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CORROSION ENGINEERING FOR GEOTHERMAL HEATING SYSTEMS

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ABSTRACT

The economic utilization of geothermal resources with temperatures ranging from 49°C-105°C 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 selection and design choices are to be made.

Based on a study of 20 low temperature direct utilization systems in the United States and abroad, general corrosion engineering guidelines are presented. Piping, valves, and heat exchange equipment are considered. These guidelines are applicable to a large number of resources in the United States.

INTRODUCTION

Direct utilization of geothermal resources with temperatures ranging from 49°C-105°C can displace a significant demand on fossil fuels for heating purposes. The economic use of these energy sources requires systems with long plant life and minimum operation and maintenance (O&M) costs. Development of such systems requires proper materials and design decisions (corrosion) engineering).

For a number of years Radian Corporation has been working for the DOE Division of Geothermal Energy to develop a materials selection handbook. The First Edition: Material Selection Guidelines for Geothermal Power Systems was completed in 1978 and is available from NTIS as document ALO-3904-1. This edition was limited to liquid dominated resources of power generating potential in the United States. Work is nearing completion on a Second Edition: Material Selection Guidelines for Geothermal Energy Systems. Previous data are updated and materials test data and operating experience from existing geothermal power plants around the world are included, as well as tests results from over twenty geothermal resources with temperatures as low as 49°C.

As a part of this effort, Radian's Material Science Laboratory has performed failure analyses on numerous failed and non-failed components from several geothermal direct utilization systems in the United States and has studied materials problems of geothermal systems abroad. From this base of experience, general guidelines about material selection and appropriate design to minimize corrosion problems in space and domestic water heating systems have been derived.

KEY SPECIES

Geothermal fluids commonly contain seven key chemical species that produce a significant corrosive effect (DeBerry *et al.*, 1978). The key species are:

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

Corrosive phenomena that can be observed with different materials due to the presence of some or all of these species in conjunction with physical factors such as fluid temperature, pressure, and velocity, are:

- Uniform (general) corrosion
- Pitting
- Crevice corrosion
- Stress corrosion cracking
- Hydrogen blistering
- Intergranular corrosion
- Galvanic corrosion
- Corrosion-fatigue
- Dealloying
- Exfoliation

These phenomena naturally are to be avoided in order to decrease downtime, increase plant life and minimize operation and maintenance (O&M) costs. Proper materials selections and design choices (corrosion engineering) can achieve these goals.

CLASSIFICATION OF GEOTHERMAL RESOURCES

While developing the Second Edition: Material Selection Guidelines for Geothermal Energy Systems, it was noticed that presently developed resources could be divided into six provisional classes based on certain key chemical species, wellhead temperature, and similarities of corrosion behavior. This classification does not eliminate the need for site specific evaluation of corrosion problems, but does allow some generalization about expected materials performance and design requirements. One of the provisional classes includes most low temperature resources. It has the following characteristics:

- Total key species (TKS) <5000 ppm
- Chloride fraction in TKS 3-72% but > 10 ppm
- pH 6.5-10
- Total sulfide 0.01-5 ppm
- Temperature 49°C-105°C

The rest of this paper will consider corrosion engineering guidelines for systems utilizing resources of this class.

PERFORMANCE OF MATERIALS

Carbon Steel

The uniform corrosion rates of carbon steel in oxygen-free (<10ppb) water with pH >9 are usually less than 25 μm/yr. (Einarsson, et al., 1977), while in the range pH 6-9, rates are typically 25-125 μm/yr. Pit penetration rates are reported to vary from zero to 760 μm/yr. Saturation with air increases the corrosion rate at least ten-fold (DeBerry et al., 1978; Hermannson, 1970).

Carbon steel piping has been used widely but carbon steel tube-and-shell heat exchangers have been satisfactory only in systems where 10 ppm excess sulfite is added continuously as oxygen scavenger. Zinc galvanizing does not control corrosion (Hermannson, 1970).

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 presence of traces of sulfide species. Copper tubing rapidly becomes fouled with cuprous sulfide films more than 1mm thick. Serious crevice corrosion occurs at cracks in the film and uniform corrosion rates of 50-150 μm/yr appear typical based on failure analyses (Ellis, 1980; Griess, 1977; Mitchell, 1980). These corrosion rates are more than ten-fold greater than the rates measured by coupons (Lund, et al., 1976 Howard et al., 1980) in low velocity (∿ 0.03 m/sec) fluid at the same or similar resources.

