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CORROSION REFERENCE FOR GEOTHERMAL
DOWNHOLE MATERIALS SELECTION

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March 1983

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Radian Corporation
Austin, Texas

U. S. DEPARTMENT OF ENERGY
Geothermal Energy

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Austin, Texas

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1.0 INTRODUCTION

This reference was prepared by Radian Corporation for the United States Department of Energy under DOE Contract No. DE-AC03-81SF11503. It includes a review of geothermal downhole conditions that may affect the performance and reliability of selected materials and components used in the drilling, completion, logging, and production of geothermal wells. It also discusses the results of specific research and development efforts aimed at improvement of materials and components for downhole contact with the hostile physicochemical conditions of the geothermal reservoir.

1.1 Background

Because of the many uncertainties associated with the development of geothermal energy and the relatively small size of the current geothermal market, the private sector has viewed this technology as a high-risk venture and has been reluctant to support extensive materials research and development. To reduce these risks and stimulate industrialization, the Department of Energy has taken the lead role in administering research, development, and demonstration programs for high-risk, high-payoff projects under the Geothermal Energy Program. An important part of DOE's geothermal program is to develop economically feasible solutions to technical problems which may arise during the various activities involved in exploitation of a geothermal resource.

Exploitation requires that very large quantities of potentially corrosive fluids, containing up to 300,000 ppm of total dissolved solids (TDS) and acid gases (hydrogen sulfide and carbon dioxide), must be produced cost-effectively and disposed of safely. Most materials problems are a result of a combination of these conditions which must be taken into consideration when selecting materials and components for downhole applications.

A key consideration in solving these problems is the reliability of materials and components used downhole during drilling, completion and logging of geothermal wells, and downhole equipment used during long term production and disposal of geothermal fluids. Such reliability will significantly affect the reduction of the cost of geothermal wells and will aid in the private sector acceptance of geothermal energy as a cost-effective and reliable energy source.

1.2 Purpose

The selection of materials and components which can withstand the harsh environment sometimes found downhole in geothermal wells is technologically and economically complex. This reference is a collective and interpretive summary of existing data on the performance of materials and components in actual or simulated downhole geothermal conditions. The use of this reference will enable those responsible for various activities involved during the life of a geothermal well to benefit from the knowledge gained from extensive research efforts in these areas. The information may alleviate additional lengthy testing of materials at each new geothermal site. It provides help in the screening of potential well construction materials and components used in downhole equipment that may be affected by the geothermal environment.

1.3 Scope

This reference presents a discussion of the performance of materials and components used in downhole applications, with regard to the effects of corrosion, thermal degradation, and physical/mechanical properties problems caused by the geothermal environment. Discussion is limited primarily to materials and components developed and tested during specific research efforts, many of which have been government-sponsored.

The terms "materials" and "components" in this reference include equipment used over the entire lifetime of a well, as well as equipment that may be used over relatively short periods of time or intermittently. Long-

term equipment includes casing, cement, and downhole production equipment. Short-term equipment includes equipment used during actual drilling and completion operations as well as during logging and evaluation of the resource. Only equipment which contacts the chemical environment of the geothermal well is considered.

For both long-term and intermittent use, limitations for current and proposed downhole equipment technology are defined from a materials perspective. Conclusions are based upon results of current research and may aid in the identification of areas where available well technology is still deficient.

Geothermal resources include hydrothermal (liquid- and steam-dominated), geopressured, and hot dry rock resources. In the U.S. some of these resources have been designated as known geothermal resource areas (KGRA's).

Materials performance considerations based upon results of this generic research have applications to all of these resources. However, since the possible commercialization of geopressured and hot dry rock resources is still being investigated, use of this information will be most beneficial for application to liquid- and steam-dominated hydrothermal resources. These resources are currently being exploited commercially for thermal energy recovery and electrical power generation.

This reference considers only materials for downhole use. For a discussion of materials used in surface equipment, from the production well-head through surface components of the disposal system, the reader is referred to Materials Selection Guidelines for Geothermal Energy Utilization Systems [Ellis and Conover 1981].

This reference does not include a detailed technical description of the various activities involved in drilling, completion, logging, and production of a geothermal well. It is not a review of current downhole technology

as used in the oil and gas industry, although materials problems and research efforts discussed do point out the limitations of direct transfer of such technology to the geothermal environment. Economic assessment is also considered beyond the scope of this document.

1.4 Overview

Section 2 identifies the downhole conditions that materials and equipment components encounter in the geothermal environment. The problem of reliability of materials used downhole is a very complex issue, and may be a result of not only operations dictated by the physical nature of the formation being drilled but also the chemical composition of the resource fluids and gases encountered.

Sections 3 through 9 present specific materials-related problems with components used downhole and both detailed and summarized results of research efforts to develop materials and components. Because of the difficulty in presenting a concise description of problems and research for specific materials of construction, these sections are generally divided according to equipment components used downhole. The only exceptions to this method of presentation are Section 4 for stainless steels and non-ferrous metals, used for a variety of high temperature downhole applications, and Section 6 for elastomeric materials, which have a wide variety of applications as sealing and protective elements in several component areas. The other sections are as follows: (3) tubular goods, (5) cements, (7) drilling and completion tools, (8) logging tools, and (9) downhole pumps.

Each of the sections 2 through 9 is preceded by a brief summary. The summaries, which usually consist mainly of tables of results and conclusions, contain no in-depth discussions, but are intended as overviews of section material. The reader is referred to the sections for caveats, qualifications and references cited for material presented in the summaries.

1.5 References

Ellis, P. F., and Conover, M. F., 1981. Materials Selection Guidelines for Geothermal Energy Utilization Systems. DOE Contract AC02-79ET27026, NTIS Pub Code DOE/RA/27026-1. Radian Corporation, Austin, TX, January.

SUMMARY

This summary is a quick reference to the material discussed in Section 2. Please refer to the Section for caveats, qualifications, and references cited for the data presented here.

The physical and chemical characteristics of geothermal producing formations are different from those typically encountered in oil or gas wells. And the corrosive chemistry of high-temperature liquid-dominated geothermal formations is significantly different from the corrosive chemistry of the produced fields from these formations.

The temperature of a geothermal response can range to nearly 700°F. Of the identified geothermal resources in the United States with temperatures $\geq 250^\circ\text{F}$, ten percent have an estimated reservoir temperature $\geq 376^\circ \pm 27^\circ\text{F}$. Two of these resources, the Salton Sea KGRA and the Geysers, CA, have reservoir temperatures $\geq 550^\circ \pm 27^\circ\text{F}$.

Pressures of most liquid- or steam-dominated geothermal formations are generally hydrostatic or less, but some Gulf coast formations are geopressured.

Geothermal reservoir rocks range from sedimentary to igneous. Some formations are hard, abrasive, and highly fractured.

Most corrosion in geothermal environments is caused by seven key corrosive species:

- o oxygen (from atmospheric contamination),
- o hydrogen ion,
- o carbon dioxide species,
- o hydrogen sulfide species,

- o ammonia species,
- o chloride ion, and
- o sulfate ion.

Distributions of these species in vapor-dominated and liquid-dominated resources are summarized in Table 2.0-1. This table represents sources for which data was available.

When the fluid from a high-temperature liquid-dominated resource is produced by lowering the pressure (flashing), much of the carbon dioxide, hydrogen sulfide, and ammonia partition into the steam phase. Therefore, the unflashed fluid has significant carbon dioxide fugacity (0.9 - 160 psia) and a pH about 2.6 units lower than that of the separated fluid.

Because there is such diversity of geothermal resource chemistry and a great range of temperatures, a corrosivity classification system was developed during a previous effort. The system was based on the weight sum in ppm of the key corrosive species, resource phase domination, plant inlet temperature, and above-ground corrosion of carbon steel. Though the classification system was developed and intended for above-ground use, and though the quantitative corrosion downhole may be significantly different, the system may well serve as a provisional classification system for downhole corrosivity trends. The six classes of the system are described in Tables 2.2-5 through 2.2-11.

INTRODUCTION

Although most geothermal well technology is based on technology developed by the petroleum industry, the equipment used in the geothermal well may be subjected to more adverse downhole conditions. The reliability and performance of well materials now in use is affected by various physical resource characteristics unique to geothermal formations, as well as by the specific corrosive nature of the geothermal fluid encountered. Materials-

TABLE 2.0-1. RANGES OF CORROSIVE SPECIES CONCENTRATIONS IN SELECTED GEOTHERMAL RESOURCES

Parameter	High-Temperature Vapor-dominated Resource	High-Temperature Liquid-dominated Resource (Unflashed)	Low-Temperature Resource
pH		2.0 - 10.2	6.7 - 10.25
Carbon Dioxide (ppm)	290-200,000	47 - 25,500	12 - 600
Hydrogen Sulfide (ppm)	5-1600	2 - 625	0.03 - >5
Chloride (ppm)	0.1 - 20	18 - 155,000	8 - 530
Ammonia (ppm)	9 - 1660	0.02 - 410	0.4 - 0.7
Sulfate (ppm)	trace-25	8 - 335	2 - 2340

Note: ppm by weight in all cases.

related problems in the geothermal environment result from a complex interaction between these downhole conditions and the materials commercially available for use in the well.

In Section 2.1, the physical characteristics of geothermal resources are briefly discussed. Section 2.2 presents a more detailed discussion of the factors which control the corrosive nature of the geothermal fluid and the effects of these factors.

2.1 Physical Characteristics of Geothermal Resources

The physical characteristics of geothermal producing formations are different from those typically encountered in oil and gas wells. Downhole temperatures, ranging to nearly 700°F, are higher than in similar depth oil and gas wells. Table 2.1-1 indicates reservoir temperatures and well depths for 33 high temperature geothermal resources worldwide. Figure 2.1-1 illustrates the temperature and energy distribution of U.S. geothermal resources with temperatures greater than or equal to 250°F. Of the 248 identified U.S. geothermal resources with temperatures greater than or equal to 250°F, 10 percent have an estimated reservoir temperature of at least 376°±27°F and estimated heat content of 663 Quads (quadrillion Btu's). One percent of the resources have an estimated resource temperature of at least 550°±27°F. Only two such resources have been identified in the U.S., the Salton Sea KGRA and the Geysers, California. The resources with temperatures between 250°F and 376°±27°F have an estimated heat content of 1446 Quads.

Geothermal reservoir rocks range from sedimentary, as normally found in petroleum exploration, to igneous. Some formations are hard, abrasive, and highly fractured formations. Formations are generally underpressured (hydrostatic or less), except for geopressured formations where reservoir pressures are greater than hydrostatic pressures. Table 2.1-2 illustrates general reservoir characteristics for several KGRAs in the U.S. A summary of general well materials problems related to the physical characteristics of geothermal resources is shown in Table 2.1-3. A more detailed description of these problems and research efforts attempting to solve them is discussed in Sections 3 through 9.

