

**COMPANION STUDY GUIDE
TO
SHORT COURSE ON GEOTHERMAL CORROSION
AND MITIGATION IN LOW TEMPERATURE
GEOTHERMAL HEATING SYSTEMS**

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INTRODUCTION

The economic utilization of geothermal resources with temperatures less than 220°F for purposes other than electric power generation (direct utilization) requires creation of systems with long plant life and minimum operation and maintenance costs. Development of such systems requires careful corrosion engineering if the most cost effective material selections and design choices are to be made. This study guide presents guidelines for materials selection for low-temperature geothermal systems (120 - 200°F), as well as guidance in materials design of heat pump systems for very-low-temperature geothermal resources (less than 120°F).

This guideline is divided into five sections and an Appendix.

1.0	Key Corrosive Species
2.0	Modes of Geothermal Corrosion
3.0	Geothermal Corrosivity Classification System
4.0	Corrosion Engineering of Low-Temperature Direct Utilization Systems
5.0	Geothermal Heat Pumps
Appendix	Worksheets for Chemical and Scaling Properties of Low-Temperature Geothermal Waters

These guidelines are based on Radian's geothermal materials database, containing materials performance data from more than 20 low-temperature geothermal sites worldwide, as well as results of numerous component failure investigations conducted by Radian's Materials Sciences Laboratory (MSL). Much of this data is summarized in two DOE reports:

Materials Selection Guidelines for Geothermal Energy Utilization Systems.
and the Addendum to this report (the first two citations in the list of references).

Unless otherwise indicated, the information herein is taken from these two documents.

1.0 KEY CORROSIVE SPECIES

Geothermal fluids commonly contain seven key chemical species that produce a significant corrosive effect. The key species are:

- Oxygen (generally from aeration)
- Hydrogen ion (pH)
- Chloride ion
- Sulfide species
- Carbon dioxide species
- Ammonia species
- Sulfate ion

The principal effects of these species are summarized in Table 1, except as noted, the described effects are for carbon steel.

Two of these species are not reliably detected by standard water chemistry tests and deserve special note. Dissolved oxygen does not naturally occur in low-temperature (120 - 220°F) geothermal waters which contain traces of hydrogen sulfide, though because of slow reaction kinetics, oxygen from air inleakage may persist for some minutes. Preventing oxygen contamination once the geofluid is produced is extremely difficult, especially if pumps other than downwell submersible pumps are used to move the geofluid. Even though the fluid system may be maintained at positive pressure, air inleakage at the pump seals is likely, particularly in light of the level of maintenance likely in many installations.

Hydrogen sulfide is ubiquitous at low part-per-million (ppm) or part-per-billion (ppb) levels in geothermal fluids above 120°F. This corrosive species also occurs naturally in many cooler groundwaters. For those alloys such as cupronickels which are strongly affected by it, hydrogen sulfide concentrations in the low parts-per-billion range may have a serious detrimental effect, especially if oxygen is also present. At these levels, the characteristic rotten egg odor of hydrogen sulfide may be absent, and detection requires use of field methods. Hydrogen sulfide levels down to 50 ppb can be detected using a simple field kit provided by CHEMetrics. Even absence of hydrogen sulfide at this low level may not preclude damage by this species. Field spectrophotometry, which requires a spectrometer and different kit (K9503) has a detection limit of less than 10 ppb.

Two other key species must also be measured in the field: pH and carbon dioxide species. This is necessary because most geothermal fluids will rapidly off-gas carbon dioxide, causing a rise in pH. DOE has published a manual for complete chemical analysis of geothermal well waters, giving recommended procedures (Kindle and Woodruff, 1981).

2.0 MODES OF GEOTHERMAL CORROSION

A number of different corrosive phenomena have been observed in geothermal systems. In low- and very-low-temperature geothermal systems, the following are most likely to be significant:

Uniform corrosion is the even wastage of metal from the component. This is the form of corrosion which is expressed as a “corrosion rate,” often mils/yr or mpy. Uniform corrosion is a useful measure of corrosion resistance only if the other modes of corrosion described below do not occur.

Pitting is localized corrosion forming cavities or holes in the metal surface. The rate of pit penetration is highly unpredictable, and it is not practical to design around (or allow for) pitting. Pitting is particularly serious in heat exchangers (HX) because of the thin walls and large area of the HX, and because a single pin hole perforation may constitute a failure.

Table 1. Principle Effects of the Key Corrosive Species

Key Corrosive Species	Principle Effects
Oxygen	<p>Extremely corrosive to carbon and low alloy steels. 30 ppb* shown to cause four-fold increase in carbon steel corrosion rate.</p> <p>Concentration above 50 ppb cause serious pitting.</p> <p>In conjunction with chloride and high temperature, less than 100 ppb dissolved oxygen can cause chloride-stress corrosion cracking (chloride-SCC) of some austenitic stainless steels.</p>
Hydrogen ion (pH)	<p>Primary cathodic reaction of steel corrosion in air-free brine is hydrogen ion reduction. Corrosion rate decreases sharply above pH 8.</p> <p>Low pH (less than about 5) promotes sulfide stress cracking (SSC) of high strength low alloy (HSLA) steels and some other alloys coupled to steel.</p> <p>Low pH may cause breakdown of passivity of stainless steels.</p> <p>Acid attack on cements.</p>
Carbon dioxide species (dissolved carbon dioxide, bicarbonate ion, carbonate ion)	<p>Dissolved carbon dioxide lowers pH, increasing carbon and HSLA steel corrosion.</p> <p>Dissolved carbon dioxide provides alternative proton reduction pathway, further exacerbating carbon and HSLA steel corrosion.</p> <p>May exacerbate SSC.</p> <p>Strong link between total alkalinity and corrosion of steel in low-temperature geothermal wells.</p>
Hydrogen sulfide species (hydrogen sulfide, bisulfide ion, sulfide ion)	<p>Potent cathodic poison, promoting SSC of HSLA steels and some other alloys coupled to steel.</p> <p>Highly corrosive to alloys containing both copper and nickel in any proportions.</p> <p>May cause an (active path) chloride-sulfide-SCC of nickel-based alloys at high temperatures.</p>
Ammonia species (ammonia, ammonium ion)	<p>Causes SCC of some copper-based alloys.</p>
Chloride ion	<p>Strong promoter of localized corrosion of carbon, HSLA, and stainless steels as well as of other alloys.</p> <p>Chloride dependent threshold temperature for pitting and SCC. Different for each alloy.</p> <p>Little if any effect on SSC.</p> <p>Steel passivates at high temperatures in pH 5, 6070 ppm chloride solution with carbon dioxide. 133,500 ppm chloride destroys passivity above 300°F.</p>
Sulfate ion	<p>Primary effect is corrosion of cements.</p>

* Parts per billion

Crevice corrosion is similar to pitting except that it occurs in geometrically confined spaces such as the crevices where tube and tubesheet join, where the plate ridges of flat plate heat exchangers (PHXs) overlap or under scale deposits. Like pitting, the rate of crevice corrosion penetration is unpredictable, and it is not possible to design around it.

Stress corrosion cracking is the cracking of an alloy as a result of the interaction of stress, applied or residual from forming and fabrication, and a specific environmental factor. For example, some stainless steels are cracked by chlorides under certain conditions (chloride-SCC) and some copper alloys are so attacked by traces of ammonia (ammonia-SCC). A special case of SCC can result when high strength low alloy (HSLA) steels are exposed under stress to waters containing hydrogen sulfide. This particular form of SCC is commonly called sulfide stress cracking (SSC).

Erosion-corrosion is the highly accelerated corrosion of an alloy exposed to a corrosive solution flowing faster than a critical velocity peculiar to that alloy. Characteristically, corrosion is mild at lower velocities.

Inter-granular corrosion occurs when the grain boundaries of the metallic microstructure corrode preferentially, causing the grains to fall out. This process can occur in austenitic stainless steels in low-temperature geothermal environments, but only if the stainless steel is defective in heat treatment or is improperly welded.

Galvanic corrosion is the accelerated corrosion of one metal resulting from its electrical contact with a different metal. The most common example is steel coupled to copper, resulting in accelerated corrosion of the steel.

Dealloying is the selective leaching of one constituent element of an alloy, without change in the gross shape of the component. Three forms have been observed in low-temperature geothermal components: **dezincification** of yellow brass, **graphitization** of cast iron (the iron is removed leaving the carbon matrix), and **deplumbification** (removal of lead) from a lead-tin solder.

3.0 GEOTHERMAL CORROSIVITY CLASSIFICATION SYSTEM

While developing the Materials Selection Guidelines for Geothermal Energy Utilization Systems, Radian invented a **Geothermal Corrosivity Classification System** that divided the currently developed geothermal resources into six classes based on key corrosive species, wellhead temperature, and similarities of corrosion behavior. This classification system does not eliminate the need for site specific evaluation of corrosion problems; but does allow some generalization about materials performance and design requirements.

Subsequent information led to the division of Class V, the class containing low-temperature geothermal resources, into two sub-classes, Class Va and Class Vb. This division was based on statistical evaluation of carbon steel corrosion data from 29 separate tests in different resources (Ellis, 1982). Tables 2 and 3 summarize the characteristics of these two corrosivity systems sub-classes.

