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ADDENDUM TO MATERIAL SELECTION GUIDELINES
FOR GEOTHERMAL ENERGY UTILIZATION SYSTEMS

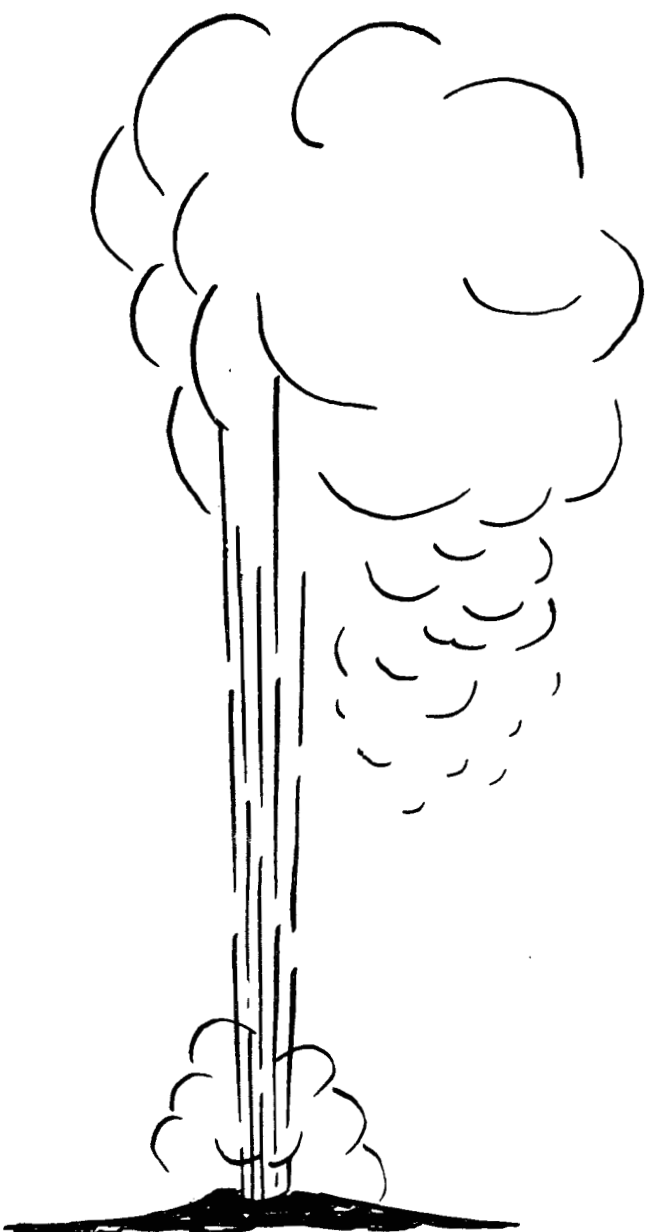
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A CORROSIVITY CLASSIFICATION SYSTEM FOR GEOTHERMAL RESOURCES

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ABSTRACT

The most important difference between traditional steam systems and those that utilize geothermal fluids is the potential for corrosion of metals. The recently developed sourcebook Materials Selection Guidelines for Geothermal Energy Utilization Systems is expected to facilitate corrosion engineering decision making and reduce the cost of geothermal systems where new resources are similar to those presented by the corrosivity classification system.

INTRODUCTION

For more than four years work has been underway to synthesize the corrosion experience from numerous worldwide geothermal operations into a rational, organized body of corrosion experience. This effort first explored the chemistry and corrosion experienced by seven liquid-dominated, power-capable resources in the U.S. Reference 1 presents fluid chemistry, materials test data, and materials operating experience for surface equipment and process streams from 45 geothermal resources with temperatures ranging from 49°C to more than 350°C. Of the 45 sites considered, 31 are located in seven countries other than the U.S.

KEY CORROSIVE SPECIES

Results of materials performance tests were analyzed based on the chemical composition of the corrosive fluid and physical factors such as temperature, exposure duration, pressure and fluid velocity. These variables must be well defined in order to use test results to predict materials performance in other mixtures.

