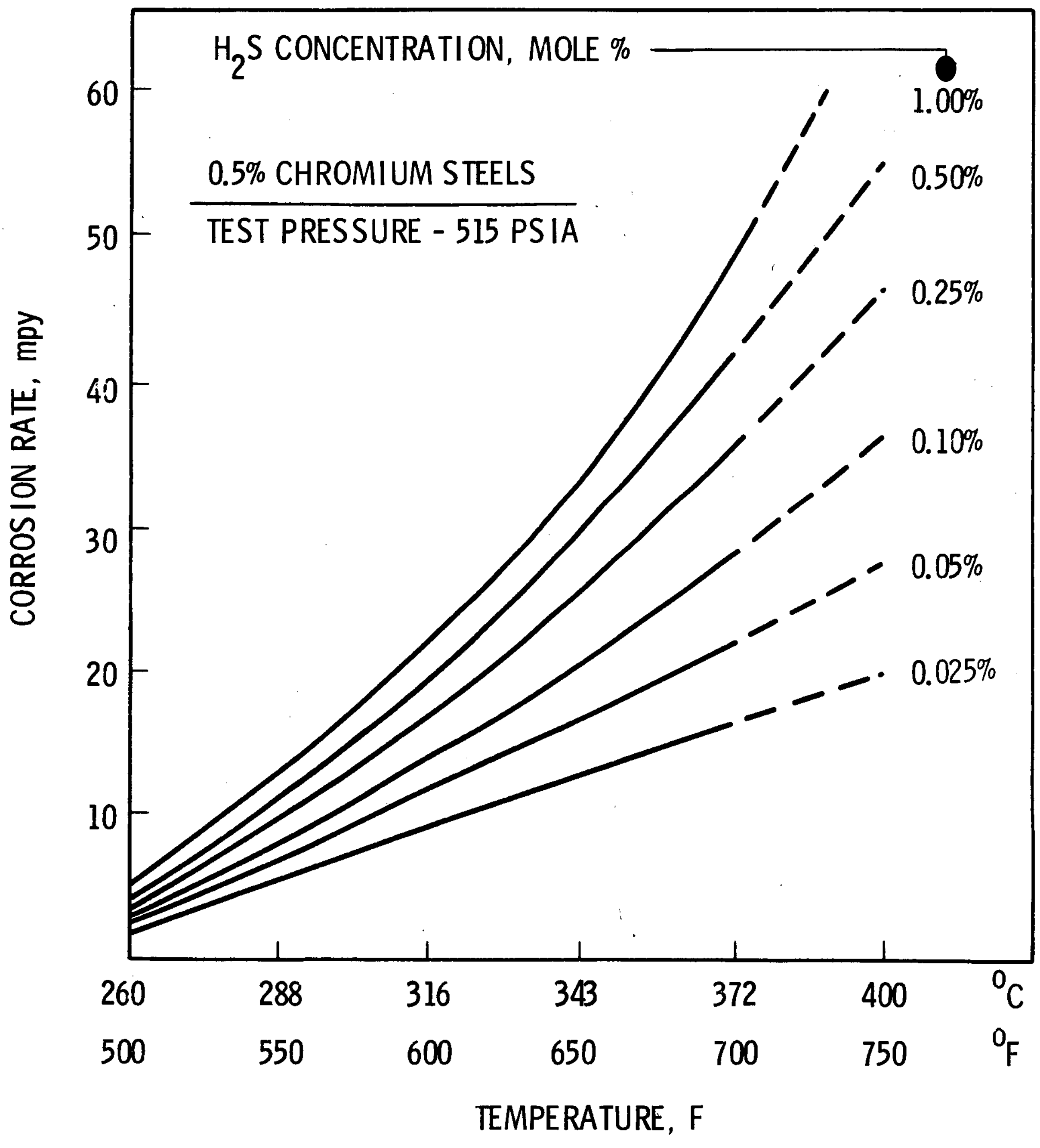


FIGURE 11. Corrosion Rate Curves for H_2/H_2S Environments

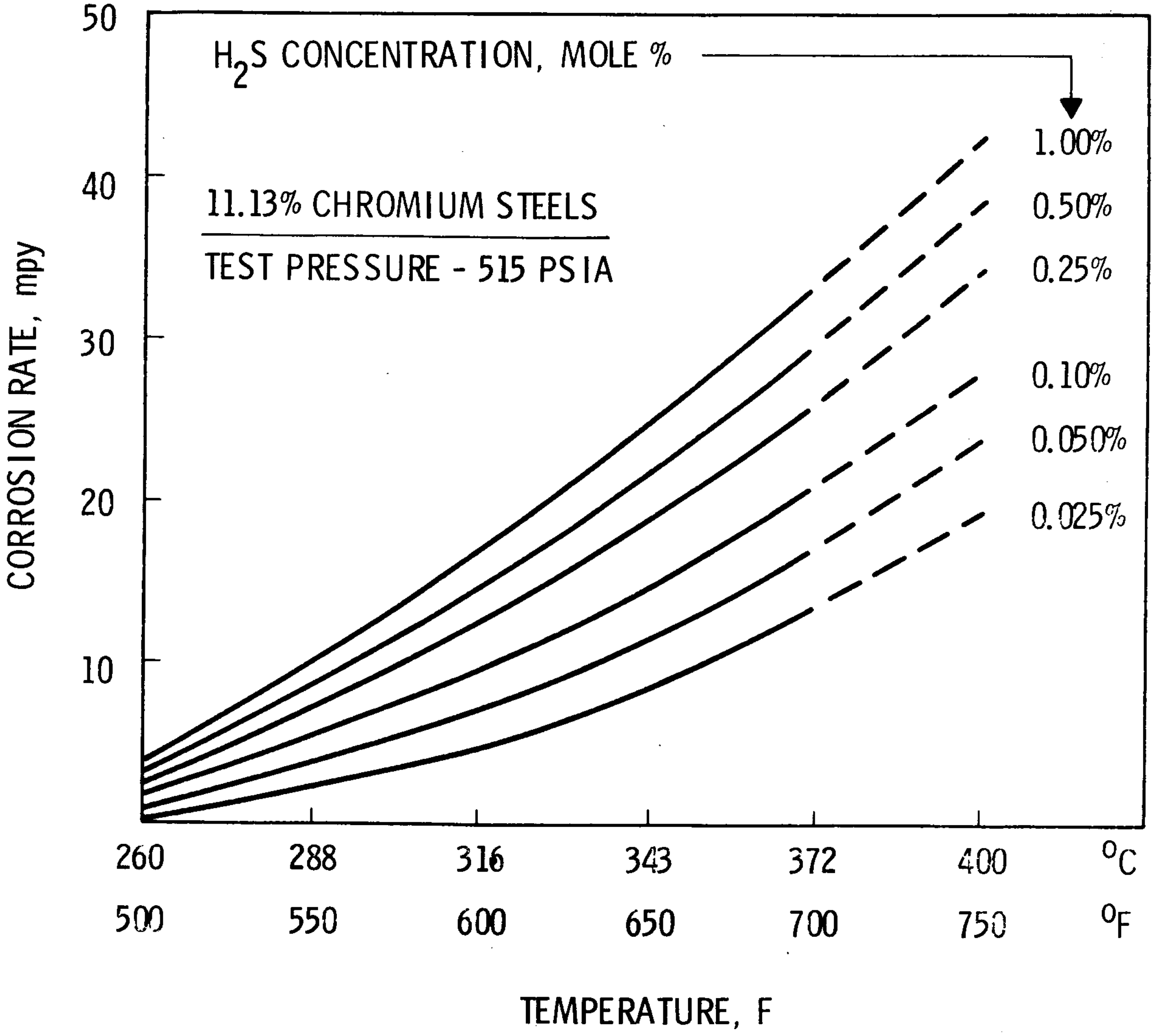
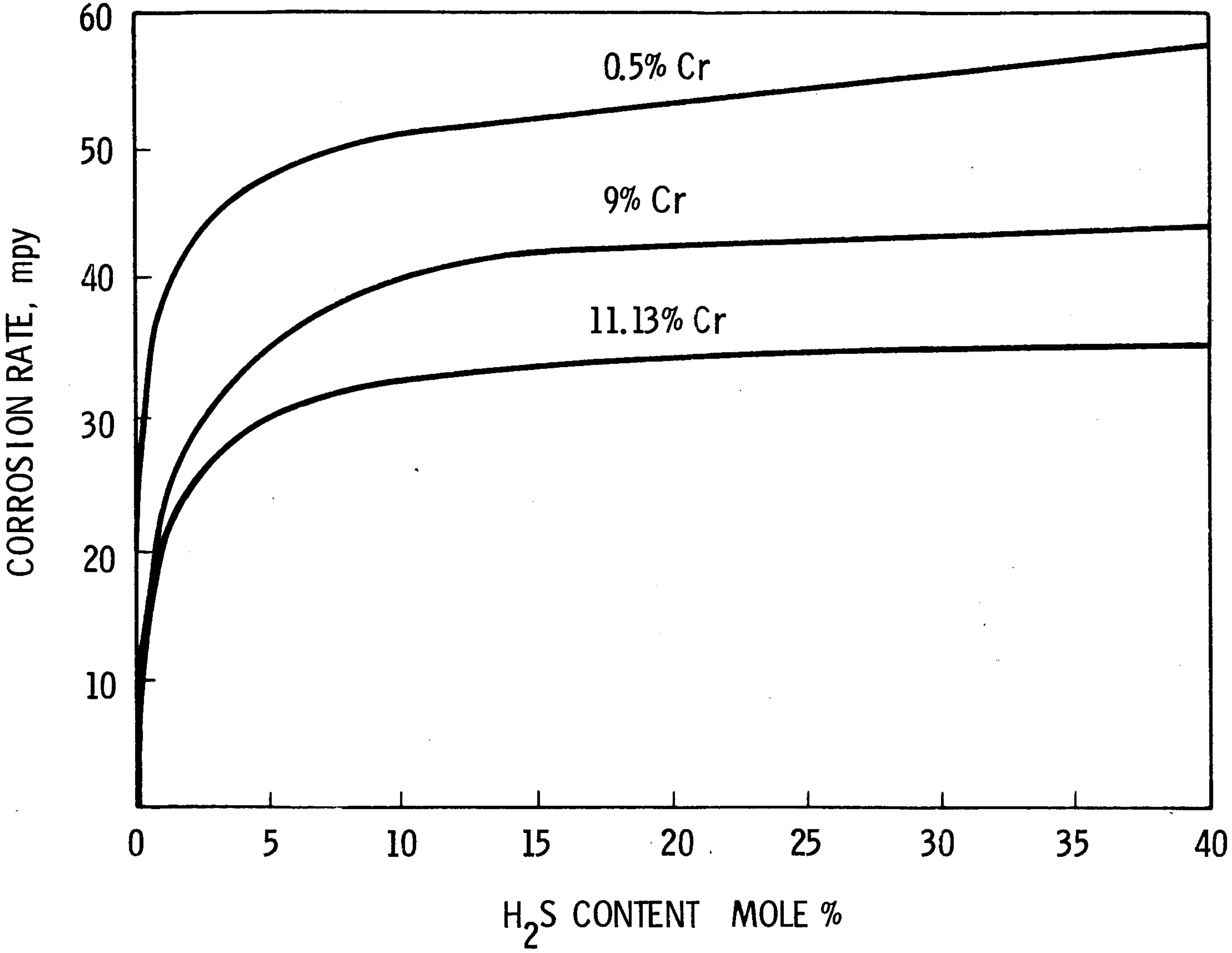
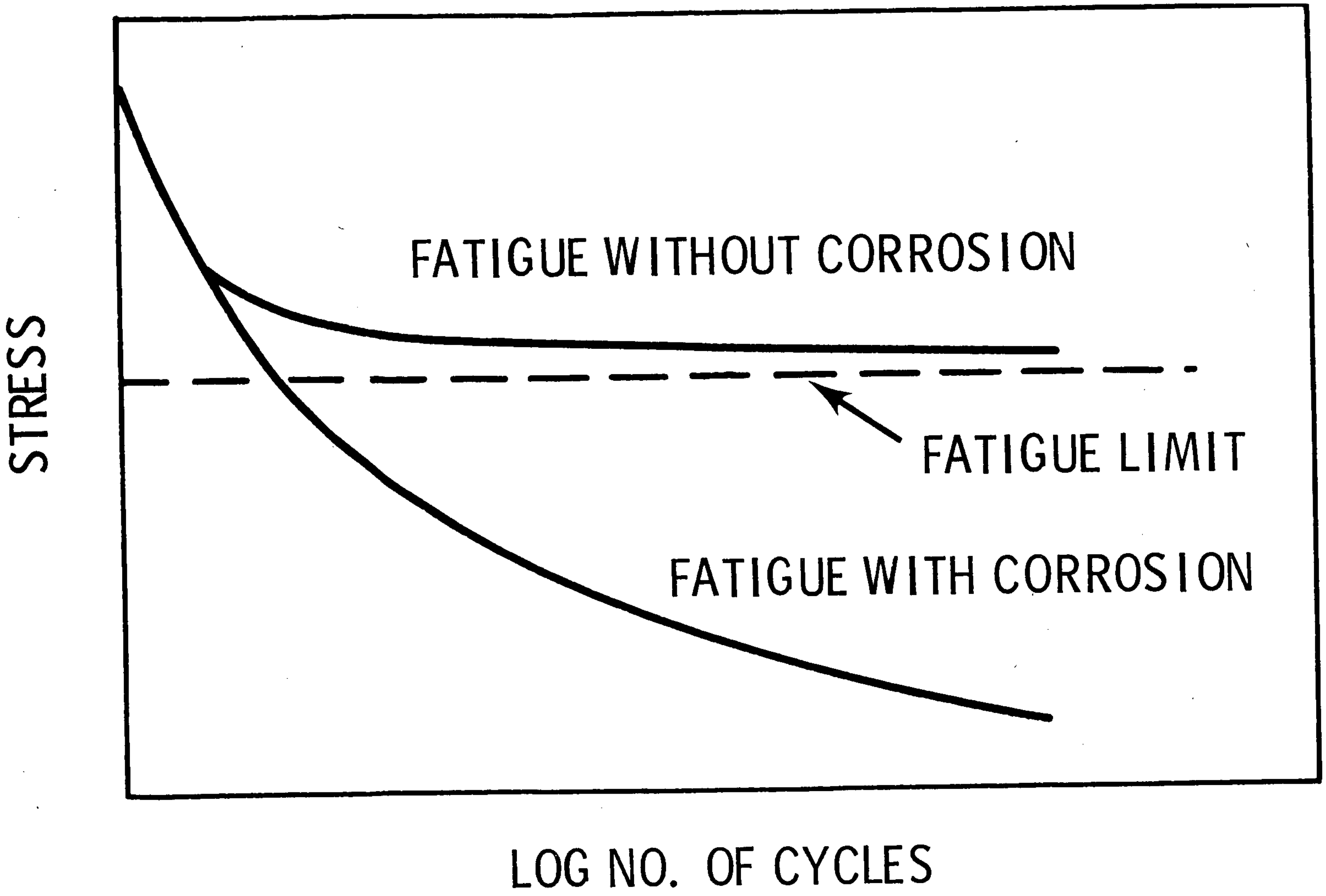


FIGURE 12. Corrosion Rate Curves for H_2/H_2S Environments



SOURCE: MORIN, 1974

FIGURE 13. Corrosion Rate versus H_2S Content in Gas for Chromium-Molybdenum Steels 370°C (700°F) and 500 psig



SOURCE: EVANS, 1960

FIGURE 14. Effect of Corrosive Media on Fatigue Life

Geothermal fluids can produce corrosion fatigue. Tolivia (1970), discusses corrosion fatigue tests at Cerro Prieto where some steel specimens exposed to geothermal steam 150 days at 147°C, and a stress of 50 kg/mm^2 failed at less than half the stress cycles of unexposed specimens. One high strength steel (B50-A125H) tensile 101 kg/mm^2 (144,000 psi) failed in geothermal steam after only 3% as many cycles as unexposed specimens.

