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CHOOSING MATERIAL FOR THE RAFT RIVER GEOTHERMAL PLANT

G. A. Reimann

H. W. Schutz

Aerojet Nuclear Company

IDAHO NATIONAL ENGINEERING LABORATORY

Idaho Falls, Idaho — 83401

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by

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ABSTRACT

Based on the known chemistry of Raft River geothermal water, no severe corrosion problems are envisioned which cannot be accommodated by plant design and conventional materials, including plastics. With a few exceptions, the use of stainless steel and other exotic materials cannot be justified and most of the Raft River plant can be constructed of low carbon-low alloy steel. It is imperative that oxygen be excluded from the system. Deposition of CaCO_3 and erosion will be troublesome.

Concrete and asbestos cement pipe can replace steel pipe at lower cost and may yield superior performance, particularly in aerated waste water. Most plastics and elastomers cannot endure continuous exposure to water temperatures above 250°F ; however, fluorocarbons are suitable for 400 to 550°F exposure and are especially resistant to accumulation of scale.

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CHOOSING MATERIALS FOR THE RAFT RIVER GEOTHERMAL PLANT

I. INTRODUCTION

Geothermal water is an effective means for transferring natural underground heat to the surface where it can be converted into electrical energy. Water is used in a similar manner to transfer the heat generated by fossil fuel or a nuclear reactor to a turbine for conversion into electrical energy. Among the problems connected with utilization of geothermal fluids are the minerals dissolved in the water as a consequence of prolonged exposure to various rock formations at high temperatures and pressures. The Raft River geothermal water is not expected to be aggressively corrosive if oxygen is not introduced, so that steel should be adequate for construction of most of the plant. However, concrete and asbestos cement appear to have cost advantages, particularly in the water transmission lines.

Certain controls may be exerted on the chemistry of water for conventional boilers, but very little control may be exerted on the chemistry of geothermal water. This heat source must be accepted "as is", particularly in view of the large volumes of "warm" geothermal water that must be handled in order to extract a useful quantity of steam. Naturally occurring contaminants in geothermal water will influence material selection and plant design. These contaminants will create problems in the form of corrosion, deposition, and erosion. The purpose of this investigation is to determine those materials applicable to the environment of a geothermal plant, located at Raft River in southeastern Idaho, which is designed to flash steam from superheated geothermal water.

II. SUMMARY

The Raft River geothermal water has not been thoroughly characterized in terms of chemistry; and because of the likelihood of mixing with cold aquifer water on the way to the surface, meaningful chemical data cannot be obtained until hot source water has actually been tapped. Based on what is known in conjunction with what may be reasonably assumed, the chemistry of Raft River geothermal water will not cause severe problems of corrosion, deposition, and erosion if suitable precautions are observed. The Raft River water will cause more materials problems than boiler feed water but fewer problems than sea water or other geothermal fluids encountered elsewhere which have higher dissolved solids. Available water chemistry data do not justify inordinate concern over corrosion in the geothermal plant; and conventional materials, which include concrete, asbestos cement, plastics, and plastic coatings, will be adequate for general plant construction.

Concrete pressure pipe and asbestos cement pipe are both cheaper than steel and can be used to carry primary geothermal water and waste water. Steel may not be satisfactory for the waste water line if waste water contains cooling tower discharge or has been exposed to the atmosphere in a settling pond. Fluorocarbons and coal tar pitch will withstand geothermal temperatures and may be useful to inhibit scale formation in the flashers and corrosion in the condenser circuit, respectively.

III. RECOMMENDATIONS

(1) API (American Petroleum Institute) 5L line pipe and its equivalent in plate specification should be suitable for 95% of the plant. Schedule 30 pipe should provide adequate corrosion allowance in most areas for the life of the facility. Subsequent experimentation may indicate that Schedule 10 pipe is sufficient, particularly if a plastic coating can be applied.

(2) In no portion of the plant (except for the turbine, certain valve and pump parts, and small critical items) can use of alloyed steel be justified in terms of corrosion protection when considering the additional cost involved. The condenser circuit, including the cooling tower, contains the most corrosive environment; and plastic components and/or plastic coatings will be most satisfactory, considering cost and serviceability. Calcium carbonate deposition will be most troublesome in the flasher unit and will remain a problem regardless of the material selected.

(3) Concrete and asbestos cement pipe will be suitable for carrying geothermal water, but their use in the larger pressurized vessels within the geothermal plant may require additional development to overcome inherent mechanical property deficiencies.

(4) Plastic coatings on steel will be useful in preventing accumulation of CaCO_3 scale; but only fluorocarbons will withstand anticipated geothermal temperatures in this application, and fluorocarbons are quite expensive.

(5) Fluorocarbons are difficult to bond firmly to steel; loose linings may be awkward but necessary if bonded linings are not satisfactory. Concrete and asbestos cement begin to decompose at fluorocarbon-curing temperatures.

(6) Some varieties of coal tar pitch are claimed to withstand 600°F and will protect steel from corrosion, but may not resist CaCO_3 encrustation. A coal tar pitch coating on steel may be useful in the condenser unit.

(7) Filament-reinforced plastic pipe is likely to deteriorate under prolonged exposure to geothermal water, even in cooler portions of the plant circuit, and this material should be viewed with caution.

(8) Complete water chemistry, including a gas analysis, is necessary before firm commitments are made regarding choice of materials.

(9) Field tests should be conducted in two phases: (a) for the short term, to determine the degree of deposition and the response of candidate materials thereto, and (b) for the long term, to monitor plant materials for the life of the plant, to investigate new materials, and to simulate other "warm" geothermal fluids that are to be utilized elsewhere for power generation.

IV. FINDINGS AND DISCUSSION

1. KNOWN WATER CHARACTERISTICS

Elements known to be present in the warmest geothermal well in the Raft River area, and their concentration in mg/l, are as follows^[1]: Si, 97 (as SiO₂, 208); Mg, 0.4; Na, 1,110; K, 35; Ca, 130; HCO₃, 36; SO₄, 61; F, 14; Cl, 1,900; calculated dissolved solids, 3,360. No gas analysis of this well is known, but the gas is believed to consist of CO₂, H₂S, CH₄, N₂, and NH₃, with CO₂ predominating. These gases will be in solution at depth but will evolve as geothermal water nears the surface and pressure is reduced.