Experience in Iceland also indicates that copper is unsatisfactory and that brasses (Cu-Zn) and bronzes (Cu-Sn) are still less suitable for heat exchanger service (Hermannson, 1970). Failure of silicon bronze by dezincification has also been observed (Ellis, 1980). Cupronickels can be expected to perform more poorly than copper in low temperature geothermal service because of trace sulfide (DeBerry et al., 1978).

Stainless Steels

The limited test results available at this time (Howard et al., 1980; unpublished Radian data) indicate that T304 and T316 stainless steels are suitable in most low temperature environments. Chloride stress corrosion cracking is possible at the higher temperatures in this fluid class, provided that the fluid is aerated and the steel is highly stressed, so parts should be stress-relieved after forming. Pitting and crevice corrosion resistance should be adequate in most cases. The 400 series stainless steels have more resistance to SCC than the 300 series, but will probably pit severely (DeBerry et al., 1978).

Aluminum

Geothermal experience to date indicates that aluminum alloys will not be acceptable in most cases because of severe pitting (Howard, 1980; DeBerry, et al., 1978).

Titanium

This material has extremely good corrosion resistance. However, it cannot be acid cleaned, and contamination with metallic iron particles can cause pitting.

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

These materials offer ease of fabrication and are not adversely affected by oxygen intrusion. Their mechanical properties at higher temperatures 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.

DESIGN TO LIMIT CORROSION PROBLEMS

It is evident, based on existing geothermal experience, that geothermal fluids impost material selection and design constraints not normally encountered in low temperature water (LTW) systems. Successful design requires special consideration of corrosion problems encountered in the geothermal environment.

Materials with adequate corrosion resistance must be selected to avoid unexpected and unacceptable maintenance and repair costs. For district sized heating projects with attendant surface storage and fluid exposure to oxygen, it may be economical to inhibit the geothermal fluid by continuous addition of excess sulfite as an oxygen scavenger. If this is done, carbon steel can be used for heat exchange equipment. System design should minimize introduction of oxygen into the geothermal fluid to reduce sulfite costs. Vented tanks should be avoided.

Sulfite addition will probably not be practical for smaller systems because the special equipment and operator requirements may prove uneconomical. If sulfite is not added to scavange oxygen, it is extremely important to minimize oxygen intrusion from the atmosphere. Even with careful design, some oxygen contamination will occur, and carbon steel heat exchangers will probably be unacceptable. The difficulty of alternate material selection is increased because of the need to use "off the shelf" components.

Even with careful materials selection, geothermal systems will require more maintenance than conventional systems. System design should minimize the number and kind of components which contact geothermal fluids. This can best be done by using an isolation heat exchanger to transfer heat to a non-corrosive secondary heat transfer medium for circulation to domestic water heaters and fan-coils. 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 higher heat transfer efficiency than tube-and-shell units, and because they are easy to clean and inspect.

DESIGN/MATERIALS INTERACTION

System design and materials selection is an interactive process in that the development of a specific design requires certain materials while selection of a given material will greatly affect design.

The appended three tables illustrate materials choice/design constraint interactions for piping, valves, and heat exchange materials. In these tables, materials have been divided into five performance categories based on the available data from 29 direct utilization systems which satisfy the conditions of chemistry and temperature stated previously. Corrosion and design cautions must be observed to obtain favorable results.

CONCLUSIONS

Low temperature (40°C-105°C) geothermal fluids impose constraints on material selection and system design not normally encountered in low temperature water systems. Reliable direct utilization systems have been built and can be built, but economical system design requires a specialized concern for the corrosion problems encountered in geothermal environments, in order to minimize material costs while assuring acceptable O&M costs.

