

CORROSION RESISTANCE OF MATERIALS FOR GEOHERMAL HEAT EXCHANGERS

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16. Abstract Corrosion resistant alloys and non-metallic coating have been tested by exposure to Glenwood Springs geothermal water in a test loop constructed for the purpose adjacent to the Glenwood Springs geothermal well. The alloys tested included stainless steels, higher Cr - Ni alloys and a Ni - Cu alloy. The coatings included several plastics and one glass coating. None of the materials showed any measurable degradation during the test. However, it is recommended that the results be applied with caution; several factors suggest that the data from these tests might be overly optimistic and that corrosive conditions in practice could be more severe. For a number of reasons, including failure of the water pump feeding the test loop and ice formation within the loop, no data were obtained on the fouling resistance or thermal conductivity of the materials tested. Based on this study and previous studies on geothermal heating of bridge decks, consideration for geothermal heating of two structures in Glenwood Canyon is underway. Implementation					
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1. Introduction

The Colorado Department of Highways is presently studying the feasibility of using geothermal heating systems for snow and ice control on parts of the proposed new interstate highway through Glenwood Canyon. A gravity operated heat-pipe system with intermediate heat exchangers between the water and the deck is preferred: this system eliminates the possibility of water freezing inside the deck and confines any corrosion and fouling problems associated with the geothermal water to those parts of the system external to the bridge-deck structure.

The essential viability of this method was tested by incorporating heat-pipes in a simulated bridge-deck structure in Glenwood Canyon⁽¹⁾. The primary heat source was a local geothermal spring. These trials demonstrated the capability of the system to reduce snow and ice coverage by levels approaching 100%. However, the efficiency of the heat exchangers was markedly reduced by severe fouling of the water-side pipe walls. For example, a 1/4" sludge layer was deposited inside one heat exchanger unit in less than three months, reducing the thermal performance ratio from 0.4 to 0.25. In addition, the geothermal water caused corrosion of the carbon steel pipe walls and immersion thermistors at localized rates of about 0.05 in/yr. This corrosion rate is sufficient to cause penetration of a 3/16 in. pipe wall in less than 4 years.

Insufficient data exist at present to predict the corrosion and fouling behavior of alternative heat exchanger materials. Materials testing has been carried out in other geothermal waters, but in each case the water conditions differ from those of the Colorado geothermal waters. The complexity of the water chemistry and of the corrosion and fouling processes

precludes direct application of the results of this testing to the present situation. The work described in this report was initiated to provide corrosion data directly relevant to the Glenwood Springs project and to be used as a basis for selection of materials for the heat exchangers.

2. Selection of Materials for Testing

The materials selected for testing were those regarded as likely to show good corrosion resistance in the Glenwood Springs geothermal water. The corrosivity of the water was evaluated from a chemical analysis supplied by Colorado Department of Highways (Table 1) prior to initiation of the materials test program. The suitability of materials considered for inclusion in the tests was determined from data reported in the open literature, briefly reviewed below, and from advice given by materials manufacturers (some of which are listed in Table 5).

2.1. Corrosion of Metals in Waters

Corrosion of metals in aqueous environments is an electrochemical process. Metal ions are released into solution from anodic areas of the metal surface:



The electrons generated by the formation of metallic ions must be removed from the metal for the corrosion reaction to continue. This takes place at cathodic sites on the metal surface. The most common cathodic reaction in the corrosion of steels in low temperature waters is the reduction of dissolved oxygen gas:



Rust precipitates as an iron hydroxide and subsequently hydrolyses to the more familiar hydrated ferric oxide (brown rust).

Recognition of the electrochemical nature of corrosion is important in understanding corrosion processes. For example, depletion of oxygen throughout the entire system will normally reduce corrosion rate, which is usually controlled by availability of oxygen at the metal surface. However, local oxygen depletion in occluded cell conditions, such as in crevices

or underneath scales, will increase the rate of corrosion in the depleted region. This latter effect occurs because the anodic (corrosion) reaction is concentrated at the depleted zone; hydrolysis of the metallic ions and chloride ions in solution results in a reduced pH which further accelerates corrosion.

Geothermal waters are potentially very corrosive to steels because of their high dissolved solids content although, in practice, low corrosion rates are often experienced due to the absence of dissolved oxygen in waters drawn directly from deep wells⁽²⁾. In the Glenwood Springs experiment, water was taken from a surface stream, thus the water would have been saturated with air (~7 ppm oxygen⁽³⁾) and high corrosion rates would be expected.

The high chloride content of most geothermal waters (4,700 ppm Cl⁻ reported in the Glenwood Springs water) increases rates of corrosion in three ways: conductivity of the water is increased, facilitating the electrochemical processes; protective corrosion product films tend to be destroyed; and locally high concentrations of hydrochloric acid (~ pH4) can be produced in occluded areas. Other ions commonly found in geothermal waters and which lead to increased corrosion rates are sulfide, ammonium, sulfate and ferric ions. Both sulfide^(4,5) and ferric ions⁽⁶⁾ can be reduced in cathodic reactions replacing or complementing the oxygen gas reduction reaction. The iron content of the Glenwood Springs water was high and, as the water was aerated, the iron would be present in the ferric state; this was confirmed in the sludge deposit⁽¹⁾ which had a high iron content and was brown (ferric) colored.