The present well temperature is given as 90°C, but the water chemistry indicates that deep drilling will tap a geothermal reservoir at 150°C. It is probable that the chemistry of the 150°C deep well water will differ from the chemistry as measured at the 90°C well since hotter water at greater pressure is capable of carrying more solids in solution. Also, between source and surface, the geothermal water intersects and commingles with the cold aquifer which contains a different ion balance. Mixing of such waters can result in reactions and precipitation, but chemical interaction has usually run its course by the time the water reaches the surface, even if increased well flow is induced.

The use of geothermal water to produce steam to power a turbine is accompanied by more severe problems than would be encountered when using boiler-produced steam. A degree of control may be exerted upon the chemistry of the boiler feed water, but controlling the chemistry of geothermal water is difficult to the point of being impractical in view of the large volume of 150°C water required to produce a useful quantity of steam. Adding 1 ppm to the water at the source is equivalent to adding 115 lb/day. Some technology is available from experience with "dry" geothermal steam, but such information is not directly applicable to utilization of geothermal water. The Raft River geothermal plant is intended for demonstrating the possibility of using warm geothermal water as an economical source of energy. The nation appears to be entering an era of shortages, hence the emphasis on geothermal resource development. Shortages also may dictate which materials are available for geothermal plant construction, and alternatives should be selected where feasible.

2. POSSIBLE PROBLEMS WITH GEOTHERMAL WATER

Material problems in the Raft River geothermal plant, which will be a direct consequence of using geothermal water, may be separated into three categories: (1) corrosion, (2) deposition, and (3) erosion. Of the ions presently known in the geothermal water, the chloride ion will have the most pronounced effect on corrosion. Problems with dissolved gases, particularly CO₂ and H₂S, should be anticipated also. Corrosion from these sources is greatly accelerated when dissolved oxygen is present. Silica and calcium carbonate

will cause deposition problems. Insufficient magnesium is present to warrant any concern, and its concentration in the deep well is not expected to be significant. The degree of erosion will be influenced by suspended particulate matter, such as silt and precipitates; but entrained gas bubbles also produce erosive effects.

2.1 Chloride Ion

Based on experience with "natural" river and sea water, the chloride ion will cause substantial corrosion on steel pipe in the presence of dissolved oxygen. Raft River geothermal water has about 1/10 the salinity of sea water. At 150°C and 70 psia, geothermal water can maintain less than 10 ml/l or about 15 ppm dissolved oxygen. This greatly exceeds any O₂ level anticipated. Assuming sodium and potassium to be present as NaCl, a concentration of 2.9 g/l (3,160 ppm, with water at 917 g/l at 150°C) is present. Uhlig^[2] provides data indicating a corrosion rate of steel at 35°C at the above NaCl concentration with 1 atm air at this temperature. The corrosion rate doubles for each 30°C temperature increase, and this rate is doubled again by the increased oxygen which could be maintained in the 150°C water by virtue of the 70 psi pressure. Thus, under the worst conditions, a corrosion rate of 0.220 inch per year could be expected. Steel geothermal plant piping will be completely corroded within 1-1/2 to 3 years, assuming uniform corrosion (no pitting) and depending on the initial wall thickness selected.

Fortunately, the geothermal water is expected to contain very low oxygen concentrations; and unless oxygen is inadvertently introduced, the corrosion rate from NaCl alone is expected to be less than 0.006 inch per year in the well and transmission line.

Small quantities of chloride ion may be carried in the steam from the flasher and will increase the tendency for stress-corrosion cracking in stainless steels which are heat treated and/or stressed. This situation can develop at very low (less than 0.1 ppm) oxygen levels. Chloride ion will not enter the steam circuit unless the steam separator is inefficient, and the steam is wet.

2.2 Hydrogen Sulfide

According to solubility data, presence of hydrogen sulfide in geothermal water at 150°C and 70 psi is limited to insignificant quantities. Based on its solubility in pure water, 15 atm (220 psi) is necessary to dissolve 50 ppm H₂S at 150°C. The presence of metal sulfides can change the situation somewhat by reacting with or releasing H₂S in response to pressure changes; however, the solubility products for compounds likely to be encountered are very small (FeS, one of the more soluble, is 1×10^{-19}) and not likely to contribute much H₂S to the system. When present, H₂S tends to accentuate chloride corrosion and cause stress-corrosion cracking in high-strength and stainless steels. When chlorides are absent or at very low concentrations, H₂S forms a protective FeS coating on mild steel which prevents further H₂S attack. This coating cannot be maintained in regions of high water turbulence or where erosion is a factor, so sulfide attack in such regions could be continuous. Few data are available which would be directly applicable to conditions found in a geothermal plant. Also, data are not yet available to indicate the actual H₂S content of

the Raft River water. Since the H_2S content is presently assumed to be quite small, its effect on steel is assumed to be insignificant in terms of corrosion rate, particularly in view of corrosion protection afforded by any deposition of $CaCO_3$.

2.3 Carbon Dioxide

Dissolved CO_2 will present no problems in any portion of the system where calcium ion is present, and calcium ion is abundant in the Raft River geothermal water. In the flasher system, the CO_2 is separated from the calcium ion and enters the steam line along with any H_2S and other gases. With reasonably dry steam, CO_2 will cause no corrosion problems. Where the steam begins to condense in the steam line, in the latter stages of the turbine and in the condenser, CO_2 attacks steel at a rate of 10 to 15% that of the same concentration of O_2 were it present^[2]. In the absence of oxygen, corrosion in the steam line due to CO_2 in the condensate should be less than 0.005 inch per year.