Figure 2.1-la. Temperature Distribution of 248 Identified U.S. Geothermal Resources with Temperatures $\geq 250^{\circ}\text{F}$ [Data drawn from White and Williams 1975]

Figure 2.1-lb. Energy Distribution of 248 Identified U.S. Geothermal Resources with Temperature $\geq 250^{\circ}\text{F}$ [Data drawn from White and Williams 1975]

TABLE 2.1-1. RESERVOIR TEMPERATURES AND WELL DEPTHS OF THIRTY-THREE HIGH-TEMPERATURE GEOTHERMAL RESOURCES

Resource	Reservoir Temperature (°F) ^a		Well Depth (ft.)	
	Avg.	Max.	Avg.	Max.
Chile				
El Tatio	446	509	3,300	6,000
El Salvador				
Ahuachapun ^b	446	509	3,300	4,600
Berlin	--	520	--	5,900
Iceland				
Krafla ^b	536	572	6,150	7,300
Namafjall ^b	482	536	3,300	4,600
Hveragerdi ^b	420	--	2,130	--
Svartsengi ^b	455	--	--	--
Indonesia				
Kawah Kamojong	428	460	2,150	2,500
Italy				
Campi Flegrei	--	--	--	6,050
Larderello ^b	383	464	2,150	14,000
Monte Amiata ^b	311	374	2,550	4,900
Japan				
Hatchobaru ^b	482	572	1,650	2,650
Matsukawa ^b	428	536	3,300	4,900
Onikope	446	550	3,300	4,450
Otake ^b	446	482	1,650	4,900
Kenya				
Olkaria	--	572	--	5,400
Mexico				
Cerro Prieto ^b	572	698	4,250	8,650
New Zealand				
Broadlands ^b	491	472	3,600	7,950
Kawerau	482	545	2,600	4,100
Wairakei ^b	446	518	2,650	7,550
Philippines				
Makiling Banahaw	--	563	--	--
Tiwi	482	--	3,100	7,550
Taiwan				
Tatun	--	559	--	4,900
Turkey				
Kizildere	374	428	2,300	3,300
United States				
Baca ^b	464	625	7,000	9,000
Brady Hot Springs ^b	338	415	--	6,900
Casa Diablo ^b	333	360	750	1,100
East Mesa ^b	353	399	7,350	9,200
Heber ^b	356	374	--	10,800
Raft River ^b	297	298	--	5,900
Salton Sea ^b	619	680	5,500	8,100
The Geysers ^b	482	545	4,900	10,200
Soviet Union				
Pauzhetsk	365	392	--	2,650

--no data available

^aThe mean difference between the average and maximum temperatures is 25°- 121°F (95% confidence interval)

^bAbove-ground corrosion data presented in Ellis and Conover 1981

Sources: Ellis and Mahon 1976; DiPippo 1980; Ellis and Conover 1981; White and Williams 1975; Cosner and Apps 1978

TABLE 2.1-2. RESERVOIR CHARACTERISTICS OF TYPICAL U.S. KGRAs

KGRA	Reservoir Type	Fluid Pressure	Primary Reservoir Rock	Average Reservoir Temperature (°F)	Reservoir Depths (ft)	Porosity and Permeability
Fenton Hill, NM	Hot Dry Rock	n.a.	Granitic	392	6,600-13,200	Hydraulic Fracturing Required
The Geysers, CA	Steam-dominated	Abnormally Low	Metagraywacke	482	6,600-13,200	Fractures
Gulf Coast, TX & LA	Geopressured	Abnormally High	Sandstone	350	10,000-15,000	Intragranular
Imperial Valley, CA	Liquid-dominated	Hydrostatic	Sandstone and Metasediments	356-698	3,300-6,600	Intergranular and Fractures
Roosevelt Hot Springs, UT	Liquid-dominated	Hydrostatic	Granitic	536	6,600-9,900	Fractures
Valles Caldera, NM	Liquid-dominated	Under Hydrostatic	Extrusive Igneous Tuff and Andesite	482	6,600-9,900	Fractures

n.a. - not applicable

Source: Varnado 1979

TABLE 2.1-3. GEOTHERMAL WELL MATERIALS PROBLEMS

Technology Area	Resource Type	
	Sedimentary	Hard Igneous
	Liquid-Dominated	Liquid and Vapor-Dominated
Cements	A, B, C	A, B, C
Tubulars	A, B, C, D	A, B, C, D, E, F
Drilling and completion tools (bits, downhole motors, etc.)	A, B	A, B, E
Logging equipment	A, B	A, B
Downhole pumping equipment	A, B	not used

Problem Key

- A - Degradation of performance due to temperature effects on elastomers, metals, cements, and electrical insulation and components.
- B - Corrosion or degradation of materials due to exposure to geothermal fluids and acid gases.
- C - Corrosion or degradation of materials due to the exposure to groundwater.
- D - Corrosion of materials due to gas entrainment in drilling fluid.
- E - Wear of materials and physical/mechanical properties problems due to hard, abrasive or fractured formations.
- F - Erosion of materials due to drilling with air.

2.2 Chemical Characteristics of Geothermal Resources

2.2.1 The Key Corrosive Chemical Species

During development of Material Selection Guidelines for Geothermal Power Systems [DeBerry, Ellis, and Thomas 1978] and subsequently of Material Selection Guidelines for Geothermal Energy Utilization Systems [Ellis and Conover 1981], it became evident that most of the corrosion in geothermal environments is controlled by the following seven principal key corrosive chemical species:

- o oxygen,
- o hydrogen ion (pH),
- o carbon dioxide species,
- o hydrogen sulfide species,
- o ammonia species,
- o chloride ion, and
- o sulfate ion.

Oxygen does not normally occur in geothermal reservoir fluids, but is introduced by atmospheric contamination. Other species such as mercury, copper, lead, arsenic, and possibly other heavy metal ions may also be significant in special cases.

The effects of the key corrosive species on materials are discussed exhaustively in Ellis and Conover [1981] and that discussion will not be repeated here. Table 2.2-1 identifies the principal effects of the key corrosive species on cements and the alloys likely to be used in geothermal down-hole operations.

TABLE 2.2-1. PRINCIPAL EFFECTS OF THE KEY CORROSIVE SPECIES

Key Corrosive Species	Principal Effects
Oxygen	<ul style="list-style-type: none"> o Extremely corrosive to carbon and low alloy steels. 30 ppb* shown to cause four-fold increase in carbon steel corrosion rate. o Concentrations above 50 ppb cause serious pitting. o 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.
Hydrogen ion (pH)	<ul style="list-style-type: none"> o Primary cathodic reaction of steel corrosion in air-free brine is hydrogen ion reduction. Corrosion rate decreases sharply above pH 8. o 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. o Low pH may cause breakdown of passivity of stainless steels. o Acid attack on cements.
Carbon dioxide Species (dissolved carbon dioxide, bicarbonate ion, carbonate ion)	<ul style="list-style-type: none"> o Dissolved carbon dioxide lowers pH, increasing carbon and HSLA steel corrosion. o Dissolved carbon dioxide provides alternative proton reduction pathway, further exacerbating carbon and HSLA steel corrosion. o May exacerbate SSC. o Strong link between total alkalinity and corrosion of steel in low temperature geothermal wells.
Hydrogen sulfide Species (hydrogen sulfide, bisulfide ion, sulfide ion)	<ul style="list-style-type: none"> o Potent cathodic poison, promoting SSC of HSLA steels and some other alloys coupled to steel. o Highly corrosive to alloys containing both copper and nickel in any proportions. o May cause a chloride-sulfide (active path)-SCC of nickel-based alloys at high temperature.
Ammonia Species (ammonia, ammonium ion)	<ul style="list-style-type: none"> o Causes SCC of some copper-based alloys.
Chloride ion	<ul style="list-style-type: none"> o Strong promoter of localized corrosion of carbon, HSLA, and stainless steels as well as of other alloys. o Chloride dependent threshold temperature for pitting and SCC. Different for each alloy. o Little if any effect on SSC. o Steel passivates at high temperature in pH 5, 6070 ppm chloride solution with carbon dioxide. 133,500 ppm chloride destroys passivity above 300°F
Sulfate ion	<ul style="list-style-type: none"> o Primary effect is corrosion of cements.

*Parts per billion

2.2.2 Variation in Geothermal Resource Chemistry

Geothermal resources show a tremendous range of chemistries. Table 2.2-2 illustrates the reported chemistries of four vapor-dominated geothermal resources. These resources produce dry steam containing about 290-200,000 ppm (wt) carbon dioxide and about 5-1600 ppm (wt) hydrogen sulfide. They produce only traces of chlorides. Because the resources are vapor-dominated, there is probably little difference between the compositions of the reservoir steam and the produced (wellhead) steam.

Tables 2.2-3a and 2.2-3b illustrate the range of chemistries of high temperature liquid-dominated resources. These tables give the key corrosive species chemistry of both the reservoir fluid and, in most cases, of separated fluid from the same resource. Table 2.2-3a shows that the chloride contents of the separated fluids range from 27 ppm to 155,000 ppm; some wells have even higher chloride concentrations.

Perhaps the most important fact shown by Tables 2.2-3a and 2.2-3b is the effect of flashing on geothermal fluid chemistry. The reservoir fluid of liquid-dominated geothermal resources is single-phase water. When the fluid is produced by dropping the pressure -- either in the wellbore, or above grade -- the superheated liquid flashes into two-phase fluid. Much of the dissolved carbon dioxide partitions into the steam phase along with most of the hydrogen sulfide and ammonia. This means that the pH of unflashed geothermal fluid is significantly lower than the pH of the separated fluid. A survey of eleven liquid-dominated high-temperature geothermal resources showed that complete degassing causes a pH rise of 2.6 ± 0.8 units (two sigma limits). In short, Tables 2.2-3a and 2.2-3b show that the reservoir fluid chemistries of liquid-dominated resources are significantly different from those indicated by the produced separated fluid. The major differences are lower pH -- about 2.6 units lower -- and significant carbon dioxide fugacity, 0.9 - 160 psia.