Nakanishi (1970) reports the fatigue limit drops 7.5 kg/mm (11,000 psi) for 12% Cr steel in 150 days in Cerro Prieto steam. However, it must be kept in mind such tests are time dependent and the fatigue strength would be expected to drop further in longer tests.

Corrosion fatigue is especially important in geothermal turbines where corrosive conditions and high cyclic stresses are encountered. There have been several turbine blade and band failures in the 12% Cr Type 410 steel in the Geysers plant turbines which probably are caused by corrosion fatigue (Shannon 1974).

It is clear the 12% Cr steels now used for turbine blades in geothermal turbines are subject to pitting in geothermal steam (Shannon 1974, Nakanishi 1970, Marshall 1957, Yoshida 1968). Since it is axiomatic that a material that pits is especially prone to corrosion fatigue, it would appear that an R&D test program to find a replacement turbine blade material is needed.

The corrosion resistance of the 12% Cr steels depends upon the formation of a passive Fe-Cr oxide film. With the equilibrium oxygen activity in geothermal steam approximately $fo_2 = 10^{-40}$ to 10^{-50} atm we showed in Figures 9 and 10 that this passive protective film may not be stable and pitting corrosion can begin. Chlorides also promote breakdown of the passive film and this may be involved, too.

At the very low equilibrium oxygen levels in geothermal steam one can speculate that very small air leaks could raise the oxygen chemical activity and create a non-equilibrium situation where O_2 is high enough (e.g., even 1 ppb) to achieve a passive film and reduce pitting of 12% Cr steels.

This suggests it might be of interest to test very small O_2 additions to the steam as it enters the turbine.

The cure to corrosion fatigue in geothermal turbines is partly to reduce cyclic stresses to the minimum. However, a more fundamental cure would be a blade material with inherent passivity to the geothermal steam as well as adequate mechanical properties.

Speculating about the passivity aspects only (not the mechanical requirements) titanium, aluminum alloy additions or coatings, and the Ni-Cr-Mo alloys may be of interest. The excellent performance of aluminized Cr-Mo steel in H_2S is interesting (McCoy 1974). There are some organic coatings for service at temperatures < 400°F in geothermal systems that could be explored. It would appear we do not now have optimum geothermal turbine materials. Geothermal projects to data have been too sparsely funded and the geothermal turbine market too small to support R&D for improvements.

Erosion Corrosion

When geothermal brine impinges on steel at high velocity the protective passive film can be mechanically removed as fast as it forms. This will result in accelerated attack, especially in more acid solutions. Erosion corrosion problems would be especially severe on brines containing suspended solids which would "sandblast" the protective film.

Erosion corrosion would not be limited to Fe alloys but is a general problem with all corrosion construction materials that depend on passive films for corrosion resistance.

Applications where erosion corrosion is to be expected are valve seats, pipe turns, turbine parts, and orifice plants. The proposed use of impulse turbines (Austin 1973) on hot brines may be subject to severe erosion corrosion on the impeller blades.

Sulfide Cracking and Hydrogen Embrittlement

In an H_2S - brine-oil mixture the H_2S promotes the absorption of nacent corrosion product hydrogen into the metal lattice. In soft steels this can lead to blisters in the steel where nacent hydrogen recombines to H_2 in metal voids creating internal pressure. In higher strength steels brittle fracture occurs. The cure to the problem is illustrated in Figure 15. By specifying the hardness of all steels below R_c22, cracking is minimized. Some failures still have occurred however, but in every case it appears localized work hardening or tool marks increased local hardness which caused failure (Tuttle 1974). The hydrogen embrittlement problem can decline as the temperature increases since H_2 diffuses out of the metal lattice.

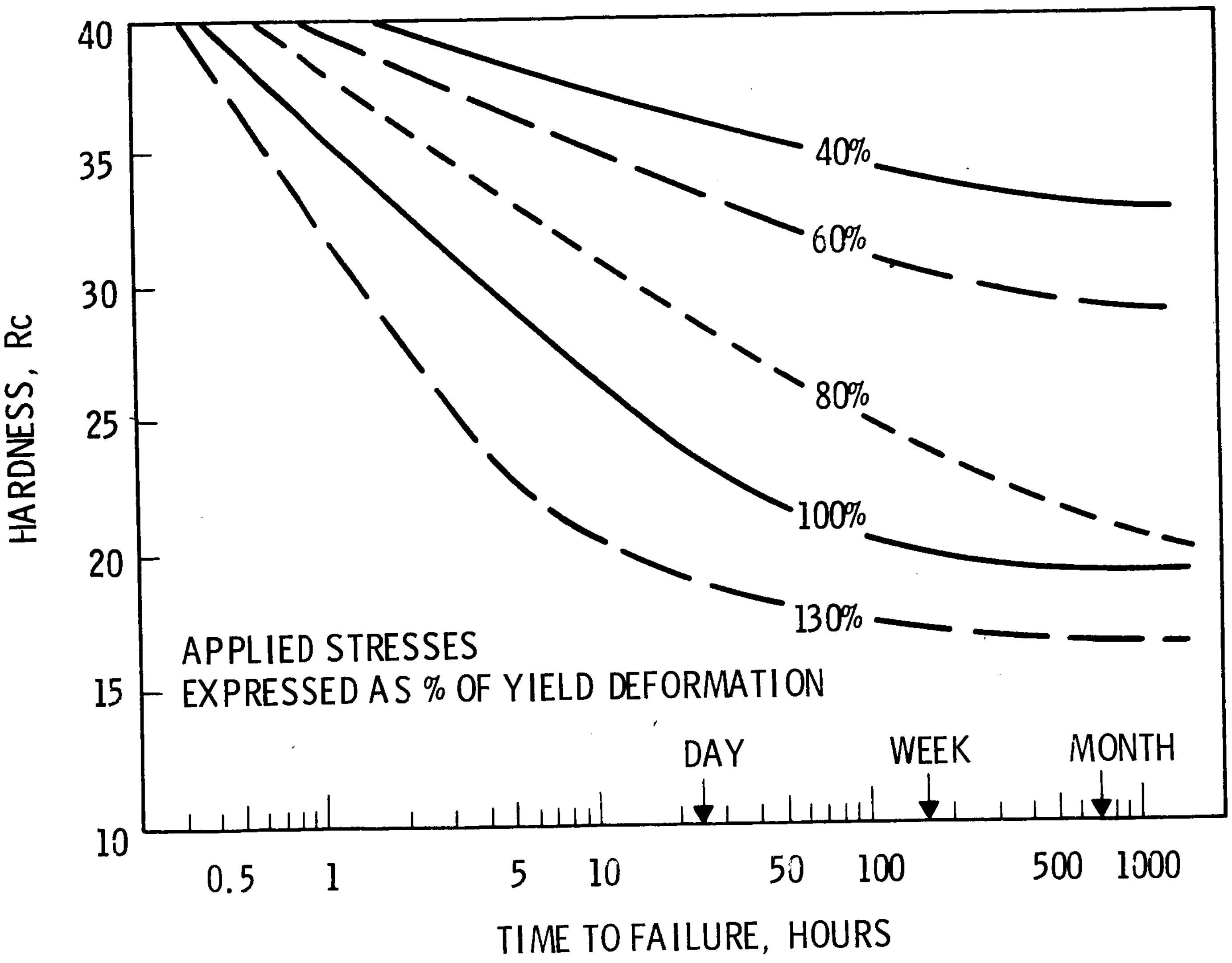
There is a significant engineering and cost impact imposed by the Rc22 hardness limitation. This eliminates many high strength steels that would produce a lighter, cheaper mechanical design. In some cases materials strength is limiting so the search goes on for both high strength and H_2S cracking resistance. A list of promising high strength materials based on 28-day laboratory tests (not yet field tested) is given in Table 5 (Rice, et al., 1973).

Type 410 stainless steel (12% Cr) is very subject to hydrogen embrittlement cracking if in the hardened condition. However, tests in geothermal steam (Marshall 1957, Haldane 1962) have shown Type 410 steel resists cracking if in the soft, annealed condition.

Effect of Scale Deposits on Corrosion

It has been known for years that scale deposits of calcium and magnesium carbonates substantially reduce the uniform corrosion of steel piping in water systems. In geothermal waters such carbonate scales are often seen. Another very significant scale forming species is silica. The formation of these scales on the inside of steel pipe can reduce corrosion rates substantially. However, the practical problem may turn from pipe corrosion to pipe plugging due to scale. Pitting under deposited scale may sometime occur.

The formation rates of scale are a highly specific function of the individual water chemistry under consideration. Carbonate scales occur if CO_2 is lost. Silica scales form on cooling if the solubility of silica is exceeded. Tests must be conducted on specific waters to determine what effect, if any, scale deposits will have on corrosion and deposition. Where



SOURCE: NACE CORROSION DATA SURVEY, 1974

FIGURE 15. Approximate Correlation of Hardness, Time to Failure, and Applied Stress for Carbon Steels (3000 ppm H_2S in 5% NaCl)

TABLE 5. Promising High Strength Materials to Resist Sulfide Cracking Based on Laboratory Tests (Rice et al., 1973)

Criteria:

(1) 0.2% offset yield stress

(2) 10 ft lb minimum and average 18 ft lb average full size transverse Charpy V impact strength at -70°F (-57°C).

(3) Minimum 0.2% offset tensile yield stress of 60,000 psi

(4) Resist sulfide cracking in sour crude oil drilling operations

(no preferred order of merit)

AlSi 4340 (Quench & Tpmper, 26 Rc)

Vulcan Steel Astralloy (Quench & Temper, 25 Rc)

INCO k Monel (mill annealed & age hardened 29 Rc)

A286 (solution treated 1800°F (982°C) & Age 1325°F (718°C) all by mill 32 Rc)

Titanium Alloy 6 Al- 4 V mill annealed 33 Rc

J&L 304 N (cold worked by mill 26 Rc)

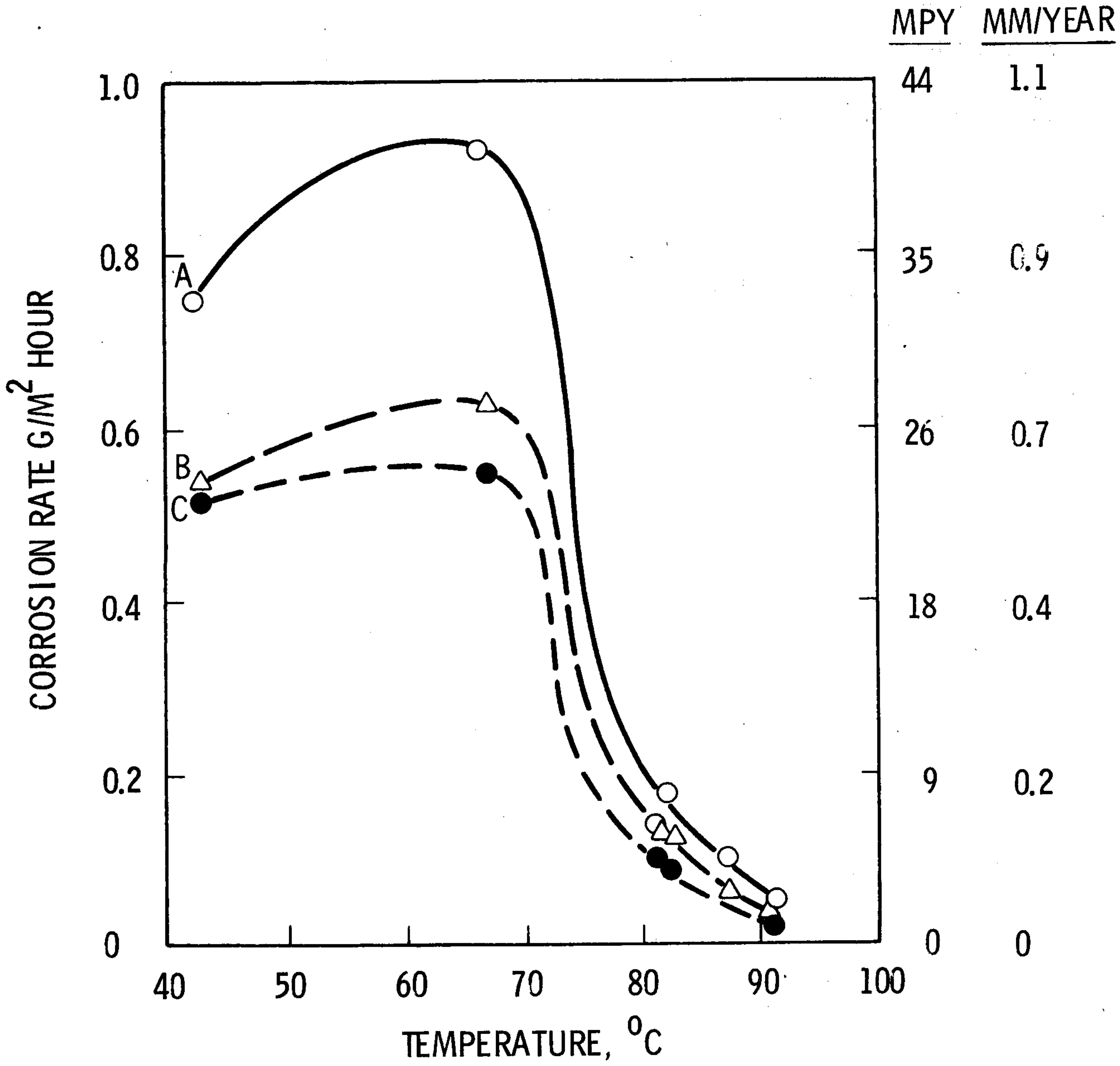
Armco 22-13-5 (cold worked by mill to 26 Rc)

Armco pH 13-8 Mo (Annealed & heat treated to condition H 1150 M 30 Rc) such waters are used in cooling towers the adjustments to cooling tower water chemistry must be considered. There is a voluminous literature on this subject which is beyond the scope of this report.