The corrosiveness of waters is strongly influenced also by their hardness; this in turn is dependent primarily on carbonate content, pH and the level of dissolved carbon dioxide. Hard waters precipitate a film of solid carbonates, mainly on the cathodic areas, which acts as a barrier

between the metal and its environment. Hard waters, therefore, tend to be less corrosive than soft waters. The hardness of the Glenwood Springs water was high and, taken on its own, would suggest that carbonate precipitation would occur. However, the high saline content of water would counter the tendency toward precipitation; "saturation index" calculations indicate that the water would, in fact, behave as a soft water.

A number of investigations have been carried out in which corrosion rates in geothermal waters have been measured. The more salient results are discussed below in terms of potential materials for the heat-pipe heat exchanger core tubes.

2.2. Carbon and Low Alloy Steels

Pit depth measurements on the carbon steel pipe wall from the Glenwood Springs trial⁽¹⁾ indicated localized penetration rates of up to 50 mils per year (mpy). This rate is not untypical of carbon steels in aerated saline solutions. A review of corrosion studies in U.S. geothermal waters⁽⁷⁾ reported localized rates of up to 200 mpy. The temperature of the waters responsible for these high rates (105-140°C) was well above that in Glenwood Springs (~26°C), but the reported compositions of the waters appeared considerably less aggressive. Corrosion behavior in sea water may give some guidance to expected behavior in geothermal waters. Carbon steels immersed in quiet seawater corrode at a rate typically about 5 mpy. Local rates can be up to 10 times this general rate. The temperature of Glenwood Springs water was about 10°C higher than that of typical seawater, and corrosion rates in these conditions can be regarded as increasing by a factor of about two for every 10°C increase in temperature⁽⁹⁾. Thus, localized rates of ~ 100 mpy would be predicted.

Several failures of carbon steel components in geothermal environments have been reported⁽¹¹⁾. Some of these failures resulted from high water

velocity and are not relevant here. Water velocity in the Glenwood Springs equipment was up to 5 ft/sec. Velocities of this level are unlikely to accelerate corrosion of carbon steel to a significant extent; the tendency for higher rates of corrosion brought about by the improved supply of oxygen to the metal surface as velocity increases is countered by the disruption of occluded cell (crevice) conditions as velocity rises. At velocities above 10 ft/sec, rates of corrosion tend to increase rapidly.

Field corrosion tests were carried out in the East Mesa Known Geothermal Resource Area (KGRA), California⁽¹²⁻¹⁴⁾ in waters nominally similar to that at Glenwood Springs but at much higher temperatures (~150°C). The corrosion rates reported after the 22 week exposures were remarkably low: 2-3 mpy with no apparent localized attack. The reason for these unusually low rates is unclear. It was reported that fouling did not occur, indicating that the water composition was, in fact, different from that in Glenwood Springs, where severe fouling was found. The absence of fouling could, in itself, reduce corrosion in that there would be less opportunity for occluded cell conditions to be set up.

In summary, no corrosion data are available for carbon steel in conditions known to be comparable to those in Glenwood Springs. Corrosion rates in other geothermal waters are highly variable. No systematic attempt appears to have been made to date to relate corrosion rate to variables in water composition and temperature; frequently, the data reported are insufficient to permit this.

The addition of low alloy levels to carbon steel has little influence on corrosion behavior during immersion in saline solutions^(8,10).

AISI Type 1020 carbon steel samples were included in the tests reported here for baseline data.

2.3. Stainless Steels

Stainless steels depend for their corrosion resistance on a thin film of corrosion product, usually regarded as a chromium oxide, which passivates the metal by providing a barrier between the metal surface and the environment. This passive film can suffer local breakdown under certain conditions, leading to localized attack such as pitting and stress corrosion cracking. Chloride ions are most commonly responsible for film breakdown; their effect becomes more severe at increased temperatures and low pH levels.

Austenitic stainless steels (i.e. containing $>8\%Ni$) are widely used in preference to ferritic stainless steels because of their superior mechanical properties, better fabrication characteristics and, in many environments, higher corrosion resistance. However, they are rarely used in seawater because of their susceptibility to pitting. Pit depths of 6 mils have been observed in AISI Types 304 and 316 stainless steels after one year's exposure to seawater. The molybdenum-bearing grades (Types 316 and 317) are more resistant to pitting and crevice corrosion than Type 304 but, once initiated, pits propagate at comparable rates.

Pit penetration rates of up to 40 mpy have been reported from tests of Types 304 and 316 in geothermal waters at high temperature ($133^{\circ}C$)⁽⁷⁾. In other geothermal waters at temperatures of $<100^{\circ}C$, Type 304 was reported not to be significantly affected by pitting⁽⁷⁾. However, stainless steels are very sensitive to small changes in environment. Moderate flow rates generally reduce corrosion, stagnant waters promoting locally aggressive conditions. Fouling can lead to accelerated attack of stainless steels by occluded cell mechanisms.