Geothermal system fluids may contain seven key chemical species that produce a significant corrosive effect on construction materials. These key species were identified from an extensive corrosion analysis and an examination of chemical composition data on fluids from liquid-dominated and steam-dominated geothermal resources. They are the most common and aggressive corrosive species, and, therefore, are the ones that should always be identified as a basic, minimum set. These key species are:

- Oxygen (usually from atmospheric contamination)
- Hydrogen ion (pH)
- Chloride ion
- Hydrogen sulfide
- Carbon dioxide, carbonate, and bicarbonate ions
- Ammonia, ammonium ion
- Sulfate ion

Corrosive phenomena that have been observed due to the presence of some or all of these species are:

- Corrosion fatigue
- Crevice corrosion
- Dealloying
- Erosion-corrosion
- Exfoliation
- Galvanic corrosion
- Hydrogen blistering, embrittlement
- Intergranular corrosion
- Pitting
- Stress corrosion cracking (SCC)
- Sulfide stress cracking (SSC)
- Uniform (general) corrosion

Naturally, these phenomena are to be avoided in order to decrease down time, increase plant life and minimize operation and maintenance (O&M) costs. Proper materials selections during the design phase can achieve these goals.

UTILIZATION MODES EFFECTS
ON MATERIALS SELECTION

General fluid properties that influence the applicability of utilization modes to a particular geothermal resource are the temperature, pressure, velocity, key species concentrations in the water or steam, the interaction of the species present, and the nature of the material exposed to the environment.

Systems utilizing geothermal energy can be as varied as the engineer's imagination permits. However, all schemes can be conveniently divided into two categories:

- Direct utilization
- Power generation (Indirect utilization)

In the direct case, geothermal fluid is used on the spot to provide actual heat energy for an end-product purpose. In the power generation case, geothermal energy is converted to another energy form (electrical) whereby much wider use can be realized over a large geographical area.

Various power cycles can be selected for use in generating electricity according to the nature of the resource. Because National interest is focused on steam-dominated and liquid-dominated resources, the power cycles listed below were studied and reported on to acquaint future materials engineers with the environmental parameters which may be encountered in geothermal power production.

- Steam-Dominated Resources
 - Rankine cycle
- Liquid-Dominated, Natural Pressure Resources
 - Flash steam cycles
 - Binary steam cycles
 - Two-phase expander cycle
- Liquid-Dominated, Pumped Resources
 - Direct binary cycle
 - Flashed steam binary cycle
 - Two-phase expander cycle

In similar manner, three methods of extracting heat for direct utilization of geothermal energy are based on the water quality, and end use.

- Direct contact systems
- Indirect contact systems
- Isolation systems (Binary)

Direct contact systems are characterized by the end product's direct, intimate contact with the fluid. Examples are sparge heating, aquaculture and hot mineral baths. In indirect contact

systems, the end product is separated from the geothermal fluid by an end use heat exchange device such as fan-coil in a space heating system. There is no effort to limit the contact of geothermal fluid with components of these systems.

Isolation systems use two (binary) fluids. A primary (isolating) heat exchanger separates the corrosive geothermal fluid from a secondary heat transfer fluid--such as water or antifreeze--so as to minimize the contact of geothermal fluid with system components. An example is a space heating system with a secondary water loop.

SITE-SPECIFIC MATERIALS TEST DATA
AND OPERATING EXPERIENCE GUIDELINES

Materials test results, geochemistry and available operating experience have been acquired, analyzed and presented in Reference 1 from geothermal sites around the world including:

Country	Resource
El Salvador	Ahuachapan
Iceland	High Temperature Areas (4 sites) Low Temperature Areas (10 sites)
Italy	Boraciferous Region (10 sites)
Japan	Hatchobaru Matsukawa Otake
Mexico	Cerro Prieto
New Zealand	Broadlands Wairakei
United States	Baca, NM Brady H.S., NV Casa Diablo, CA East Mesa, CA Heber, CA Klamath Falls, OR Madison Aquifer, SD Raft River, ID Salton Sea, CA The Geysers, CA

Information about each site is presented in four parts which include utilization mode, typical fluid geochemistry, corrosion tests methods and results, and, finally, the available operating experience. A method for categorizing each site according to its corrosivity has been developed and each site has been assigned to one of six such corrosivity classes.

Materials test results for the sites are presented in two formats. The first is a Material Selection Guideline Table which gives a broad screening overview of materials performance at a given

site. This presentation classifies corrosion rates in one of the following four categories based on uniform rates in mils per year (mpy):

<u>Category</u>	<u>Uniform Corrosion (mpy)</u>
A	rate < 1
B	1 < rate < 10
C	10 < rate < 50
D	rate > 50

In addition to materials selection guidelines tables, detailed summary tables show the actual materials test results. Uniform and localized corrosion rates are presented in tabular form. Pitting and crevice corrosion rates are standardized by assuming linearity to permit site comparisons: however, judicious interpretation must be employed.