Effect of Temperature

The corrosion rate of iron alloys about doubles for every 10°C temperature rise if all other factors stay the same. However, in the general case the other factors never stay the same. This is illustrated by Figure 16 where corrosion decreases with increasing temperature because H_2S and CO_2 are less soluble in the liquid at 1 atm pressure at 90°C than at 60°C, so the pH changes with the partial pressures. The CO_2 and H_2S change concurrently with temperature.

The fluid chemistry, mineral stability fields, solubilities of scale forming minerals and reaction rates and equilibria are all highly temperature dependent. Thus it is not feasible to plot corrosion rate versus temperature diagrams until the environment is very carefully specified.



SOURCE: TSKHVIRSHVILI et al., 1972

FIGURE 16. Dependence of the Corrosion Rate of Carbon Steel on the Temperature of Natural Waters at the Mouths of Different Springs. A-2000, B-4500 and C-9100 Hours

AUSTENITIC STAINLESS STEELS

Pitting Corrosion and Passive Films

The 300 series 18% Cr - 8% Ni steels are successfully used for some geothermal applications. However, the role of the passive protective film on these steels must never be overlooked. Under oxidizing conditions the 300 series steels are much more stable than in the reducing conditions of a geothermal plant. Chlorides are effective in destroying the passive character of the protective film. When passive film breakdown occurs pitting corrosion results, often penetrating the steel faster than corrosion of carbon steel under the same conditions.

Successful Use in Desalting Plants

Stainless steel (especially Type 316) has been successfully used in desalinization plant service at 250°F (Lawson 1974). Some characteristic pitting or crevice corrosion was reported.

Stainless steels perform well in refreshed seawater (which has dissolved oxygen) but pit to failure rapidly under biological growths where localized oxygen depletion occurs (Fink 1970). Molybdenum additions (type 316SS) reduce pitting tendencies (Kopecki 1973). The necessity of dissolved oxygen to maintain passivity in choride brines suggests poor performance of stainless steels for geothermal brine service.

Application to Geothermal Systems

Allegrini (1970) describes pitting corrosion failures of AISI 316 stainless steel in the steam system at Larderello, Italy, after only a few months at 130°C - 220°C. Carbon steel bellows which lasted eight to nine years were replaced by stainless steel pipes that failed in two to six months. Marshall (1957) also reports significant pitting of 18/8 CrNi steels in steam at Wairekei, NZ.

In the general case the corrosion performance of austenitic steels in chloride containing geothermal steam or water will be inferior to carbon steel, and the extra cost for stainless steel unjustified.

However, in the steam condensate systems of geothermal plants, temperatures and chlorides are much lower. Thus, austenitic stainless steels (especially Type 316) perform well and are used extensively in the condensed steam parts of the system. Corrosion rates are almost unmeasurable in chloride-free condensate below 100°C. The passivity of the stainless steel is maintained and affords much more protection tothe acidic, and occasionally oxygen containing environment, than carbon steels would (Marshall, 1957, Yoshida 1970, Tolivia 1970).

Stress Corrosion Cracking

Austenitic stainless steels are notorious for brittle fractures due to stress corrosion cracking. Generally both chlorides and oxygen must be present, although the amounts required are only in the ppm range. Alternate wetting and drying can concentrate chlorides and increase the possibility of stress corrosion cracking. Marshall (1958) reported severe stress corrosion cracking of austenitic stainless steels in aerated geothermal steam at Wairekei, N.Z., however, no cracking occurred in air-free geothermal steam. Allegrini (1970) reports stress corrosion cracking of austenitic stainless steel at Larderello, Italy, geothermal steam systems.

Except where chlorides and temperatures are low (such as in steam condensate systems) the probability of stress corrosion cracking of austenitic stainless steels in geothermal fluids is extremely high. Latanision and Stahle (1967) surveyed many aspects of stress corrosion cracking of austenitic steels and gave data that 75°C and very dilute chloride solutions are adequate to produce cracking. Generally, however, stress corrosion cracking is more common above 100°C. The number of documented cases of stress corrosion cracking in the 150°C to 300°C temperature range fill the literature.

It would be dangerous to assume the normal lack of oxygen in geothermal fluids will prevent stress corrosion cracking in a geothermal system. Systems are periodically exposed to the air for maintenance. Given the right combination of stress, chloride, oxygen level, and temperature, austenitic stainless steels can crack in minutes!

Application to Water-Binary Cycle and Hot Dry Rock Systems

Chlorides will be at a significant concentration in almost any geothermal fluid. Because of the severe impact of chlorides on austenitic stainless steel pitting corrosion and cracking, there will be few applications for austenitic steels, with the notable exception of handling steam condensate below temperatures of about 100°C - 120°C. Even in this temperature range there is a risk of stress corrosion cracking.

ALUMINUM AND ITS ALLOYS

Corrosion in Geothermal Water and Steam

Aluminum is a very chemically active metal which has corrosion resistance due to a passive protective film. Aluminum alloys are subject to pitting and crevice corrosion, especially in chloride containing oxygen-free systems. Like austenitic stainless steels, aluminum can pit badly under scale (Verink 1974) or biological fouling.

The protective film is generally stable over a pH range of 4.5 to 8.5 (Dix 1961), which is the pH range often encountered in geothermal systems. Corrosion rates are usually lowest about pH 6. Corrosion rates for aluminum in geothermal steam and in steam condensate are given in Table 6.

TABLE 6. Corrosion of Aluminum Alloys in Geothermal Systems

	Steam 140°C-150°C mm/yr	Steam Condensate 100°C mm/yr	pH
Wairakei, N.Z.	0 (P)	0.005 (P)	6
Matsukawa, Japan	0.06 mm (P)	0.025 (P) pitting rate 1.1	4.5
Cerro Prieto, Mexico	0	0.08 (P)	6

(P) = Corrosion pitting observed

It can be seen from Table 6 that pitting corrosion is the major corrosion problem encountered with aluminum and once a corrosion pit forms complete perforation can occur rapidly. Note the pitting rate of 1.1 mm/yr (43 mils/yr) measured at Matsukawa, Japan.

The Al clad aluminum was developed to resist pitting attack. An aluminum tube is clad by metallurgically bonding to another aluminum alloy that is anodic to the base alloy. When a corrosion pit reaches the base alloy, the clad cathodically protects the base metal from further penetration until the clad is consumed. There are no specific references to the AL clad technique being used in geothermal plants, but it would appear promising for those low temperature applications where the structural properties of aluminum are satisfactory.

Aluminum has been used successfully in the steam condensate lines at the Geysers plant (Finney 1973) and other low temperature applications in other geothermal plants (Haldane 1962).

Because of low cost, good general corrosion resistance to H_2S brines, and good heat transfer, aluminum alloys may have considerable application to the lower temperature-binary cycle systems and related applications.

Galvanic Corrosion

Aluminum is highly susceptable to galvanic corrosion effects which must be considered in any design. Coupling aluminum to steel (or stainless steel) make aluminum the anode and subject to accelerated attack. Electrical insulators and/or coatings must be used in mixed metal systems. Aluminum is subject to rapid failure by contamination with copper, or its compounds. As would be expected, the 2000 series Al-Cu alloys have poor corrosion resistance in chloride brines.

Stress Corrosion Cracking

There are numerous reports of stress corrosion cracking of high strength aluminum alloys (see Fink, 1970, for cracking in seawater). Generally stress corrosion cracking is confined to those alloys especially formulated and heat treated for high strength. Chloride solutions are especially aggressive, and a 3.5% NaCl solution is often used as a laboratory test medium for stress corrosion tests.

Stress corrosion cracking should not be a serious problem for geothermal applications so long as the proper alloys are used. However, in high temperature applications where strength may be limiting, caution should be used about specifying high strength aluminum alloys; stress corrosion cracking is likely to occur.

It should be mentioned mercury causes catastrophic corrosion and cracking of all aluminum materials.

Atmospheric Corrosion

Aluminum alloys have outstanding corrosion resistance to the H_2S contaminated air atmospheres around a geothermal plant. Aluminum has been successfully used for transmission lines and hardware (Finney 1973). Galvanic corrosion must be considered if aluminum is used in the same structure as other metals, especially crevices where rain water can collect.

TITANIUM AND ZIRCONIUM

Titanium and zirconium are both extremely active elements that form very protective oxide films.

Titanium

Titanium is an outstanding material for a great many corrosive environments. Corrosion resistance is excellent in salt water. Fink (1970) lists three problem areas with titanium in salt water environments:

1) corrosion pitting observed in oxygen-starved crevices above temperatures of 120°C (250°F),

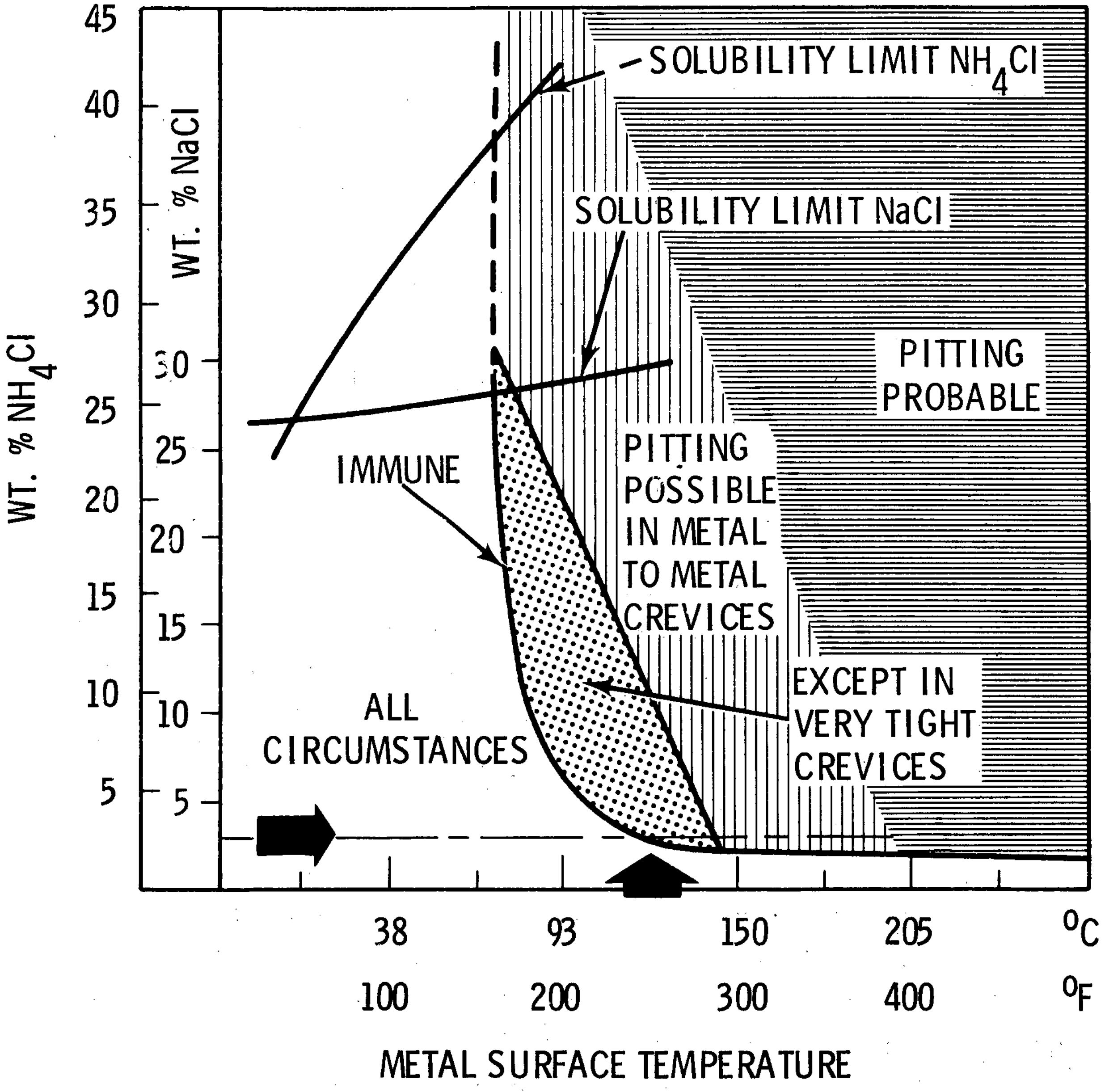
2) stress corrosion cracking under tensile stress with a surface flaw,

3) stress corrosion cracking under tensile stress in dry NaCl above 260°C (500°F).

For geothermal applications, the pitting tendencies are the most serious, as all geothermal fluids are low in oxygen. In Figure 17 the pitting tendency is plotted. These data indicate excellent performance at NaCl concentrations below 1 to 2% and all NaCl brines below 120°C (250°F).

Titanium has performed well in a number of applications, relating to geothermal service, see Table 7.

Titanium may be the best material for heat exchangers involved in the proposed binary cycle geothermal plant, especially if the pH is below about 7 and the water is below 3% NaCl. (Above about pH 7-8 carbon steel is possible). As the salinity and temperature increase, the tendancy to pit increases and any proposed applications of titanium in the "pitting" zone of Figure 14 should be checked by field tests (especially tests for crevice corrosion).



SOURCE: FEIGE, 1969

FIGURE 17. Anticipated Performance of Unalloyed Titanium in Chloride Brines and Under NaCl or NH_4Cl Deposits

TABLE 7. Successful Use of Titanium in Service Related to Geothermal Plants

Environment	Temperature	Corrosion	Remarks
Geothermal Steam Matsukawa, Japan (Joshida, 1970)	140°C	~ 0	steam contained 0.06% H_2S
"Sour Brine" 5% NaCl, - H_2S at pH 2.8 (Rice 1973)	ambient 28 days	no cracking	Ti-6Al-4V alloy
High Pressure Salt Water Well Injection Pump (Stormer 1972)	ambient	no corrosion fatique after 584 million cycles operating at 4000-5000 psi	Ti-Cp70
Refinery Sour water stripper (Hildebrand 1974)	180°F-200°F refluxing brine in H_2S	"slight etching after 3-4 years service"	one case of pitting failure under carbonate scale
Desalinization Plants	up to 250°F	~ 0	Ti used to replace failed copper alloys

Zirconium

No data are available on application of zirconium and its alloys to geothermal systems. Zirconium has excellent corrosion resistance to dilute acids, neutral salts (except Fe^{+3} and Cu^{+2}), and alkaline solutions up to 100°C. Few high temperature data are available except for the outstanding corrosion resistance of Zircaloy-2 up to 750°F in nuclear reactor service. These facts suggest zirconium alloys could have applications to geothermal systems if the high initial material cost could be overcome by superior performance.

HIGH NICKEL ALLOYS

Alloys with high nickel content have not been extensively used in geothermal plants except for some application of Monel. In today's geothermal plants, materials problems have been solved with less expensive materials.