Truman⁽¹⁶⁾ tested Type 304 in several chloride solutions and found that, over an 18 month test period, a chloride level of 10^4 ppm was required to initiate pitting in a pH7 solution at $40^{\circ}C$. At $20^{\circ}C$, 10^5 ppm chloride was

required. The chloride content of the water in the Glenwood Springs trials was reported to be 4.7×10^3 ppm, i.e. below that required to cause pitting. Other factors are likely to influence the behavior of the steel in practice, however; most notably the fouling tendency and high dissolved solids content of the Glenwood Springs water.

Austenitic stainless steels have been found to be susceptible to stress corrosion cracking (SCC) in some high temperature geothermal waters^(11,14). SCC of correctly heat-treated (i.e. non-sensitized) austenitic steels does not occur at temperatures $< \sim 60^\circ\text{C}$ (except under special laboratory conditions), thus SCC is unlikely to be a problem in the Glenwood Springs water (26°C).

Ferritic stainless steels tend to be more resistant to pitting and SCC than do the austenitics. However, both these types of localized attack have been observed with ferritics in geothermal waters at high temperatures^(11,14). The conventional ferritics (AISI 400 Series) suffer from pitting in ambient temperature seawater⁽⁸⁾, but the newer "superferritics" are considerably more resistant and have been reported to be very resistant to high temperature geothermal waters⁽¹⁵⁾ and seawater. In addition to their superior corrosion resistance, the superferritics exhibit better fabrication characteristics and improved low temperature toughness compared to the conventional ferritics.

Thus stainless steels, particularly the superferritics, were included in the list of candidate materials for testing in the Glenwood Springs water.

2.4. Copper Alloys

Copper alloys have not been widely tested in geothermal waters. Copper-nickel and copper-zinc alloys (brasses) were exposed to high temperature geothermal brines by Idaho National Engineering Laboratories⁽¹⁷⁾. The brasses were found to be more corrosion resistant in this environment than the copper-nickel alloys but both types of alloy suffered localized attack

in the form of pitting. All copper-base alloys are susceptible to attack by sulfide-bearing waters and the above tests⁽¹⁷⁾ suggested that sulfides were the principal aggressive species in the geothermal water. Hydrogen sulfide levels as low as 0.1 ppm have been reported to cause failure⁽¹⁸⁾ of copper alloys. Stress corrosion cracking of copper alloys can occur in waters containing ammonia which is often found in water from geothermal sources.^(6,11)

Copper alloys were not regarded as suitable for inclusion in the present tests.

2.5. Nickel Alloys

A wide range of nickel alloys are available and are widely used for seawater applications, notably for seawater-cooled condenser systems. Monel 400 (~70Ni - 30Cu) was tested for high temperature geothermal systems⁽⁷⁾: rates of general corrosion were low but pitting rates of up to 80 mpy were reported. The Ni-Cr-Mo alloys offer better resistance to geothermal waters. A number of the Inconel and Hastelloy alloys have shown a high degree of corrosion resistance in geothermal environments^(11,14,18), although some of the lower alloyed variants have suffered pitting attack.

The Nicloy alloy was included in the tests as the most promising candidate from the nickel alloys.

2.6. Other Metals

Aluminum alloys have been reported as having a corrosion resistance considerably less than that of carbon steel in high temperature geothermal environments⁽¹²⁾ and in the Glenwood Springs water⁽¹⁹⁾. However, alloys of aluminum are considerably less resistant to corrosion than is the pure metal, principally because of local galvanic cells set up on the alloy surface between intermetallic particles and the aluminum matrix. To overcome this, aluminum alloys with pure aluminum cladding are produced.

Pure aluminum sprayed coatings of 10 mil thickness have been reported to protect steel in marine immersion for over five years⁽¹⁰⁾. In geothermal applications, aluminum or its alloys may be susceptible to crevice corrosion under fouling deposits, and to galvanic corrosion if any noble metals (such as the iron in the Glenwood Springs water) present in the water plate out on the aluminum surface. This latter effect arises because aluminum, one of the more active metals, can displace from solution more noble metals, such as copper. An additional problem with aluminum will arise if the circulating water contains sufficient abrasive solids to damage the passivating oxide film causing degradation by erosion-corrosion.

Aluminum alloys were not regarded as viable candidate materials.

2.7. Coatings

The corrosion resistance of carbon steel piping can be increased by the application of either metallic or non-metallic coatings. The latter are likely to be the less susceptible to fouling, but because of their low thermal conductivities, will reduce heat transfer across the pipe wall.

Metallic coatings can be applied in a number of ways, e.g. hot-dipping, electroplating, spraying. Any metal can be applied by at least one of the available techniques, but cost and availability frequently limit realistic candidate materials. Few, if any, are readily available as coatings on the inside of tubing. The most widely used metallic coating is zinc, applied by hot-dipping or electro-galvanizing processes. To the author's knowledge, this is the only metallic coating which has been tested in geothermal environments: pitting rates of ~30 mpy were reported⁽⁷⁾ for galvanized steel in 80°C geothermal water which, from the composition reported, appeared less aggressive than that at Glenwood Springs. As the coatings are normally only a few mils in thickness, such a rate would not be acceptable. Zinc coatings are not normally recommended for immersion service.