2.4 Oxygen

In the condenser system, which includes the cooling tower, oxygen is introduced into the water up to its solubility limit. The water enters the cooling tower at $42^\circ C$ and is cooled by evaporation to $24^\circ C$. Oxygen, in equilibrium with air, ranges between 6 and 8 ppm over this temperature range. Excess CO_2 will be lost through aeration, and any H_2S will be oxidized to sulfur and sulfate. The cooling tower receives 650 gpm of water from condensed steam and evaporates 1,000 gpm to achieve the reduction in temperature. Thus, an additional 350 gpm must be added to the tower circuit to compensate for evaporation plus any quantity needed to compensate for drift losses. Makeup water to compensate for losses and to control the concentration of tower effluent will be supplied by a well from the cold aquifer, and ions will be introduced which would not be found in the steam. Calcium ion will lessen the corrosive effect of dissolved CO_2 , which will be present in the range of 5-8 ppm, depending on salinity. The presence of oxygen is a certainty in this circuit and, in combination with chlorides, sulfates, and dissolved CO_2 , may be expected to produce a corrosion rate on mild steel of 0.100 inch per year. Substituting stainless steel will reduce the corrosion rate considerably, but not sufficiently to offset the tremendous increase in cost.

2.5 Silica

Two components are present in Raft River water which can cause troublesome deposition, namely SiO_2 and $CaCO_3$. From Wohlberg^[3], $150^\circ C$ water can maintain between 500 and 700 ppm amorphous silica in solution. The 208 ppm silica in solution in the Raft River geothermal water will tend to precipitate between 30 and $60^\circ C$. Consequently, no silica precipitation should be anticipated anywhere in the system, except at the bottom of the cooling tower, where evaporation may concentrate silica from the cold aquifer water (20-30 ppm)^[4] to levels where precipitation will occur at $24^\circ C$.

2.6 Calcium Carbonate

Calcium in the residue of the geothermal water was reported as equivalent to 130 mg/l. This value is equivalent to 325 mg/l (353 ppm) of CaCO_3 assuming none of the calcium is in the form of sulfate, fluoride, or chloride. Insufficient bicarbonate is reported to produce 325 mg/l CaCO_3 ; however, enough CO_2 could have evolved from solution prior to the analysis to compensate for this insufficiency. Water at 150°C and 70 psi can maintain 1,375 mg/l (1,500 ppm) of CO_2 in equilibrium^[5] which is more than adequate to maintain 325 mg/l (353 ppm) of CaCO_3 in solution as $\text{Ca}(\text{HCO}_3)_2$.

Since no gas analysis is available, it is uncertain whether sufficient CO_2 is actually available to maintain calcium ion in solution. It is likely that some CaCO_3 will precipitate in the transmission pipe. This would be beneficial in terms of inhibiting the corrosive action of other ions and detrimental if the deposit accrues to the extent of restricting flow.

If calcium is in solution in the transmission line, it certainly will precipitate where the water reaches the flasher. The temperature drops from 150 to 115°C , and the pressure drops from 70 to 24 psi. Water at 116°C and 24 psi will maintain about 230 mg/l (242 ppm) CaCO_3 and 640 mg/l CO_2 under equilibrium conditions. The change of temperature and pressure causes loss of 95 mg/l of CaCO_3 and 0.735 mg/l CO_2 . At a flow rate of 10,400 gpm (40,000 lpm) and assuming all excess CaCO_3 will deposit in the flasher unit (including the hot well), deposition will occur at the rate of 4.1 kg/min, or 8.94 lb/min. The deposit will accumulate at a rate of 90,000 lb/wk, or 4,690,000 lb/yr. The evolved CO_2 is equivalent to 15,000 l/min STP, or 21,300 l/min ($5,635 \text{ ft}^3$) at 116°C .

The above situation would represent a formidable disposal problem. The rate of deposition was not taken into account, however; and since CaCO_3 deposition and CO_2 evolution will not occur instantly, a significant proportion of the deposition and evolution may take place in the waste water return line or in a second flash unit, if one is used. The flasher units are designed for cleaning access, and it would be more convenient if all deposition occurred in the flashers even though deposition around valves could be very troublesome. The pumps that return the waste hot water to the reinjection well must repressurize the fluid for this long journey. Repressurization will restrict further gas evolution and CaCO_3 deposition, although nucleated gas bubbles will contribute to erosion and facilitate cavitation.

2.7 Erosion

No estimate can be given for erosion from suspended silt. The high well water velocities required for plant supply at 10,400 gpm compared to the present unassisted well flow of less than 100 gpm make such estimates difficult. Initially, the silt load will be high and will diminish as the well stabilizes. Restarting shutdown wells will impose intermittent silt loads on the system. Corrosion will be more severe where silt abrades protective reaction products and keeps fresh metal surfaces exposed. Also, entrained gas bubbles will produce similar erosive effects in some areas. Erosion protection is achieved by minimizing changes

in fluid direction and abrupt changes in cross section or projections into the fluid stream. Such precautions are difficult in valves and pumps. The steam separator should prevent particles greater than 10 microns from entering the steam circuit, but turbine bucket protection should be considered for these small particles.

3. MATERIALS SELECTION

3.1 Division of Plant for Isolating Materials Problems

The Raft River plant may be divided into seven areas, for the purpose of identifying material problems, as follows:

- (1) The well
- (2) The transmission line to the plant
- (3) The flasher system, which separates steam from the hot water
- (4) The steam circuit
- (5) The turbine
- (6) The waste hot water line and the reinjection well
- (7) The condenser system.

3.2 Well Casing and Well Pumps

The final geothermal well depth is expected to exceed 6,000 feet. This casing will require some strength beyond that available in the existing casings in the 400-500-foot wells. Very high strength casings, such as "P110" should be avoided due to susceptibility to sulfide attack. The maximum casing hardness should not exceed 22 Rc, with 16-18 Rc values preferred. A "C-75" or equivalent should be suitable.

Exposure of the exterior of the casing to oxygenated water near the ground surface is inevitable, and double casing or effective grouting is necessary. Also, encroachment of oxygen into valve and pump shaft packing will accelerate corrosion in these parts. Simply plating these areas should be sufficient, and galvanic protection may be employed where parts are in contact with the earth and where other means of protection are difficult.