With the exception of the 54Ni-15Cr-16Mo alloys (Hastelloy C, Inconel 625), most nickel alloys are subject to crevice corrosion and pitting corrosion in saline systems, and high nickel alloys are not much better than Type 316 stainless steel which costs less. This is especially true of crevice corrosion, and corrosion under scale and fouling. Even the Ni-Cu alloys (Monel), which are excellent in oxygenated seawater, pit badly in oxygen deficient systems (Fink 1970). The addition of Mo increases the resistance of nickel alloys to pitting (as it does for Type 316 stainless). The corrosion of Hastelloy C and Inconel 625 in seawater is excellent, equaled only by titanium. These alloys may be candidates for pumps, heat exchangers and other geothermal components where less costly materials are not adequate. Field tests in geothermal fluids would be essential.

There are very few data available for nickel alloys in geothermal systems. Table 8 gives data from Marshall (1957) and data from International Nickel Co. (Banning 1973). Hildebrand (1974) reports a test in some brine strippers where Hastelloy B and C performed well in refluxing H_2S brine at 180°F.

As a general rule pure nickel does not have good corrosion resistance to sulfur and H_2S at high temperatures. Thus one should not expect nickel base alloys to have good high temperature corrosion resistance in geothermal steam. Swardby (1963) indicates the 54Ni-15Cr-16Mo alloys are resistant to H_2S atmospheres up to 300°F.

TABLE 8. Corrosion of Nickel Alloys in Geothermal Systems(1)

	Geothermal Steam 140-150°C	Aerated Steam 110°C	Gas Rich Steam Condensate 70°C (containing H_2S & CO_2)
Wairakei, NZ (Marshall, 1956)			
Inconel (78% Ni, 13 Cr, 9Fe)	0.0000	2 mm yr (80 mils/yr)(2)	Not reported
Monel (Ni-30% Cu)	0.1 mm/yr (4 mils/yr)	0.25 mm/yr (10 mils/yr)	0.1 mm/yr 4 mils/yr)(3)

GT Paul International Nickel Co.
(Published by Banning & Oden 1973)

	Geothermal Steam 150°C		Steam Condensate 115°C pH 5.25	
Monel	0.13 mm/yr	5.0 mils/yr	0.13 mm/yr	5.2 mils/yr
Nickel	0.06	2.3	0.07	2.8
Inconel	0.003	0.1	0.003	0.1
Ni-O-Nel	< 0.003	< 0.1	< 0.003	< 0.1
Hastelloy F	< 0.003	< 0.1	< 0.003	< 0.1
Ni-Resist	0.09	3.8	0.07	2.4

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1. No stress corrosion cracking observed.
2. Aerated steam test-carbon steel only corroded 20 mils/yr and Type 316 stainless steel was essentially zero.
3. Steam condensate tests (carbon steel corroded 3 mils/yr and Type 316 stainless steel was essentially zero.

COPPER AND COPPER ALLOYS

Tests conducted to date on copper alloys have indicated moderate to high corrosion rates in geothermal fluids, especially when oxygen leaks into the system. Copper is avoided in electrical instruments, relays and switch gear because of attack by H_2S (Finney 1973). Corrosion rates for several copper materials in geothermal steam and condensate are given in Table 9.

Hermannsson (1970) reports mixed results in using copper alloys for transporting hot, geothermal water in Iceland. He states the use of copper alloys is limited by the content of alkali sulfide in the water and Cu-Zn and Cu-Sn alloys have given "very bad" results. Where copper materials were successful it was because the water chemistry and velocity permitted the formation of a protective--cuprosilcate film. Marshall (1957) and Tskhvirashvili (1970) report dezincification of brass.

The effect of H_2S on copper alloys in desalting plants is discussed by Morin (1974) where 0.5 to 1 ppm H_2S in seawater produced severe attack to copper alloys, most of which are being replaced with titanium.

In H_2S contaminated water copper alloys form copper sulfide film which is more cathodic than the oxide film (Fink 1970). When breaks occur in the sulfide film the large cathode area causes stimulated local attack. The available data suggest copper alloys will not have very wide application to geothermal systems which contain H_2S. Certainly no copper alloys should be specified without careful field tests.

TABLE 9. Corrosion of Copper Alloys in Geothermal Systems mm/yr

	Geothermal Steam 140 - 150°C	Aerated Steam 110°C	Gas Rich Steam Condensate 70°C (containing H_2S & CO_2)
Wairakei, NZ (Marshall 1956)			
Copper	0.05 (2 mpy)	1.0 (40 mpy)	0.13 (5 mpy)
Silicon Bronze	0.08 (3 mpy)	0.5 (20 mpy)	--
Phosphor Bronze	0.05 (2 mpy)	0.2 (9 mpy)	--
Brass	0.01 (0.4 mpy)	1.0 (40 mpy)	--
Aluminum Bronze	0.08 (3 mpy)	0.2 (10 mpy)	0.005 (0.2 mpy)
Cerro Prieto, Mexico (Tolivia 1970)			
Copper	--	0.6 (25 mpy)	0.2 (9 mpy)
Naval Brass	--	--	0.06 (3 mpy)
Matsukawa, Japan (Yoshida, 1968)			
Copper	0.4-1.0 (16-40 mpy)	--	0.07 (3 mpy)
Phosphor Bronze	0.05-0.3 (2-14 mpy)	--	--
Naval Brass	0.05-0.4 (2-16 mpy)	--	0.03 (1 mpy)

MATERIALS APPLICATIONS

This section has been placed last in the hope that an engineer seeking quick answers will consider the preceding discussion before jumping to rash conclusions.

In Table 10 are listed some general guides to materials selection for geothermal systems. The usefulness of Table 10 is limited to materials selection for economic analyses of geothermal concepts and to select candidate materials for field tests. The big data gap in geothermal water above 180°C is an obvious problem. Even in the 120°C - 180°C range corrosion rate data are inadequate, but some extrapolation is possible. The brief comment in the problems column is to flag some of the significant problem areas which were discussed in preceding sections.

TABLE 10. Candidate Materials for Oxygen-Free Geothermal Systems

	<120°C (250°F)		120°C-180°C (250°F-350°F)		>180°C (>350°F)	
	Material	Problems	Material	Problems	Material	Problems
Dry Steam	Carbon steel Low alloy steels 12 Cr steel	Corrosion fatigue Erosion High corrosion if steam condenses	Carbon steel Low alloy steels 12 Cr steel Titanium Zirconium	Corrosion fatigue Erosion Specify corrosion allowance	Cr-Mo steels 12 Cr steels	Corrosion fatigue Erosion Specify significant corrosion allowance R&D on turbine materials
					Zirconium Titanium	Lack of data
Water						
pH >8	Carbon steel	Erosion	Carbon steel Low alloy steels	Hydrogen embrittlement Erosion Specify corrosion allowance	Alloy steels (for strength	Hydrogen embrittlement Erosion Specify corrosion allowance Need R&D for data
pH 6-8	Carbon steel	Erosion	Carbon steel Low alloy steels	Erosion Specify corrosion allowance	R&D Required	
	Aluminum	Test for pitting				
	Titanium		Aluminum	Test for pitting	Use titanium or 56Ni-15Cr-16Mo* for cost studies. Iron alloys with heavy corrosion allowances	
	316 SST	<50 ppm Cl^- required	Titanium	Test for pitting and crevice corrosion (especially in brines)		
			56Ni-15Cr-16Mo			
pH 4-6	Carbon steel	Short life uses only				
	Aluminum	Test for pitting	Aluminum	Pitting Test required		
	Titanium		Titanium			
	Zirconium		Zirconium		R&D Required Use titanium or 56Ni-15Cr-16Mo* for cost studies	
	316 SST	<50 ppm Cl^- required	56Ni-16Cr-16Mo*			
	56Ni-15Cr-16Mo*					
pH 4	Titanium	R&D Required	Titanium	R&D Required	R&D Required	
	Zirconium		Zirconium			
	56Ni-15Cr-16Mo*					

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* Such as Hastalloy C

GEOCHEMICAL AND MATERIALS CONSIDERATIONS IN ECONOMIC MODELING OF GEOTHERMAL ENERGY SYSTEMS

INTRODUCTION

The geothermal water and steam chemistry will affect both the plant capital cost and operating costs:

Capital Cost Factors

- equipment needed to control scaling and corrosion
- materials selection to combat corrosion

Operating Cost Factors

- operation of scaling and corrosion control equipment, including temperature and pressure losses caused by such equipment
- replacement of equipment that fails by corrosion in less time than plant life
- loss of plant availability during forced shutdowns caused by scaling and corrosion.

The chemistry parameters which affect plant costs have been discussed in previous sections and are summarized in Table 11. This section will concentrate on methods to evaluate the economic impact of those parameters.

It would be desirable to have equations describing plant costs as functions of each parameter in Table 11. However, the present state-of-the-art and published data do not permit such an idealized approach. This is because the listed parameters are functions of each other, and very little experimental work has been done to describe the interrelationships, rather the practical approach has been to measure scaling and corrosion rates in field tests at a specific geothermal site and tailor the plant design to cope with the specific problems. Thus, geothermal plant design and cost estimating is best handled on an iterative basis:

TABLE 11. Parameters Affecting Scaling and Corrosion in Geothermal Plants

Scale and Incrustation

- Silica (SiO_2)
- Calcite ($CaCO_3$)
- Gypsum ($CaSO_4$-$2H_2O$)
- Soluble Salts and Salt Carryover
- Temperature and Temperature Changes
- Pressure changes including partial pressure change in CO_2, H_2S, NH_3
- Velocity and Turbulence
- Residence time in each part of plant
- Surface effects and surface to volume ratio effects.
- Phase (e.g., steam or water)

Materials Corrosion

- pH of water (pH is affected by temperature, gas partial pressure, and mineral content)
- Temperature and ΔT
- Phase (e.g. water or steam?)
- Moisture carryover if steam phase
- Partial pressures of CO_2, H_2S, NH_3, H_2
- O_2 leakage into system.
- Stress levels in materials and especially cyclic stresses
- Crevices
- Presence or absence of scale deposits
- Passive or active state of metal protective films
- Velocity
- Suspended solid content
- Ionic strength
- Galvanic coupling of dissimilar metals

Step 1. With a knowledge of the thermodynamic, chemical, and corrosion properties of the geothermal fluid, scope a plant design to extract power and cope with the obvious problems.

Step 2. Define the range of values for parameters in Table 1 for various parts of the plant--since the literature data are limited, lab and field tests are needed for accuracy.

Step 3. Select materials of construction to cope with corrosion problems and decide what methods will be used to cope with scaling problems.

Step 4. Estimate the capital and operating costs for the plant.

Step 5. Iterate back to Step 1 to affect design and cost optimization.

CASE 1 - LOW SALINE HOT WATER - GEOTHERMAL RESOURCE - FLASH WATER TYPE PLANT

Examples of the flash water type plant are at Cerro Prieto, Mexico, and Wairakei, New Zealand (Figure 18). This geothermal resource is characterized by a large underground reservoir of high temperature water under sufficient hydrostatic pressure to maintain a 100% liquid phase in the reservoir.

Wells drilled into this reservoir do not produce steam initially. First the column of water must be blown out of the well (by air injection) to reduce the hydrostatic head. With reduced pressure, boiling begins within the well, and a self sustaining two-phase flow begins. The steam-water mixture has cooled substantially by the time it reaches the steam separator at the surface. Steam temperature, pressure, well flow rate, and reservoir life are interrelated variables and their optimization is beyond the scope of this report. For our purposes here the important considerations are:

- The geothermal fluids have cooled 100-200°C in the process of production up to the well head by adiabatic expansion
- About 20-25% if the mass flow leaves the steam separator as steam (remainder as waste water)

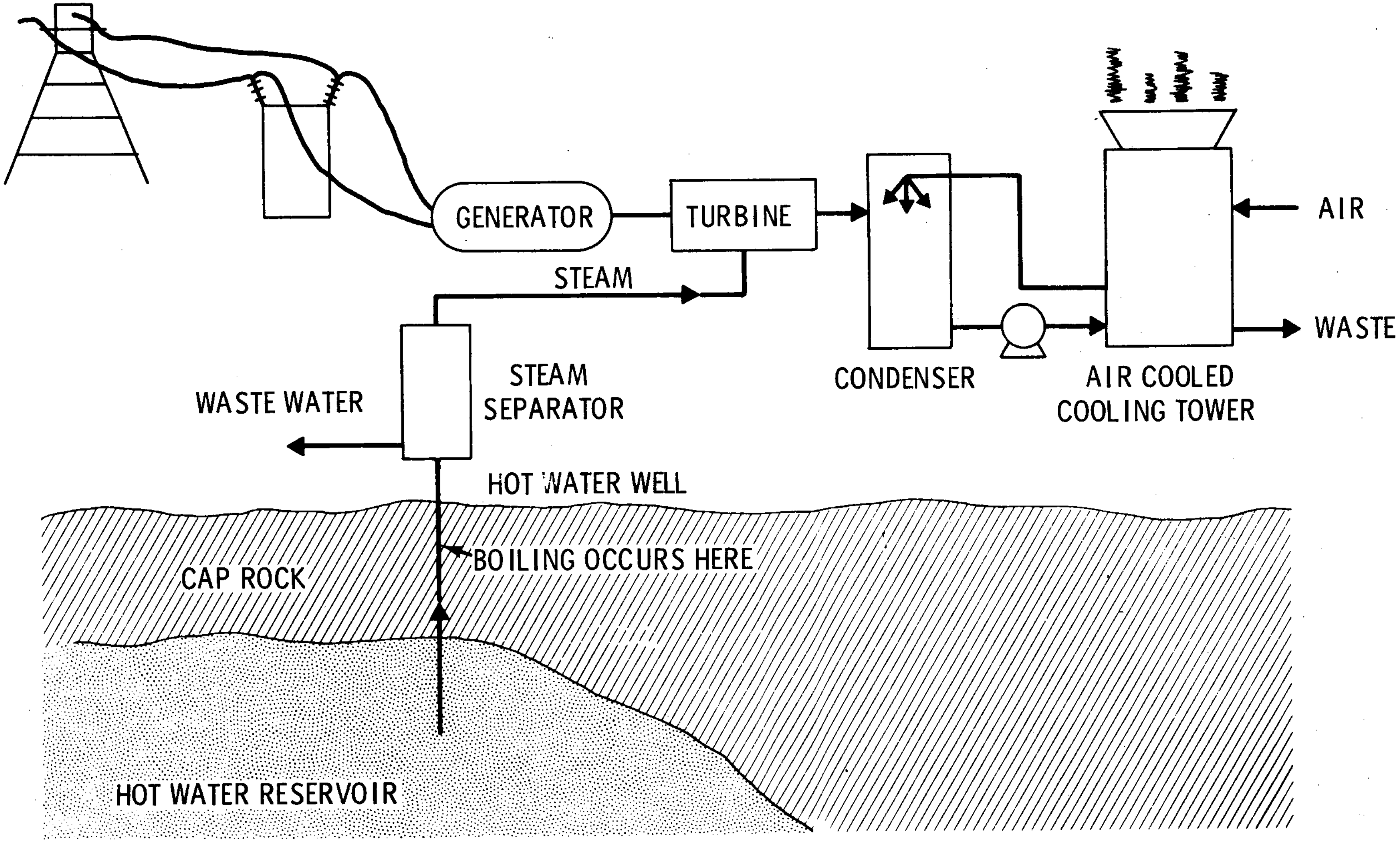


FIGURE 18. Hot Water - Flash Steam Geothermal Plant

- The gases CO_2, H_2S, NH_3 largely fractionate with the steam phase.
- The soluble salts largely fractionate in the liquid phase.