TABLE 2.2-2. CORROSIVE CHEMISTRY OF FOUR VAPOR-DOMINATED GEOTHERMAL RESOURCES

Parameter	Larderello Region Italy	Monte Amiata Region, Italy	Travale Region Italy	The Geysers, CA United States
Temperature - resource				
Range (°F)	285 - 464	280 - 374	387 - 516	-- - 545
Average (°F)	383	311	476	482
Noncondensable gases (total)				
Range (ppm wt)	30,000-44,000	--	--	1,200 - 34,1000
Average (ppm wt)	37,000	200,000	90,000	3,980
Carbon dioxide				
Range (ppm wt)	29,000 - 43,000	--	--	290 - 30,600
Average (ppm wt)	35,000	197,000	88,000	3,260
Hydrogen sulfide (total)				
Range (ppm wt)	630 - 990	--	--	5 - 1,600
Average (ppm wt)	910	1,290	1,000	222
Ammonia (total)				
Range (ppm wt)	--	--	--	9 - 1,660
Average (ppm wt)	--	--	--	194
Chloride				
Range (ppm wt)	0.5 - 20	0.1 - 0.3	0.3 - 1.0	1
Sulfate				
Range (ppm wt)	tr - 70	3 - 25	10 - 20	--
Arsenic (Total as As)				
Range (ppm wt)	0.007 - 0.24	0.003 - 0.014	0.05 - 0.20	0.002 - 0.050

-- data not available, tr = trace

Sources: Ellis and Conover 1981; DiPippo 1980; Ellis and Mahon 1977

TABLE 2.2-3a. CORROSIVE CHEMISTRIES OF UNFLASHED AND SEPARATED LIQUID FROM THIRTEEN HIGH-TEMPERATURE LIQUID-DOMINATED GEOTHERMAL RESOURCES--NONVOLATILE SPECIES

Resource	Separation Pressure (psia)	pH	Chloride (ppm)	Sulfate (ppm)	Corrosivity Class ^a	Additional Comments
Ahuachapan, El Salvador	Unflashed 81-93	-- 7.0	[8349] 9770	[36] 42	IV	Calculated by summation and/or proportion []
Baca, NM	Unflashed 150	-- 7.2	[2340] 3061	[49] 64	IV	
Brady Hot Springs, NV	Unflashed Ambient	-- 7.0	942 1,100	320 335	IV	
Broadlands, New Zealand	Unflashed Ambient	-- 8.3	1340 1743	8 10	IV	
Casa Diablo, CA	Unflashed --	6.5 --	227 --	96 --	IV	
Cerro Prieto, Mexico	Unflashed Ambient	5.3 7.9-8.2	9,040-11,400 10,100-16,100	9-27 10-18	III	
East Mesa, CA	Unflashed	6.5	555	170	IV	Well 16-29; Typical of resource Well 6-1 anomalous well Well 6-1 anomalous well
	Unflashed	5.5	15,850	43	III	
	Unknown	7.7	19,670	20	III	
El Tatio, Chile	Unflashed --	2.0 --	5600 --	-- --	II	Aquifer
Hveragerdi, Iceland	Unflashed Ambient	7.8 9.6	125 152	65 76	IV	
Namafjall, Iceland	Unflashed Ambient	7.5 10.2	18 27	38 56.3	IV	
Salton Sea, CA	Unflashed --	4.5 --	155,000 --	56 --	I	
Svartsengi, Iceland	Unflashed --	-- --	12,200 --	32 --	IV	
Wairakei, New Zealand	Unflashed Ambient	6.3 8.4	1520 2215	8 35	IV	Aquifer (Hole 20)

-- No data available

^aCorrosivity classes discussed in Section 2.2.3

Sources: Ellis and Mahon 1977; DeBerry, Ellis, and Thomas 1978; Cosner and Apps 1978; Helgeson 1968; McCright 1981; Vetter, Cambell, and Walker 1978; Union 1980; White and Williams 1975; Ellis and Conover 1981

TABLE 2.2-3b. CORROSIVE CHEMISTRIES OF UNFLASHED AND SEPARATED LIQUID FROM THIRTEEN HIGH-TEMPERATURE GEOTHERMAL RESOURCES--VOLATILE SPECIES

	Carbon Dioxide Species			Sulfide Species		Ammonia		Corrosivity Class
	PCO ₂ * (psia)	Total (ppm)	Ionized (ppm)	PH ₂ S* (ppm)	Total (ppm)	PNH ₃ * (psia)	Total (ppm)	
Ahuachapan, El Salvador	0.9	372-699	--	0.004	--	--	0.1	IV
	--	--	18	--	--	--	--	
Baca, NM	--	8830	--	--	65	--	--	IV
	--	--	107	--	2	--	--	
Brady Hot Springs, NV	--	47	41	--	3	--	0.02	IV
	--	73	--	--	--	--	--	
Broadlands, N.Z	160	25518	--	1.6	192	0.015	5-20	IV
	--	128	--	--	1	--	2.1	
Casa Diablo, CA	--	180	--	--	14	--	0.1	IV
	--	--	--	--	--	--	--	
Cerro Prieto, Mexico	100	1270-2608	20-28	2.9	310-624	--	--	III
	--	--	32-43	--	--	--	--	
East Mesa, CA	--	1085	463	--	--	--	--	IV
	--	--	148	--	3	--	41	III
	--	--	31	--	--	--	55	III
El Tatio, Chile	23	792	--	0.004	7	--	--	II
	--	--	--	--	--	--	--	
Hveragerdi, Iceland	2.0	176	--	0.073	30	--	--	IV
	--	48	--	--	8	--	--	
Namafjall, Iceland	--	62	--	--	107	--	--	IV
	--	18	--	--	40	--	--	
Salton Sea, CA	38	5000	--	--	16-35	--	409	I
	--	--	--	--	--	--	--	
Svartsengi, Iceland	--	298	--	--	4	--	--	IV
	--	--	--	--	--	--	--	
Wairakei, N.Z	15	363	16	0.3	9	0.0004	0.23	IV
	--	17	--	--	1.7	--	0.2	

-- No data available

* Calculated partial pressure for reservoir fluid

[] Calculated by summation and/or proportion

Sources: Ellis and Mahon 1977; DeBerry, Ellis, and Thomas 1978; Cosner and Apps 1978; Helgeson 1968; McCright 1981; Vetter, Cambell, and Walker 1978; Union 1980; White and Williams 1975; Ellis and Conover 1981

Table 2.2-4 shows the key corrosive species chemistry of 21 low-temperature geothermal resources. In this table, the "pH" column gives the reported fluid pH, while the "pHs" column gives the calcium carbonate saturation pH -- above which calcium carbonate can precipitate. It seems unlikely that the fluid in the reservoir would remain supersaturated with calcium carbonate; therefore, Table 2.2-4 indicates a significant loss of carbon dioxide. With the exception of the Marlin, Texas, resource, the sampling technique was not reported, but the pH rise shown in this table is consistent with that for samples shipped to a laboratory.

2.2.3 Geothermal Corrosivity Classification System

The data in Section 2.2.2 illustrates the great diversity of geothermal resource chemistry while Section 2.1 illustrates the great range of temperatures. To avoid having to deal with each resource, and perhaps each well, as a unique case, it is extremely desirable to group or classify the resources so that estimates of potential downhole problems can better be made. A corrosivity classification system was invented during a previous effort [Ellis and Conover 1981]. This system was based on the Total Key Species (weight sum in ppm of the key corrosive species)--total dissolved solids having been shown not to be a useful parameter--resource phase domination, plant inlet temperature, and corrosion of carbon steel above ground.

Table 2.2-3b showed that the downhole corrosive chemistry of high-temperature geothermal resources is significantly different from the corrosive chemistry of the produced fluid from those resources. Therefore, the corrosion resistance of carbon steel and other materials will be different--probably worse--downhole. However, the limited data available on tubular goods corrosion (Section 3.1.1) seems to indicate a qualitative correlation in corrosivity trends between downhole experience and the corrosivity classification system.

TABLE 2.2-4. CORROSIVE CHEMISTRY OF TWENTY-ONE LOW TEMPERATURE GEOTHERMAL SYSTEMS

	Temp. (°F)	pH	pHs ^a	Chloride (ppm)	Sulfate (ppm)	Carbon Dioxide (ionized) (ppm as CO ₂)	Hydrogen Sulfide (Total) (ppm as H ₂ S)	Ammonia (Total) (ppm)
<u>Iceland</u>								
Boholt	181	9.55	8.79	27	17	27	0.3	--
Dalvik	131	10.25	9.01	8	14	20	nd	--
Hunavellir	124	9.50	8.46	8	59	34	2.2	--
Husavik	176	9.55	7.89	10	28	41	1.0	--
Hrisey	145	9.30	8.04	342	42	12	nd	--
Hsammstangi	176	9.45	7.97	141	137	15	0.4	--
Mogilsa	144	7.90	7.80	28	49	97	1.5	--
Olafsfjordur	117	10.10	9.02	9	2	20	nd	--
Reykir	163	9.70	8.58	15	15	29	0.1	--
Reykjahlid	187	9.55	8.52	13	22	30	1.6	--
Saudar Krokur	167	9.85	7.31	19	41	21	0.5	--
Selfoss	180	8.75	7.65	245	51	30	<0.1	--
Seltjarnarnes	183	8.50	7.45	528	180	15	0.1	--
Storutjarnir	149	9.65	8.79	17	31	27	2.5	--
<u>United States</u>								
Diamond Ring Ranch, SD	147	6.90	6.30	185	1087	92	0.20	--
Edgemont, SD	135	7.60	6.60	225	315	145	0.02	--
Klamath Falls, OR	189	8.70	7.62	49	370	28	0.3	0.7
Marlin, TX	153	7.02	7.30	93	2340	125	0.13	--
Pagosa Springs, CO	140	6.70	5.78	160	1520	594	>5	--
Philip, SD	160	7.20	6.43	21	633	117	0.03	--
Susanville, CA	170	8.50	8.4	120	325	13	0.5	0.4

-- = no data available

nd = not detected

^apH above which calcium carbonate precipitates at the resource temperature (calculated by Radian).

Sources: Howard, Carda, and Cieslewicz 1980; Ellis 1980; Radian unpublished data; Ellis and Anliker 1981; Ellis and Pearsall 1981; Ellis and Conover 1981

For example, resources defined as Class IV in that system show minor metal-loss corrosion of carbon steel in separated water. Casing experience from two resources in that class also indicate that metal loss corrosion is rarely a problem. Class III resources have more severe above ground corrosion of carbon steel, and some casing failures due to metal loss have been reported in wells tapping a Class III resource. The produced separated waters of Class I resources cause severe localized corrosion of carbon steel, while downhole experience indicates casing life of less than four years due to metal loss corrosion.

Thus, though the Corrosivity Classification System was developed and intended for above-ground use, and though the quantitative corrosion behavior downhole may be significantly different, the system may well serve as a provisional classification system for trends in downhole corrosivity as well.

Because of the tentative qualitative correlation between trends in above-ground and downhole corrosivity, reference to the Geothermal Corrosivity Classification System is made a number of times in Sections 3 and 4. Tables 2.2-5 through 2.2-11 present an updated version of the system. Defining parameters are those found at the wellhead. Resource temperatures of the reference sites have been added.

TABLE 2.2-5. GEOTHERMAL RESOURCE CORROSIVITY CLASS I

Defining parameters:

Resource type	Liquid-dominated
Total key species (TKS) ^a	Greater than 100,000 ppm
Chloride fraction in TKS	99 percent
pH (unflashed fluid)	Less than 5
pH (flashed fluid)	5 - 6
Vol. gas in steam	Less than 2.5%
Plant inlet temperature	Greater than 390°F

Sites Reviewed^b

USA - Salton Sea, CA (619°F)^c

Observed Corrosion of Carbon Steel:

- o In nonaerated, separated fluid, the uniform rate exceeds 50 mpy at 390°F but may decrease to about 15 mpy at 300°F. Serious localized corrosion.
 - o In separated nonaerated steam, the corrosion rate is 10 to 50 mpy with serious pitting. Scrubbing steam does not reduce corrosion rate.
-

General Performance of Other Alloys:

- o T316 stainless steel susceptible to pitting, crevice corrosion, and stress corrosion cracking.
-

^aTotal chloride + sulfate + carbon dioxide species + sulfide species + ammonia species in separated fluid.