Table 2. Geothermal Resources Corrosivity Class Va

Defining Parameters

Resource type	Liquid-dominated
Total key species (TKS) ^a	Less than 5,000 ppm
Chloride fraction in TKS	3 to 72 percent
Total alkalinity	207-1329 ppm CaCO ₃
pH (unflashed fluid)	6.7 - 7.6
pH (flashed fluid)	Not applicable
Vol. gas in stream	Not applicable
Plant inlet temperature	120 to 205°F
Resource temperature	Same

Sites Reviewed

Madison Aquifer, SD (3 sites)
Pagosa Springs, CO
Marlin, TX

Corrosion of Carbon Steel

- In non-aerated produced fluid, the median uniform (weight-loss) corrosion rate is 12.5 mpy, with a probable range (95 percent confidence limits) of 4.9 mpy - 20.2 mpy.
- One of nine tests showed no pitting, others showed severe pitting as high as 83 mpy.
- Aeration may cause a 4- to 15-fold increase in weight-loss corrosion as pitting.

General Performance of Other Alloys

- In non-aerated fluid, uniform corrosion of copper in heat transfer service is 1 to 10 mpy with severe crevice corrosion under corrosion product scale. Brasses and cupronickels are less suitable than copper for heat transfer.
- Type 316 stainless steel is resistant to uniform corrosion, pitting and crevice corrosion, and stress corrosion cracking in many applications.

a. Total chloride + sulfide + carbon dioxide species + sulfide species + ammonia species in produced fluid.

Table 3. Geothermal Resources Corrosivity Class Vb

Defining Parameters

Resource type	Liquid-dominated
Total key species (TKS) ^a	Less than 5000 ppm
Chloride fraction in TKS	3 to 72 percent
Total alkalinity	Less than 210 ppm CaCO ₃
pH (unflashed fluid)	7.8 - 9.85
pH (flashed fluid)	Not applicable
Vol. gas in stream	Not applicable
Plant inlet temperature	120 to 205°F
Resource temperature	Same

Sites Reviewed in the Guidelines

Iceland (15 sites)
USA - Klamath Falls, OR (5 wells)

Corrosion of Carbon Steel

- In non-aerated produced fluid, the median uniform (weight-loss) corrosion rate is 0.12 mpy with an upper limit (95 percent confidence) of 1.65 mpy.
- Pitting - 28 percent no detectable pitting. Additional 40 percent pitted at less than 5 mpy. Maximum observed pitting rate was 20 mpy.
- Aeration may cause a 4- to 15-fold increase in weight-loss corrosion with probably heavy pitting.

General Performance of Other Alloys

- In non-aerated fluid, uniform corrosion of copper in heat transfer service is 1 to 10 mpy with severe crevice corrosion under corrosion product scale. Brasses and cupronickels are less suitable than copper for heat transfer.
- Type 316 stainless steel is resistant to uniform corrosion, pitting and crevice corrosion, and stress corrosion cracking in many applications.

a. Total chloride + sulfate + carbon dioxide species + sulfide species + ammonia species in produced fluid.

4.0 CORROSION ENGINEERING FOR LOW-TEMPERATURE GEOTHERMAL SYSTEMS

4.1 Performance of Materials

Carbon Steel

For many years, the Ryznar Index (discussed in the Appendix), has been used to estimate the corrosivity and scaling tendencies of potable water supplies. However, the statistical study discussed in Section 3 found no significant correlation (at the 95 percent confidence level) between carbon steel corrosion and Ryznar Index. Therefore, the Ryznar Index, and other indices based on calcium carbonate saturation, should not be used to predict corrosion. The Ryznar Index may be predictive of calcium carbonate scaling tendencies.

Table 2 summarizes the expected performance of carbon steel in Class Va geothermal fluids. Under these conditions, corrosion rates of about 5 to 20 mpy can be expected, often with severe pitting.

Table 3 summarizes the expected performance of carbon steel in Class Vb geothermal fluids. Carbon steel piping has given good service in a number of systems, provided the system design rigorously excludes oxygen. However, introduction of 30 ppb oxygen under turbulent flow conditions causes a four-fold increase in uniform corrosion. Saturation with air often increases the corrosion rate at least 15-fold. Oxygen contamination at the 50 ppb level often causes severe pitting. Chronic oxygen contamination causes rapid failure. These fluids are characteristic of those used by Icelandic district heating systems. In those systems, steel piping has been generally successful, but carbon steel shell-and-tube heat exchangers have been satisfactory only in systems where 10 ppm excess sodium sulfite is added continuously as an oxygen scavenger.

In the case of buried steel pipe, it is critical that the external surfaces be protected from contact with groundwater. Such groundwater is aerated, and has caused pipe failures by external corrosion in a least two U.S. systems. Required external protection can be obtained by use of coatings or pipe-wrap, provided the selected material will resist the system operating temperatures and thermal stresses.

At temperatures above 135°F, galvanizing (zinc coating) will not protect steel from either geothermal or groundwater.

Hydrogen sulfide inhibits the reaction of atomic hydrogen on the steel surface, itself a product of the proton reduction step of the corrosion processes, to form molecular hydrogen. The atomic hydrogen enters the steel lattice and, in the case of carbon (mild) steels, accumulates as molecular hydrogen in microvoids, causing hydrogen blistering. Hydrogen blistering can be prevented by use of void-free, or “killed” steels.

Low alloy steels (steels containing not more than four percent alloying elements) have corrosion resistance similar, in most respects, to carbon steels. As in the case of carbon steels, sulfide promotes entry of atomic hydrogen into the metal lattice. If the steel exceeds Hardness Rockwell C22, sulfide stress cracking may occur.

Copper and Copper Alloys

Copper fan-coil units and copper-tubed heat exchangers have a consistently poor performance in U.S. geothermal fluids due to the presence of traces of sulfide species. Copper tubing rapidly becomes fouled with cuprous sulfide films more than 0.4 inches thick. Serious crevice corrosion occurs at cracks in the film and, uniform corrosion rates of 2 - 6 mpy appear typical, based on failure analyses. These corrosion rates were measured by coupons in low velocity (1 ft/sec) fluid at the same or similar resources.

Experience in Iceland also indicates that for heat exchange service, copper is unsatisfactory and most brasses (Cu-Zn) and bronzes (Cu-Sn) are still less suitable. Cupronickels can be expected to perform more poorly than copper in low-temperature geothermal service because of trace sulfide.

Much less information is available about copper and copper alloys in non-heat-transfer service. Copper pipe shows corrosion behavior similar to copper heat exchange tubes under conditions of moderate turbulence (Reynolds numbers of 40,000 - 70,000). The internals of the few yellow brass valves analyzed by Radian showed no significant corrosion. However, silicon bronze CA 875 (12-16-CR, 3-5-Si, <0.05-Pb, <0.05-P), an alloy normally resistant to dealloying, failed by this mode in less than three years when used as a pump impeller. Leaded red brass (CA 836 or 838) and leaded red bronze (SAE67) appear viable as pump internals. Aluminum bronzes have also shown potential for heavy-walled components, based on corrosion tests at a few Class Va sites.

Another problem area associated with copper equipment is solder. Lead-tin solder (50-Pb, 50-Sn) was observed to fail by dealloying after a few years exposure. Silver solder (1Ag-7P-Cu) was completely removed from joints in less than two years. Radian does not endorse the circulation of geothermal fluids through copper components. However, if the designer elects to accept this risk, then solders containing at least 70 percent tin should be used.

Stainless Steels

Unlike copper and cupronickels, stainless steels are not affected by traces of hydrogen sulfide. Their most likely application will be as heat exchange surfaces. For economic reasons, most heat exchangers will probably be of the plate type. Again, for economic reasons, most plate heat exchangers will be fabricated with Type 304 or Type 316 austenitic stainless steel; since, these are the two standard alloys. In addition, some pump and valve trim may be fabricated from these or other stainless steels.

These alloys are subject to pitting and crevice corrosion above a threshold chloride level which depends upon the chromium and molybdenum content of the alloy, and upon the temperature of the geofluid. Above this temperature, the passivation film, which gives the stainless steel its

corrosion resistance, is ruptured in local areas and/or in crevices. These ruptured area then corrode in the form of pitting and crevice corrosion. Figure 1 shows the relationship between temperature, chloride, and occurrence of localized corrosion of Type 304 and Type 316. For example, this figure indicates that localized corrosion of Type 304 may occur in 80°F geofluid if the chloride level exceeds around 210 ppm; while, Type 316 is resistant at that temperature until the chloride level reaches about 510 ppm. Type 316, as shown in Figure 1, is always more resistant to chlorides than is Type 304, due to its 2 - 3 percent molybdenum (Mo) content. The fact that localized corrosion can occur does not predict the rate, but one should expect more severe attack as the chloride-temperature conditions intrude further and further into the localized corrosion region. These alloys can be used in this region, provided that oxygen is rigorously excluded, but there would be a risk of rapid failure should even traces of oxygen intrude.

These alloys can also fail by stress corrosion cracking above about 140°F. In practice, however, no such failures have, to Radian's knowledge, occurred in low-temperature (120 - 220°F) geothermal applications. As a precaution, heat exchanger plates should be stress relieved after forming.

Other austenitic stainless steels with increased chromium and molybdenum contents, compared to Type 316, can be expected to be resistant to pitting, crevice corrosion, and stress corrosion cracking under virtually any conditions encountered with resources of this fluid class, but are not routinely available as HX plates.