We will now examine the scaling and corrosion problems in the waste water, steam, and well systems for significant design and cost impacts.

Waste Water System

1) Silica - SiO_2

Silica is highly soluble in the reservoir water and has been shown to be in equilibrium with quartz at reservoir temperatures (Ellis, 1964). During the cooling that occurs during production, quartz solubility is quickly exceeded, and the higher solubility limit of amorphous silica may be exceeded. Deposition rate data are not available, but it is known if the amorphous silica solubility is exceeded precipitation is rapid, (in minutes). The slow precipitation of quartz (over years) may be involved in slow deterioration of well production, but is not as important to plant design as is the effect of exceeding the amorphous silica solubility.

The solubility of SiO_2 in the reservoir is a function of reservoir temperature, T_R over the range of 25 to 300°C:

$$S_Q(\text{ppm}) = (60060) \times 10^{\left[0.23 - \frac{5.38}{0.00458 T_R}\right]}$$

where T_R is in °K $= C° + 273$ $\quad 25° \leq T \leq 300°C$

(Above 300°C quartz solubility drops slightly so use T - 300°C for range 300 - 370°C)

The solubility of amorphous silica is:

$$S_A = 40 + (3.8)\, T_M \text{ where } T_M \text{ is in °C}$$

where T_M is the minimum temperature in that region of the plant where the precipitation potential is to be evaluated.

Only about 75 to 80% of the total flow (F_T) ends up as waste water (F_W) thus concentrating the silica in the water phase. The potential suspended silica in the waste water, S_W is :

$$S_W = S_Q \left(\frac{F_T}{F_W} \right) - S_A$$

The total potential rate of silica deposition, S_T is:

$$S_{T(\text{lb/day})} = F_{W(\text{MGD})} \times 8 \times S_W$$

Example: In a 100 MWe geothermal plant, what is the potential deposition rate of silica at a waste water reinjection pump, given the following parameters:

T_R = Temperature Reservoir = 300°C

T_M = Temperature at Reinjection Pump = 100°C

F_T = Total Flow = 10×10^6 lb/hr
= 1.2×10^6 gal/hr

$\frac{F_W}{F_T}$ = 0.75 Thus, F_W = 0.94×10^6 gal/hr
= 22.5×10^6 gal/day

Calculate the following

$$S_Q = (60060) \times 10^{\left[0.23 - \frac{1175}{573}\right]} = 907 \text{ ppm}$$

$$S_A = 40 + 3.8\,(100) = 420 \text{ ppm}$$

$$S_W = (907)(1.25) - 420 = 714 \text{ ppm}$$

$$S_T = 22.5 \times 8 \times 714 = 128 \times 10^3 \text{ lb/day}$$

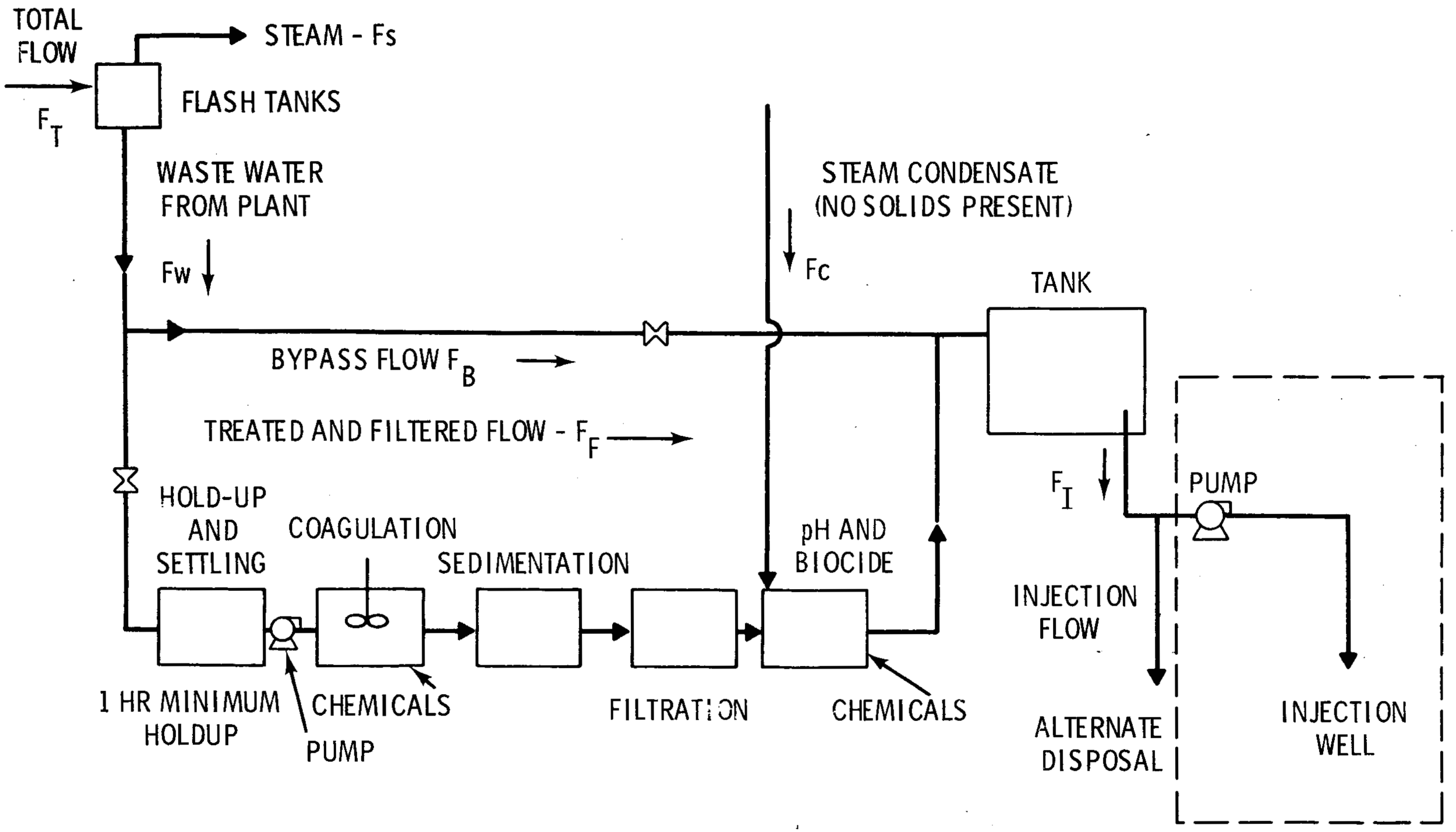
This enormous potential silica deposition is readily seen by observers in the waste canals at flash water plants. The past practice of dumping these wastes to a river or surface pond are unacceptable under present environmental laws. Thus reinjection is often cited. It is quite probable that attempts to reinject such massive suspended solids would plug the reinjection formation in a short time. Thus we conclude the economic impact of a silica filtration system should be evaluated. Such a filtration plant is shown in Figure 19. For purposes of cost study we have assumed such a plant would be analogous to a municipal water treatment plant and have developed cost equations based on a study reported in Office of Saline Water Report OSW 257. In order to permit evaluation of the economic impact of various degrees of filtration the parameter, S_I = allowable suspended solids, is specified as input. By varying the values of S_I from 0, where most of the waste flow is filtered, to values of S_I above S_W, where filter plant flow and costs become zero, any desired degree of filtration can be evaluated. Credit is taken for any steam condensate waste Fc, which contains no suspended solids, to dilute F_W. Details of the cost evaluation are given in Appendix A.

2) Materials for Waste Water System

The corrosion of carbon steels is sufficiently low in the pH 7-8 waste waters at Wairakei, N.Z., to provide 20 years' service. At least no significant replacement costs are indicated in published reports. The pH of the waste water is of major importance in establishing corrosion rates. Carbon steel in some of the Salton Sea (pH 4.5 - 5) brines lasts only a couple of years. An estimate of carbon steel waste water piping replacement times is:

≥ pH 7	≥	20 years	± 5
pH 6	-	10 years	± 5
pH 5	-	5 years	± 3
pH 4	-	2 years	± 2

Below pH 6 the use of corrosion inhibitors or plastic-lined pipe should be evaluated. An extensive technology has been developed for using filming corrosion inhibitors in oil field flooding operations where mildly acid "sour brines" are pumped into the field.



NOTE: INJECTION PUMP AND WELL COSTS NOT INCLUDED

FIGURE 19. Filtration Plant Model for Silica Removal

An order of magnitude cost estimate is that a 100 MWe plant producing 10^7 lb/hr of waste water would use $1000 of inhibitor per day. This is a cost of 4 mils/kW-hr; rather expensive!

Alternate materials such as aluminum and stainless steel cannot be recommended because of potential pitting problems.

Steam System

1) Silica (SiO_2)

Silica is soluble in steam. At steam pressures used in conventional boilers, silica above 0.1 ppm in the steam causes serious turbine deposits. However, flash water type geothermal plants operate at steam temperatures and pressures (around 75 to 100 psig) where silica solubility in steam is a minor problem. Cleaning the turbine once a year during a maintenance shutdown is sufficient. However, if plant designs call for steam above about 230°C and 400 psi, silica scale deposits will become significant. Such high steam temperatures would not be expected in a flash water type plant.

2) Soluble Salt Transport in Moisture Droplets and Need for Scrubbers

The steam-water separation in a flash type plant leaves 0.5 to 1% moisture droplets in the steam. These droplets contain dissolved salts at the same concentration as the water phase. Mechanical carryover results in scale buildup as these moisture droplets evaporate in the steam system and turbine. This mechanism has been the largest source of steam piping scale in flash water plants. Obviously as the salt content of the feed water goes up, the carryover of dissolved salts increases, too.

This same mechanical carryover problem occurs in conventional boilers and is controlled by limiting boiler water to 4000 ppm dissolved solids and 1 ppm carryover in steam. A geothermal water containing 35,000 ppm salt or even 350,000 ppm exceeds these limits.

One solution is to insert a scrubber as shown in Figure 20. The scrubber washes the steam to remove the carryover salt content to 1 ppm. The volume of scrub water to do this can be estimated as follows:

F_S = steam flow (lb/hr)

F_W = Scrub water flow (lb/hr)

C_W = Concentration of dissolved solids in water phase in steam separator (ppm)

C_S = Concentration of carryover solids in steam from steam separator (ppm)

C_S' = Concentration of solids in steam out of scrubber
= 1 ppm by specification

Steam separator efficiency 99% (e.g., 1% moisture carryover)

$$\frac{(C_S \times F_S}{(C_{SW} \times F_{SW}} = \frac{100}{1}$$

$$F_{SW} = \frac{C_S\ F_S}{100\ C_{SW}}$$

The design basis of scrubber efficiency is CS'≤ 1 ppm when $C_{SW} \leq 100$ ppm.

$$\therefore\ F_{SW} = \frac{C_S\ F_S}{(100)(100)} = \frac{C_S\ F_S}{10^4}$$

$$\text{Since}\ \frac{CS}{CW} = \frac{1}{100}$$

$$\text{Then}:\ F_{SW} = \frac{C_S\ F_S}{10^6}$$

The scrubber water flow increases as the salt content of the geothermal water increases. There is a thermodynamic cost of heating the scrub water that must be subtracted from steam enthalpy.

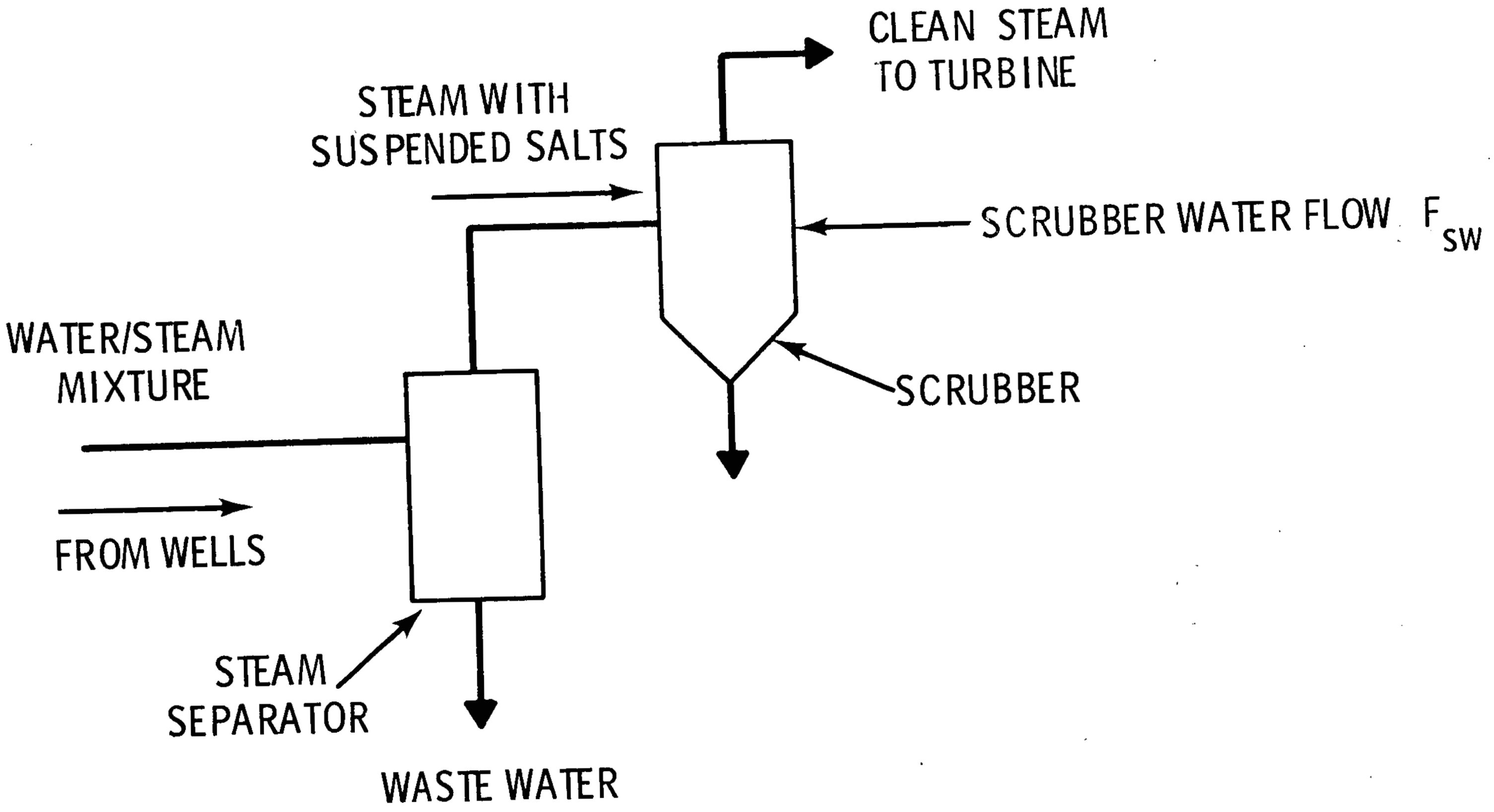


FIGURE 20. Scrubber Flow Sheet for Removal of Salts from Steam

For this application, carbon steel probably would have a short life (<5 years) due to the acid characteristics of the scrub water absorbing CO_2 and H_2S. Titanium would probably be the best material for scrubber construction, which would cost about \$30/ft^2 of material used. The size of the unit will depend on plant size. Austenitic stainless steel and nickel alloys probably would fail rapidly due to pitting (or stress corrosion cracking for austenitic stainless steel).