^bIn Ellis and Conover 1981.

^cAverage resource temperature.

TABLE 2.2-6. GEOTHERMAL RESOURCE CORROSIVITY CLASS II

Defining parameters:

Resource type	Liquid-dominated
Total key species (TKS) ^a	1000 to 10,000 ppm
Chloride fraction in TKS	Not established
pH (unflashed fluid)	Much less than 4.5
pH (flashed fluid)	Less than 4.5
Vol. gas in steam	Not established
Plant inlet temperature	250° to 350°F

Sites Reviewed^b

Japan - Matsukawa^c (428°F)^d

Corrosion of Carbon Steel:

- o On basis of pH, the corrosion rate in nonaerated separated fluid should exceed 50 mpy. No test data available.
- o Corrosion rate in separated nonaerated steam is 20 to 25 mpy with crevice corrosion.

^aTotal chloride + sulfate + carbon dioxide species + sulfide species + ammonia species in separated fluid.

^bIn Conover and Ellis 1981.

^cAfter its classification as a Class II resource, the Matsukawa resource dried out and now produces dry steam, Class VI.

^dAverage resource temperature.

TABLE 2.2-7. GEOTHERMAL RESOURCE CORROSIVITY CLASS III

Defining parameters:

Resource type	Liquid-dominated
Total key species (TKS) ^a	10,000 to 20,000 ppm
Chloride fraction in TKS	45 to 99 percent
pH (unflashed fluid)	5 to 6
pH (flashed fluid)	Greater than 6
Vol. gas in steam	Not established
Plant inlet temperature	300° to 375°F

Sites Reviewed^b

Mexico - Cerro Prieto (572°F)^c
 U.S.A. - East Mesa (6-1)^d, CA (353°F)

Corrosion of Carbon Steel:

- o In nonaerated separated fluid, the uniform corrosion rate is typically 5-10 mpy at temperatures of 300 to 375°F. Some localized attack occurs.
- o Steam separated with <0.01% moisture is equivalent to Class VI.

General Performance of Other Alloys:

- o Type 316 stainless steel is susceptible to pitting and stress corrosion cracking in liquid streams.
- o High strength low alloy (HSLA) steels are susceptible to sulfide stress cracking.
- o Monel 400 and cupronickels are unsatisfactory.

^aTotal chloride + sulfate + carbon dioxide species + sulfide species + ammonia species in separated fluid.

^bIn Ellis and Conover 1981

^cAverage resource temperature

^dEast Mesa Well 6-1 is an anomalous well

TABLE 2.2-8. GEOTHERMAL RESOURCE CORROSIVITY CLASS IV

Defining parameters:

Resource type	Liquid-dominated
Total key species (TKS) ^a	500 to 10,000 ppm
Chloride fraction in TKS	45 to 99 percent
pH (unflashed fluid)	Greater than or equal to 5
pH (flashed fluid)	Greater than 6
Vol. gas in stream	Less than 2.5 percent
Plant inlet temperature	250° to 390°F

Sites Reviewed^b

El Salvador - Ahuachapan (446°F) ^c	New Zealand - Wairakei (446°F)
Iceland - HTA (four sites) (420° - 536°F) ^d	U.S.A. - Baca, NM (464°F)
Japan - Hatchobaru (482°F)	U.S.A. - Brady, N.S., NV (338°F)
Japan - Otake (446°F)	U.S.A. - Heber, CA (356°F)
New Zealand - Broadlands (491°F)	U.S.A. - Raft River, ID (279°F)

Corrosion of Carbon Steel:

- o In nonaerated separated fluid at 250° to 390°F, uniform corrosion rates are typically less than 5 mpy with minor pitting.
- o High strength low-alloy steels are susceptible to sulfide stress cracking.
- o Steam separated with <0.01% moisture is equivalent to Class VI.

General Performance of Other Alloys:

- o Type 316 stainless steel is susceptible to stress corrosion cracking in aerated fluid.
- o Corrosion-fatigue of 12 Cr turbine blades by geothermal steam is twice as severe as corrosion-fatigue by boiler quality steam.

^aTotal chloride + sulfate + carbon dioxide species + sulfide species + ammonia in separated fluid.

^bIn Ellis and Conover 1981.

^cAverage resource temperature.

^dRange of average temperatures.

TABLE 2.2-9. GEOTHERMAL RESOURCE CORROSIVITY CLASS VA

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	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)^b
 Pagosa Springs, CO^c
 Marlin, TX^c

Corrosion of Carbon Steel:

- o In nonaerated 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.
- o One of none tests showed no pitting, others showed severe pitting as high as 83 mpy.
- o Aeration may cause a 4- to 15-fold increase in weight-loss corrosion as pitting.

General Performance of Other Alloys:

- o In nonaerated 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.
- o Type 316 stainless steel is resistant to uniform corrosion, pitting and crevice corrosion, and stress corrosion cracking in many applications.

^aTotal chloride + sulfate + carbon dioxide species + sulfide species + ammonia species in produced fluid.

^bIn Ellis and Conover 1981.

^cIn Ellis 1981.

TABLE 2.2-10. GEOTHERMAL RESOURCE 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

Iceland (15 sites)^b
 U.S.A. - Klamath Falls, OR (5 wells)^c

Corrosion of Carbon Steel:

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

General Performance of Other Alloys:

- o In nonaerated 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.
- o Type 316 stainless steel is resistant to uniform corrosion, pitting and crevice corrosion, and stress corrosion cracking in many applications.

^aTotal chloride + sulfate + carbon dioxide species + sulfide species + ammonia species in produced fluid.

^bIn Ellis and Conover 1981.

^cIn Ellis 1982.

TABLE 2.2-11. GEOTHERMAL RESOURCE CORROSIVITY CLASS VI

Defining parameters:

Resource type	Vapor-dominated
Noncondensable gas (Vol. percent)	Less than 5
Chloride	Less than 1 ppm (wt)
Plant inlet temperature	320° to 360°F

Sites Reviewed

Italy - Boraciferous Region (10 sites) (350°F)^b
 U.S.A. - The Geysers, CA (482°F)

Corrosion of Carbon Steel:

- o Less than 5 mpy uniform corrosion common.
- o Carbon steel is widely used.
- o Aeration of steam or steam condensate causes severe corrosion.

General Performance of Other Alloys:

- o Type 316 stainless steel susceptible to stress corrosion cracking in aerated moist steam.
- o Type 316 stainless steel and lead coated steel used in aerated condensate without hydrogen sulfide abatement chemicals. Hydrogen sulfide abatement chemicals increase corrosiveness of condensate.
- o Geothermal steam causes more severe corrosion-fatigue of 12Cr turbine blades than does boiler quality steam.

^aIn Ellis and Conover 1981.

^bAverage reservoir temperature.

2.3 References

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SUMMARY

This summary is a quick reference to the material presented in Chapter 3. Please refer to the section for caveats, qualifications, and references cited for the material presented here.

Well casing problems have historically resulted from thermal stress, Sulfide Stress Cracking (SSC), cementing inadequacies, and internal or external corrosion of the casing. The main problems with drillstem have been wear and erosion, localized corrosion, and corrosion-fatigue resulting in twist-offs.

The need for low-strength steels to resist Sulfide Stress Cracking conflicts directly with the need for high strength to resist thermal stress. There is therefore a need for high hot toughness steels with high yield strength, resistance to SSC, and increased resistance to localized corrosion.

Fortunately, the same metallurgical features which lead to improved resistance to SSC in casing also lead to improved toughness and resistance to corrosion fatigue. Microstructure affects the SSC-resistance of steels with the same hardness; composition is significant only as it affects hardening and microstructure. The most SSC-resistant microstructures consist of fine spheroidized carbides uniformly dispersed in ferrite. These result from the tempering of martensite at high temperatures. Minor alloying can significantly improve localized corrosion resistance. A summary of material selection suggestions for casing and drillstem in the various resource classes is given as Table 3.0-1.

An amine-based corrosion inhibitor has been developed for the geothermal air drilling environment at one installation. Use of the inhibitor, along with maintenance of pH 9.5-11, reduced the metal-loss rate of the drill pipe by 92%.

TABLE 3.0-1. CASING AND DRILLSTEM MATERIALS SELECTION SUMMARY

Application	Cautions and Constraints	Materials Selection Suggestions
Resource Class I <u>Casing</u>	<ul style="list-style-type: none"> Continuous complete cementing with corrosion-resistant cement required to prevent external corrosion by groundwaters and thermal buckling. Subject to sulfide stress cracking (SSC) during "killed" periods. Risk of thermal stress failure as result of low strength requirements for SSC resistance vs. large thermal cycle of normal operations. Severe to catastrophic corrosion of API J-55 grade casing. 	<ul style="list-style-type: none"> Common API casing grades are a poor risk in this resource class. Composition controlled (AISI and ASTM) steels superior to property controlled (API) grades for both SSC and metal-loss corrosion resistance. Preliminary results suggest that a moderate alloy steel such as ASTM A387 gr 2, gr 7, or gr 9 heat-treated to API specifications for C-90 or C-95 may offer the best combination of localized corrosion resistance and SSC resistance.
Resource Class II <u>Casing</u>	<ul style="list-style-type: none"> Extreme corrosion of carbon and low-alloy steels as result of the <4.5 pH of reservoir fluid. 	Not addressed in this chapter, but see Chapter 4.
Resource Class III <u>Casing</u>	<ul style="list-style-type: none"> Continuous complete cementing with corrosion resistant cement required to prevent external corrosion by groundwaters and thermal buckling. Subject to sulfide stress cracking (SSC) during "killed" periods. Risk of thermal stress failure as result of low strength requirements for SSC resistance vs. large thermal cycle of normal operations. Isolated instances of serious localized internal corrosion. 	<ul style="list-style-type: none"> J-55 grade is "industry standard." Steels with very low sulfur and finely dispersed inclusions are more resistant to pitting and SCC allowing higher strength while maintaining SSC resistance. Heat treatment should avoid "soaking" at temper embrittlement temperatures. Molybdenum additions promote high hardenability, reducing risk of temper embrittlement. AISI 4130 Mod, high-purity 4130, and Republic Steel 115 all have SSC resistance to yield strengths of at least 120 ksi, a significant advantage over the 55 ksi minimum for J-55 casing. Also likely to have improved resistance to localized corrosion.
Resource Class IV <u>Casing</u>	<ul style="list-style-type: none"> Continuous complete cementing with corrosion resistant cement required to prevent external corrosion by groundwaters and thermal buckling. Subject to sulfide stress cracking (SSC) during "killed" periods. Risk of thermal stress failure as result of low strength requirements for SSC resistance vs. large thermal cycle of normal operations. Internal corrosion not a significant factor. 	See Resource Class III.
Resource Class Va and VI <u>Casing</u>	<ul style="list-style-type: none"> Continuous cementing through overlying groundwater horizons required to prevent external corrosion and heat "theft." Steel casing subject to SSC. Steel casing likely subject to serious metal loss corrosion in Class Va resource. 	<ul style="list-style-type: none"> Non-metallic casings suggested for Class Va resources due to potential serious metal-loss corrosion. SSC resistant steel casing grades suitable for Class Vb resources. Non-metallic casing may be economically attractive.
Resource Class VI <u>Casing</u>	<ul style="list-style-type: none"> Continuous complete cementing with corrosion resistant cement required to prevent external corrosion by groundwaters and thermal buckling. Subject to sulfide stress cracking (SSC) during "killed" periods. Risk of thermal stress failure as result of low strength requirements for SSC resistance vs. large thermal cycle of normal operations. Internal corrosion not a significant factor. 	<ul style="list-style-type: none"> SSC-resistant API grades "industry standard."
Drillstem	<ul style="list-style-type: none"> Major problems: <ul style="list-style-type: none"> oxygen pitting corrosion fatigue originating from pits susceptibility to SSC Pitting control by use of high-temperature polymerizing amine resin inhibitor shown highly effective in air and air/water drilling. Pitting control by use of nitrogen or inerted diesel exhaust shown highly effective in air and air/water drilling. Careful, frequent inspection and rejection of pitted drillstem a key to avoidance of twist-off and subsequent fishing costs. 	<ul style="list-style-type: none"> AISI 4130 Mod, high purity 4130 and similar low alloy steels with finely dispersed inclusions in micro-structure likely to have best combination of mechanical properties.
Injection Well <u>Casing</u>	<ul style="list-style-type: none"> To date, geothermal injection wells designed like production wells--no injection tube packed-off at the top of the injection zone. Injection volumes of binary plants will be very large ($>10,000$ bpd/MW net). Water must be completely deaerated or inhibited prior to injection into steel casing. 	<ul style="list-style-type: none"> API casing steels usually used. No data basis for optimum material selection.