Non-austenitic stainless steels are generally resistant to chloride stress corrosion cracking. But many, especially grades containing about 12 percent chromium and less than two percent molybdenum, will probably pit severely, especially in aerated environments. More highly alloyed "super ferritics" offer considerable promise but have not been tested in these environments. Type 444 (18Cr-2Mo) has pitting resistance similar to Type 316. SeaCure (26Cr-3Mo), Allegheny-Ludium 29-4 (29Cr-4Mo) and Allegheny-Ludium 29-4-2 (29Cr-4Mo-2Ni) should resist any environment resulting from use of fluids of this class. ASTM XM27 (26Cr-1Mo) is of intermediate resistance. All these alloys resist chloride stress corrosion cracking.

Aluminum

Geothermal experience to date indicates that aluminum alloys will not be acceptable in most cases because of catastrophic pitting.

Titanium

This material has extremely good corrosion resistance and should serve as heat exchanger plates in any low-temperature geothermal fluid, regardless of dissolved oxygen content. Great care is required if acid cleaning is to be performed. The vendor's instructions must be adhered to. In addition, care must be taken to avoid scratching the titanium with iron or steel tools, since this can cause pitting.

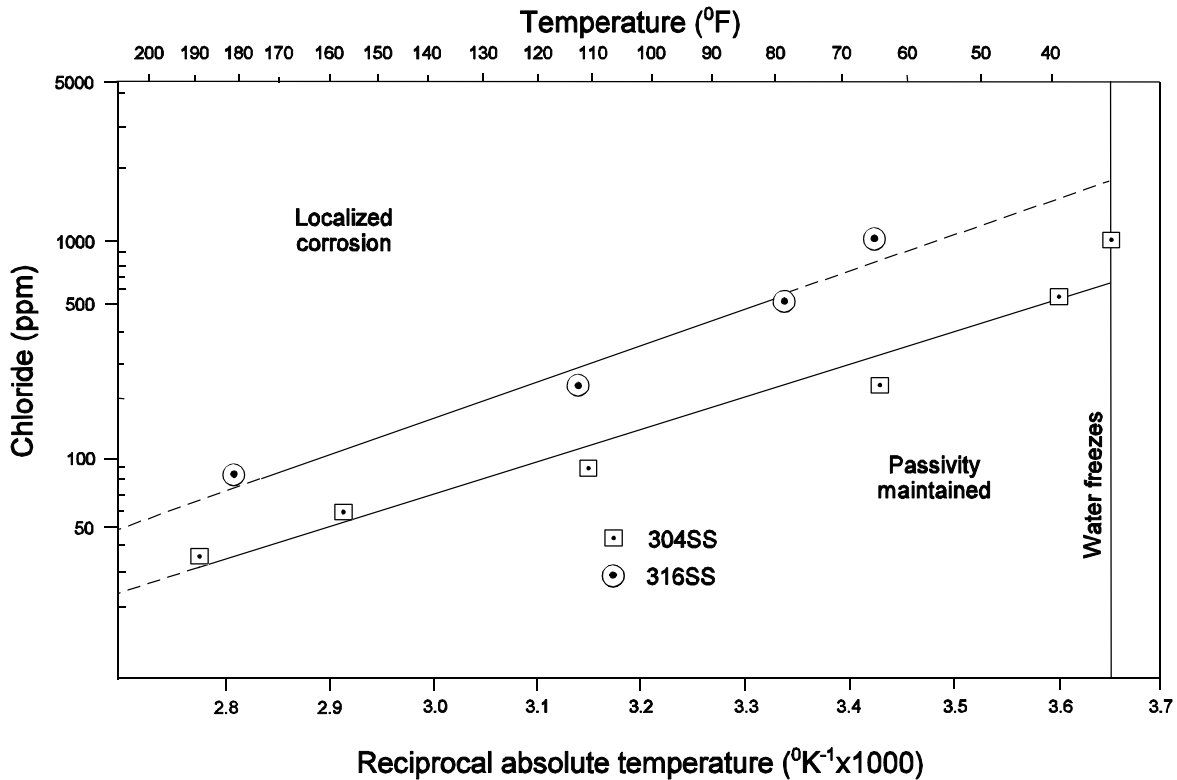


Figure 1. Chloride required to produce localized corrosion of Type 304 and Type 316 as a function of temperature (Data from Efirid and Moller, 1978).

Note: The lines are linear regression best fits having correlation factors ≈ 0.98 .

CPVC (Chlorinated Polyvinyl Chloride) and FRP (Fiber Reinforced Plastic)

These materials offer ease of fabrication and are not adversely affected by oxygen intrusion. External protection against groundwater is not required. Their mechanical properties at higher temperatures may vary greatly from ambient temperature properties and care must be exercised not to exceed the mechanical limits of the materials. The usual mode of failure is creep rupture and the creep rupture strength decays with time. Design data are available from manufacturers, based on extrapolation of 10,000-hour test results to 100,000 hours. The effect on mechanical properties of exposures longer than 100,000 hours is not known.

The manufacturer's directions for joining must be followed explicitly to avoid premature failure of joints.

Elastomeric Seals

Tests of O-ring materials by Radian in a low-temperature system in Texas, indicate that Viton is the best material with Buna-N being acceptable. Neoprene, which developed extreme compression set, was a failure. Natural rubber and Buna-S should also be avoided.

4.2 Corrosion Engineering and Design

The design of the geothermal system is as critical in controlling corrosion as the selection of suitable materials. Furthermore, the design/material selection process is interactive in that certain design decisions force the use of certain materials; while, selection of materials may dictate design. In all cases, the objective should be the same: to produce an adequately reliable system with the lowest possible life-time cost.

Three basic corrosion engineering design philosophies for geothermal systems are apparent:

1. Use corrosion resistant materials throughout the system,
2. Exclude or remove oxygen and use carbon steel throughout the system.
3. Transfer the enthalpy via an isolation heat exchanger to a non-corrosive working medium so that the kind and number of components contacting the geothermal fluid are minimized, and make those components of corrosion resistant materials.

The first philosophy would produce a very reliable system requiring little maintenance. However, the cost would be very high, and at least in the United States, many of the desired components are not available in the required alloys.

The second philosophy may be considered for district-sized heating projects with attendant surface storage and potential for oxygen intrusion, because it may be economical to inhibit the geothermal fluid by continuous addition of excess sulfite as an oxygen scavenger. When this is done, carbon steel can be used for heat exchange equipment, provided fluid pH is greater than 8. This second philosophy is widely and successfully used for municipal heating systems in Iceland. If this approach is used, system design should minimize the introduction of oxygen to reduce sulfite costs. Use of vented tanks should be minimized.

The second philosophy has three major drawbacks. First, the sulfite addition plant is relatively complex and requires careful maintenance and operation. Second, failure of the sulfite addition plant, or insufficient treatment, is likely to cause rapid failure of the carbon steel heat exchangers. Third, sulfite addition will probably not be economical for smaller systems because of the first point above. Without oxygen scavenging, and even with careful design, some oxygen contamination will occur and carbon steel heat exchangers will probably not be satisfactory.

The third philosophy, transferring the enthalpy via isolation heat exchangers to a non-corrosive secondary heat transfer medium and minimizing the kind and number of components exposed to the geothermal fluids, has several advantages for systems of all sizes. The resultant system is much simpler to operate, and therefore, more reliable than above. Only a small number of geothermal resistant components are required and it is feasible to design systems in which oxygen exclusion is not critical. Retrofitting of existing fossil-fired hot water is also simplified since the isolation heat exchanger may either entirely replace the existing heater, or be located in-line with the water supply to the existing heater. Finally, even with careful material selection and design,

geothermal heating systems require more maintenance than conventional systems. Minimizing the number and kind of components in contact with geothermal fluids will further reduce maintenance costs.

All geothermal components should be easily disassembled for maintenance. Scale deposits from geothermal fluid may make threaded joints almost impossible to disassemble; so, this type of joint should be avoided. Similarly, plate heat exchangers may be very desirable, both because they have much higher heat transfer efficiencies than tube-and-shell units, and because they are easy to clean and inspect.

Tables 4 through 6 illustrate materials choice/design constraint interactions for piping, valves, and heat exchanger. In these tables, materials have been divided into five performance grades, based on the available data from 29 direct utilization systems. The corrosion and design cautions must be followed to obtain favorable results. Where specific reference is not made to geothermal corrosivity Class Va or Class Vb, the data presented are equally applicable to either class of resource.

5.0 GEOTHERMAL HEAT PUMPS

From a materials selections standpoint, the geothermal resources of the United States have been divided into low-temperature resources (120 - 220°F) and high-temperature resources. Another class of resource, having temperatures ranging from 10°F above the average ambient air temperature up to 120°F, can readily be called very-low-temperature geothermal resources according to this scheme. These resources cannot usually be used economically in direct utilization systems, but greatly extend the amount and distribution of low-temperature geothermal resource if used with water-source heat pumps (WSHPs) to boost the delivery temperature to more than 120°F for process or other direct use. A delivery temperature of 140 - 220°F would be desirable in many cases. The apparent current state-of-the-art limitation on delivery temperature is about 230°F (Neiss, 1980).

Water-source heat pumps have been shown to be economically attractive, particularly where the alternative is electric resistant heating, and some systems have operated for a number of years with few maintenance problems (Hildebrandt, et al., 1979). Other systems have not fared well, due to poor materials/design factors (Ellis, 1980).