Turbine Failures and H_2S in Steam

Turbine blade failures have occurred at the Geysers, CA, Matsukawa, Japan, and Larderello, Italy, geothermal plants. No definitive causes have been published but corrosion fatigue appears most likely. At the Geysers plant the failures are reducing plant availability at least 10% (Finney, 1974). See Table 12. It is believed H_2S in the steam is the

TABLE 12. Turbines Operating Availability - Geysers, CA

Turbine No.	1972 %	1973 %
1	87.6	90.6
2	77.2	90.3
3	79.3	82.0
4	79.1	91.8
5	87.4	78.7
6	86.2	82.2
7	79.2	80.7
8	84.2	87.3
9	--	63.9
10	--	90.4
Average	82.5	83.8

Note: Capacity factors average about 71% (allowing for lost production due to operating turbines with stages out).

Source: G. Horton, Plant Engineer, PGE, Personal Communication prime corrosive agent. No such failures have been reported at Wairakei, N.Z.; however, their H_2S is an order of magnitude lower than the above plants. Cerro Prieto has high H_2S, but has had no blade failures in one year of operation--perhaps insufficient time for the problem to show up.

In the absence of more definitive information the economic impact of H_2S in the steam can be estimated:

H_2S Content	Plant Factor	Shutdowns	Turbine Maintenance Cost
500 - 3000 ppm	82%	1 per year	\$100,000/yr
50 - 500 ppm	92%	1 per 5 years	\$ 20,000/yr

Raising plant factor 10% with a total of 500 MW of installed capacity represents 50,000 kW x 8760 hr x 0.92 x 0.01 = \$4,300,000/yr increased revenues at an electricity price of 10 mils/kW-hr. There is considerable incentive to develop solutions to the turbine blade cracking problem.

Condenser and Cooling Tower Piping

All the materials handling steam condensate should be of austenitic stainless steel or aluminum for condensate piping. The steam condensates are acid due to H_2S and CO_2. No significant problems or corrosion failures have been reported in this application. Note that chlorides are very low in steam condensate, thus avoiding the pitting corrosion of austenitic stainless steel often cited. Austenitic stainless steel would not be acceptable if chlorides are present. Specific limiting chloride concentrations have not been established for geothermal condensate systems.

Plugging of Production Wells

Because boiling occurs in the well casing in a flash type plant, wells plug periodically and require rework. A. Majon (1974) of Cerro Prieto indicated low enthalpy wells (e.g., ∿400 Btu/lb) plug with calcite in about one year; high enthalpy wells (∿650 Btu/lb) are expected to plug with silica in 3 to 4 years. Cleaning the well involves redrilling with a small rig and takes 5 to 10 days at Cerro Prieto costing about 15,000 pesos/day (\$1200/day).

Costs would expect to be higher in the U.S. Assuming the rework rig was available with no "move charge," a rework cost of $10,000 to $30,000 is estimated.

Analytical expressions to predict well plugging rates require data not yet developed.

CASE 2 - LOW SALINE HOT WATER RESOURCE - VAPOR TURBINE - BINARY CYCLE TYPE PLANT

In the vapor turbine-binary cycle concept a secondary fluid such as isobutane or Freon is boiled by hot geothermal water. The entire turbine and condensor system operates with the organic fluid in a sealed system between the hot let geothermal water heat exchanger and a cold leg cooling water heat exchanger (Figure 21). Anderson (1973) discusses the concept in detail.

The major application of such a system would be to extract power from medium temperature geothermal water that cannot provide economic quantities of flash steam to drive a turbine. Because of the lower temperature involved, this system must move large quantities of water (70 to 200 lb H_2O per kW-hr generated) and must have large heat exchangers. Wells will require mechanical pumps since the geothermal water remains pressurized and does not flash boil to make wells self pumping as in Case 1.

Some of the potential scaling and corrosion problems in this concept are:

- Fouling of heat exchangers
- Plugging of reinjection wells with silica
- Corrosion of heat exchangers and pumps
- Cooling water supply and corrosion control

Silica Deposits

The binary cycle type plant may be subject to heat exchanger fouling due to silica deposits because of the temperature drop in the heat exchangers.

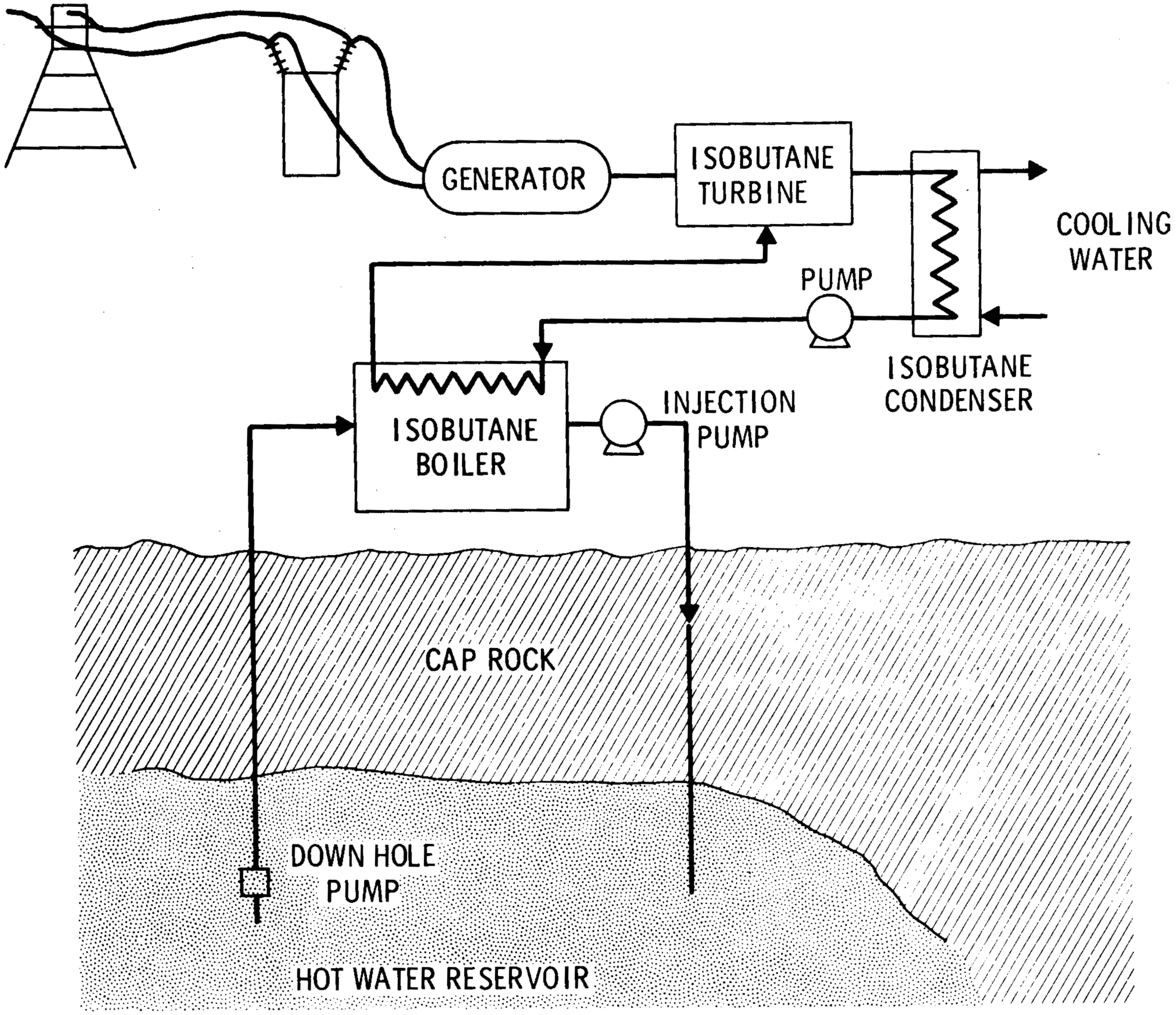


FIGURE 21. Vapor Turbine - Binary Cycle Geothermal Plant

The equations developed in Case 1 are applicable to estimate potential suspended silica contents, (except a correction does not need to be made for concentration of silica due to steam loss).

Silica in Hot Water:

$$S_Q \text{ (ppm)} = (60060) \times 10^{\left[0.23 - \frac{5.38}{0.0458T_R}\right]}$$

T_R = T°C - 273

For example, at T_R = 297 K = 204C = 400 F

S_Q = 440 ppm

Solubility of amorphous silica:

S_A = 40 + 3.8(TM)

With water leaving the heat exchanger at 50°C (123°F)

S_A = 40 + 3.8(50) = 230 ppm

S_W = suspended solids = S_Q - S_A = 440 - 230 = 110 ppm

At a water flow rate of 3.7 million gallons per day required for a 10 MWe plant, the potential silica deposition rate is:

S_T = 3.7 MGD x 8 lb/gal x 110 ppm = 3,256 lb/day

This silica could pose a serious problem in heat exchanger fouling and injection well plugging. The actual rate of deposition probably would be substantially lower because of kinetic effects. R&D is needed.

However, a different set of water temperatures can prevent silica insolubilities, if S_A is larger than S_Q. For example, if the geothermal water is 163°C (325°F) at heat exchanger inlet and exits at 50°C (123°F):

S_T = S_Q - S_A = 205-220 = -15 ppm

Or at a water temperature of 204°C (400°F) entering the heat exchanger and leaving at 106°C (223°F):

S_T = S_Q - S_A = 440 - 443 = -3 ppm

There is a tradeoff that must be further evaluated to determine if accepting a thermodynamic loss is more economical than alternative approaches to preventing silica problems. For example, dual heat exchangers could be installed and cleaned periodically. The expensive silica filtration plant discussed in Case 1 may be needed if reinjection of large quantities of suspended silica is planned, however, the problem can be avoided by keeping silica soluble.

Calcite Deposition

The binary cycle concept avoids problems with calcite deposition because the system remains pressurized thus keeping the CO_2 partial pressure high. Since calcite solubility increases on cooling, the binary cycle should avoid calcite incrustation of medium enthalpy wells.

Corrosion and Materials Considerations

The pH of the geothermal water will be of major importance in the material selection and life of pumps, pipe, and heat exchangers in the geothermal circuit. In water of pH 8-9, which occurs in Iceland, carbon steel components would have adequate life (probably 20 years). In the pH 7-8 range carbon steel still would suffice, but failure of thin-wall heat exchanger tubes might occur in about 10 years. Below pH 6 carbon steel heat exchangers would have short lives.

Titanium should be considered for yeat exchangers for acid geothermal water although pitting and crevice corrosion must be considered above 300°F in high saline brines above 3% NaCl.

For acid salt brines (>3% NaCl, pH 6) at temperatures above 300°F there are no proven materials of construction, except expensive materials such as zirconium, tantalum, gold, platinum, and possibly 54Ni-15Cr-16Mo alloys.

Cooling Water Problems

The binary cycle system does not have large quantities of steam condensate to cool the condensers like natural steam or flash water geothermal plants do. Thus a cooling water source or dry cooling towers (air) will have to be considered.

One obvious source of water is the large volume of geothermal water exiting the hot leg heat exchanger. This water source has numerous problems:

- calcite deposition when CO_2 pressure is released
- silica deposition in the cooling process
- soluble salt deposition when water is evaporated
- H_2S release to the atmosphere

The scaling rates in a cooling tower operated on high solids geothermal water have not been measured, but one would predict they would prove unacceptable. However, it might be possible on some low dissolved solids waters. An alternative would be to flash distill part of the water (e.g., a small desalting plant) and then use the steam condensate in the cooling towers. Economics would have to be evaluated.

A conventional solution using cooling towers and local rivers or ground water is another alternative if water is available. The solutions to conventional cooling tower corrosion and scaling problems are within established technology.

CASE 3 - HIGH SALINE HOT WATER GEOTHERMAL RESOURCES

The major example of a high saline, high temperature geothermal brine occurs in the Salton Sea areas of California. Various attempts have been made to utilize these brines including an unsuccessful attempt to generate electricity from separated steam. The problems encountered have included high pipe scaling rates and general corrosion problems handling the brine.

Silica

The potential rate of deposition of silica depends primarily on the temperature changes between reservoir and plant. High saline brines should have about the same silica deposition potential as low saline brines since silica solubility is largely independent of pH and salt content. Equations developed for estimating the potential insoluble silica were given in Case 1.

However, comparing observed pipe scaling rates between high saline Salton Sea brines and low saline Cerro Prieto brines, it has been observed scaling rates are much higher with the Salton Sea brines. Skinner, et al. (1967) report deposition of 2 to 3 tons per month of siliceous scale in pipes from one Salton Sea well (No. 1 Imperial Irrigation District). This is in marked contrast to experience at Cerro Prieto where silica does not deposit in significant quantities except in the waste water system. Silica content in the brine at Cerro Prieto is 400 to 1000 ppm (Mercado 1970) which, if anything, is higher than silica contents reported for Salton Sea brines of 400 ppm (Helgeson 1968, Skinner 1967).

In attempting to resolve this apparent discrepancy in silica deposition rates it must first be observed that neither system approaches the maximum potential scaling rate. For example the IDD No. 1 well at a flow rate of 50,000 gal/hr and cooling from 325°C to 150°C has a potential silica deposition rate of about 2 to 3 tons/day; much more than the 2 to 3 tons/month observed. Thus, we can conclude kinetic factors are playing a major role in the rate of scaling.

One factor which could cause higher scaling rates in Salton Sea brines is the precipitation of iron and copper sulfides. Skinner, et al., (1967) reports the composition of pipe scale is a 60-70% amorphous silica matrix surrounding sulfide minerals (30-40%) rich in copper, iron and silver (in that order). These sulfides become insoluble on the temperature-pressure drop accompanying two-phase flow up the well. Since the Salton Sea brines have much higher concentrations of cations such as Fe, Cu, Ag than the Cerro Prieto brines, it is not surprising sulfide scaling occurs. The deposition of these sulfides could provide deposition sites that would increase the adhesion of silica to the pipe wall.