CORROSIVITY CLASSIFICATION SYSTEM

It has been noted for years that there was a relationship between a geothermal resource's total dissolved solids (TDS), temperature, and its corrosiveness. Yet, TDS and temperature alone could not predict the corrosiveness of a geothermal fluid. A more definitive set of parameters was needed.

Classification Rationale

Comparisons of a large body of materials test data showed that apparently rather different geothermal chemistries tended, in many cases, to yield similar corrosion results with common construction materials such as carbon steel. This led to the invention of an empirical system of corrosivity classification based upon the key corrosive species (mentioned above), reservoir phase domination, plant inlet temperature, and similarities and differences in the corrosion behavior of carbon steel.

In the development of this system, the term total key species, or TKS, was developed. Analogous to total dissolved solids, the TKS is the sum, in ppm, of chloride, sulfate, carbon dioxide, bicarbonate, carbonate, total sulfide species and total ammonia species. For most liquid dominated resources the bulk of the TKS is chloride, sulfate, and bicarbonate, with only minor weight contributions from ammonia and sulfides. Because adequate analytical data on unflashed fluid chemistry is lacking from many resources, separated fluid

chemistry was used as the basis for classifying liquid-dominated resources.

In the case of steam-dominated resources, the term TKS, as defined above, has little significance and is replaced by the volume percent of noncondensable gases in the steam.

The reservoir temperatures, for the sites studied, ranged from 49°C to more than 350°C, a range of more than 300°C. However, little quantitative data are available relating to downhole materials performance (accumulation of this data is underway) and the Geothermal Corrosivity Classification System uses the plant inlet temperature as a defining criterion. For power plants using a flashed steam cycle, the plant inlet temperature is taken to be the first stage steam separator temperature as this separator is generally located at the wellhead. The first stage steam separator temperatures are rarely more than 200°C at existing or proposed plants.

For plants using direct binary cycles, the temperature drop from the reservoir is minimized and flashing is not desired. The plant inlet temperature, approximately the wellhead temperature, ranges from 100°C to 200°C in currently proposed or operating plants.

For the lower temperature (49°C - 105°C) resources there is little temperature drop as the fluid is extracted from the resource.

Description

The Geothermal Corrosivity Classification System is presented in detail in Reference 1. Figure 1 depicts the corrosivity to carbon steel of the four classes of liquid-dominated geothermal resources occurring in the United States as a function of the class Defining Parameters (Total Key Species, noncondensable gases, pH, and plant inlet temperature). Figure 1 depicts only the uniform corrosion of carbon steel. The Geothermal Corrosivity Classification System considers other corrosion modes as well as other materials.

It is important to observe that the carbon steel corrosion rates, TKS, and temperatures of the four presented corrosivity classes fairly well separate into distinct groups. Listed below are reference geothermal resources that fall into the four classes:

Conover

<u>Class*</u>	<u>Geothermal Resources</u>	REFERENCE
I	Salton Sea, CA	
III	Cerro Prieto, Mexico East Mesa, CA (one zone)	1. Ellis, P.F., and M.F. Conover, 1981, <u>Material Selection Guidelines for Geothermal Energy Utilization Systems</u> , DOE Contract No. DE-AC02-79ET27-026, NTIS Pub Code DOE/RA/27026-1, Radian Corporation, Austin, TX, January.
IV	Ahuachapan, El Salvador Baca, NM Brady H.S., NV Broadlands, New Zealand East Mesa, CA (other zones) Hatchobaru, Japan Heber, CA High Temperature Areas, Iceland Otake, Japan Raft River, ID Wairakei, New Zealand	
Va	Klamath Falls, OR Low Temperature Areas, Iceland	
Vb	Edgemont, SD Marlin, TX Midland, SD Pagosa Springs, CO Philip, SD	