To be economically viable, the WSHP installation, which uses low- or very-low-temperature geofluid as its heat source—a geothermal heat pump (GHP) system—must have a long, essentially trouble-free life and require a minimum of operation and maintenance (O&M) costs. Experience with other low-temperature geothermal systems has shown that proper materials selection for corrosion control (corrosion engineering) is essential if this objective is to be obtained. This aspect of GHP system design is generally not addressed by the heat pump manufacturer, and is the responsibility of the system designer or owner, who usually purchases the heat pump as a package.

Table 4. Material/Design Interaction Matrix for Piping

Material	Corrosion Comments	Design Comments
Carbon steel	<p><u>Grade I</u> in Class Vb resources</p> <p><u>Caution:</u> Oxygen must be rigorously excluded. Aeration will cause 10-fold or greater increase in corrosion rate.</p> <p><u>Grade IV</u> in Class Va resources</p>	<p>Oxygen contamination may cause very serious localized corrosion.</p> <p>Minimize oxygen intrusion into the system.</p> <p>Do not vent tanks, especially recirculation tanks unless oxygen scavengers are also used.</p> <p>Protect exterior surfaces from groundwater.</p>
Galvanized steel Copper	<p><u>Grade IV</u></p> <p>Zinc not protective at operating temperatures and may cause rapid pitting.</p> <p><u>Grade III</u></p> <p>May be acceptable in thick walled applications.</p> <p><u>Caution:</u> Crevice corrosion at cracks in the cuprous sulfide corrosion product scale has been observed.</p> <p><u>Caution:</u> No suitable solders have been verified.</p>	<p>If used, design should provide for easy replacement.</p> <p>Limit fluid velocity to less than 3 ft/sec.</p>
CPVC and Fiber Reinforced Plastic	<p><u>Grade V</u></p> <p>Oxygen intrusion should have no effect.</p> <p>Failure by degradation of creep rupture strength with time. No data are available for estimating allowable stress after 100,000 hrs (11.4 yrs).</p> <p><u>Caution:</u> Properties deteriorate significantly at elevated temperature.</p>	<p>Observe manufacturer's temperature, pressure and stress limits.</p> <p>Fabricate joints exactly as prescribed by manufacturer.</p>

- Grade I: Can be reliably used in most cases, with little or not testing, provided corrosion and design cautions are observed.
- Grade II: Acceptable in many cases, but confirmatory tests are advisable. Corrosion and design cautions must be observed.
- Grade III: Acceptable in a limited number of cases. Confirmatory tests strongly advisable. Corrosion and design cautions must be observed.
- Grade IV: Probably not acceptable.
- Grade V: Long-term suitability has not been verified.

Table 5. Material/Design Interaction Matrix for Valves

Material	Corrosion Comments	Design Comments
Carbon steel body with carbon steel trim	<p><u>Grade IV</u></p> <p>Trim life not adequate in many cases.</p> <p>Localized corrosion at stem/seal/air interface.</p> <p><u>Caution:</u> Aeration will cause rapid failure.</p>	<p>Probable failure mode trim related. Valves should be easy to remove and maintain. Flange or water designs favored. Minimize threaded parts.</p>
Carbon steel body with non-austenitic stainless steel trim	<p><u>Grade III</u></p> <p>Pitting of trim significant risk.</p> <p><u>Caution:</u> Aeration will cause rapid corrosion of body.</p>	<p><u>Plug (globe) valves</u> not recommended for frequent cycle duty because of plug/stem corrosion problems and reciprocating stem motion which causes seal failure or seizing.</p>
Carbon steel body with austenitic stainless steel	<p><u>Grade I</u></p> <p><u>Caution:</u> Aeration will cause rapid corrosion of body.</p>	<p><u>Gate valves</u> not recommended for frequent cycle duty because reciprocating stem motion causes seal failure or seizing.</p>
Brass body with brass trim and brass or austenitic stainless steel stem	<p><u>Grade III</u></p> <p><u>Caution:</u> Cathodic to steel, but effect probably not severe in most cases.</p> <p><u>Caution:</u> Dezincification may be significant risk. Use only red brass or red bronze.</p>	<p><u>Ball or Butterfly valves</u> recommended for frequent cycle duty because rotation of stem minimizes stems/seal problems. Austenitic stainless steel or elastomeric (Buna-N, Viton, TFE) seat satisfactory.</p>
<p>CPVC body and trim</p> <p>Fiber reinforced plastic body and trim</p>	<p><u>Grade V</u></p> <p>Failure of materials by degradation of creep rupture strength with time. Data not available for estimating allowable stress after 100,000 hrs (11.4 yrs).</p> <p>Oxygen intrusion should have no effect.</p> <p><u>Caution:</u> Properties deteriorate greatly at elevated temperatures.</p>	<p>Observe comments above.</p> <p>Observe manufacturer's limitations on temperature, pressure and stress.</p>

Grade I: Can be reliably used in most cases, with little or no testing, provided corrosion and design cautions are observed.

Grade II: Acceptable in many cases, but confirmatory tests are advisable. Corrosion and design cautions must be observed.

Grade III: Acceptable in a limited number of cases. Confirmatory tests strongly advisable. Corrosion and design cautions must be observed.

Grade IV: Probably not acceptable.

Grade V: Long-term suitability has not been verified.

Table 6. Materials/Design Interaction Matrix for Heat Exchangers

Materials	Corrosion Comments	Design Comments
Carbon steel	<p><u>Grade IV</u> if oxygen scavenger is not used.</p> <p><u>Grade II</u> if the resource is Class Vb and the water is continuously treated with excess sulfite.</p>	Continuous use of oxygen scavenger required.
	<p><u>Grade IV</u> if the resource is Class Va</p>	
Copper	<p><u>Grade IV</u></p> <p><u>Caution:</u> Heat exchange corrosion rates typically order of magnitude greater than coupon rates. Serious degradation by ppb H₂S. Suitable solders not identified.</p>	
Aluminum	<p><u>Grade IV</u></p> <p>Extremely severe corrosion with catastrophic pitting.</p>	
Austenitic stainless steels	<p><u>Grade II</u></p> <p><u>Caution:</u> SCC of T304 possible above 140°F. Resistance to SCC increases with molybdenum additions.</p> <p><u>Caution:</u> Pitting and crevice corrosion of T304 possible at high temperature, high chloride conditions, with oxygen. Fitting and crevice corrosion resistance increases with molybdenum additions. See Figure 1.</p> <p>Can be acid cleaned.</p>	<p>Plate-type heat exchangers recommended for ease of cleaning and economic reasons.</p> <p>Stress relief after forming is recommended.</p> <p>Fibrous gaskets should be avoided. Viton gaskets recommended.</p> <p>Minimum aeration recommended.</p>
Titanium	<p><u>Grade I</u> in absence of fluoride ion.</p> <p><u>Caution:</u> Care required when acid cleaned. Avoid scratching with steel tools.</p>	<p>Plate-type heat exchangers recommended over tube-and-shell for economic reasons and ease of cleaning.</p>

- Grade I: Can be reliably used in most cases, with little or no testing, provided corrosion and design cautions are observed.
- Grade II: Acceptable in many cases, but confirmatory tests are advisable. Corrosion and design cautions must be observed.
- Grade III: Acceptable in a limited number of cases. Confirmatory tests strongly advisable. Corrosion and design cautions must be observed.
- Grade IV: Probably not acceptable.
- Grade V: Long-term suitability has not been verified.

This section presents guidelines for evaluating the suitability of commercially available water-source heat pump evaporator materials for use with low- and very-low-temperature resources. As previously defined, a low-temperature resource has a temperature of 120 - 220°F. A very-low-temperature resource has a temperature less than 120°F, but greater than 10°F above the average annual ambient air temperature at the resource.

5.1 Basic Geothermal Heat Pump System Description

A geothermal heat pump consists of three basic components: an evaporator, a compressor, and a condenser. The evaporator is a water-to-freon heat exchanger. Geothermal water entering this heat exchanger gives up some of its enthalpy, vaporizing the freon. The compressor compresses the freon and drives it to the condenser. The condenser may be a freon-to-air heat exchanger in small space heating projects, but is more likely to be another freon-to-water heat exchanger in larger projects. The heat released by condensation of the freon is transferred to the circulating air or water, depending on the nature of the condenser.

Evaporators come in three basic configurations:

- tube-in-tube with water in the inner tube,
- tube-in-tube with water in the annulus; and
- tube-in-shell.

The first two configurations are typical of small (residential) GHPs; while, the latter is usually used for larger units. Tube-in-tube evaporators can only be chemically cleaned, and the second variety is likely to be particularly prone to erosion-corrosion problems. Tube-and-shell evaporators are equipped with either U-tubes or straight tubes. This latter design allows mechanical cleaning, an important consideration if scaling (mineral deposition) is a problem.

5.2 Forms of Corrosion Affecting Geothermal Heat Pumps

Of the forms of corrosion discussed in Section 2, only the following four are likely to be significant in the life of most GHPs.

Pitting and crevice corrosion are potentially very serious because the evaporator has a large area of thin-walled tubing, and a single pinhole perforation will cause a rapid loss of the freon charge. Therefore, alloys which show pitting or crevice corrosion cannot be expected to give long trouble-free service. The rate of pit or crevice penetration is highly unpredictable, and it is not possible to design around (allow for) pitting.