Diffusion coatings of aluminum and chromium applied to steels are commonly used for high temperature applications, including high temperature waters, but no test results are available relevant to geothermal systems. Diffusion coatings differ from the more conventional metallic coatings in that the surface presented to the environment consists of intermetallic compounds between iron and the coating metal, rather than the pure coating metal. Under many conditions this leads to corrosion properties superior to those of either the steel or the coating metal on their own.

Non-metallic coatings have not been proven in geothermal environments^(11,20). Many non-metallics have been tested in bulk form as candidates for construction materials in geothermal systems, but the properties required for bulk construction differ from those required of the same materials in coating form. For example, limited water permeability and surface cracking may be of little consequence in a thick-walled plastic pipe, but would result in failure of a coating by permitting corrosion of the metallic substrate. A large number of polymers have been exposed to high temperature geothermal water; all have shown sufficient degradation to raise doubts as to their value as coatings. No data are available for lower temperature applications. Epoxy coatings are widely used for corrosion protection but are not generally recommended for prolonged immersion in aggressive waters^(11,21). The high solids content of the Glenwood Springs water could lead to erosion problems with polymer coatings or thin metallic coatings.

Epoxy coatings, being relatively low cost and easily applied, were included in the test, as were polypropylene and polyphenolformaldehyde. Glass coatings, also included, are attractive because of their higher thermal conductivity than polymers and their abrasion resistance.

2.8. Deposition and Fouling

Several models of fouling in heat exchangers have been developed⁽²²⁾, but none appears able to predict rates of deposition from complex saline

solutions such as geothermal waters, nor dependence of deposition on surface characteristics.

In the Glenwood Springs trials, the carbon steel surfaces of the heat-exchanger pipes were severely fouled, whereas the PVC feed lines were virtually unaffected. The extent to which this can be attributed to the lack of heat transfer across the PVC pipe walls or to the nature of the PVC surface cannot be determined from presently available data.

Precipitation from saturated or near saturated solutions will occur on suitable surfaces even without a temperature reduction because of the reduced activation energy for nucleation on the surface. However, deposition on a plastic surface is expected to be less than that on a ferrous metal, irrespective of thermal effects. Again, this results from the activation energy for nucleation. A steel surface in contact with oxygenated water will be covered with a layer of ferric hydroxide (this is eventually converted by hydrolysis to a hydrated ferric oxide, the more familiar form of rust). This provides ideal epitaxial compatibility for precipitation of ferric hydroxide from solution, i.e. the crystallographic parameters of the surface and of the precipitate are identical and the energy associated with creation of a new surface on precipitate nucleation is effectively absent. A plastic surface has extremely poor epitaxial compatibility with any inorganic precipitate, hence the nucleation energy is high and precipitation is retarded.

The influence of heat transfer rate on precipitation of solids from solution is complicated because the solubility of many salts present in geothermal waters exhibits inverse temperature dependence^(11,23). In addition, the solubilities of the many species present are interdependent. Thus, temperature dependence of fouling is too complex to be predicted from present knowledge.

To help predict deposition rates, the test loop was fabricated from pipe sections, each approximately six inches long, so that real deposition behavior on the surfaces of the candidate materials could be observed. Sections of two diameters were used as a means of varying the flow rate of the water.

3. Experimental Procedure

The materials tested, their chemical analyses or descriptions, and the suppliers of the test samples are listed in Tables 3, 4 and 5. The author acknowledges with gratitude the cooperation of those companies which supplied the test samples. These companies represent the major manufacturers and/or suppliers of the materials tested.

A loop was constructed on the test site at Glenwood Springs. The geothermal water was pumped at an estimated rate of 50 gallons per minute from a natural geothermal well. The loop consisted of sections of pipe of about six inches length joined together by Raychem "Thermofit" shrink-fit plastic sleeves. The sections of pipe were of either the test materials or PVC, the latter used to house the racks containing the test coupons. The loop was, effectively, in two parts: one made from approximately 3.0 inch diameter pipe sections, the other from approximately 2 inch diameter sections. The objective of using two diameters was to have the materials exposed to two flow rates. It was hoped that this would supply information on the effect of flow rate on both corrosion and deposition rates. All the test coupons were included in the larger diameter sections.

The metal test specimens exposed included plain coupons, welded coupons of some materials, and U-bend coupons of some materials to evaluate stress corrosion cracking (SCC) behavior (see Tables 3 and 4 for details). The test specimens, other than the U-bends, were accurately weighed before testing. Two coupons were retained to check the calibration of the balances during

the final weighings. The coupons were assembled in plexiglass racks in which they were held in position by flexible plastic tie-strips. Galvanic contact was rigorously avoided. The racks were held in the PVC pipe sections by screws; the specimens were orientated so that they were parallel with the direction of water flow.