The water pressure at the well heads will not likely supply 10,400 gpm without assistance; so a well pump will be necessary, and it will be similar to a deep well irrigation pump. The impeller would be located at a depth of approximately 300 feet (500 feet maximum), and one may anticipate erosion problems from suspended solids. The shaft will

be long and subjected to cyclic tensile and torsional stresses. Bearings should be located inside the casing to minimize shaft whip. Copper alloys (i.e., bronze) or other bearing materials that might be susceptible to sulfide attack must be selected with care. Bearing and shaft seals must be evaluated, and copper components in the pump motor should be shielded from H_2S .

3.3 Transmission Line

Schedule 10, API 5L, Grade B pipe will be sufficient both for the 15- and 30-inch-diameter transmission lines. This pipe is very similar to ASTM A53, which does not yet include sizes above 26 inches in diameter. The API specification requires a double submerged arc weld and subsequent pressure testing. It is recommended that the 15-inch pipe be purchased to the API 5L specification. Also, the A53 specification permits electric resistance welded (ERW) seams. The ERW seam is in effect a continuous spot weld; and this process would be more likely to concentrate a band of oxide at the joint than would an arc weld which, by virtue of the flux and molten pool, is better able to disperse and float out oxides. If the ERW seam represents a significant cost reduction, it may be necessary to subject representative sections to test loop examination to verify suitability. The API 5L pipe may be obtained from Geneva Works in 40-foot lengths or more, which could substantially cut field welding costs.

Seamless pipe to the ASTM A106 specification is available from some suppliers. Benefits in terms of corrosion resistance are not known presently, and preference for this specification may be determined solely by relative cost and availability. The rougher inside surface of A106 pipe may result in additional transmission losses unless deposition offsets it.

3.4 Flasher Units

Four flasher units will comprise the steam generator system, with three flashers operating and one on standby. The flasher tanks measure 8 feet in diameter and 30 feet in height. These units will be fabricated from 3/4- to 1-inch-thick plate, for which the specifications have not been established. The 10,400 gpm geothermal fluid will be divided between the three operating flashers, and 6-1/4% of this volume will be flashed to steam. The geothermal fluid will be subjected to a substantial environmental change in this portion of the plant. The temperature will fall about 30°C, and the pressure will decrease suddenly by 15 psi. In addition to the generation of steam, dissolved gases will evolve, the pH will change, the remaining solution will become more concentrated, and precipitation will begin. Whether scaling will be more troublesome in the turbulence of the flasher, in the relative quiescence of the adjacent hot well, or in the waste water line is unknown at this time; but some estimate will be required.

Scaling in the flasher circuit may be controlled by mechanical and/or chemical means or by a plastic liner. Scale removal by mechanical means will require personnel entry and may result in damage to the interior, particularly liner materials. Cleaning by chemical means will require resistance to any corrosive effects of the cleaner and may require separate disposal of this solution. Thermosetting plastics, CPVC, and a number of other compounds

have properties well suited for a protective coating in the flasher except for heat resistance. The liner must give long service at 116°C in the presence of turbulent water and evolved gases, and no candidate materials other than fluorocarbons can be offered at this time in this application. It may not be good practice to send dislodged scale through the waste line pumps.

While the flasher unit sees pressure of 25 psia or less and thus circumferential stress is not a problem if steel is used for construction, the units will be subject to considerable vibration; and the effects of cyclic loading must be considered, particularly in the connected piping. A tendency toward fatigue-type failure could be aggravated by the presence of chloride and sulfide ions. The steam pipe, which the plant sketch shows as free-standing inside the flasher, should be supported at the top.

The hot well will encounter the same problems as the flasher with regard to deposition; and it is likely that deposition will continue in the hot well outlets, the isolation valves, and in portions of the waste water pumps.

3.5 Steam Circuit

The steam line measures 48 inches in diameter and will collect the 116°C steam and other gases from the flashers and direct it to the turbine. This line will be fabricated from 1/2-inch plate (A-283, A-285, or equivalent) and will include an expansion bellows below the turbine.

3.6 Turbine

This area falls within the province of the manufacturer who, it is assumed, has the benefit of his own research in this area. His judgement will hinge on the completeness and accuracy of our chemical analysis of the geothermal fluid. The turbine buckets and the adjacent shroud are critical parts. The 400-series stainless steels have been employed in dry steam geothermal applications with good results with more problems from deposition and erosion than from corrosion. A washing method is under investigation at "The Geysers" in an attempt to control this deposition. The degree of erosion is a function of steam separator efficiency, although turbine buckets and shrouds will suffer from the erosive effect of wet steam regardless of separator efficiency.

The turbine blades will be "soft" and stubby to resist stress-corrosion cracking from sulfides and chlorides. Erosion shields will be required on these soft blades.

The turbine casing must be tightly sealed to prevent entry of oxygen, especially in the low pressure regions. Shaft seals must be carefully designed for the same reason. The generator commutator must be protected from H₂S, or rapid attrition will result.

3.7 Waste Hot Water Line

This line is required because it is not permissible to carry boiling water to the reinjection site in an open ditch. It may be constructed of the same materials and to the same specifications as the transmission line with the following exception: Scaling should be less of a worry after precipitation has occurred in the flasher circuit and the waste water is repressurized for transmission several miles to the reinjection site. Remaining corrosives in solution are slightly more concentrated, however, and the pH is increased by removal of dissolved gases.

If cooling tower effluent is injected into the waste water line, or in the event a settling pond is used in order that reactions have time to go to completion and to allow settling of particulate matter, waste water will acquire sufficient oxygen to preclude the use of mild steel pipe in the waste water line.

3.8 Condenser System

Original plans called for use of 10°C aquifer water in the barometric condenser; however, calculations indicated a large amount of power was required to circulate and reinject this water. A cooling tower has been substituted for a heat sink. This unit will supply 21,000 gpm to the condenser at 24°C and recover this quantity plus 650 gpm of condenser steam at 42°C. Evaporation of 1,000 gpm will be required to maintain this temperature differential, and makeup water will be necessary to compensate for evaporation and drift losses as well as to control the composition of the tower output.