Replacement of the air with an inert gas, such as cryogenically distilled nitrogen or specially combusted diesel exhaust, has also been shown to suppress pitting corrosion of drillstem steel if the concentration of dissolved oxygen in the water film coating the steel is kept below 0.05 ppm.

INTRODUCTION

This section summarizes the corrosion behavior of a large number of alloys which have been used, or may be used, as geothermal casing or drillstem. All of the alloys considered have not more than 10 percent non-ferrous alloy content. Those degradation phenomena which result from the combined interaction of alloy, temperature, and corrosive chemical environment are considered.

Section 3.1 explores the corrosion problems of casing. Section 3.2 considers drill string in high-temperature geothermal operations. Section 3.3 considers casing corrosion in low-temperature--not greater than atmospheric boiling--geothermal resources. In this section, both steel and nonmetallic casing are discussed. Section 3.4 discusses the special corrosion problems of injection wells.

3.1 Casing in High-Temperature Geothermal Operations

Traditionally, high-temperature geothermal resources have been exploited for electric power generation by the direct use of the steam of vapor-dominated resources, or, in the case of liquid-dominated resources, by the use of separated steam in a flashed-steam cycle. This sort of utilization has typically required resource temperatures of at least 300°F. The development of the binary cycle plant makes it feasible to use lower temperature resources. For example, the Raft River Binary Plant utilizes geofluid at about 265°F (design plant inlet temperature).

3.1.1 Corrosion Problems Encountered by High-Temperature Geothermal Well Casings

During more than 40 years of large-scale geothermal-electric exploitation, many problems relating to well casing have occurred. These problems have resulted from thermal stress, Sulfide Stress Cracking (SSC), cementing inadequacies, and internal or external corrosion of the casing. Table 3.1-1 presents an overview of these problems. The estimated reservoir conditions of the resources in Table 3.1-1 are summarized in Table 3.1-2, while Tables 3.1-3 through 3.1-5 give available details of the casing programs used at the different resources.

Tables 3.1-3 through 3.1-5 illustrate some significant differences between high-temperature geothermal wells and oil wells. One major difference is size. Production casing diameters of 9-5/8 inch to 13-5/8 inch or bigger are employed in geothermal wells due to the requirement to produce large quantities of fluid. Also, in contrast to oil wells, geothermal wells are produced through the production casing, which is cemented for its full length, rather than through a production tube packed-off at the top of the producing formation.

Table 3.1-1 indicates that most casing problems result from cementing difficulties, the conflict between low strength requirements for SSC resistance and the severe thermal stresses inherent in high-temperature operations, and a few cases of serious localized corrosion. Each of these classes of problems is discussed in more detail in the following paragraphs. Where applicable, information about currently employed mitigation practices is also included.

Cementing

Complete void-free cementing of the various strings of casing is essential to the life of the geothermal well. Such cementing is required to support the casing and to prevent collapse, buckling, or joint failure as a result of thermal stress [Snyder 1979].

TABLE 3.1-1. SUMMARY OF HIGH-TEMPERATURE CASING FAILURE EXPERIENCE 1950-1981

Location/ Resource Class	Casing Program	Summary of Major Casing Experience and Recognized Potential Problems
Wairakei, N.Z. Class IV	Table 3.1-3	<ul style="list-style-type: none"> o Development began in 1950. By 1981 there were more than 243 wells with an average depth of 2400 ft. <p><u>Problems/Failure Mode</u></p> <ul style="list-style-type: none"> o Severe erosion by ejecta from open bores. Mitigated with slotted liners. o Insignificant downwell metal loss corrosion of production casing. Casing wall of 0.333 inch adequate for 30 yr life. o Demonstrated risk of sulfide stress cracking of N-80 and P-110 casing. J-55 normally used. o Forty-seven (47) casing joint parting failures due to severe thermal stresses during first decade of operations. <ul style="list-style-type: none"> - Thermal stress in cemented casing is 250 psi/ F and normal operations, including injection of cold water to kill wells, causes temperature changes of 430 F or more. The resultant stress is greater than the yield stress of API J-55 casing. - Partially mitigated by use of buttress thread rather than thread joints, and complete cementing at joints. o Casing collapse due to the expansion of water trapped in voids in incomplete cement jobs as well as brought on-line. o Few cases of serious external corrosion by groundwaters, but no production casing failures.
Brady Hot Springs, NV Class IV	Table 3.1-5	<ul style="list-style-type: none"> o External corrosion lead to blowout of 20-year old well Brady No.5. <ul style="list-style-type: none"> - Surface conductor, intermediate casing and associated cements entirely corroded away. - Production casing corroded through around circumference about 7 ft below ground. - Little evidence of internal corrosion
Cerro Prieto, MX Class III	Table 3.1-4	<ul style="list-style-type: none"> o Numerous casing problems, including 4 blowouts, 10 casing collapses, 12 casing partings, parting and collapse in 7 wells. o Much of casing collapse and parting problems due to extreme thermal stress, on the order of 85-120 ksi produced by well killing operations. o Erosion-corrosion failure of dogleg in sidetracked well. o Isolated cases of severe localized attack, usually attributed to external corrosion by groundwaters. Some cases of severe internal corrosion. o Corrosion-fatigue failure of threaded wellhead anchor. Wellheads now attached by welding.
Salton Sea, CA	Table 3.1-5	<ul style="list-style-type: none"> o Severe localized corrosion of J-55 casing. <ul style="list-style-type: none"> - >120 mpy in upper casing, above flash zone. - 500-2000 mpy, in production zone. - Well Sinclair 4 abandoned after 6 months due to localized casing corrosion. - Estimated life of upper casing typically less than 2 years.
See Table 3.1-2 for resource conditions		

Sources: Fooks, 1964; Fooks, 1981; Smith, 1964; Snyder, 1979; Marshall and Tombs, 1969; Aguirre and Blanco, 1981; Mercado, S., 1978; Mercado, A., 1976; Aguirre and Garcia, 1981; Dominguez and Vital, 1976; Ellis, 1979; Quong and Owen, 1980; Tresedor and Weiland, 1976.

TABLE 3.1-2. TYPICAL DOWNWELL CONDITIONS AT FOUR HIGH-TEMPERATURE LIQUID-DOMINATED GEOTHERMAL RESOURCES

	Wairakei, New Zealand	Brady Hot Springs, Nevada	Cerro Prieto, Mexico	Salton Sea, California
Physical Properties				
Reservoir Depth				
Range (ft)	1200 - 5200	~500	1970 - 2300	4900 - 5900
Resource Temperature				
Typical (°F)	--	338	--	--
Range (°F)	480 - 518	? - 415	482 - 651	500 - >660
Key Corrosive Species				
pH				
Typical	6.34	7.18*	--	4.5
Range	--	--	5.3 - 5.4	--
Chloride				
Typical (ppm)	1520	1100	--	--
Range (ppm)	--		8220 - 11,400	85,700 - 135,900
Sulfate				
Typical (ppm)	7.6	301	--	--
Range (ppm)	--		3 - 27	1.2 - 108
Carbon Dioxide				
(Total) Typical (ppm)	510	Gas lost on sampling.	--	--
(Total) Range (ppm)	--	Bicarbonate 98 ppm.	1250 - 2580	4472 - 7000
Partial Pressure (psia)	11.46		106	37.5
Hydrogen Sulfide				
(Total) Typical (ppm)	9.2	ND	--	--
(Total) Range (ppm)	--	--	310 - 624	30 - 35
Partial Pressure (psia)	0.3	--	2.9	--
Total Ammonia Species				
Typical (ppm)	0.19	--	--	--
Range (ppm)	--	--	--	--

-- Data not available.

* Gas lost on sampling. Actual pH may be 1-2 units lower.

ND Not Detected.

Sources: Cosner and Apps, 1978; DePippo, 1980; Domingues and Vital, 1976; Ellis and Mahon, 1977; Ellis, 1979; Helgeson, 1968; McCright, 1981; Smith, 1964; Treseden and Weiland, 1976; Truesdell and Singers, 1964;

TABLE 3.1-3. TYPICAL CASING PROGRAMS AT WAIRAKEI, NEW ZEALAND

	<u>Typical in 1961</u>		<u>Typical in 1980</u>
	<u>Production Wells</u>	<u>Exploratory Wells</u>	<u>Exploratory Wells</u>
<u>Conductor Casing^a</u>			
O.D. (in)	18	18	22
Weight (lb/ft)	73	73	86.6
Grade	H-40	H-40	H-40
Joint	BT ^c	BT	BT
Setting Depth (ft)	60-100	60-150	130
<u>Surface Casing^a</u>			
O.D. (in)	13-3/8	13-3/8	16
Weight (lb/ft)	48	48	65
Grade	H-40	H-40	H-40
Joint	BT	BT	BT
Setting Depth (ft)	400	400-600	390
<u>Intermediate Casing^a</u>			
O.D. (in)	<u>None</u>	--	11-3/4
Weight (lb/ft)		--	47
Grade		--	J-55
Joint		--	BT
Setting Depth (ft)		1000	820
<u>Production Casing^a</u>			
O.D. (in)	8-5/8	8-5/8	8-5/8
Weight (lb/ft)	36	36	36
Grade	J-55	J-55	J-55
Joint	BT	BT	BT
Setting Depth (ft)	1600-1800	1600-1800	2000-2300
<u>Slotted Liner^b</u>			
O.D. (in)	6-5/8	6-5/8	6-5/8
Weight	24	24	24
Grade	J-55	J-55	J-55
Joint	BT	BT	BT
Total Depth	to 3980	--	3950-5250

-- no data available

^aCemented back to surface.