In Figure 22 the three scaling rates observed in the No. IID well piping (Skinner 1967) are plotted versus the average temperature of the pipe at that point. This is compared with the difference in the solubilities of quartz and amorphous silica, $S_Q - S_A$. It appears the scaling rate (S_R) is proportional to $S_Q - S_A$:

$$S_R = k\,(S_Q - S_A)$$

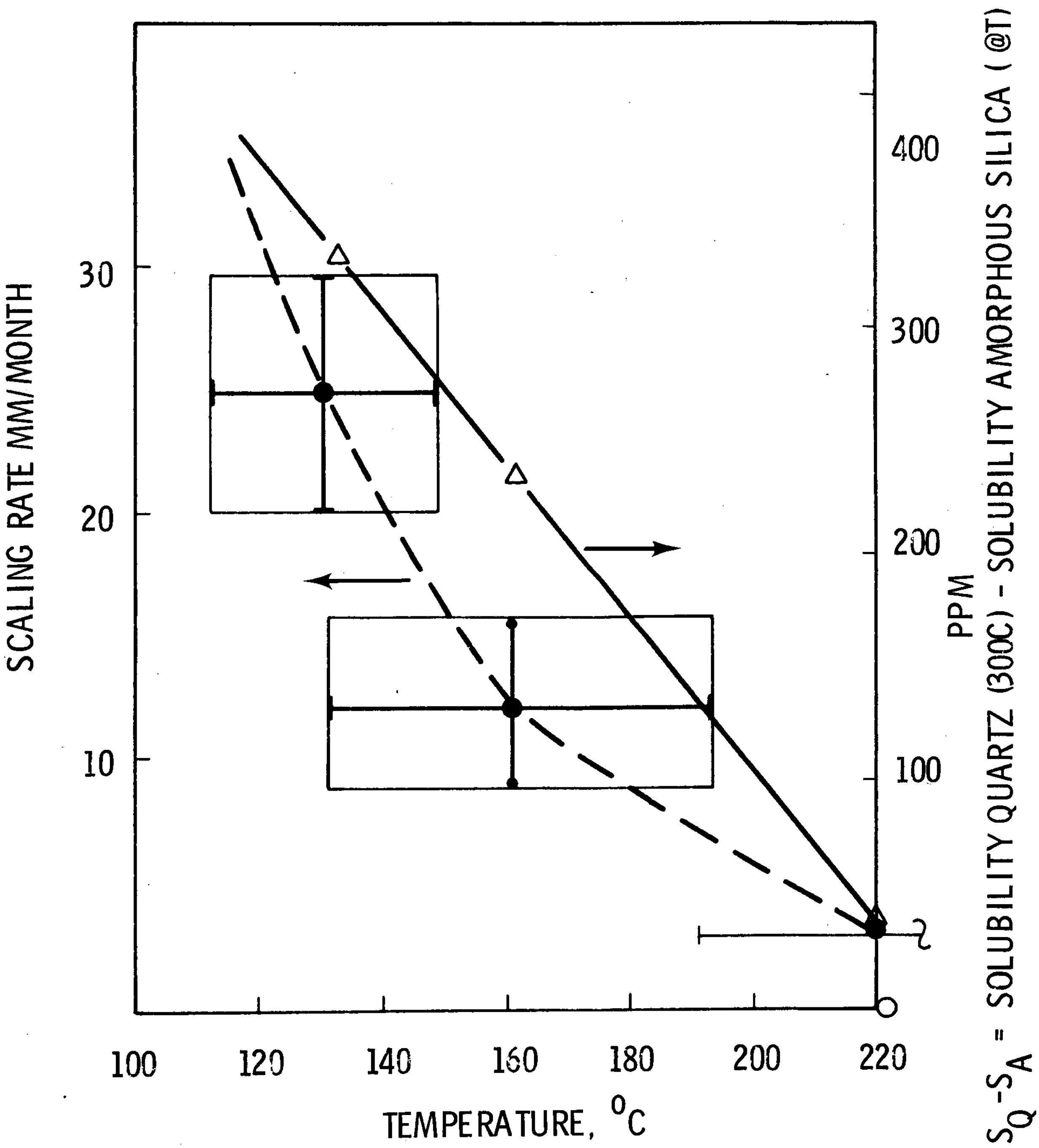


FIGURE 22. Rate of Scale Formation in Pipe Compared with Calculated Silica Insolubility (-2 Phase Brine Flow IID, No. 1 Well, Salton Sea)

The values of k for the three rates reported for by Skinner are given in Table 13. Considering the tenuous nature of the data, k is rather remarkably constant, averaging 0.05.

TABLE 13. Values of k for Scaling in Salton Sea Brine

Sample No.		T °C	Scaling Rate S_R mm/mo	Calculated S_Q (300°C) - S_A (T) ppm	k
W769	high	250	2.8	-83	-0.03
	avg	220	2.8	31	0.09
	low	190	2.8	145	0.02
W767	high	200	9	107	0.08
	avg	170	12.5	22	0.06
	low	130	16	373	0.03
W768	high	150	20	297	0.07
	avg	130	28	373	0.08
	low	110	35	449	0.08
				avg	0.05

These values of k are specific for this well and flow rate but should be useful in estimating scaling rates in other Salton Sea brines. Well flow was not stated by Skinner, however, these measurements appear to be made during a 3-month flow test where the well flow was about 200,000 kg/hr or 55,000 gal/hr (Helgeson 1968).

The high scaling rates in this brine have discouraged use of flash boiling-steam cycle geothermal plants.

Economic Considerations in a Flash Water Type Plant

Economic considerations for such a flash water plant include these rough estimates made in the absence of published data on these parameters:

Well Rework - Plugging in two-phase flow regions in about 3 years. Requiring $10,000 to clear.

Steam-Water Piping - 50% downtime for cleaning. (Piping should be installed in duplicate from wellhead, if continuous plant operation is expected.)

Scrubber - Steam scrubber will be required to remove carryover salts, as discussed and sized in Case 1.

Turbine - Assume 85% availability.

Silica Filtration Plant - Suspended silica removal from brine prior to reinjection should be included in cost estimates. The Salton Sea reservoir permeability may be high enough that full flow filtration will not be needed.

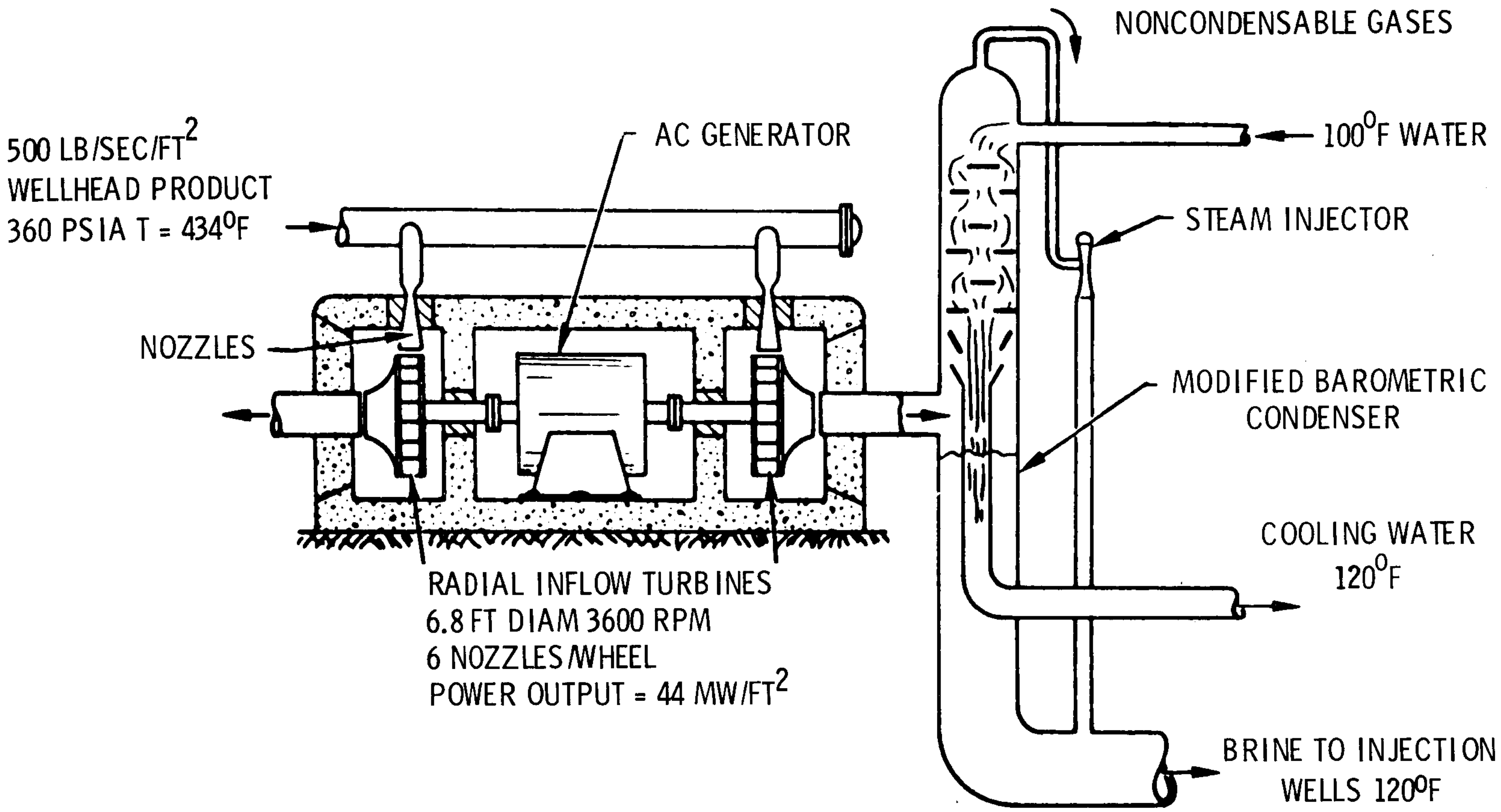
Corrosion of Materials - Use carbon steel with 5-year life for well casing, 5-year estimated life for all waste brine piping; 20-year life for steam and condensate system.

The Total Flow Concept

The total flow concept of power generation from high saline brines has been proposed by Austin, et al. (1973). In this concept no attempt is made to generate steam for a conventional turbine; rather the two-phase steam-water mixture is directed directly to an impulse turbine to generate electricity by direct use of kinetic energy, Figure 23.

Austin discusses some of the serious corrosion and scaling problems inherent in this concept. They conclude there are no inexpensive metals with sufficient corrosion resistance to the acid Salton Sea brines. Consideration is given to plastics and ceramics or tantalum coatings. They conclude a materials development program would be needed.

They present an analysis of salt solubilities and conclude most chlorides will remain soluble throughout the power cycle. This means that the total high saline content is not the factor that causes the high scaling rate, since most constituents in the brine remain soluble.



SOURCE: AUSTIN LLL

FIGURE 23. Schematic of a Total Flow System

They mention the observed buildup of magnetite (Fe_3O_4) and Hausmanite (Mn_3O_4) and silica (SiO_2) in well head equipment. We disagree however with their proposed mechanism of formation by reaction of H^+ with iron well casing by the reaction they propose:

$$Fe^{+3} + Fe^{+2} + 4H_2O \rightleftarrows Fe_3O_4 + 8H^+$$

More likely the deposits simply reflect a shift of the equilibrium. Fe^{+2} and Mn^{+3} in solution, which are in equilibrium with reservoir-minerals precipitate as depressurization and cooling occur. Since iron and manganese concentrations are quite high in Salton Sea brine (Fe, 2000 ppm, Mn 1560 ppm) there is considerable source material.

This means, however, that the scaling is inherent in the cooling process and cannot be readily prevented by avoiding construction materials that react with acids as Austin, et al., suggest.

Using the relationship $S_R = 0.05 (S_Q-S_A)$ developed above, scaling rates in the total flow concept can be roughly estimated as in Table 14. Obviously there are so many unknowns such as the effect of flow rate. The scaling rates in Table 14 are of limited use, but demonstrate scaling rates may be very high.

TABLE 14. Estimated Scaling Rates in Total Flow System Using Salton Sea Brine (Reservoir T - 300°C)

Location	P_{psi}	T °C	Scaling Rate mm/mo
Inlet Pipe	360	223 (434°F)	1 (0.04 in/mo)
Turbine Outlet Stage	1.5	46 (115°F)	35 (1.4 in/mo)
Condensor	1.5	46 (115°F)	35 (1.4 in/mo)

Austin, et al., estimate the potential for silica deposition to be 25,920 lb/day/ft^2 of well; which is consistent with this report.

The above considerations indicate that the impulse turbine and condensor system will be subject to heavy scaling rates. For economic evaluations a turbine availability rate of 50% with 50% downtime for cleaning should be used, e.g., 1 month on--1 month off.

Because of the acidic pH of Salton Sea brines corrosion rates will be high. The following component lifetimes should be used in economic analysis until specific test data are available:

Well Casing, Piping, and Condensor System	5 years
Turbines (assuming successfully developed)	10 years

As in the other hot water concepts it is not clear that the reinjection wells can tolerate the heavy silica level, so the cost of a silica filtration plant should be evaluated.

CASE 4 - HOT DRY ROCK - STEAM CYCLE PLANT

In this concept wells are drilled into a hot rock mass and fractured. Water is then injected to generate steam or hot water, which is withdrawn under pressure to drive a turbine. Two basic concepts are to recover the geothermal fluid as pressurized water or as pressurized steam.

Since plants of this type have not been built yet, analysis will necessarily be speculative.

Pressurized Water

From the point of view of corrosion and scaling, recovery of pressurized water from hot rock appears less promising than recovering steam.

In the medium temperature case (e.g., water 150-200°C), the problems are quite analogous to those discussed in the binary cycle vapor treatment plant in Case 2. The pH of the recovered water will dictate corrosion rates, heat exchanger fouling, reinjection of suspended solids, makeup water, and cooling water sources will be problems as discussed in Case 2.

If attempts were made to recover hotter water (>200°C) under pressure, the corrosion and scaling problems would be magnified. Unless the recovered water is alkaline (>pH 8), where low alloy steels can be used, corrosion rates will probably be unacceptable. However, there are no actual corrosion rate data available yet.

The potential scaling rates will become large, because of the range difference in silica solubility that occurs with the large system ΔT, and the large total silica in solution at high temperatures (900 ppm at 300°C). Other shifts in other mineral solubilities will also increase scaling rates.

Steam Cycle

Scaling and corrosion rates in geothermal steam are much lower than in water at the same temperature. A concept to inject water into hot fractured rock and recover steam which is fed to a turbine is illustrated in Figure 24.

If steam is recovered at about 115 psi and 180°C at the turbine inlet, plant design and economics would be quite similar to a natural steam plant such as the Geysers, CA, plant (Figure 25). Unless sulfide minerals are encountered and decompose, the H_2S levels in a Hot Dry Rock plant might be lower than at the Geysers plant. Plant availability could be over 90%. No data are yet available on steam purity composition in equilibrium with hot rock to judge actual problem areas.

If it is planned to use high temperature high pressure steam above 200°C, considerable caution should be used in evaluation of the economics. Corrosion and scaling data are largely unavailable, but certain problems are predictable.