Stress corrosion cracking is the cracking of an alloy as a result of the interaction of stress, applied or residual from forming and fabrication, and a specific environmental factor. For example, some stainless steels are cracked by chlorides under certain conditions, and some copper alloys are so attacked by traces of ammonia.

Erosion corrosion is the highly accelerated corrosion of an alloy exposed to a corrosive solution flowing faster than a critical velocity peculiar to that alloy. Characteristically, corrosion is mild at lower velocities.

Uniform corrosion is the even wasting away of the alloy. This is the form of corrosion which is expressed as a “corrosion rate.” For corrosion resistant alloys, it is probably the least significant form of corrosion.

These forms of corrosion are caused by the key corrosive species discussed in Section 1. Two of these species are not reliably detected by standard water chemistry tests and deserve special note because of their potentially profound effect on GHP life. Dissolved oxygen does not naturally occur in low-temperature (120 - 220°F) geothermal waters which contain traces of hydrogen sulfide, though because of slow reaction kinetics, oxygen from air leakage may persist for some minutes. Preventing oxygen contamination once the geofluid is produced is extremely difficult, especially if pumps other than downwell pumps are used to move the geofluid. Even though the fluid system may be maintained at positive pressure, air leakage at the pump seals is likely, particularly in light of the level of maintenance likely in most GHP installations. Some very-low-temperature geothermal waters may contain traces of dissolved oxygen in the formation. Since even part-per-billion levels of oxygen can have a profound effect on many construction metals, it is prudent and conservative to assume that very-low-temperature geofluid will contain traces of dissolved oxygen.

Hydrogen sulfide is ubiquitous at low part-per-million (ppm) or part-per-billion (ppb) levels in geothermal fluids above 120°F. This corrosive species also occurs naturally in many cooler groundwaters. For those alloys such as cupronickels which are strongly affected by it, hydrogen sulfide concentrations in the low parts-per-billion may have a serious detrimental effect, especially if oxygen is also present. At these levels, the characteristic rotten egg odor of hydrogen sulfide may be absent, and detection requires use of field methods. Hydrogen sulfide levels down to 50 ppb can be detected using a simple field kit provided by CHEMetrics. Even absence of hydrogen sulfide at this low level may not preclude damage by this species. Field spectrophotometry, which requires a spectrometer and different kit (K9503) has a detection limit of less than 10 ppb.

5.3 Performance of Standard Geothermal Heat Pump Materials

Due to the need for minimal initial costs to allow GHP systems to have an acceptable payback period, it is considered likely that most systems will be compelled to use off-the-shelf GHPs. Table 7 presents a summary of a 1982 survey of water-source heat pump manufacturers. This survey shows that most manufacturers offer evaporators in steel, **copper**, cupronickel, or stainless steel. In most cases, cupronickel refers to **90-10 cupronickel** (CA 706), though some manufacturers may offer **70-30 cupronickel** (CA 715). Likewise, stainless steel usually means **Type 304** stainless (18CR-9Ni). Some manufacturers also offer **Type 316** (18Cr-18Ni-2Mo). Companies offering “any alloy” use package tube-and-shell evaporators, and though custom evaporators of many alloys can be provided, there is likely to be a major cost penalty.

Table 7. Equipment of Residential and Commercial/Industrial Water-Source Heat Pumps

Company Name	Trade or Brand Name	Evap/Cond. Medium	Size Range (10³ Btu/hr)	Std. Max. Evaporator Inlet Temp. (°F)	Max. Evap. Inlet Temp. w/Special Circuit or Control	Standard Evaporator Materials	Optional Evaporator Materials	Evaporator Cleaning
American Air Fileter Co., Inc.	Emercon	Water/Air	7.7-150	90	--	Copper	None	Chemical
American Solar King Corp.	Solar King	Water/Air	33.5-68.0	90	--	Copper	Cupronickel, Stainless	Chemical
Bard Manufacturing Co.	Bard	Water/Air	3.2-42.0	75	--	Cupronickel	None	Chemical
California Heat Pump Co.	California Heat Pump	Water/Air	8.1-70.0	130	--	Copper	Cupronickel	Chemical
Carrier Air Conditioning	Weathermaker	Water/Air	8.1-86.0	90	--	Cupronickel, Steel	Copper	Chemical
Celsius Energy Co.	Celsius	Water/Air	8.4-134	70	--	Cupronickel	Copper	Chemical
Command-Aire Corp.	Command-Aire	Water/Air	13.5-156	120	--	Copper	Cupronickel, Steel	Chemical
Fedders Corp.	Carnot II	Water/Water	20-80	120	--	Cupronickel	Copper	Chemical
FHP Manufacturing Division Of Leigh Products, Inc. (Florida Heat Pump Corp.)	Energy Miser	Water/Air	14.2-156	90	--	Cupronickel	Copper	Chemical
Friedrich Air Conditioning and Refrigeration Co.	Friedrich-Geo Thermal Series	Water/Air	33.5-77.0	100	--	Cupronickel	None	Chemical
Heat Exchangers, Inc.	Koldrave	Water/Air	6.4-134	72	--	Copper	Cupronickel	Chemical
Lear Siegler, Inc., Mammoth Division	Hydrobank	Water/Air	8.4-134	90	--	Copper	Cupronickel	Chemical
Marvair Co.	Marvair	Water/Air	25.5-53.0	80	--	Cupronickel	None	Chemical

Table 7. Equipment of Residential and Commercial/Industrial Water-Source Heat Pumps (Continued)

Company Name	Trade or Brand Name	Evap/Cond. Medium	Size Range (10³ Btu/hr)	Std. Max. Evaporator Inlet Temp. (°F)	Max. Evap. Inlet Temp. w/Special Circuit or Control	Standard Evaporator Materials	Optional Evaporator Materials	Evaporator Cleaning
Northrup, Inc.	Energy Exchange Sys. (Ex-En)	Water/Air	10.1-85.0	95	--	Cupronickel	None	Chemical
The Singer Co., Climate Control Division	Electro-Hydronic	Water/Air	10-124	85	-	Cupronickel	Copper, Steel	Chemical
Solar Oriented Environmental Systems, Inc.	SOESI-Power Saver	Water/Air	17.3-126	95	-	Copper/Plastic	Cupronickel, Stainless	Chemical
The Trane Co	Trane	Water/Air	10-82	90	--	Copper	Cupronickel	Chemical
Dunham-Bush, Inc.	Dunham-Bush	Water/Air Water/Water	24-20,400	90	--	Any Tube Material	--	Rod & Brush
Sulliar		Water/Water	1200-24,000	125	--	Carbon Steel	Stainless, Carpenter 20	Rod & Brush
The Trane Co.	Recip. Cold Generators Centravac	Water/Water	12-2400 1600-20,000	90	--	Copper	Cupronickel, Titanium	Chemical Rod & Brush
Vilter	VHP	Water/Water	24-4800 3600-60,000	120	--	Any Tube Material	--	Rod & Brush
Westinghouse	Templifier	Water/Water	70-1000 1000-10,000	120 Custom	-- >180	Any Tube Material	--	Rod & Brush
York Division of Borg-Warner Corp.	Yorkpak	Water/Water	12-48,000	Custom	>180	Any Tube Material	-	Rod & Brush

- No data or not offered.
(Compiled from literature and other information provided by the companies listed.)

Steel

Wide experience with steel in low-temperature geothermal systems has shown that addition of parts-per-billion levels of dissolved oxygen causes a significant increase in the rate of corrosion and causes pitting (Ellis and Conover, 1981). As was discussed earlier, oxygen contamination of most GHP systems is probably inevitable, and therefore, the large thin-walled area of steel evaporator tube would be at serious risk of early failure by pitting. Also, some apparently innocuous waters are extremely aggressive to steel, and at least for geothermal waters above 120°F, corrosion indices such as the Ryznar Index are not predictive (Ellis, 1982). Steel is, therefore, not recommended for GHP systems unless an isolation heat exchanger is used. In an isolation system, careful treatment of the intermediate fluid to control corrosion would be prudent.

Copper and Cupronickel

Cupronickels are generally quite corrosion resistant to fresh waters and even seawater brine if these waters are absolutely free of hydrogen sulfide. In fact, the cupronickels were developed expressly for sea-water-cooled condensers. Given the above required absence of hydrogen sulfide, these alloys should give long trouble-free service. However, traces of hydrogen sulfide, especially in combination with traces of dissolved oxygen, cause serious pitting of both 90-10 cupronickel and 7030 cupronickel, with 90-10 cupronickel being more susceptible than 70-30. Even as little as 7 ppb hydrogen sulfide can pit these alloys (Gudas, et al., 1978). As discussed earlier, pitting is a corrosion mode to be absolutely avoided if the evaporator is to have a long life.

Copper is also subject to severe corrosion in fresh water containing part-per-billion traces of hydrogen sulfide and oxygen. Either one alone does not appear to be as damaging (Syrett, 1977). As discussed earlier, it is prudent and conservative to assume that in most practical systems the circulating geofluid will eventually contain traces of dissolved oxygen. Thus, if the geofluid contains any detectable hydrogen sulfide (down to at least 10 ppb), copper is also contraindicated.