^bHung from production casing -- not cemented.

^cButtress thread

Sources: Fooks 1964; Fooks 1981

TABLE 3.1-4. TYPICAL CASING PROGRAMS AT CERRO PRIETO, MEXICO

Construction Period	1964	1966-74	1977-78	1978-80	1980
Number of Wells	4	29	18	26	nr ^a
Mean Depth (ft)	6530	4490	6450	7880	8530
<u>Conductor Casing</u> ^b		<u>None</u>		<u>None</u>	
O.D. (in)	22		22		30
Weight (lb/ft)	65.24		nr		98.93
Grade	B		CED 40		B
Joint	weld		weld		weld
<u>Surface Casing</u> ^b					
O.D. (in)	16	16	16	20	20
Weight (lb/ft)	65	65	75	94	106.5
Grade	H-40 ^d	H-40	K-55 ^e	H-40	J-55
Joint	R.T.	R.T.	B.T.	R.T.	R.T.
<u>Intermediate Casing</u> ^b	<u>None</u>				
O.D. (in)		11-3/4	11-3/4	13-3/8	13-3/8
Weight (lb/ft)		47 or 60	65	61	68
Grade		J-55 or K-55	K-55	K-55	K-55
Joint		B.T.	B.T.	B.T.	B.T.
<u>Production Casing</u> ^b					
Mean Depth	3600	2950	3280	6560	6560
O.D. (in)	11-3/4	7-5/8	7-5/8	9-5/8	9-5/8
Weight (lb/ft)	47	26.4	45.3	43.5	47
Grade	J-55	K-55	K-55	N-80	C-75
Joint	B.T.	B.T.	Hydril S.E.U.	B.T.	Hydril S.E.U.
<u>Slotted Liner</u> ^c		<u>None</u> ^f	<u>None</u> ^f		
O.D. (in)	7-5/8			7	7
Weight (lb/ft)	26.4			29	29
Grade	N-80			N-80	C-75
Joint	B.T.			Hydril S.E.U.	Hydril S.E.U.

^anot reported^bcemented back to surface^chung from production liner -- not cemented^dAPI Round Thread Joint^eAPI Buttress Thread Joint^fProduction casing extends through the producing zones and is perforated below the depth indicated under production casing.

Source: Aguirre and Garcia 1981

TABLE 3.1-5. TYPICAL CASING PROGRAMS AT BRADY HOT SPRINGS, NV
AND SALTON SEA, CA

	Brady Hot Springs	Salton Sea
<u>Conductor Casing</u> ^a		
O.D. (in)	20	20
Weight (lb/ft)	--	--
Grade	--	--
Joint	--	--
Setting Depth (ft)	20	100
<u>Surface Casing</u> ^a	<u>none</u>	
O.D. (in)		13 5/8
Weight (lb/ft)		54.5
Grade		K-55 or H-40
Joint		BT ^b
Setting Depth (ft)		--
<u>Intermediate Casing</u> ^a		
O.D. (in)	16	--
Weight (lb/ft)	--	--
Grade	--	--
Joint	--	--
Setting Depth (ft)	100	--
<u>Production Casing</u> ^a		<u>liner</u> ^c
O.D. (in)	13 3/8	8 5/8
Weight (lb/ft)	--	32
Grade	--	K-55 or J-55
Joint	--	BT
Setting Depth (ft)	550	3900-6600
<u>Slotted Liner</u> ^d	<u>none</u> ^e	
O.D. (in)		6 5/8
Weight (lb/ft)		27.65
Grade		J-55 or K-55
Joint		Flush
Total Depth		--

-- data not available

^a cemented back to surface

^b Buttress Thread

^c liner hung 200 ft into surface casing, cemented for full length.

^d hung 200 ft from bottom of production liner -- not cemented

^e production casing extends to bottom of well and is perforated in production zone

Sources: Ellis 1979; Snyder 1979; Cromling 1972

Water- or mud-filled voids in the cement job do not provide support, of course, and may also cause collapse due to expansion of trapped water. For example, in two early wells at Wairakei, the production casing inside the surface pipe collapsed. In these cases, the production casing was 8-5/8 inch diameter, 32 lb/ft, H-40 casing, while the surface pipe was 10-3/4 inch, 40.5 lb/ft, H-40. Investigations showed that cement was absent from several feet of the annulus of the production and intermediate casing. It was concluded that this void was filled with water during cementing. As the bore heated up during production, the pressure of the confined heated water--on the order of tens of thousands of psi--collapsed the casing [Smith 1964]. In later wells, the production casing collapse resistance was made greater than the surface pipe burst resistance to prevent similar collapses [Fooks 1964].

Joint failure is also apparently related to cement voids. During the first decade of drilling at Wairakei, 47 cases of production casing failure by separation of joints were documented in 21 wells [Fooks 1964]. There was no apparent relationship between depth and occurrence. The joints used were short or long API round thread. The short joint has a strength rating of 0.79 relative to solid casing, while the long thread has a relative strength of 0.88 [Smith 1964]. The maximum tensile strength of the casing is 88 ksi; therefore, the probable thermal stress exceeds the rated strength of the joints. These joints have been replaced with API butress joints, which have strengths comparable to that of the casing. Such joints appear to now be the industry standard.

In all documented cases of joint failure, measurements during repair operations indicated an absence of cement in the area of the joints. The most likely cause of joint failure is an initial failure in compression due to rise in temperature, followed by pull-out upon cooling. However, in some cases the initial failure appears to have been tensile [Smith 1964]. Both modes are certainly possible given the range of downhole temperatures which can occur.

Clearly, adequate--void-free--cementing is required and every precaution should be taken to assure the quality of the cementing job. New Zealand experience has shown that increasing the annular spacing between the casing strings has been quite beneficial [Fooks 1981].

Hydrogen Damage

Hydrogen damage may take the form of Sulfide Stress Cracking (SSC) or Hydrogen Induced Blister Cracking (HIBC). The mechanism--inhibition of the recombination step of the hydrogen ion reduction reaction--by which the atomic hydrogen enters the steel matrix is the same in both cases. However, the way in which it causes damage differs. Some ambiguity exists in naming SSC. In some literature it is called stress corrosion cracking (SCC) and in other reports it may be referred to as delayed hydrogen fracture or other names. For sake of clarity, SSC is contrasted with chloride-induced stress corrosion cracking (chloride-SCC) in Table 3.1-6.

Sulfide stress cracking (SSC) is delayed brittle failure of high strength alloys. It results from hydrogen embrittlement promoted by the presence of hydrogen sulfide. In SSC, atomic hydrogen accumulates in the steel matrix and tends to concentrate in the regions of high stress in front of notch defects. When it reaches sufficient concentration, embrittlement occurs and a crack propagates normal to the steel surface.

In HIBC, atomic hydrogen encounters a discontinuity in the matrix at the boundary of an inclusion and precipitates as molecular hydrogen. Molecular hydrogen cannot diffuse into the steel lattice, therefore it pressurizes the void at the inclusion. Theoretically, pressures of a hundred thousand atmospheres or more are possible [Fontana and Green 1967], but in fact, cracks propagate parallel to the steel surface, relieving the pressure somewhat. If these cracks are near the surface, blisters also form. It is not uncommon for the HIBC cracks to link up, giving a stairstep appearance when the steel is sectioned; hence the name stepwise cracking.

TABLE 3.1-6. COMPARISON OF CHLORIDE-SCC AND SSC IN GEOTHERMAL ENVIRONMENTS^a

Chloride-SCC	SSC
1. Mechanism: active path dissolution (rapid metal dissolution at crack tip)	1. Mechanism: cathodic hydrogen embrittlement
2. Promoting species: chloride ion in aqueous solution	2. Promoting species: hydrogen sulfide in aqueous solution
3. Austenitic steels most sensitive	3. Martensitic and ferritic steels most sensitive; austenitic steels are highly resistant or immune
4. Not notch sensitive	4. Notch sensitive
5. Severity increases with increasing temperature	5. Severity decreases with increasing temperature
6. PPM oxygen causes drastic increase in severity of attack	6. PPM oxygen has little if any effect on severity of attack
7. Bulk pH has little effect	7. Low pH greatly accelerates failure
8. No threshold stress	8. Threshold of stress below which failure does not occur
9. Crack propagates normal to the applied stress	9. Crack propagates normal to the applied stress

^aIn this document, chloride stress corrosion cracking (chloride-SCC) and sulfide stress cracking (SSC) are considered to be subsets of stress corrosion cracking. Stress corrosion cracking is a general term which includes any environmental fracture of metal under static tensile stress.

Source: Ellis and Conover 1981

HIBC resistance depends on the same metallurgical factors as resistance to SSC. Therefore, SSC resistant microstructures have good HIBC resistance. The most damage-susceptible microstructures are those with long stringers of manganese sulfide inclusions [Wilde, Kim, and Phelps 1980; Herbsleb, Popperling, and Schivenk 1980; Taira et al. 1981; Williams 1981].

A number of factors in the geothermal environment affect SSC and HIBC of casing steels. The effects of several environmental factors are summarized in Table 3.1-7. Most notably, SCC failures of high-strength API casing grades have been documented at hydrogen sulfide concentrations of 0.1 ppm, approximately the same concentration that occurs in reservoir fluid at Wairakei. Hydrogen damage has been demonstrated at 0.02 ppm hydrogen sulfide in laboratory tests. Therefore essentially all geothermal environments can be considered to be "sour" to some degree.

Early research at Wairakei showed that high strength (high-hardness) casing steels are subject to SSC when exposed to cooled borehole discharge fluids [Fooks 1964] and to condensate [Marshall and Tombs 1969]. Indeed, the rationale for specifying J-55 or other low strength casing is to preclude SSC. This practice has been followed at most other high-temperature resources and appears to be an informal industry standard. Thus, common practice is to limit casing hardness to HRC 22 or less, and yield strength to around 100ksi, (80ksi in the case of J-55).