After testing, the racks were disassembled and the specimens cleaned following National Association of Corrosion Engineers' recommended practice TM-01-69. The specimens were reweighed and examined under a stereo optical microscope for pitting. No pitting was detected on any of the specimens, therefore taking cross-sections for further metallographic examination was not required. The U-bend specimens were cleaned and examined under the stereo optical microscope for cracks.

The coupons of coated steel were treated somewhat differently. Two coupons of each type were exposed, one with a complete coating and one with a scratch deliberately made through the coating. The coupons were mounted for testing in the same manner as the metal coupons. After exposure, the scratched coupons were examined with the stereo optical microscope to estimate the extent of undercutting of the coating adjacent to the scratch. The unscratched coupons were placed in a glass beaker containing a 3% NaCl solution and, using a stainless cathode, were made the anode of an electrochemical cell. Six volts d.c. was applied across the cell and the current flowing was measured to determine the permeability of the coating.

The internal walls of the test pipe sections were examined visually for damage and for deposition.

Because the thermal conductivity of the materials and coatings is seen as being an important factor in the final materials selection decision, and because the conductivity of the materials tested covers a broad range, thermocouples were taped to the outside of each pipe section, excluding the

PVC pipe (the PVC pipe was used only to house the test coupons). Two additional thermocouples were extended into the water inside the loop, one at the inlet side and one at the outlet side. This was intended to provide a measure of the temperature gradient across the pipe walls.

4. Results and Discussion

4.1. Operation of Test Loop

The ancillary equipment supporting the test loop (feed pipe, pump, flow meter, etc) were supplied and assembled by the Colorado Department of Highways. The loop operated successfully when first set up except for the flow meter, which was inoperative during the whole period.

Unfortunately the pump failed twice during the test period. The monitoring of the loop by Colorado Department of Highways staff was irregular and only occasional, so that the exposure time when water was actually flowing through the pipe is not known accurately. The second pump failure occurred probably during January and resulted in the water in the test loop freezing. Any deposition which occurred during the test was largely removed by the ice, thus it was not possible to evaluate the susceptibility to fouling of the test materials and coatings. A further effect of the freezing is that corrosion probably did not occur during the period when the water was frozen, thus the effective time of exposure of the specimens is not known.

4.2. Water Analysis and Temperature

The chemical analysis of the Glenwood Springs geothermal water initially provided by Colorado Department of Highways is given in Table 2. The chloride and total dissolved solid (TDS) contents of this water approach those of seawater, which typically contains about 19,000 ppm chloride and 34,500 ppm TDS⁽²³⁾. As such, it can be regarded as very corrosive to most metals except a number of specialized alloys, such as some Cu-Ni alloys, the newer "superferritic" stainless steels, the higher Cr-Ni-Mo stainless

steels, and a number of metals normally regarded as exotic, such as titanium and zirconium.

A subsequent water analysis, Table 2, provided by the Colorado Department of Highways indicated a much less aggressive composition, in which more conventional stainless steels (e.g. 316 or 317) might survive. However, there has at this time been no systematic evaluation of the chemistry of the Glenwood Springs geothermal water and of any seasonal variations which might occur. Until such data are available it might be prudent to regard the more aggressive water represented by the first analysis as typical.

The temperature of the water, recorded from thermocouples in the test loop, at the beginning of the test period was 31°C at the inlet side of the loop and 30°C at the outlet. Ambient air temperature at that time was 29°C.

Unfortunately, the Colorado Department of Highways was unable to provide the effort required for periodic monitoring of water temperature during the test. The temperature of the water at the end of the test, when the water in the loop was frozen due to pump failure, was measured by the thermocouples as - 26°C. The test covered the months of August to February.

4.3. Performance of Test Samples

The results of the weight loss measurements on the metal test coupons are presented in Table 6. All of the weight change figures, with the exception of those for carbon steel, are regarded as zero, within the limits of accuracy of the weighing equipment. The corrosion rate of the carbon steel samples was about 4 mpy (i.e. 4×10^{-3} inches per year). This rate is a factor of about ten less than would be predicted for carbon steel (section 2.2) in water of the analysis in Table 1 at 30°C, and is closer to that which would be expected in water of the second analysis (Table 2), suggesting that the second analysis is more typical of the conditions to which the test coupons were exposed.

None of the coupons nor the pipe sections from the remaining - the more corrosion resistant - metals showed any measurable corrosion damage. No pitting or stress corrosion cracking was detected on any of the samples. However, in using these results as a basis for materials selection, two points should be recognized: first, the water chemistry during the test run may have been markedly less aggressive than that at other times (see Tables 1 and 2); second, the failure of the pump for an indetermined part of the test run and the consequent freezing of the water in the test loop renders uncertain the exposure time figures used in the calculation of corrosion rates.

The results from the coated steels were equally negative. None of the coatings, either on the coupons or the internal walls of the test pipe sections, showed any measurable signs of deterioration. None of the scratched coupons showed undercutting of the coating at the scratches. None of the impressed current tests gave rise to a measurable current (the limit of detection was 0.0005A).