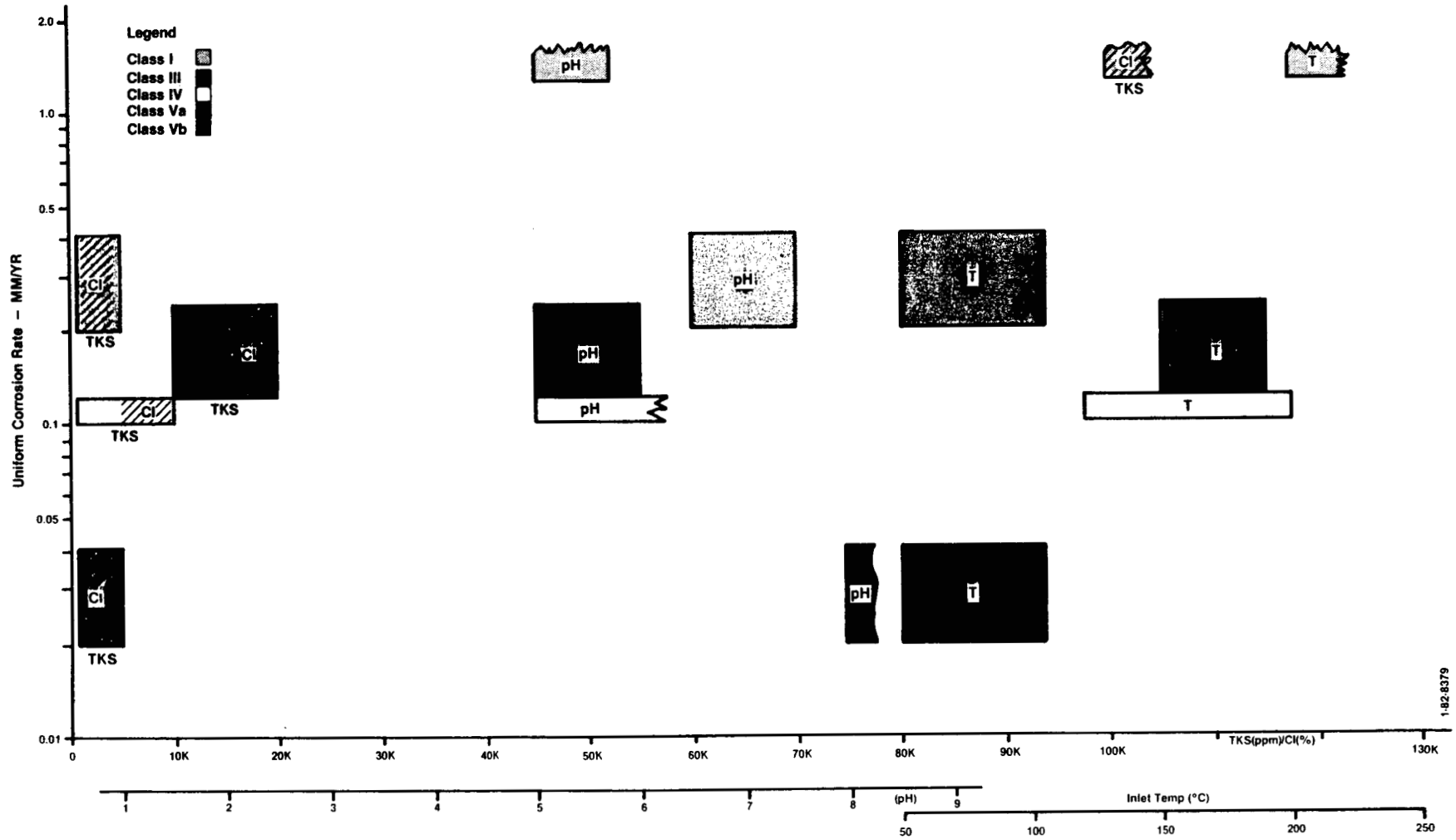
* Class II is still undefined. Class VI covers steam-dominated resources.

Use and Limitations

The most important source of information for the corrosion engineer is prior experience with comparable resources. Operating experience is probably the most helpful in corrosion engineering decision-making, followed by material test data. By comparing the characteristics of his resource with the Defining Parameters in the Geothermal Corrosivity Classification System (Figure 1) the plant design/corrosion engineer can rapidly determine which geothermal resources (above) are most similar to his. It is expected that such resources will provide the most relevant corrosion information.

By providing general information on corrosivity and directing the plant designer/corrosion engineer to the most relevant data, use of this system can significantly reduce the uncertainty, expensive mistakes, and requirements for materials tests. Together, these benefits should reduce both the cost and time-to-completion of geothermal projects.

However, the system cannot consider the many variable factors such as velocity, localized phase transitions, and design decisions which can drastically alter corrosion behavior. Also, corrosion modes other than uniform corrosion must be considered. Thus the need for careful evaluation of materials and design decisions by persons well-versed in geothermal corrosion engineering is not precluded.



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Figure 1. Uniform Corrosion of Carbon Steel in Separated Fluid from Four Classes of Geothermal Resources.