It is also important to recognize that the high temperature of the geothermal resource does not protect against sulfide stress cracking (SSC) because cooled drilling and kill fluid is circulated. For example, in 1979 and 1980, ENEL (Ente Nazionale Per L'Energia Electrica) drilled a deep exploratory well, Sasso 22, in the Larderello geothermal area in Italy. This well completely penetrated the upper, vapor-dominated resource and was to explore the lower reservoir. The target depth of this well was 14,765 feet. Water drilling was used through hot, highly fractured, underpressured zones which would have been damaged by mud. At 1995 feet, a massive lost circulation zone

TABLE 3.1-7. ENVIRONMENTAL FACTORS AFFECTING HYDROGEN DAMAGE RESISTANCE

Environmental Factor	Role/Effect
Hydrogen Sulfide	<ul style="list-style-type: none"> o Cathodic poison--prevents the recombination step of the cathodic proton reduction half reaction of the corrosion process, but does not affect (or may even accelerate) the proton reduction step which produces adsorbed atomic hydrogen on the metal surface. o With the recombination step inhibited, atomic hydrogen readily enters the steel lattice, promoting SSC (or HIBC). o The hydrogen sulfide is <u>not</u> the source of the embrittling atomic hydrogen. o Threshold concentration of hydrogen sulfide is commonly--and incorrectly--thought to be around 2-3 ppm. o SSC failures of API P-grade casing documented at 0.1 ppm hydrogen sulfide. o Accelerated hydrogen entry into steel at 0.02 ppm. o Essentially all geothermal fluids are "sour."
Chloride	<ul style="list-style-type: none"> o Not required for SSC or HIBC. o No significant effect over range of 0 to 121,320 ppm chloride.
Liquid Water	<ul style="list-style-type: none"> o Required for SSC and HIBC.
Oxygen	<ul style="list-style-type: none"> o Negligible effect on SSC or HIBC.
Temperature	<ul style="list-style-type: none"> o 15-30 percent increase in breakpoint yield strength at 212 F as compared to 77 F in NACE solution. o No further increase in breakpoint yield strength as temperature increased to 425 F. o No ceiling temperature above which immunity to SSC occurs. o Probably no effect on HIBC.
pH	<ul style="list-style-type: none"> o Below pH 4.5 severity of SSC cracking relatively constant. o Moderate increase in apparent resistance at pH between 4.5 and 6--may be due to increased incubation time. o SSC observed at pH of 12.
Carbon Dioxide	<ul style="list-style-type: none"> o Lowers pH, increasing supply of hydrogen ions--thus atomic hydrogen--and corrosion rate. o Provides alternate pathway for proton reduction--thus an additional source of embrittling atomic hydrogen.

Sources: Hydrogen Sulfide - Hudgins, et al., 1966; Hudson, et al., 1968.
 Chloride - Baldy, 1961; Troiano and Hehemann, 1979.
 Water - Fraser and Treseder, 1952; Smialowski, 1962; Marshall and Tombs, 1969.
 Oxygen - Ellis and Conover, 1981.
 Temperature - Troiano and Heheman, 1979.
 pH - Troiano and Heheman, 1979.
 Carbon Dioxide - deWaard and Milliams, 1975a, 1975b.

was encountered and all drilling below this point was with complete lost circulation [Baron and Ungemach 1981]. The water used was a mixture of 70 percent river water and 30 percent geothermal steam condensate from a nearby power plant [Anliker 1980]. The hydrogen sulfide content of the condensate--back-calculated from the volatile hydrogen sulfide content--was 3.5 ppm at 77°F.

When the drilled depth reached 13,124 feet, the estimated bottom hole temperature was 715°-750°F. The temperature at the static water level (6562 feet) was 203°F. An instrument package was lowered on 3-1/2 inch drillstem into the cooled well to the bottom of the hole and left for 80 hours to allow temperatures to equilibrate. Upon removal it was found that numerous joints had failed at depths greater than 9840 feet. The pins of virtually every recovered joint were cracked or parted. Numerous fishing operations were required to retrieve the drillstem. The drill pins were made of French 38NCD4 steel, equivalent to AISI 9840, with a hardness of HRC 35. Failure analysis revealed that the cause of failure was SSC [Anliker 1980]. Though the reservoir temperature was at least 700°F, the drillstem and joints were exposed to the much cooler temperatures of the drilling water and cooled hole.

Thermal Stress Failure

The overwhelming majority of diagnosed well casing failures result directly from the extreme thermal stresses inherent in high-temperature geothermal operations. Because of the potential for hydrogen damage in the geothermal environments, casing steels have been limited to low yield strength grades such as J-55 and K-40. Some C-75 has also been used. The need for low-strength steels to resist sulfide stress cracking conflicts directly with the need for high strength to resist thermal stress. The problem is made worse by the reversible degradation in yield strength as a result of increased temperature above 176°F. Above 176°F, the ratio of yield strength to room-temperature yield strength is given by:

$$\frac{Y_t}{Y_o} = 1.1486 - t / 1184$$

where: Y_t = yield strength at temperature t
 Y_o = yield strength at 77°F
 t = temperature (°F)

There is no significant change in yield stress with temperature increases from room temperature up to 176°F.

Such problems have been documented at Cerro Prieto, Mexico [Mercado, A. 1976] and at Wairakei [Smith 1964]. A review of stress studies at Wairakei clearly illustrates the origin of the stresses for all high temperature resources.

Until the casing is cemented, no thermal stress is produced. Thus, the temperature at which cement bonding occurs is the temperature of zero thermal stress, or neutral temperature. At Wairakei this temperature is commonly around 175°F, based on the temperature of returns during cementing [Smith 1964]. When the well is shut in, the bottom-hole temperature is around 480°-518°F in most wells while the temperature at 500 feet is generally 390°F-410°F and may be as high as 446°F.

During well output tests, temperatures of around 445°F occur at the wellhead, while normal steam production temperatures are often 390°-470°F. The other temperature extreme occurs when the well is killed with cold surface water prior to workover or repair. The kill water is about 68°F, sometimes colder, and this temperature can occur at any depth during kill operations [Smith 1964]. Thus, temperature changes of around 340F° relative to the initial neutral temperature may occur during production activities, while changes of 100F° or more relative to the neutral temperature may occur during well killing. The maximum temperature range seen in a Wairakei geothermal well is about 450F°, but a range of 430F° is probably more likely.

The thermal stress, either compressive or tensile, produced in solidly cemented casing is a function of temperature change, coefficient of thermal expansion, and modulus of elasticity. Though there is slight variation with temperature, for practical purposes the thermal stress can be taken to be 205 psi/°F and it is independent of length. Thus, initial well heat-up can produce compressive stresses in excess of 70 ksi. For production casing of J-55 (with a specified minimum yield strength of 55 ksi) therefore, the thermal stress is probably well in excess of the yield, resulting in compressive yielding of solidly cemented pipe and resultant shortening. Well killing operations can then produce tensile stresses approaching, or even exceeding, the tensile strength of the casing [Smith 1964; Snyder 1979], causing failure. This mechanism was diagnosed as the cause of blowout of Cerro Prieto well M-5. The H-40 casing of this well parted when cold water was injected during repair operations [Mercado, A. 1976].

Metal-loss Corrosion

Metal-loss corrosion does not appear to have been a significant problem at most geothermal resources. At Wairakei, for example, above-ground tests in bore fluid at 464°F and at 250°F indicate corrosion rates of around 1-2 mpy [Foster, Marshall and Tombs 1964; Marshall and Hugall 1957]. Pieces of broken casing recovered during repair operations during the first six years at Wairakei indicated little corrosion of the deeper casing after six years [Fooks 1964]. Casing weights are selected to provide at least 0.333 inch wall thicknesses.

A few cases of serious external corrosion of the conductor by aerated ground water have been observed at Wairakei. The 0.333 inch minimum thickness of the surface conductors and the competently cemented annuli did protect the surface pipe, and no production casing failures due to external corrosion were reported in the first decade of operations [Fooks 1964].

Likewise, internal corrosion does not appear to have been significant at another Class IV resource, Brady Hot Springs, Nevada. In June 1979, a twenty-year old well at this resource was cleaned to remove a calcium carbonate plug. Inspection showed no significant damage to the internal surfaces of the casing [Ellis 1979]. However, the well did blow out upon stimulation, with the production casing parting about seven feet below grade.

The ejected wellhead assembly with the attached top seven feet of production casing were examined to determine the cause of failure. The exterior of the casing showed extensive corrosion of the steel (grade not reported) with continuous tuberculation or exfoliation of the entire buried portion. The attack appeared to become more severe with increasing depth. Some very broad shallow pits were also observed. The remaining wall thickness at the point of failure was less than 0.125 inches with some perforations of more than one inch in diameter. The interior, which had been exposed to weather since the blowout, showed a film of rust, but no tuberculation or pitting from the inside was observed.

It was concluded that failure of the casing resulted from severe external corrosion. The well was located in a mineral flat and it was proposed that during wet periods the exterior of the casing was exposed to aerated saturated chloride and/or sulfate salt solutions. These solutions appeared to have completely destroyed the surface conductor and the upper string casing and associated cements. The production casing then corroded until mechanical failure occurred.

At Cerro Prieto, a Class III resource, external corrosion has also been a problem. In a number of cases, collapse has been attributed to corrosion and metal loss, apparently occurring on the exterior of the casing and associated with defective cement jobs. This corrosion is attributable to attack by ground waters [Aquirre and Blanco 1981].

Also, in contrast to the Class IV resources, instances of serious localized internal corrosion have occurred. For example, well M-103 was built in 1978 and contained a sidetrack to bypass stuck casing. This well was completed with 9-5/8 inch diameter 43.5 lb/ft production casing. When the well was activated immediately upon completion, flow irregularities indicated downhole problems. Inspection showed severe erosion and corrosion damage in the contraflexure of the deviation. In this area, the two-phase flow separated, and the casing was eroded by impingement of the high velocity liquid droplets [Aguirre and Blanco 1981].

The most extreme corrosion problems occurred in well M-3. This well was completed in 1964 and had been used for a number of studies and investigations. In 1979 inspection showed scaling in the production zone, severe internal corrosion, external corrosion at 341 and 750 feet, collapses and fractures, and degradation of the cement between the casing and formation which lead to a dangerous concentration of hot water near the surface. The well was plugged and abandoned.

The Class I Salton Sea KGRA has the most severe above ground corrosion problems encountered to date in the United States [Ellis and Conover 1981]. Very serious downhole corrosion in the form of localized metal loss--pitting or mesa and canyon attack--has been reported at the Salton Sea KGRA. Examination of carbon steel piping just downstream of the wellhead of Magmamax No. 1 showed localized corrosion with a penetration rate of 120 mpy; similar corrosion rates were predicted for the upper-most parts of the Magmamax No. 1 casing. Also, the carbon steel casing of the Sinclair No. 4 well suffered severe enough localized corrosion to cause the operators to abandon the well after six months of operations [Quong and Owen 1980].

A 4260 ft. string of 3-1/2 inch diameter J-55 tubing was suspended for 16 days in Shell Oil Company's well State No. 1, and the well was produced. The bottom hole temperature was around 608°F. The localized corrosion rate varied from 91 mpy near the surface to more than 2000 mpy at 4260 feet. All sections of tubing showed severe pitting [Treseder and Weiland 1976].