Another critical factor to consider with copper and cupronickel is the critical velocity for erosion-corrosion. Table 8 presents the critical velocities for copper (CA 122), 90-10 cupronickel (CA 706), 70-30 cupronickel (CA 715), and a chromium modified 70-30 cupronickel (CA 722). These values were iteratively calculated from basic equations (Efird, 1977) assuming water at 77°F and 0.75 inch diameter tubing. The Reynolds Number, which can be used for scale up or scale down, is calculated on the same basis. The critical velocity will increase with increases in temperature and tube diameter. It is common and recommended practice to allow design bulk fluid velocities of only 50 percent of the critical velocity. This safety factor allows for the greater turbulence which occurs at tube inlets and outlets, bends, and similar features.

Over the likely range of pH, chloride, carbon dioxide species, sulfate, and ammonia encountered in GHP operations, these species are not likely to have any significant effect on the corrosion resistance of the cupronickels.

Table 8. Critical Velocities for Erosion-Corrosion of Four Copper Alloys

Alloy	Common Name	Critical Velocity* (ft/sec)	Reynolds Number *
CA 122	Deoxidized Copper	6.1	$1.77 \cdot 10^4$
CA 706	90-10 Cupronickel	14	$5.60 \cdot 10^4$
CA 715	70-30 Cupronickel	15	$6.00 \cdot 10^4$
CA 722	90-10 Cupronickel + Chromium	39	$1.56 \cdot 10^4$

* Values calculated based on 0.75 inch diameter tubing and 77°F water. Critical velocity calculations based on work by Efird (1977).

Note: Standard conservative design practice suggests limiting bulk fluid velocity to one-half the critical velocity to allow for turbulence at tube inlets, etc.

Stainless Steel

Unlike copper and cupronickels, austenitic stainless steels (including Type 304 and Type 316) are not affected by traces of hydrogen sulfide in the geofluid. These alloys are subject to pitting and crevice corrosion above a threshold chloride level which depends upon the temperature of the geofluid. Above this temperature, the passivation film, which gives the stainless steel its corrosion resistance, is ruptured in local areas and/or in crevices. These ruptured areas then corrode in the form of pitting and crevice corrosion. Figure 1 showed the relationship between temperature, chloride, and occurrence of localized corrosion. The fact that localized corrosion can occur does not predict its severity, but one should expect more severe attack as the chloride-temperature conditions intrude further and further into the localized corrosion region. As discussed previously, prudent design should avoid selection of materials which are subject to pitting and crevice corrosion.

5.4 ISOLATED vs. NON-ISOLATED SYSTEM DESIGNS

GHP systems can be either non-isolated or isolated systems. In a non-isolated system, the geothermal water is circulated directly through the evaporator. In isolated systems, the geofluid passes through an isolation heat exchanger where heat is transferred to treated water flowing in a closed loop between the isolation heat exchanger and the evaporator. The isolated system suffers a thermal penalty because of the temperature drop across the isolation heat exchanger, and it does require an additional heat exchanger, piping, pump and controls.

Isolation systems have the advantage of protecting the heat pump or pumps from the corrosive and scaling problems produced by the geofluid. Plate heat exchangers (PHXs) are commonly used to minimize the cost of the isolation heat exchangers, even when exotic metals like titanium are used, as well as to simplify cleaning. Indeed, the largest geothermal heat pump system in the world, a district heating system in the Paris Basin, France, uses titanium PHXs to protect banks of water-source heat pumps (Trolano, 1980).

Thus, if the GHP system designer concludes that the standard evaporator materials are not suitable for service in his geofluid, then an isolation system will probably be his best option.

Numerous factors other than corrosive resistance must be considered to achieve a successful system. Therefore, a heat pump should be selected only after system design by a competent engineer, and consultation with the heat pump manufacturer.

6.0 REFERENCES (in order of appearance in the text)

Ellis, P. F. and M. F. Conover, 1981. Material Selection Guideline for Geothermal Energy Systems, NTIS Code DOE/RA/27026-1. Radian Corporation, Austin, TX, January.

Smith, C. S. and P. F. Ellis, 1983. Addendum to Materials Selection Guidelines for Geothermal Energy Utilization Systems, NTIS Code DOE/ET/27026-2. Radian Corporation, Austin, TX, May.

Kindle, C. H. and E. M. Woodruff, 1981. Techniques for Geothermal Liquid Sampling and Analysis, NTIS Code PNL-3801. Pacific Northwest Laboratory, Richland, WA, July.

Ellis, P. F., 1982. "Critical Assessment of Carbon Steel Corrosion in Low-Temperature Geothermal Applications," Paper 74, Corrosion/82, Houston, TX, 22-26 March.

Efird, K. D. and G. E. Moller, 1978. "Electrochemical Characteristics of 304 and 316 Stainless Steels in Fresh Water as Functions of Chloride Concentration and Temperature," Paper 87, Corrosion/78, Houston, TX, 6-10 March.

Niess, R. C., 1980. "High-Temperature Heat Pumps Can Accelerate the Use of Geothermal Energy," Commercial Use of Geothermal Heat (Special Report No. 9). Geothermal Resources Council, Davis, CA, June.

Hildebrandt, A. F.; Gupta, S. D. and F. R. Elliott, 1979. Groundwater Heat Pump HVAC Demonstration Project Phase I - Design Development, Texas Energy Advisory Council Report EDF-OM, University of Houston, Houston, TX, July.

Ellis, P. F., 1980. Geothermal Analytical Report - Copper Tube-in-Heat Exchanger for Heat Pump, DCN 80-212-003-08, Radian Corporation, Austin, TX, March.

Gudas, J. P.; Hack, H. P. and D. W. Taylor, 1978. "Parametric Evaluation of Susceptibility of CuNi Alloys to Sulfide Induced Corrosion," Paper 22, Corrosion/78, Houston, TX, 6-10 March.

Syrett, B. C., 1977. "Accelerated Corrosion of Copper in Flowing Pure Water Contaminated with Oxygen and Sulfide," Corrosion, Vol. 33, No. 7, July.

Efird, K. D., 1977. "Effect of Fluid Dynamics on the Corrosion of Copper-Base Alloys in Sea Water," Corrosion, Vol. 33, No. 7, January.

Trolano, A. R., 1980. The Development of Low-Enthalpy Geothermal Energy in the Paris Basin, Trip Report to DOE, Division of Geothermal Energy Case Western Reserve University, Cleveland, OH, November.

APPENDIX A

Worksheets for Chemical and Scaling

Properties of Low-Temperature Geothermal Waters

APPENDIX A

Worksheets for Chemical Scaling Properties of Geothermal Waters (Low-Temperature)

This appendix contains a series of worksheets which guide the user in calculations relating to the quality of water analysis data (ionic charge balance) and qualitative estimations of the probability of scaling by calcium carbonate or gypsum.

Ionic Charge Balance

The total amount of positive (cation) and negative (anion) charges in a solution are necessarily equal, since solutions are electroneutral. Therefore, the ionic charge balance in an analysis should be zero – cations - anions = 0. In fact, a 10 percent difference is not uncommon. Worksheet 1 guides the user in calculation of the ionic balance.

Calcium Carbonate

The solubility of calcium carbonate is a function of temperature, the concentration of calcium ion, concentration of carbonate ion and of the other species dissolved in the fluid. The concentration of carbonate ion is dependent on fluid pH, which controls the distribution between carbonate and bicarbonate ions. In most geothermal fluids, the pH is controlled by the carbon dioxide partial pressure. Evolution of carbon dioxide causes a rise in pH which may cause deposition of calcium carbonate.

Calcium carbonate exhibits retrograde solubility (solubility increases as temperatures decreases). This means that as long as the fluid pressure within the system is maintained at a level such that carbon dioxide is not evolved, deposition of calcium carbonate should not be a problem.

The Ryznar Index gives a qualitative estimate of the calcium carbonate scaling tendencies of waters. The Ryznar Index is given by the following equation:

$$\text{Ryznar Index} = 2 \text{ pHs} - \text{pHa}$$

where - pHs = the pH above which calcium carbonate
will precipitate

pHa = measured pH of the fluid

The interpretation is as follows:

Ryznar Index	Scaling Tendency
<4.0	Extreme
4.0-5.0	Heavy
5.0-6.0	Moderate
6.0-7.0	Light
>7.0	None

Worksheet 2 guides calculation of the Ryznar Index.

Gypsum (Calcium Sulfate Dihydrate)

Calcium sulfate can precipitate as either calcium sulfate anhydrite or as calcium sulfate dihydrate (gypsum). The anhydrite is less soluble than the dihydrate, but the anhydrite does not form at temperatures less than about 200°F because of kinetic factors. Therefore, only the solubility of gypsum need be considered for most low-temperature geothermal resources.

Gypsum can precipitate whenever the product of calcium ions and sulfate ions (calcium sulfate ion product) exceeds the gypsum (calcium sulfate dihydrate) solubility product. This solubility product is a complex function with temperature and ionic strength (itself a function of species in solution) as independent variables. It is independent of pH in the range normally occurring in low-temperature geothermal fluids. Calculation of the gypsum solubility product is complex. However, Figure A-3 allows an approximate graphic determination of the gypsum solubility product.

Figure A-3 shows the logarithm of the gypsum solubility product (on a mass rather than molar basis) as a function of temperature and dissolved solids. The logarithm of the gypsum solubility product at a given temperature in fluid of a given TDS, is found at the intersection of that temperature and the appropriate iso-TDS line. This figure was generated by using a previously published extended Debye-Huckel equation for activity coefficients and an equation for the gypsum solubility product at unit activity as a function of temperature (Wilde, 1979).