Metal corrosion problems in the condenser circuit may be eliminated by minimizing the use of metal. A number of heat-resistant plastic compounds are available and suitable for cooling tower components, including cooling tower louvers. Stainless fasteners should be employed where plastic fasteners will not suffice. Cooling tower construction must withstand a winter ice load.

The condenser jet may require metal construction and is in a critical location in that it supplies the mineralized cooling tower output to the condenser and may be subjected to alternate acid and basic cleaning flushes. This unit is a relatively small component in the system; and exotic corrosion-resistant alloys, such as titanium or zirconium, may be warranted here.

Attention must be given to housings, shafts, and impellers of pumps for cooling tower output, as well as to aeration fans. Oxygenated water will contain various corrosive ions. Also, deposition and erosion will occur; and plastic coatings will not suffice in all applications, nor can stainless steel or other corrosion-resistant alloys assure extended service. Hard facing may be necessary in high intensity regions. Experience with "conventional" cooling towers will not be helpful, but cooling tower experience at The Geysers would be useful if the information can be obtained.

3.9 Concrete and Asbestos Cement, General

The suitability of concrete and asbestos cement piping for geothermal plant service has received very little attention. Both materials have had extensive exposure to cold and near-boiling water; but no information could be uncovered to detail the consequences, if any, of prolonged exposure to geothermal water at 300°F and 150 psig. The Department of Interior, Office of Saline Water, has exposed concrete and asbestos cement pipe to high temperature (over 500°F) brines; and the Bureau of Reclamation is exploring desalting and energy extraction from geothermal wells in Imperial Valley, California, although the latter agency is apparently not investigating concrete and asbestos cement in critical locations.

3.9.1 Concrete. Concrete is a cemented aggregate with each particle of aggregate surrounded by a cement and water paste. The aggregate content normally ranges between 65 and 80% of the mix. Concrete exhibits variable properties. Much of the variability is related to the aggregate, i.e., the strength, size and shape of the particles, and their tendency to react chemically with the paste. The cement and water paste requires but a small amount of water for complete chemical reaction with the cement. However, water is added in excess for placeability or mobility of the mix. Increasing amounts of water, above that required for reaction, result in proportional decreases in quality, strength, and resistance to weathering. The impermeability of concrete to water decreases as additional water is added to make the paste. Once emplaced, proper curing conditions are necessary to assure the desired properties.

Portland cement is composed of four principal compounds: tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$), and tetracalcium aluminoferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$). The proportions of the above compounds are varied somewhat for higher early strength, lower heat generation, sulfate resistance, etc. Other compositional variations, outside the scope of ASTM specifications, are used in special situations^[6,7].

3.9.2 Concrete Pipe and Vessels. Concrete pipe and vessels can be fabricated in any size currently envisioned for geothermal power generation. Concrete pressure pipe sections up to 18 feet in diameter and 20 feet long and weighing 165 tons have been produced, but shipment of such sizes is very difficult. Mechanical damage, variable properties, and susceptibility to damage from pressure surge and thermal shock become more troublesome with increasing size. "Standard" concrete pipe would not likely give satisfactory service in elevated pressure and temperature geothermal applications; however, the "pressure pipe" contains a continuous steel membrane of 16-gage steel that is prestressed by wire wrapping. The imbedded steel shell provides impermeability as well as strength. Pressure pipe in 30-inch size should be suitable for carrying primary geothermal fluid as well as waste hot water.

No direct experience is available to enable an estimate of the response of concrete pipe to continuous exposure to hot geothermal water. The possibility is always present that the cement and/or the aggregate will dissolve in the pressurized hot water, although the likelihood of this decreases with increasing pH and an excess of Ca^{++} ion. Some

manufacturers of concrete pipe claim it will last indefinitely, while suppliers of steel or asbestos cement pipe claim that concrete pipe will deteriorate rapidly. There is no substitute for field testing in such a situation, with the caution that what works well in a pilot-plant setup may not necessarily be amenable to scale-up, as the thicker walls in the larger sizes are more vulnerable to thermal stress failure. Also, materials that serve well in the geothermal water at Raft River may not be satisfactory elsewhere.

The cost of 30-inch concrete pressure pipe to handle 300°F water at 150 psig is estimated at \$35.00/running foot.

3.9.3 Other Concrete Applications. Concrete foundations and structures are considered vulnerable in desert locations regardless of the formulation^[8]. Sulfate ions and alkaline salts are the culprits, and concrete deterioration is particularly active near the groundline. Cooling tower drift accelerates deterioration. The products of reaction with the offending ions result in localized substantial volume increases causing the concrete to self-destruct when exposed. Specially formulated concrete is less affected but not immune. The problem is best solved by protective coatings, with coal tar epoxy being particularly effective as demonstrated by its use at The Geysers, California.

3.9.4 Asbestos Cement. Asbestos fiber is formed by alteration by hydrothermal reactions of basic igneous rock and is a product of selective solution and crystallization. Considering this, asbestos fiber may be vulnerable to certain geothermal waters. Fundamentally, asbestos fiber is $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ and contains variable quantities of FeO, Fe_2O_3 , Al_2O_3 , and CaO. Asbestos cement contains asbestos as a minor constituent, with silica (35%) and portland cement (40%) predominating. The fiber, finely ground silica, and portland cement are blended; and water is added to make a slurry.

3.9.5 Asbestos Cement Pipe. In the manufacturing of asbestos cement pipe, the slurry is picked up on a belt and wrapped on a steel mandrel under pressure to obtain the desired shape. Fiber orientation is random. Curing is done with steam in an autoclave at 350°F and 100 psig. Manufacturing equipment, in particular the mandrels, limits the size of asbestos cement pipe to a 42-inch inside diameter (ID) although the process could accommodate larger sizes if demand existed. Finished pipe is routinely tested at 350 psig, and geothermal water temperatures are thought to be a problem only where rubber-compound joint seals are concerned. Asbestos cement pipe deteriorates under conditions of frequent wetting and drying.