Thermal Conductivity Measurements

Unfortunately, the Colorado Department of Highways was unable to make the effort to monitor the external thermocouples on the test pipes. On the final visit of this author to the test site, for disassembling of the loop and removal of the specimens, the water in the loop was frozen because of the pump failure. Thus, no data are available from which the thermal conductivity of the test materials can be evaluated. It is likely, however, that for most of the materials included in the test approximate data can be obtained from the manufacturers or suppliers listed in Table 5.

4.5. Deposition and Fouling

One of the primary reasons for including short sections of pipe of the test materials in the loop was to evaluate the relative resistance to fouling

of the various materials and coatings tested. It was hoped that additional data on the effects of flow rate would result from use of pipe sections of two different diameters. Unfortunately, the action of the ice resulting from freezing due to the failure of the pump toward the end of the test exposure removed most of the solids deposited on the pipe walls during the test. Thus, no useful data were obtained regarding fouling behavior.

4.6. Selection of Materials for Heat Exchangers

Superficially, the results of these corrosion trials suggest that all of the materials tested are resistant to the Glenwood Springs geothermal water. However, a number of factors must be taken into account in applying the results in the materials selection process. The disparity in the two analyses of the water and the relatively low corrosion rate exhibited by the carbon steel samples suggest that during the test period the water chemistry may have been less aggressive than at other times. The materials selection must be based on the most aggressive water chemistry likely to be encountered. Corrosion damage, especially pitting, initiated during even short periods of highly corrosive chemistry often continues when the water reverts to a less aggressive composition.

The pump failures and consequent freezing leave in doubt the actual exposure time of the test samples. The ice formation would have suspended the corrosion processes. The length of time that the loop was frozen is not known. It should also be noted that, even without the problems caused by the pump failures, the duration of the tests, generally 161 days, is rather short as a basis for extrapolation to longer times. Many corrosion mechanisms, such as pitting and SCC, can have long incubation periods during which there is no visible damage. This is particularly so in the conditions in the test loop where a gradual build up of fouling deposits can markedly alter the chemistry of the metal surface. Crevice corrosion

mechanisms and high chloride concentrations are commonly associated with surface deposits. Finally, it should be noted that, statistically, the probability of finding an incidence of localized corrosion, such as pitting, and of the severity of the corrosion found increases as the surface area tested increases. The specimens used in these trials were necessarily small. There remains a probability that much larger specimens - and therefore, of course, the heat exchangers eventually constructed - could suffer damage from pitting.

None of the coatings tested showed any signs of deterioration. Here again, the statistical effect of size of surface area must be taken into account. Thin coatings such as those tested (with the exception of the Dow polypropylene lining) are traditionally regarded as always containing defects. Hence the need, for example, for cathodic protection to reinforce the protection offered by the coatings applied to long gas transmission pipelines. The probability of there being a defect increases as the coated area increases. If coatings were to be used for the heat exchanger, a thorough test of the coatings, after installation, is strongly recommended. An electrochemical method, such as that used to evaluate the specimens in the tests reported here, is more sensitive than traditional electrical "holiday detectors". Coatings, of course, are less likely to suffer fouling than are metal surfaces.

Although the results of these tests are inconclusive, they do suggest that all of the materials and coatings tested are appropriate candidates for the heat exchanger. The final selection decision must be based on factors such as cost, availability and ease of fabrication. Evaluation of these factors will depend on the final designs for the heat exchangers and on the contract procedures involved and is outside the scope of this work. In any event, it is strongly recommended that coupons of the selected material

and of alternate materials are included in the heat exchangers and monitored regularly. Electrochemical corrosion monitoring equipment is also likely to be valuable in performance surveillance.

5. Conclusions

1. All of the alloys and coatings tested showed acceptable corrosion resistance in the corrosion tests. However, because of the factors mentioned below, these results should be applied with caution.
2. Doubts concerning the validity of the data arise from a number of sources. Failure of the pump which circulated water through the loop and consequent freezing of the water in the loop give rise to uncertainties in the actual exposure time of the specimens. Disparity in the chemical analyses of the water and the relatively low corrosion rates of the carbon steel samples suggest that the water circulated through the loop during the test period was possibly considerably less aggressive than that from the same well at other times. Finally, extrapolation of data from short term corrosion tests to longer periods is always questionable and a large margin of error should be allowed for.
3. Failure of the pump in the test loop prohibited obtaining any useful data on the fouling resistance of the materials tested.
4. Inavailability of effort from Colorado Department of Highways compounded by the pump failure prohibited obtaining any useful data on the relative thermal conductivities of the materials and coatings tested.