The relative saturation with respect to gypsum at a given temperature can be calculated by:

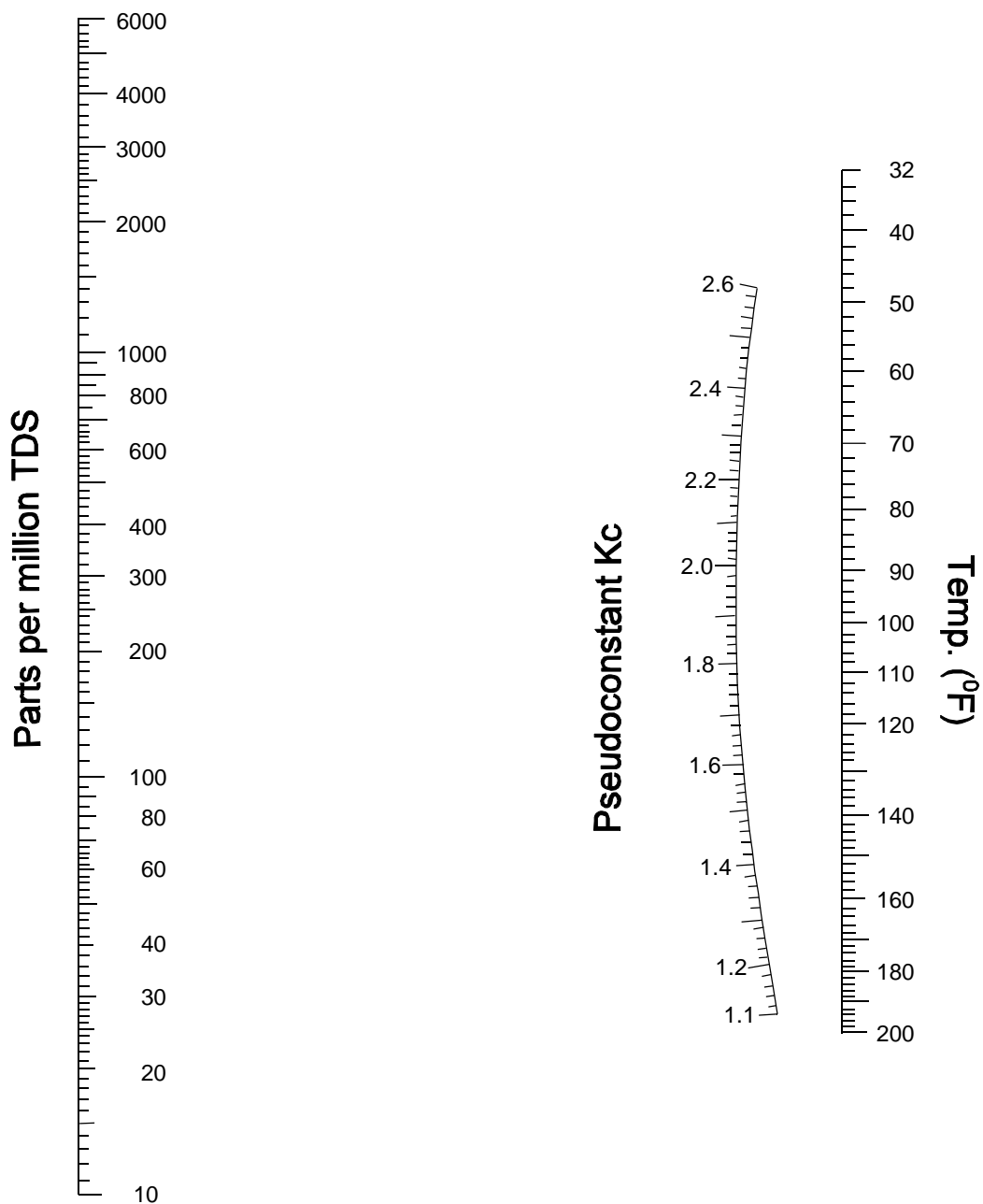
$$\text{gypsum R. S.} = 10^{(\log \text{ ppm Ca} + \log \text{ ppm SO} - \log K \text{ gypsum})}$$

Values of less than unity indicate sub-saturation and no scaling by gypsum; while, values greater than unity indicate super-saturation and possible scaling. The relative saturation does not indicate the rate of deposition. Because a number of simplifying assumptions were required in generation of Figure A-3, interpretation of relative saturations between 0.9 and 1.1 are problematic.

Figure A-1

Determination of K_c for geofluids containing less than 6000 ppm or mg/l Total Dissolved Solids (TDS).

Using a straightedge, connect the ppm TDS on the “Parts-per-Million” scale with the fluid temperature on the “Temp. °F” scale. Read the value of K_c on the Pseudoconstant K_c scale.

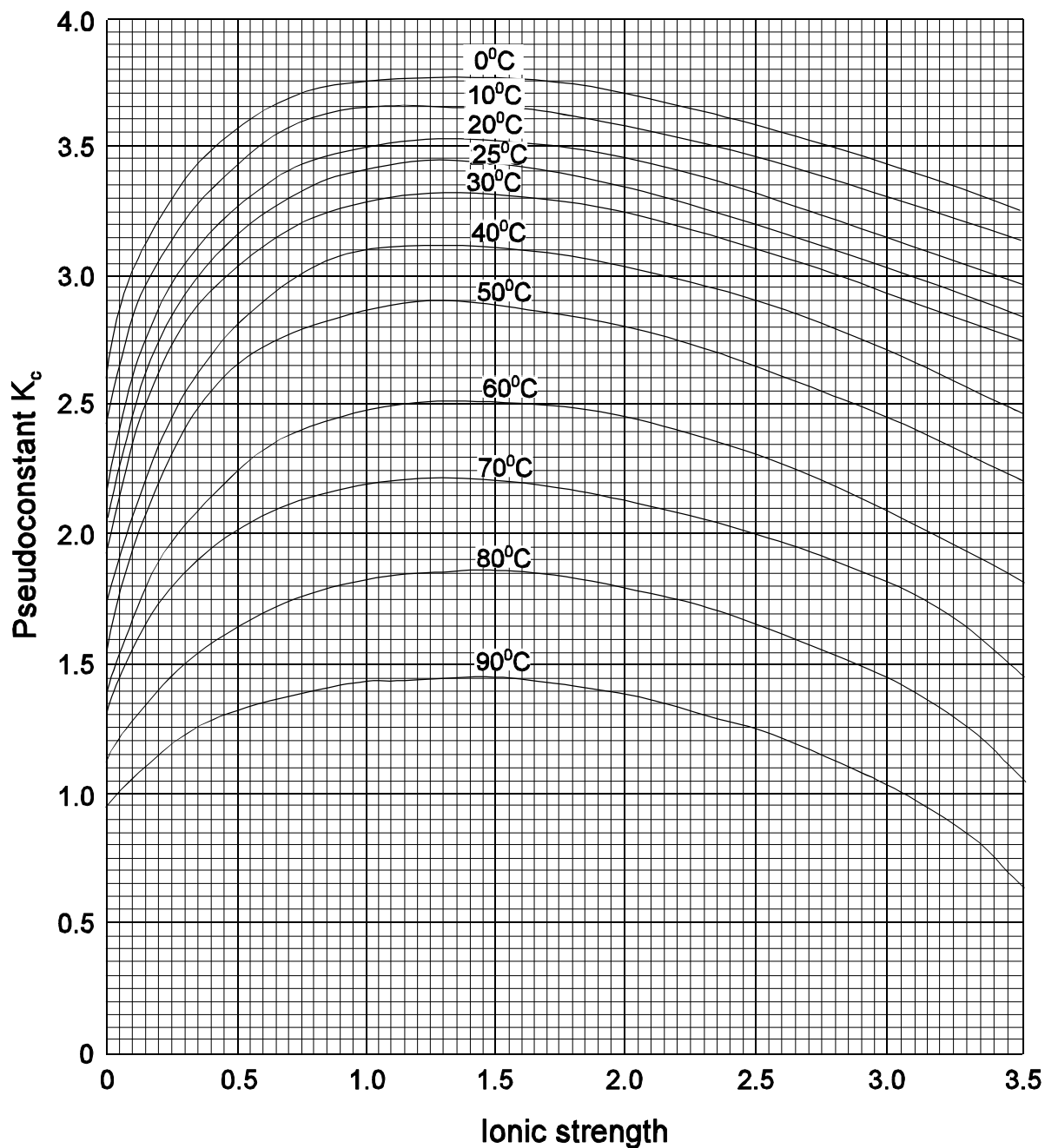


(Adapted from Lund, et al., 1976)

Figure A-2

Determination of K_c for geofluids containing more than 600 ppm TDS.