One major advantage of asbestos cement (and concrete) pipe is that no expansion loops are necessary as dimensional shifts are compensated for in flexible elastomer seal joints. Also, these materials are unaffected by increasing oxygen content in heated water; and they can be buried without cathodic protection. No incidents of attack by desert soils on asbestos cement pipe have been reported. Asbestos cement pipe, 30 inches in diameter and tested at 350 psig, is estimated at \$26.00/running foot compared to 200-psig concrete pressure pipe at \$38.00/foot and API 5L Schedule 10 line pipe at \$47.00/foot.

3.10 Other Nonmetallics

Nonmetallics such as carbon, graphite, and ceramics are ordinarily too susceptible to impact damage, too vulnerable to attack by water, or too expensive. Also, some nonmetallics (carbon, graphite, CaSO_4 , Fe_2O_3 , etc.) are known to increase the rate of precipitation^[9]. Nonmetallics most worthy of consideration for geothermal power uses are the organics: plastics and elastomers.

3.10.1 Plastics, General. Besides the ability of many organics to absorb punishment by flexing, compressing, etc., the largest single advantage is resistance to scale precipitating from ground waters. Dow Chemical's Saran-lined Pipe Co. says it has found no scale formation in any of the plastic-lined pipe it supplies lined with Teflon TFE or FEP, Kynar (VF_2), Penton, Saran, and polypropylene. Another advantage of the same smooth surface when used to line piping is reduced pumping friction. The main handicap to the use of plastics is high-temperature effects, especially reduced strength and, sometimes, chemical deterioration by hydration^[10]. Embrittlement has been encountered in some plastics, such as polyvinyl chloride (PVC), when exposed to geothermal fluids for extended periods^[8].

Loss of high-temperature strength can be overcome to an extent by use of plastic-lined steel pipe or by glass fiber reinforcement. The success of lined pipe depends on the liner's ability to produce a metal-to-plastic bond resistant to weakening due to a small-but-finite penetration of the lining by the contained liquid. No plastic is completely impermeable (see Section VII, Table I). However, at times, this fact may be capitalized upon by realizing that the three gases to which plastics are ordinarily most permeable are hydrogen, helium, and carbon dioxide. It may be possible to vent small volumes of CO_2 and H_2 directly through the wall of a plastic vessel.

Glass fiber reinforcement permits strengthening of vessels in preferred (usually circumferential) directions, but it usually reduces flexibility to limits impractical for cracking off scale. Reinforcement permits a significant increase in temperature stability but only if the glass fiber can be protected against direct contact with water. Hydration is the Achilles' heel of glass fibers and of several otherwise high-temperature plastics such as polyimides^[11].

Plastics like PVC owe much of their room-temperature usefulness to incorporation of organic plasticizers such as di-2-ethylhexyl phthalate. Exposure to hot water, however, quickly leaches out the plasticizer, leaving a relatively brittle remainder. Plastics containing plasticizers should be avoided for geothermal work. Maximum recommended service temperatures for a number of plastics are listed in Table II (Section VII).

3.10.2 Elastomers. Specially compounded elastomers such as silicone rubber, nitrile, Hytrel, etc., will withstand geothermal temperatures; but these materials are quite permeable to water (relative to fluorocarbons) and generally lack sufficient mechanical strength for use as thin linings. They should be well suited for use in joints, seals, and gaskets.

3.10.3 Information from Supplier Contacts. None of the suppliers could offer any reference for direct geothermal experience to demonstrate the response of various coatings to geothermal water, particularly regarding resistance to formation of CaCO_3 scale. Most of the following items of information were obtained from sales literature and telephone contacts with suppliers and appliers. A list of telephone contacts is compiled under Section VI.

(1) The list of suitable nonmetallics (plastics) that will withstand 240 to 300°F temperatures for prolonged periods is quite short. The more common coatings (Saran, PVC, CPVC, polypropylene, etc.) are limited to 150-220°F and may have some application in cooler portions of the circuit, such as the waste water line, but not in the primary water line or in the flashers.

(2) The most suitable plastics appear to be the fluorocarbons, some of which are serviceable up to 550°F. These include polymers of tetrafluoroethylene (TFE, to 500°F), fluorinated ethylene propylene (FEP, to 400°F), vinylidene fluoride resin (VF_2 , to 340°F when laminated), and perfluoro-alkoxy (PFA, to 550°F). These compounds have outstanding corrosion resistance; however, in the geothermal application, this feature is secondary to heat resistance and "nonstick" characteristics since geothermal water is not aggressively corrosive if oxygen is excluded.

(3) The nonstick characteristics of fluorocarbons make it difficult or impractical to achieve a secure bond to the vessel wall. A thermal expansion coefficient 10 times that of steel may compound this difficulty, particularly where frequent temperature cycling is encountered.

(4) All plastics are permeable (see Table II), especially to water molecules, and permeability increases with temperature. This feature is an additional hindrance to bonded coatings. Fluorocarbon suppliers and appliers speak in terms of loose vessel linings, although one applier claimed the ability and the facilities to enable durable bonded coatings of FEP to steel. For nonbonded loose linings, the vessel wall should be vented to prevent water accumulation behind the lining. Allowance for escape of water vapor from these vents must be considered when insulating the vessel exterior.

(5) Suppliers of fluorocarbons would not give assurance that CaCO_3 would not adhere to these linings in service. In one case, barnacles were able to attach themselves and grow on Teflon-coated ship hulls, although they could be removed easily. However, it is reasonable to speculate that any CaCO_3 accumulation will not adhere sufficiently to permit continuous buildup in the turbulence within water lines or in the flasher vessel. Such a circumstance might be entirely acceptable if it eliminated the requirement of periodic opening of the flasher and hot well vessels for cleaning. The waste water pumps would receive a higher particulate load than the well pumps if this condition occurs, and dislodged pieces of scale too large to be swept out by high water velocity could grow into large stones by accretion.