6. References

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Table 1. Chemical Analysis of Glenwood Springs Geothermal Water

Glenwood Springs Area: Graves Springs

Location: 39°33'14"N. Latitude; 107°20'08"W. Longitude; T. 6 S., R. 89 W.,

Sec. 9 bb, 6th. P.M., Garfield County

	Date Sampled	Glenwood Springs
	9/75	
Arsenic (As), (UG/L):	0	
Boron (B), (UG/L):	1,000	
Cadium (Cd), (UG/L):	0	
Calcium (Ca), (MG/L):	770	
Chloride (Cl), (MG/L):	11,000	4700
Flouride (F), (MG/L):	2.9	
Iron (Fe), (UG/L):	70	
Lithium (Li), (UG/L):	690	
Magnesium (Mg), (MG/L):	150	
Manganese (Mn), (UG/L):	50	
Mercury (Hg), (MG/L):	0	
Nitrogen (N), (MG/L):	0.04	
Phosphate (PO ₄)		
Ortho diss. as P, (MG/L):	0.05	
Ortho, (MG/L):	0.15	
Potassium (K), (MG/L):	180	
Selenium (Se), (UG/L):	0	
Silica (SiO ₂), (MG/L):	32	
Sodium (Na), (MG/L):	7,000	
Sulfate (SO ₄), (MG/L):	2,000	
Zinc (Zn), (UG/L):	20	
Alkalinity		
As Calcium Carbonate, (MG/L):	610	
As Bicarbonate, (MG/L):	744	
Hardness		
Noncarbonate, (MG/L):	1,900	
Total, (MG/L):	2,500	
Specific conductance (Micromohs):	33,500	
Total dissolved solids (TDS), (MG/L):	21,500	
pH, Field	7.0	
Discharge (gpm):	5	
Temperature (°C):	46	

Remarks: Located at 0281 164 Road in Glenwood Springs

Taken from James K. Barrett and Richard Howard Pearl, HYDROGEOLOGICAL DATA OF THERMAL SPRINGS AND WELLS IN COLORADO, Colorado Geological Survey, 1976.

Table 2. Chemical Analysis of Glenwood Springs Geothermal Water

Date:	8/29/83	
Laboratory No.	C/1653	
Origin of Sample	<u>Glenwood Yard - Geothermal Spring</u>	
Normal Carbonate Alkalinity as CaCO ₃	None	ppm
Bicarbonate Alkalinity as CaCO ₃	310	ppm
Chlorides (Cl)	2,267	ppm
Sulfates (SO ₄)	444	ppm
pH (Above 7.0 Alkaline; Below 7.0 Acid)	6.9	
Total Solids	-	
Organic Matter	-	
Resistivity (ohm - cm)	900	
CR No.	-	

Table 3. Metals Tested

Description	C	Mn	S	P	Si	Cr	Ni	Cu	Mo	Al	Fe	N	Other	Spec. ¹ Type	Supp- ² lier
Nicloy 400	0.12	1.24	0.001	0.0013	0.26	0.04	65.22	31.62	0.01	0.10				LSP	1
Nicloy 400	0.09	1.08	0.001	0.001	0.11	0.03	65.67	31.51	0.01	0.093				LSP	1
Inconel 625 ³						21.5	61		9		2.5		3.6Nb/Ta	LSPW	2
Incoloy 825 ³						21	42							LSPW	2
HAI G ³						22	44	2	6.5		19		2.1Nb/Ta	WU	2
904L ³	0.02					21	25	1.5	4.7		ba1			SWU	2
Hastelloy C276 ³						15	60		16		4.7		4W	LSP	3
Ferrallium 255 ³						26	5.5	1.7	3		ba1			LP	3
Sea-Cure	0.021	0.32	0.001	0.025	0.28	27.08	1.22	0.13	3.38	-	ba1	0.021	0.52 Ti	P	4
VDM	0.010	1.70	0.004	0.021	0.35	22.35	5.45	-	2.76	-	ba1	0.13		P	4
317L4	0.013	1.75	0.005	0.016	0.30	18.20	16.30	0.16	4.06	-	ba1	0.14		P	4
254SMO	0.014	0.049	0.006	0.023	0.37	20.00	17.80	0.78	6.13	-	ba1	0.21		P	4
1925HMO	0.015	1.31	0.010	0.018	0.27	24.85	20.55	1.67	5.90	-	ba1	0.15		P	4
AL 29-4C	0.021	0.81	0.002	0.026	0.38	28.89	0.40	0.11	3.84	0.05	ba1	0.02	0.62 Ti	P	5
Carbon Steel ³	0.20													LSP	

Notes

1. Specimen types: L = Large diameter pipe section (-3" dia. x 6" length)
 S = Small diameter tube section (-2" dia. x 6" length)
 P = Plain coupon
 W = Welded Coupon

U = U-bend stress corrosion specimen

2. See Table 5.

3. Nominal Composition

Table 4. Coatings Tested

Coating/Lining	Description	Spec. Type ¹	Supplier ²
CR - 68H glass	Glass Coating	L	6
Thick PPL Lining	Polypropylene lining	LSP	7
PPL Coating	Polypropylene	LS	8
Kynar Coating	Polyvinylidene Fluoride (PVDF)	LS	8
Teflon Coating	Polytetrafluoroethylene (PTFE)	LS	8
Si 14E Coating	Polyphenolformaldehyde	LS	9
TK 2 Coating	epoxy	LSP	10
TK 69 Coating	epoxy	LSP	10
TK 75 Coating	epoxy	LSP	10
TK 77 Coating	epoxy	LSP	10