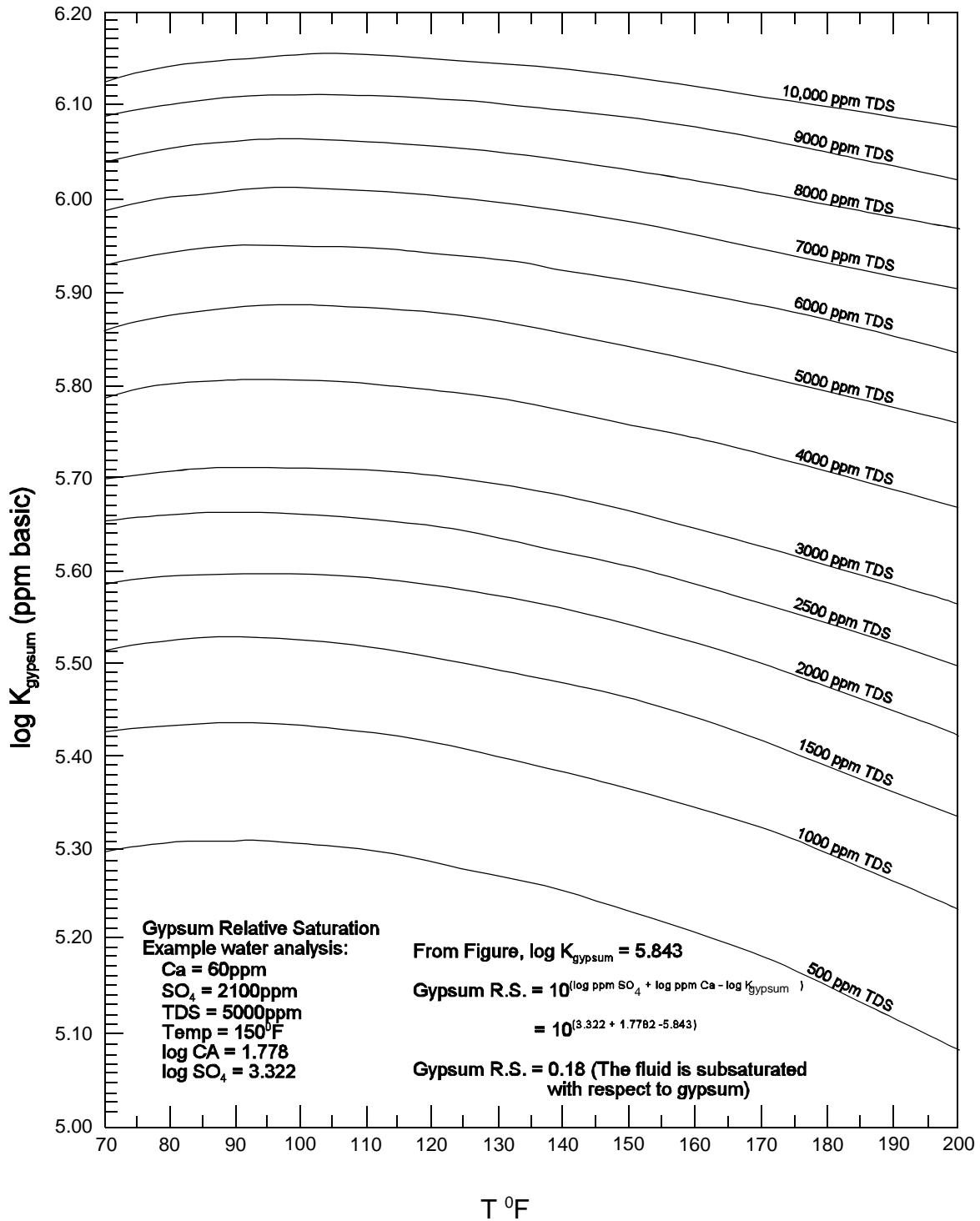
Calculate the ionic strength using Worksheet 2A. Read K_c from the graph below.



(Adapted from Ostroff, 1979)

Figure A-3

The solubility product of gypsum (calcium sulfate dihydrate) in low-temperature geothermal waters. The solubility product is expressed on a ppm mass basis, rather than a molar basis, and is corrected for ionic strength and temperature.



WORKSHEET 1 - IONIC BALANCE

TDS = _____ ppm or _____ mg/l

Cations

			<u>moles/l</u>	<u>eq/l</u>
pH	_____	$10^{-\text{pH}}$	= _____	x 1 = _____
	ppm ÷ D	=	mg/l ÷ FW(mg)	= _____
Na ⁺	_____	=	_____ ÷ 22989.2	= _____ x 1 = _____
K ⁺	_____	=	_____ ÷ 39102.0	= _____ x 1 = _____
Ca ⁺²	_____	=	_____ ÷ 40080.0	= _____ x 2 = _____
Mg ⁺²	_____	=	_____ ÷ 24312.0	= _____ x 2 = _____

Total Cations (eq/l) _____

Anions

SO ₄ ⁻²	_____	=	_____ ÷ 96061.6	= _____ x 2 = _____
HCO ₃ ⁻	_____	=	_____ ÷ 61017.3	= _____ x 1 = _____
CO ₃ ⁻²	_____	=	_____ ÷ 60009.4	= _____ x 2 = _____
Cl ⁻	_____	=	_____ ÷ 24312.0	= _____ x 2 = _____

Total Anions (eq/l) _____

The total cations should equal the total anions.
A 10 percent difference is acceptable.

Note:

1. For solutions containing less than 14,000 ppm Total Dissolved Solids (TDS), ppm = mg/l with less than 1 percent error.
2. $D = \text{density in Kg/l} = (1 \div 6.95 \cdot 10^{-7} \text{ TDS [mg/l]}) = 1 / ([1 - 6.95 \cdot 10^{-7} \text{ TDS ppm}]) = \underline{\hspace{2cm}}$.
3. If carbon dioxide species are expressed as Total Alkalinity (TA) as mg/l CaCO₃, equate the TA to HCO₃⁻. $\text{CaCO}_3 \times 0.8196 = \text{HCO}_3^-$.

WORKSHEET 2 - RYZNAR INDEX

1. Calculate pHs

$$\text{pHs} = \text{pCa} + \text{pALK} + \text{Kc}$$

$\text{pCa} = -\log(\text{Ca})$ where (Ca) is the molar concentration of calcium from Worksheet 1

$$\text{pCa} = \underline{\hspace{2cm}}$$

$$\text{pALK} = -\log(\text{ALK})$$

If total Alkalinity is given as mg/l CaCO_3 ,

then $(\text{ALK}) = \text{mg/l CaCO}_3 \div 100089.4$

$$= \underline{\hspace{2cm}}$$

If analysis gives HCO_3^- and CO_3^{2-} , then use the molar concentrations and pH from Worksheet 1 to solve:

$$(\text{ALK}) = (\text{HCO}_3^-) + 2(\text{CO}_3^{2-}) + 10^{\text{pH}-14} - 10^{-\text{pH}}$$

$$= \underline{\hspace{2cm}}$$

$$\text{pALK} = -\log(\text{ALK})$$

$$= \underline{\hspace{2cm}}$$

“Kc” is a complex term involving two equilibria constants and activity coefficients; all temperatures dependent terms. Its calculation is quite complex and is beyond the scope of this method. Fortunately, however, graphical methods for estimating “Kc” are available. Furthermore, Kc is relatively insensitive to minor errors introduced by the assumption required for the two graphical methods.

If TDS is less than 6000 ppm, refer to Figure A-1 and determine the value for Kc.

If TDS is greater than 6000 ppm, complete Worksheet 2A and use the calculated ionic strength to derive Kc from Figure A-2.

$$\text{Kc} = \underline{\hspace{2cm}}$$

$$\text{pHs} = \underline{\hspace{2cm}}$$

2. Calculate the Ryznar Index

$$\text{Ryznar Index} = 2 \text{pHs} - \text{pHa}$$

$$= \underline{\hspace{2cm}} - \underline{\hspace{2cm}}$$

$$= \underline{\hspace{2cm}}$$

FLUID PROPERTIES WORKSHEET 2A - IONIC STRENGTH

Perform only for calcium carbonate scaling calculations when TDS exceeds 6000 ppm.

<u>ion</u>	<u>moles/l^a</u> ÷ Kg H ₂ O/l ^b	=	<u>moles/kg H₂O</u>
pH	_____	=	_____ x 1 = _____
Na ⁺	_____	=	_____ x 1 = _____
K ⁺	_____	=	_____ x 1 = _____
Ca ⁺²	_____	=	_____ x 4 = _____
Mg ⁺²	_____	=	_____ x 4 = _____
SO ₄ ⁻²	_____	=	_____ x 4 = _____
HCO ₃ ⁻	_____	=	_____ x 1 = _____
CO ₃ ⁻²	_____	=	_____ x 4 = _____
Cl ⁻²	_____	=	_____ x 1 = _____

x 0.5

molal ionic strength =

- a. From mole/l column of Worksheet 1.
- b. Kg H₂O/l brine = (D - TDS mg/l) ÷ 1,000,000,
where D is defined on Worksheet 1.

APPENDIX REFERENCES

Lund, J. W.; Silva, J. F.; Culver, G.; Lienau, P. J; Svanevik, L. S. and S. D. Anderson, 1976. Corrosion of Downhole Heat Exchangers, Appendix A, DOE Contract E(10-1)-1548, Oregon Institute of Technology, Klamath Falls, OR, October.

Ostroff, A. G., 1979. Introduction to Oilfield Water Technology, Appendix 1, National Association of Corrosion Engineers, Houston, TX.

Wilde, K. A., 1979. Radian Technical Note 210-344-02, EPRI Research Project RP 1261-1, Stearns-Roger Project C-21385: Equilibrium Model Documentation, DCN 79-210-344-06, Radian Corporation, Austin, TX, January.