(6) The cost of applied fluorocarbons is considerably higher than the more commonly applied plastics. This increase is related to the high cost of "raw" material. For example, Kynar in powder or pellet form lists for \$5.00/lb in quantities less than 5,000 lb; and dispersions list for \$45.00/gallon in 5-gallon containers, as of 1 March 1974. One applier quoted \$15.00/square foot for bonded coatings (approximately \$12,000 per flasher vessel), and another estimated \$25,000 per vessel if loose linings were used. Price estimates were based on the inside surface of flasher only and did not include the attachment fittings or the steam pipe.

(7) No one seemed eager to discuss application of fluorocarbon coatings to concrete and asbestos cement pipe. Portland cement experiences significant water losses with corresponding property degradation at temperatures above 450°F, and 500-700°F is required for curing fluorocarbon coatings. Extra wall thickness can compensate for property loss if necessary. More rapid heating to minimize exposure time of vessels near fluorocarbon-curing temperature can cause spalling and cracking. Also, evolving water vapor can interfere with bonding. Concrete and asbestos cement pipe can be particularly susceptible to CaCO_3 encrustation if no coatings or linings are used. In view of the foregoing, concrete and asbestos cement should not be considered for the flashers and hot wells or for nearby portions of the water circuit likely to experience heavy CaCO_3 deposits.

(8) Another potential vessel coating is "Super Service Black" by Koppers Co., Pittsburgh. This material is a heavy coal tar pitch with fillers added to decrease a tendency to sag when hot. Its maximum service temperature is 600°F. Naphtha is added as a solvent to enable application and must be evaporated between coats. Super Service Black is relatively cheap, easily applied to steel, concrete, and asbestos cement; and it will withstand expected geothermal temperatures. Its resistance to scale formation is unknown but will likely be inferior to the fluorocarbons. Its main advantage should be in protecting steel from corrosion, especially in the condenser circuit. Coal tar epoxies are not suitable in elevated temperature environments as they become embrittled upon long-term exposure and spall from the surfaces they are supposed to protect.

(9) This review of nonmetallics has raised some questions regarding the application of filament-reinforced plastics. In addition to the resin tending to become brittle at elevated temperatures, these compounds exhibit a relatively high permeability to water. This factor adversely affects the reinforcing glass fibers and results in substantial strength loss. Pipes can begin leaking in a relatively short time, and leaking worsens rapidly once it starts. Steel protected with coal tar pitch may be considered as an alternative to fiber-reinforced plastics where such plastics were previously recommended for consideration.

(10) Successful prevention of CaCO_3 scale accumulation in the flashers and hot wells will result in high quantities of suspended solids in the waste water. This condition will cause more rapid attrition of the waste water pumps, subject the waste water line to abrasion, and present the risk of clogging or sealing off the porous formation into which the waste water is to be reinjected.

The above difficulties could be minimized or eliminated entirely by dumping the hot well waste water directly into a settling pond. Such a pond may require considerable volume to allow sufficient water residence time for complete precipitation with an input of 10,000 gpm, but it would provide waste water pumps with water relatively free of solids and provide a means for disposal of cooling tower effluent.

The use of a settling pond exposes geothermal water to the atmosphere for the first time, and metal corrosion problems will develop where previously they were of little concern. The presence of a higher concentration of oxygen in the hot waste water will require consideration of a material other than steel to conduct this water to the reinjection site; and, for this reason, concrete and asbestos cement pipe would likely yield better performance if used in this portion of the plant circuit.

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VI. TELEPHONE CONTACTS

1. Amer. Concrete Pressure Pipe Assn., 1501 Wilson Blvd., Arlington. Va. 22209
Mr. Joe Willet 703-524-3939
2. Ameron, Inc., 400 S. Atlantic Blvd., Monterey Park, Calif. 91754
Research Lab., Southgate
W. R. Dana 213-564-6626
Engineering, 750 NE Columbia Blvd., Portland Oregon 97211
Don Munroe 503-285-2531
(MFR Conc. Pressure Pipe)
3. Bureau of Reclamation, Dept. of Interior, Denver Federal Center, Denver, Colo. 80225
Applied Science Branch
Case Van Hoek 234-3211 (Geothermal)
Jack Grimsley (Concrete Pipe) 234-4794
Jim Warden (Asb. Cem. Pipe) 234-4294
Jerry Dodd (Geology) 234-3117
Haley Warren (Publications) 234-3007
4. Chapman Industries, Rt. #1, State Road, Avondale, Pa. 19311
Frank Chapman
Ted Starr 215-268-2252
(apply linings to vessels)
5. Dow Chemical Corp., Bay City, Michigan
Jim Ayres 517-684-4330
(Saran, Kynar lined pipe, max. 14 in. Dia)
6. DuPont Company, Polymer Group, Wilmington, Del. 19898
Dr. Larry Ferris 302-999-3749
Fabrics & Finishes Dept., Wynnewood, Pa. 19096
Mr. John Enrich
Mr. Rist 215-896-2249
Elastomer Chemical Dept., Akron, Ohio 44308
Margaret Lonsberry 216-253-5571
7. Fluorodynamics, Inc., P. O. Box 1202, Newark, Del. 19711
Wyatt Smythe 302-368-2511
(apply coatings to vessels)

8. Johns-Manville, Littleton, Colo.
Louis F. Benton
Elmo Brundrett 303-770-1000
Boise, Idaho
Phil Sloan 343-3260
9. Koppers Company, Inc. 1420 Koppers Bldg., Pittsburgh, Pa. 15219
Mr. Pauli 412-391-3300
(Super Service Black, Coal Tar Epoxy)
10. Minnesota Mining and Manufacturing Co., 3M Center, St. Paul, Minn. 55101
612-733-1110
Chemical Div.
Lew Cove, Ext. 0733
11. Office of Saline Water, Dept. of Interior, Washington D. C. 20240
Mr. Will Hahn 202-343-5965
12. Pennwalt Corp., 3 Parkway, Philadelphia, Pa. 19102
R. E. Jones 215-587-7000
(Kynar)

VII. TABLES

TABLE I
PERMEABILITY OF POLYMERS^[a,12]