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TABLE 1. MATERIAL/DESIGN INTERACTION MATRIX FOR PIPING

Material	Corrosion Comments	Design Comments
Carbon steel (mill scale free)	Class II • Caution: Oxygen must be rigorously excluded. Aeration will cause ten-fold or greater increase in corrosion rate. • Caution: Pitting may be serious in some cases. Oxygen will exacerbate pitting.	• Minimize oxygen intrusion into the system. • Do not use vented tanks, especially recirculation tanks. • Avoid threaded junctions because of maintenance problems. • Protect exterior from ground water.
Carbon steel (with mill scale)	Class III • Rapid pitting at defects in mill scale will occur in many cases. • Caution: Oxygen contamination will cause very serious localized corrosion.	
Galvanized steel	Class IV • Zinc not protective at operating temperatures and may cause rapid pitting.	
Copper	Class III • May be acceptable in thick walled applications. • Caution: Crevice corrosion at cracks in the cuprous sulfide corrosion product scale has been observed. • Caution: No suitable solders have been identified.	• If used, design should provide for easy replacement. • Limit fluid velocity to less than 1.3 meter/second.
CPVC and Fiber Reinforced Plastic	Class V • Oxygen intrusion should have no effect. • Failure by degradation of creep rupture strength with time. No data are available for estimating allowable stress after 10^5 hrs (11.4 yrs). • Caution: Properties deteriorate significantly at elevated temperature.	• Observe manufacturer's temperature, pressure, and stress limits. • Fabricate joints carefully.

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

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

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

Class IV: Probably not acceptable.

Class V: Long term suitability has not been verified.

TABLE 2. MATERIAL/DESIGN INTERACTION MATRIX FOR VALVES

Material	Corrosion Comments	Design Comments
Carbon steel body with carbon steel trim	Class IV • Trim life not adequate in many cases. • Localized corrosion at stem/seal/air interface. • Caution: Aeration will cause rapid failure.	• Probable failure mode trim related. Valves should be easy to remove and maintain. Flange or wafer designs favored. Minimize threaded parts. • Plug (globe) valves not recommended for frequent cycle duty because of plug/stem corrosion problems and reciprocating stem motion which causes seal failure or seizing. • Gate valves not recommended for frequent cycle duty because reciprocating stem motion causes seal failure or seizing. • Ball or Butterfly valves recommended for frequent cycle duty because rotation of stem minimizes stem/seal problems. AISI 300 series stainless steel or elastomeric (Buna N, Viton, TFE) seat satisfactory.
Carbon steel body with AISI 400 series trim	Class III • Pitting of trim significant risk. • Caution: Aeration will cause rapid corrosion of body.	
Carbon steel body with AISI 300 series trim	Class I • Caution: Aeration will cause rapid corrosion of body.	
Brass body with brass trim and brass or stainless steel stem	Class III • Caution: Cathodic to steel but effect probably not severe in most cases. • Caution: Dezincification may be significant risk.	
CPVC body and Trim Fiber Reinforced Plastic body and trim	Class V • Failure of materials by degration of creep rupture strength with time. Data not available for estimating allowable stress after 10^5 hrs (11.4 yrs). • Oxygen intrusion should have no effect. • Caution: Properties deteriorate greatly at elevated temperatures.	• Observe comments above. • Observe manufacturers limitations on temperature, pressure, and stress.

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

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

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

Class IV: Probably not acceptable.

Class V: Long term suitability has not been verified.

TABLE 3. MATERIALS/DESIGN INTERACTION MATRIX FOR HEAT EXCHANGERS

Material	Corrosion Comments	Design Comments
Carbon steel	Class IV if oxygen scavenger is not used. Class II if water is continuously treated with excess sulfite and pH > 9. Class III if water is continuously treated with excess sulfite and pH 6.5-9.	- Continuous use of oxygen scavenger required.
Copper	Class IV - Caution: Heat exchange corrosion rates typically order of magnitude greater than coupon rates. Serious degradation by ppb H_2S. Suitable solders not identified.	
Aluminum	Class IV - Extremely severe corrosion with catastrophic pitting.	
AISI 300 series stainless steels	Class II - Caution: SCC of T304 possible above 70-85°C. Resistance to SCC increases with molybdenum additions. - Caution: Pitting and crevice corrosion of T304 possible at high temperature, high chloride conditions, with oxygen. Pitting and crevice corrosion resistance increases with molybdenum additions. - Can be acid cleaned.	- Plate type heat exchangers recommended for ease of cleaning and economic reasons. - Stress relief after forming is recommended. - Fiberous gaskets should be avoided. - Minimum aeration recommended.
Titanium	Class I - Caution: Can not be acid cleaned. Avoid scratching with metal tools.	- Plate type heat exchangers recommended over tube-and-shell for economic reasons and ease of cleaning.

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

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

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

Class IV: Probably not acceptable.

Class V: Long term suitability has not been verified.