Notes

1. See Table 5.

2. Specimen Types: L = Large diameter pipe section (~3" dia. x 6" length)
 S = Small diameter pipe section (~3" dia. x 6" length)
 P = Plain coupons

Table 5. Suppliers of Test Materials

Ref. No.	Company	Materials Supplied
1.	Babcock and Wilcox, Tubular Products Division, Beaver Falls, PA.	Nicloy 400
2.	Huntingdon Alloys, Huntingdon, WV.	Inconel 625 Incoloy 825 HAIG 904L
3.	Cabot Corporation, Kokomo, IN.	Hastelloy C276 Ferralium 255
4.	Colt Industries, Crucible Research Center, Pittsburg, PA.	SEA-CURE VDM 317L4 254SMO 1925HMO
5.	Allegheny Ludlum Industries Research Center, Allentown, PA.	AL 29-4C
6.	The Ceramic Coating Company, Newport, KY.	CR-68H glass coating
7.	Dow Chemical Company, Denver, CO.	Heavy Polypropylene lining
8.	Fluorolined Systems, Inc., Saint Charles, Missouri.	PPL coating Kynar coating Teflon coating
9.	Heresite - Saekaphen, Manitowoc, WI.	Si 14E polyphenolformaldehyd coating
10.	AMF Tubescope, Houston, Texas.	TK 2, TK 69, TK 75, TK 77 epoxy coatings

Table 6. Results of Corrosion Tests on Corrosion Resistant Alloys

Spec. No.	Material	Area (cm ²)	Initial Weight (g)	Final Weight (g)	Exposure (Days)	Corr. Rate (mpy ¹)	Appearance ²
1.	C-Steel	27.06	17.3344	16.7494	94	4.186	R
2.	C-Steel	26.38	18.7819	18.3147	94	3.429	R
3.	Nicloy	22.30	36.3015	36.2912	94	0.089	N
4.	Nicloy	20.43	26.5437	26.5283	94	0.146	N
5.	IN 625	118.91	338.58	338.59	94	-0.02	N
6.	IN 625	110.11	319.19	319.18	94	0.02	N
7.	IN 825	120.77	347.51	347.53	94	-0.03	N
8.	IN 825	113.34	322.64	322.64	94	0	N
9.	HAI G	109.66	336.57	336.60	94	-0.05	N
10.	HAI G	123.71	350.29	350.30	94	-0.02	N
11.	904L	118.65	336.23	336.23	94	0	N
12.	904L	111.48	328.57	328.52	94	0.09	N
13.	Hast C276	62.22	81.3436	81.3446	161	-0.002	N
14.	Hast C276	63.02	80.6150	80.6173	161	-0.004	N
15.	Hast C276	62.22	81.1874	81.1891	161	-0.003	N
16.	Ferr 255	69.88	79.7022	79.7028	161	-0.001	N
17.	Ferr 255	65.42	81.0832	81.0851	161	-0.003	N
18.	Ferr 255	65.77	82.3088	82.3100	161	-0.002	N
19.	Ferr 255	65.77	78.9483	78.9510	161	-0.005	N
20.	Sea-Cure	30.76	14.1696	14.1681	94	0.009	N
21.	Sea-Cure	30.34	15.1308	15.1302	94	0.004	N
22.	Sea-Cure	29.75	15.2615	15.2610	94	0.003	N

Tabel 6. (continued)

Spec. No.	Material	Area (cm ²)	Initial Weight (g)	Final Weight (g)	Exposure (Days)	Corr. Rate (mpy ¹)	Appearance ²
23.	VDM	31.02	33.7315	33.7305	161	0.004	N
24.	VDM	31.02	32.1405	31.1400	161	0.002	N
25.	VDM	32.06	33.7028	33.7010	161	0.006	N
26.	317L4	24.23	60.7471	60.7439	161	0.015	N
27.	317L4	35.38	62.2354	62.2333	161	0.007	N
28.	317L4	35.38	62.2874	62.2840	161	0.011	N
29.	317L4	35.32	62.2354	62.2838	161	-0.155	N
30.	254SMO	29.50	21.6613	21.6600	161	0.005	N
31.	254SMO	31.54	21.0488	21.0479	161	0.003	N
32.	254SMO	30.52	21.3277	21.3262	161	0.006	N
33.	1925HMO	31.29	33.0628	33.0621	161	0.003	N
34.	1925HMO	33.10	32.7341	32.7357	161	-0.006	N
35.	1925HMO	32.32	33.0655	33.0651	161	-0.001	N
36.	A1 29-4C	57.29	14.7726	14.7724	161	0.000	N
37.	A1 29-4C	59.97	14.8342	14.8337	161	0.001	N
38.	A1 29-4C	58.05	14.6619	14.6625	161	-0.001	N
39.	A1 29-4C	58.05	14.8792	14.8789	161	0.001	N

Notes

1. mpy = mils per year (0.001 inch per year)
2. R = Rusted
N = No corrosion damage detectable