1) Silica

In conventional steam boilers silica deposition on turbine blades becomes a problem if silica content in the steam becomes too high. Staub (1946) showed that silica content of steam above 0.1 ppm caused turbine deposition. Boilers operate with silica below 5 ppm in feedwater to control

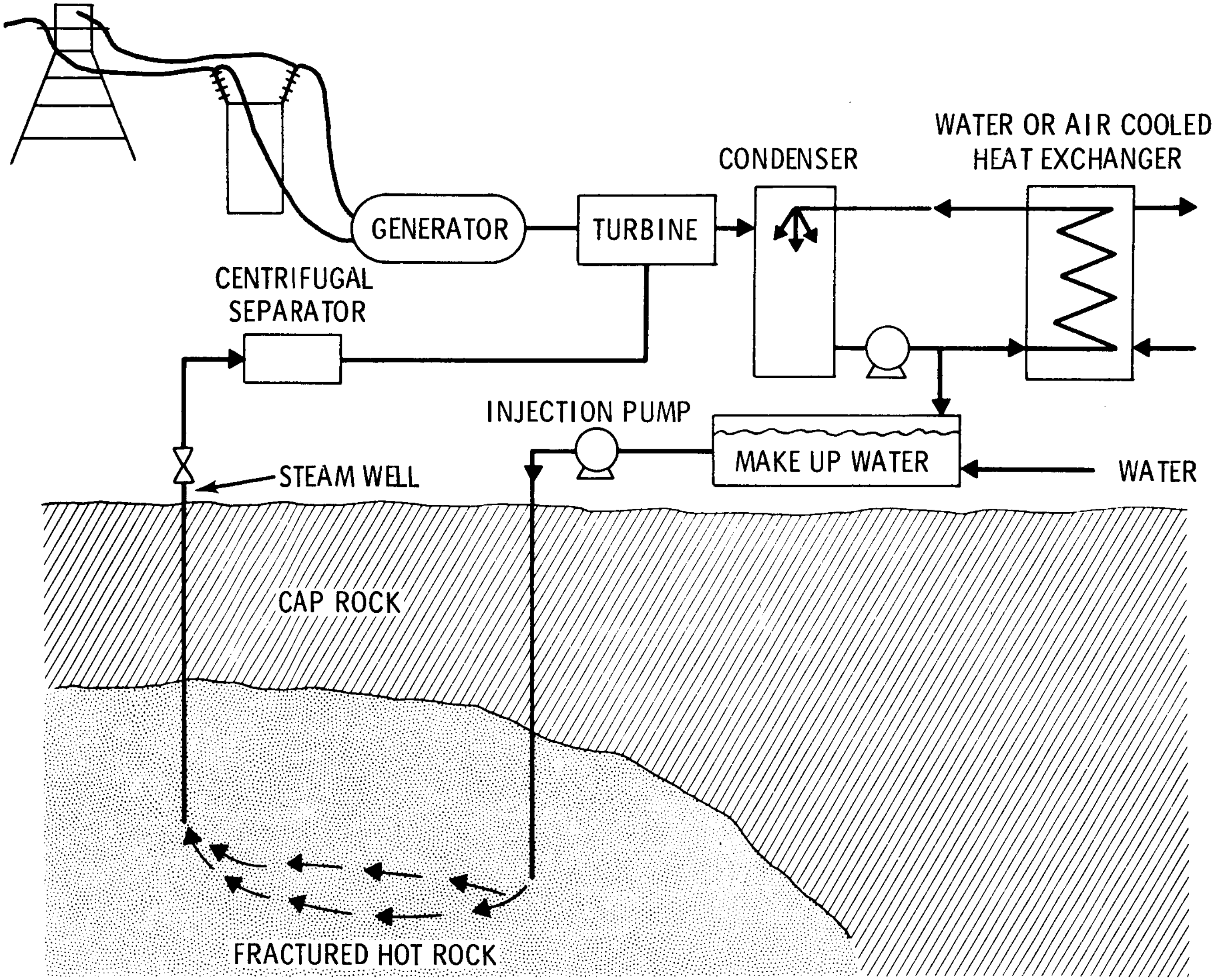


FIGURE 24. Hot Dry Rock Geothermal Plant

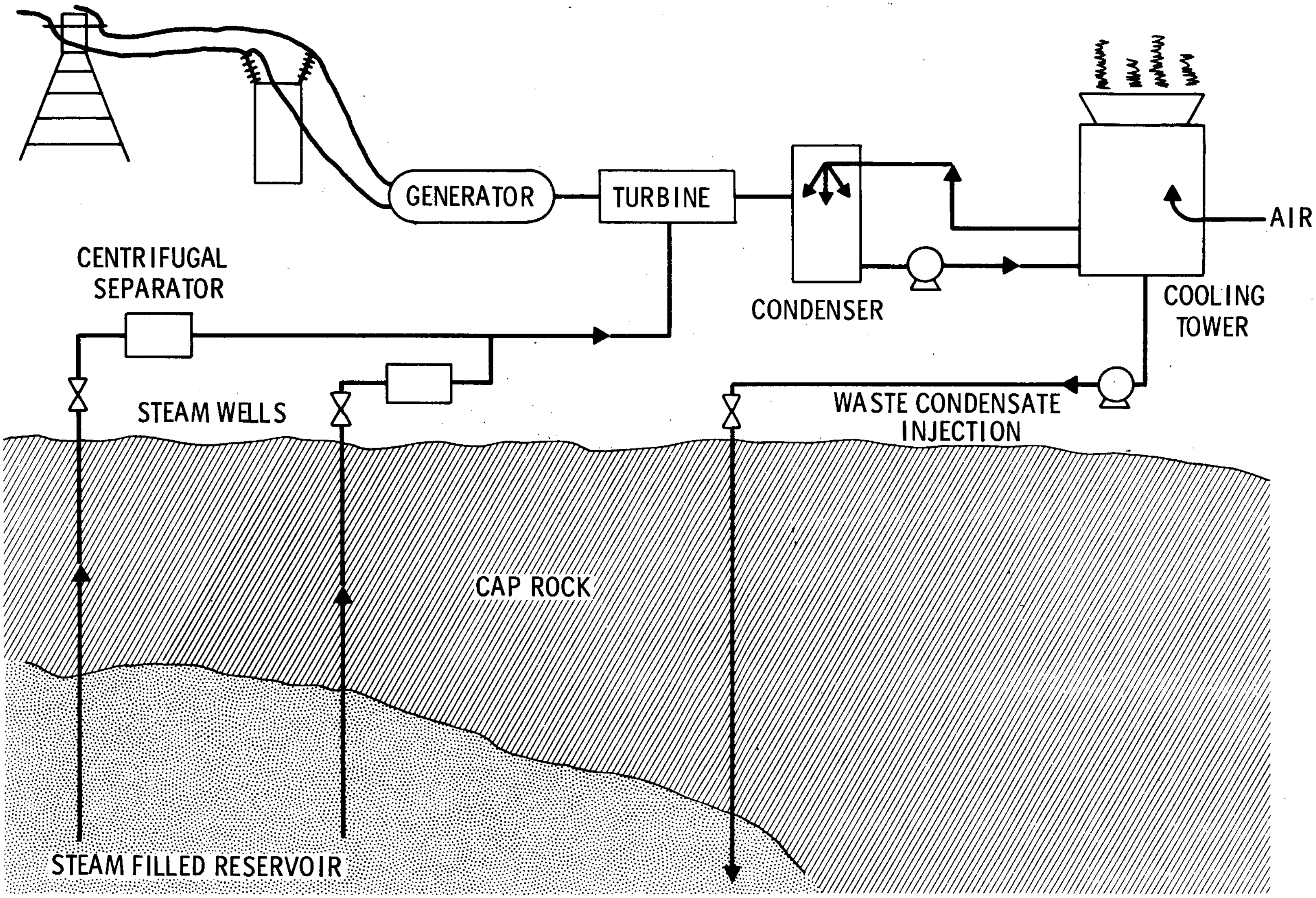


FIGURE 25. Natural Steam Geothermal Plant

silica in steam to below 0.05 ppm. Silica turbine deposits are so difficult to remove that prevention of deposits is the preferred method of combating the problem. The silica solubility in steam reaches 0.1 ppm at about 230°C (400 psi) (K. Krikurian 1973). As turbine inlet temperatures increase above 230°C, silica removal from the steam will be increasingly necessary. As discussed above (pp. 14-16) there are many reasons why silica content in the steam may not be even close to the calculated equilibrium value. However, until better data become available the use of scrubbers and the associated cost penalties appear likely above 230°C. See page 89 for discussion on evaluating scrubber water flow.

Staub (1946) indicates the deposition of silica in the turbine increases as steam superheat increases. Thus in the wet parts of a condensing turbine, silica deposition will be less because the silica distribution coefficient favors solution in the condensing water. Attempts to generate superheated steam above 230-250°C are likely to encounter serious silica deposition in the turbines. Development of silica removers that do not degrade steam quality would appear necessary to exploit very high temperature hot dry rock.

2) Corrosion Rates

The corrosion rates of carbon steel or low alloy steels would be completely satisfactory in dry geothermal steam up to at least 500°C. The major uncertainties would be the acidity of moisture droplet carryover, and the H_2S content of the steam. For purposes of initial cost estimates carbon steel steam components can be considered satisfactory. The steam condensate and cooling tower piping components (at below 100°C) should be estimated using austenitic stainless steel, since acid pH is likely.

3) Cooling and Makeup Water

Considerable quantities of makeup water are required for the hot dry rock concept, since no natural water reservoir is tapped.

Equipment for makeup water will be required and includes:

- filtration to remove suspended solids
- softening to remove calcium and magnesium (which would precipitate on heating and plug the formation)
- oxygen removal (vacuum on gas sparging)
- possible biocide treatment
- possible adjustments of pH and cation content (see page 14)

If a dry cooling tower is used with a completely sealed steam condensate system, the makeup water and treatment facilities will be minimized. Costs should be compared for a sealed steam condensate system versus an open wet cooling tower system (like the Geysers plant) which will require considerable makeup water.

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APPENDIX A

COST CALCULATIONS - GEOTHERMAL WASTE WATER TREATMENT PRIOR TO REINJECTION

1) START
2) Obtain total waste water flow from program step __ = F_W'(lb/hr)

   convert to million gal/day - F_W

   F_W = _____ 10^6 gal/day (MGD)

3) Obtain residual steam condensate flow left after cooling towers from program step _____ = F_C' (lb/hr)

   convert to million gal/day = F_C

   F_C = _________MGD

4) Calculate suspended solids content in waste = S_W

   a. Input reservoir temperature = T_R °C and total bore flow F_T (lb/hr)

   b. From data on Quartz solubility obtain silica content of bore water:

   $$S_Q = (60060)(10)^{\left[0.23 - \frac{5.38}{0.00458\, T_k}\right]}$$

   $$T_k = T_R + 273$$

   c. Input minimum temperature of settling tank = T_M, °C

   d. From data on amorphous silica solubility obtain silica (amorphous) soluble at $T_M \div S_A = 40 + 3.8\ (T_R)$

   e. Calculate suspended solids in flow = S_W

   (F_W' = F_W converted to lb/hr)

   $$S_W = S_Q \left(\frac{F_T}{F_W'}\right) - S_A$$

   S_W = __________ ppm

f. Print out S_W

g. Calculate total suspended solids load per day

S_T = F_W x X8 x S_W

lb/day = (Mgal/day x lb/gal x lb/10^6lb

5) Input max. permissible suspended solids content in injection water to avoid plugging in well or formation: S_I = ________ ppm

6) Test $S_W > S_I$

yes - go to 7

no - $F_F = 0$ and skip step 7

7) Calculate water filtration plant flow = F_F (MGD)

$$F_F = F_W - \frac{S_I}{S_W} (F_W + F_C)$$

8) Test: if F_F is negative enter $F_F = 0$

9) Print out F_F = ______

10) Calculate filtration plant capital cost (Data from OSW 257)

Note: Escalation of equations based on Engineering News Construction Index

$$\frac{1974}{1966} = \frac{1993}{658} = 3.03 = E$$

a) Construction Cost

For $0 \leq \text{capacity} \leq 1$ MGD
$\$\text{Cost} - 240{,}000\ (F_F)^{0.56}\ (E)$

For $1 \leq \text{capacity} \leq 10$ MGD
$\$\text{Cost} = 240{,}000\ (F_F)^{0.72}\ (E)$

For $10 \leq \text{capacity} \leq 100$MGD
$\$\text{Cost} = 240{,}000\ (F_F)^{0.76}\ (E)$

Select correct formula based on value of F_F

b) Calculate engineering and contingencies

$\$\text{Cost} = 0.21$ (cost of a)

c) Calculate interest on construction funds

Capital Cost of filtration plant = a + b + c

11. Calculate Operating Cost of Filtration Plant

a) Power consumed 1 kW-hr/1000 gal filtered

$\text{kW-hr/day} = 1000(F_F)$

Subtract from plant output - kW-hr/day

b) Calculate cost of operation and maintenance of filtration plant

$$\frac{1993 \text{ (June 1974)}}{658 \text{ (1966)}} = 3.03$$

E - escalation factor - Engineering News Construction

For $0 \leq \text{capacity} \leq 0.4$ MGD

C_F = cost ¢/1000 gal $6.31 - [6.75 \times \log F_F](E)$

Select correct formula based value of F_F

For $0.4 \leq$ capacity ≤ 10 MGD

C_F = Cost ¢/1000 = $(6.64 - [4.46 \times \log F_F] + 1.74 [\log F_T]^2)(E)$

For 10 MGD $\leq$ capacity $\leq$ 100 MGD

C_F = Cost ¢/1000 gal = $4.35 - (1.31 \times \log F_F)(E)$

C_{FT} = Operating $ Cost/day = $\frac{C_F}{100} \cdot F_F \times 1000 = 10\, C_F F_F$

Printout C_{FT} = $/day x operating days/year - cost/year

c) Filtration chemicals = 2¢/1000 gal

Cost/day - $(F_F \times 1000 \times 0.02)(E)$

Printout cost/day x operating days/yr = $ Cost/yr

d) Amortize Plant Costs Per Year

e) Interest/year on Capital Invested

Total Operating Cost/Year = b + c + d + e

DERIVATION OF F_F EQUATION

F_W = Waste Water - MGD

F_C = Condensate - MGD

F_F = Filter plant flow

S_I = Solids content injected water (ppm)

S_W = Solids content waste water (ppm)

$$S_I = S_W \left(1 - \frac{F_F}{F_W}\right)\left(\frac{F_W}{F_W + F_C}\right)$$

$$S_I \left(\frac{F_W + F_C}{F_W}\right) = S_W - \frac{F_F\ S_W}{F_W}$$

$$S_I F_W + S_I F_C = S_W F_W - F_F S_W$$

$$F_F S_W = S_W F_W - S_I F_W - S_I F_C$$

$$\text{Filtered Flow} = F_F = F_W - \frac{S_I}{S_W}(F_W + F_C)$$

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