Chemical Type	Example ^[b]	Nitrogen	Oxygen	Carbon dioxide	Permeability to water ^[d]
Polyvinylidene chloride	Saran	0.01	0.05	0.29	14-1,000
Polyvinyl fluoride	Tedlar	0.04	0.2	0.9	3,300
Polyethylene terephthalate	Mylar	0.05	0.3	1.0	1,300-2,300
Rubber hydrochloride ^[e]	Phofilm	0.08-6.2	0.25-5.4	1.7-18.2	250-19,000
Polychlorotrifluoroethylene ^[f]	Kel-F	0.09-1.3	0.25-5.4	0.48-12.5	3-360
Phenol-formaldehyde	Bakelite	0.95	---	---	---
Polyamide	Nylon	0.1-0.2	0.38	1.6	700-17,000
Epoxy ^[g]	Epon-1001	---	0.49-16	0.86-14	---
Poly(styrene-methacrylonitrile)		0.21	1.6	---	---
Polyformaldehyde (acetal)	Delrin	0.22	0.38	1.9	5,000-10,000
Polyvinyl chloride		0.4-1.7	1.2-6	10.2-37	2,600-6,300
Poly(styrene-acrylonitrile)		0.46	3.4	10.8	9,000
Cellulose acetate ^[h]		1.6-5	4.0-7.8	24-180	15,000-106,000
Poly(butadiene-acrylonitrile) ^[h]	Hycar	2.4-25	9.6-82	75-636	10,000
Polycarbonate		3	20	85	7,000
Polystyrene		3-80	15-250	75-370	10,000
Poly(isobutylene-isoprene) 98/2 ^[i]	Butyl rubber	3.2	13	52	400-2,000
Polyethylene ^[j]		3.3-20	11-59	43-280	120-2,100
Poly(vinylidene fluoride-hexafluoro-propylene)	Viton A	4.4	15	78	520
Polypropylene		4.4	23	92	700
Polyurethane ^[k]	Adiprene	4.9	15.2-48	140-400	3,500-125,000
Polydimethylbutadiene	Methyl rubber	4.8	21	75	---
Chlorosulfonated polyethylene	Hypalon	11.6	28	208	12,000
Polychloroprene	Neoprene	11.8	40	250	18,000
Fluorinated ethylene-propylene copolymer	Teflon FEP	21.5	59	17	500
Polytetrafluoroethylene	Teflon	---	---	---	360
Poly(butadiene-styrene)	Buna-S	63.5	172	1240	24,000
Polybutadiene		64.5	191	1380	49,000
Natural rubber		84	230	1330	30,000
Ethylcellulose		84	265	410	14,000-130,000
Silicone rubber		---	1000-6000	6000-30,000	106,000
Polyvinyl alcohol		---	---	---	29,000-140,000

[a] Units: cc(STP)/cm²/mm/sec/cm Hg X 10¹⁰.

[b] The table is not intended to be exhaustive. Because of the considerable variation of permeability with crystallinity, density, plasticizer content, monomer ratio in copolymers, source, and other parameters, the values should be considered only as examples of permeability values observed with some, not necessarily the best, representative of each polymer class. These values are also not necessarily those characteristic of the materials listed in the column headed "Example". Neither do the ranges cover the total spectrum of permeabilities obtainable for each polymer class.

[c] At 20 to 30°C except where noted otherwise.

[d] At 20 to 30°C.

[e] The high values for nitrogen and carbon dioxide apply to the plasticized material.

[f] The low values for gases apply to the 80% crystalline material at 40°C.

[g] The low values are for Epon 1001; the high values are for Hysol.

[h] The low values for gases apply to a 61/39 butadiene acrylonitrile ratio (Hycar OR 15). The high values apply to an 80/20 ratio.

[i] The low value for water applies to a quinoid-cured, carbon-black-filled butyl rubber compounded at the U. S. Naval Applied Science Laboratory for Hydrophone encapsulation.

[j] The low values apply to high density polyethylene (0.954-0.960 g/cc). The high values apply to low density polyethylene (0.92 g/cc).

[k] The high water permeability was reported for Vorite-Polyein (system 21) by the Baker Castor Oil Co. The high value was observed at the U. S. Naval Applied Science Laboratory for Moca-cured Adiprene L-100 and other polyether-based polyurethanes. A value of 29,000 was observed for the cured and filled polyester-based polyurethane Estane-58029.

TABLE II
MAXIMUM RECOMMENDED SERVICE TEMPERATURES FOR PLASTICS
AND ELASTOMERS^[10,13]

Plastics	In Air (°F)	In Water (°F)
Teflon TFE (polytetrafluoroethylene)	500	500
Teflon TFE (confined, as in a gasket)	650[a]	650[a]
Teflon FEP (tetrafluoroethylene-hexafluoropropylene copolymer)	400	---
Kynar (polyvinylidene fluoride, etc.)	340	---
Kel-F (polychlorotrifluoroethylene)	380	---
Penton (chlorinated polyether)	250-275	---
Vespel (polyimide)	500	175
Nylons (polyamides)	250[a]	200[a]
Delrin (polyacetal)	195	---
Celcon (acetal copolymer)	220	better than homopolymer
Lexan (polycarbonate)	250	---
Dacron, Mylar (polyethylene terephthalate)	250-400	---
Polyethylene - low density	175	175
Polyethylene - high density	230	230
Polypropylene	230	230
Lucite, Plexiglas (polymethylmethacrylate)	140-200	---
Silicones	500	---
Polystyrene	not recommended	---
Alkyd (glycerol-phthalic anhydride)	300	---
Elastomers		
Natural rubber (cis-polyisoprene)	180	---
Buna-S (butadiene-styrene copolymer)	180	---
Buna-N (butadiene-acrylonitrile copolymer)	300	---
Nitrile	300	---
Butyl (isobutylene-isoprene)	300	---
Neoprene (polychloroprene)	240	---
Ethylene-propylene terpolymer (EPT or EPDM)	250[a]	450 (steam 500)[a]
Ethylene-propylene (EP)	250[a]	400 (steam 450)[a]
Viton (vinylidene fluoride-hexafluoropropylene copolymer)	400	350
Silicone	600	300[a]

[a] Taken from RDT Standard M11-1T.

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