In 1979, 1662 feet of J-55 tubing were suspended in well Woolsey No. 1 for 69 days. This well has a bottom hole temperature of 500°F and a well-head temperature of 366°F during production. Flow from the well was intermittent, 904 hrs with brine flow, 752 hrs shut-in. Pitting corrosion occurred in all joints of the J-55 pipe, with maximum penetration rates ranging from 11 mpy at 332 feet to a maximum of 577 mpy at 1495 feet [Quong and Owen 1980]. The results of these two tests are presented graphically in Figure 3.1-1. Lawrence Livermore Laboratories has estimated that the lifetime of J-55 well casing will be less than four years even for the upper portion of the well [Quong and Owen 1980]. Even more severe corrosion is expected at depth, as shown in Figure 3.1-1.

It appears that SSC is a risk to be considered at any high-temperature resource, forcing use of SSC-resistant steels. However, these steels may not sustain the high thermal stresses produced by normal well operations. In most cases, however, localized corrosion does not appear to be significant in Class IV resources. This corrosion mode has caused some difficulties at Class III resources, and appears to be the major problem in Class I resources. Thus, the two identified development needs for high temperature well casing are for:

- o increased yield strength with resistance to sulfide stress cracking and other hydrogen damage, and
- o increased localized corrosion resistance.

The first is needed for all high-temperature resources. The latter is essential only for Class I resources, though it would also be beneficial to Class III, and perhaps even to Class IV.

Figure 3.1-1. Localized Corrosion Penetration Rates of J-55 Casing in Two Salton Sea Geothermal Wells
[Data from Quong and Owen 1980; Treseder and Weiland 1976]

3.1.2 Developments in SSC Resistant Casing Steels

A number of different accelerated methods are used in the laboratory to measure resistance to SSC. All define SSC resistance in relationship to the applied stress which causes SSC failure, but the exact way in which this is defined varies from test to test. There is also considerable variation in test methodology. For these reasons, though the various tests usually give the same relative ranking of materials, results from one test method cannot be quantitatively compared with results from other methods. Table 3.1-8 compares the three most commonly used test methods. This table also defines NACE solution, as well as three common evaluation parameters: threshold stress, median survival stress and breakpoint yield strength.

Yield strength (YS) and microstructure are the most important material factors in SSC resistance of low-alloy steels. Yield strength, or hardness if YS cannot be measured, is the standard criterion for SSC susceptibility. The (NACE) standard for sour (hydrogen sulfide) service is 90 to 100 ksi yield strength, or HRC 22. This is based on performance of steels stressed to 100 percent YS in NACE solution [NACE Standard MR-01-75 (1980 rev.)]. See Table 3.1-8 for other details of this test method.

Strength and hardness are inadequate for defining susceptibility to SSC [Bowers, McGuire and Wiehe 1952]. Microstructure affects the SSC resistance of steels with the same hardness, while composition is significant only as it affects hardening and microstructure [Greer 1975; Hudgins et al. 1966; Snape 1967; 1968]. Quenched and tempered steels are superior to normalized and tempered steels of comparable yield strengths [Snape 1967]. Normalized and tempered steels are superior to normalized steels [Kane and Greer 1976].

The most resistant microstructures consist of relatively fine, spheroidized carbides uniformly dispersed in ferrite. These microstructures result from tempering martensite at high temperatures. Alloying additions which increase required tempering temperature increase SSC resistance by their

TABLE 3.1-8. COMPARISON OF THREE COMMONLY USED SULFIDE STRESS CRACKING (SSC) TESTS

Method	NACE Test (TM-01-77)	Modified Shell Test	Case Western Reserve University Test
Test Solution	<u>NACE Solution</u> : deionized water plus 5 percent sodium chloride and 0.5 percent acetic acid, continuously saturated with hydrogen sulfide gas at one atmosphere absolute pressure.	NACE Solution	NACE Solution
Test Specimen and Loading Mode	Machined cylindrical tensile specimens under pure uniaxial tensile load.	Three-point, bent-beam specimen similar to ASTM G39 specifications. Beam is 0.06 x 0.19 x 3.0 in with two (2) No. 70 holes drilled 0.06 in. apart on transverse center lines.	Two-point, bent-beam specimens prepared according to ASTM G39 specifications.
Test Duration	720 hrs	Usually 720 hrs	720 hrs
Ranking Criteria	<u>Threshold Stress</u> : the maximum stress at which no SSC is observed.	<u>Median Survival Stress</u> : applied stress at which one-half of specimens of given yield strength fail.* Often designated 1Sc1 and having units of 10 ksi.	<u>Yield Strength Breakpoint</u> : maximum yield strength at which failure of specimens loaded at 100 percent of their yield strength does not occur in 720 hrs.
Comparability with Other Test Methods	Gives same ranking. Results <u>not</u> quantitatively comparable to other methods.	Gives same ranking. Results <u>not</u> quantitatively comparable to other methods.	Gives same ranking. Results <u>not</u> quantitatively comparable to other methods.

Note: Underscored terms are followed by definitions.

*At a given yield strength, the range of applied stress at which some specimens crack and some do not is about 40 ksi.

Sources: NACE Standard TM-01-77; Fraser and Treseder, 1955; Fraser, Eldridge, and Treseder, 1958; Troiano and Heheman, 1979.

effect on microstructure. Steels high in chromium, sulfur, or phosphorus are less resistant [Snape 1968]. Because of the need for fine microstructure, high hardenability is necessary [Troiano and Hehemann 1981a].

The next most resistant microstructures contain coarse globular and/or laminar carbides [Snape 1968]. Sulfur also tends to form "stringers" of inclusions which favor cracking by producing a less resistant microstructure than globular sulfides. [Okhi, et al. 1977]. Laboratory heats of very low sulfur steels or steels with trace lanthanide additions are very resistant to SSC [Okhi, et al. 1977; Snape 1968; Toriano and Hehemann 1979, 1981a; Waid and Stiglitz 1979].

Microstructures containing untempered martensite have the least resistance of all. Even very small traces of untempered martensite, especially as a network, drastically lower the threshold stress. Such steels can fail at bulk hardnesses far below HRC 22. These microstructures can occur in either quenched-and-tempered or normalized-and-tempered steels if the tempering temperature exceeds the lower critical temperature (austenizing temperature). Additions of nickel and manganese reduce the lower critical temperature, which increases the risk of forming untempered martensite. This accounts for the poor SSC resistance of steels containing more than one percent nickel: low-alloy steels containing more than one percent nickel should be tested carefully before use.

There is also evidence that temper embrittlement may be a major factor in some cases of SSC. Tempering near 1100°F or slow cooling through this range can cause temper embrittlement. The general practice of slow air cooling can lead to this form of embrittlement in large-diameter or thick-walled goods. Only recently has attention been given to fast cooling of tubular goods through the temper embrittling region.

Case Western Reserve University has recently (March 1981) concluded a several-year long program in which 11 low-alloy steels were evaluated for SSC resistance in geothermal operations. The alloys were commercially available grades or had compositional variations, principally very low sulfur (VLS) contents of less than 0.005 percent.

All of the steels were heat-treated under a nitrogen atmosphere; great care was exercised to avoid decarburization. All the low-alloy steels were quenched for martensite and given a single temper. Tempering times and temperatures were selected to produce yield strengths in the range of approximately 100-150 ksi.

The study was done with two-point bent-beam specimens as described in ASTM GR 39-73 (see also Table 3.1-8). The results of this long-term investigation are presented in Table 3.1-9a and the compositions of the alloys in Table 3.1-9b. Examination of these results indicates that of the commercially available materials, 4135 Mod has the highest yield strength breakpoint --122 ksi. A special very-low-sulfur version of this alloy had even better performance--126 ksi yield strength breakpoint. The high-purity 4130 was also better than its commercial counterpart--122 ksi yield strength breakpoint compared to 110 ksi.

Troiano and Hehemann [1981a] also reported the results of an extensive study of SSC resistance of commercially acquired tubular goods as measured by C-ring testing in NACE solution. The rings were stressed at the grade minimum yield stress. The results of this study are presented in Table 3.1-10a, while Table 3.1-10b gives the compositions of the alloys.

This table illustrates the general validity of the HRC 22 maximum hardness restriction for sour service. Fourteen steels were tested in 19 heat treatment conditions. Hardnesses ranged from HRC 19 through HRC 32. All but two of the steels with hardness greater than HRC 22 failed, while no steel with hardness of HRC 22 or less failed.

TABLE 3.1-9a. THRESHOLD STRESS/YIELD STRENGTH BREAKPOINTS OF LOW-ALLOY STEELS
IN MODIFIED NACE TEST

Steel	Breakpoint Yield Strength (ksi)				
	pH 2.5-4 77°F	pH 2.5-4 215°F	pH 2.5-4 325°F	pH 2.5-4 425°F	pH 6-7 77°F
4118	110	--	--	--	--
4123 (commercial pipe)	112	--	>131 ^c	--	--
4130	110	140	>128 ^c	140	140
4135 Mod	122	138	>138	138	140
4135 Mod VLS	126	--	--	--	--
4340	108	--	--	--	--
V1312 (VLS) ^a	118	140	--	--	140
V1313 (VLS) ^a	118	138	>126 ^c	--	142
V1397 (4130 High Purity)	122	143	--	--	142
2.25 Cr-1 Mo-0.31C ^b	120	140	--	--	--
2.25 Cr-1 Mo 0.19C ^b (Cast)	119	--	--	--	--

-- no data available

^aVery Low Sulfur, less than 0.005 percent.

^bTroiano and Hehemann 1981a

^cTroiano and Hehemann 1976

Source for other data: Troiano and Hehemann 1979

TABLE 3.1-9b. COMPOSITIONS OF CONSTRUCTIONAL STEELS TESTED

Steel	C	Mn	P	S	Si	Cr	Mo	Cb	V	Ni
4118	0.20	0.80	0.008	0.012	0.27	0.5	0.11	--	--	--
4123	0.23	0.84	0.036	0.016	0.36	0.93	0.20	--	--	--
4130 High Purity	0.35	0.003	0.006	0.003	0.011	1.40	0.20	0.02	0.006	0.02
4130	0.33	0.53	0.015	0.029	0.27	0.91	0.21	--	--	--
4135 Mod	0.34	0.86	0.013	0.010	0.28	1.08	0.83	0.054	--	--
4135 Mod (VLS)	0.34	0.003	0.006	0.003	0.03	0.98	0.94	0.036	--	--
4340	0.35	0.76	0.007	0.011	0.25	0.82	0.25	--	--	1.79
V1312	0.26	0.50	0.005	0.005	0.21	1.01	0.78	0.04	--	--
V1313	0.26	0.52	0.005	0.004	0.22	1.01	0.78	--	0.06	--
2.25 Cr-1 Mo	0.19	0.55	0.013	0.008	0.22	2.20	1.00	--	--	--
2.25 Cr-1 Mo (Cast)	0.15	0.75	0.015	0.007	0.23	2.73	0.92	--	--	--

-- No data available.

VLS = Very low sulfur

Source: Troiano and Hehemann 1981a

TABLE 3.1-10a. RESULTS OF C-RING SSC TESTS ON AS-RECEIVED AND RETEMPERED COMMERCIAL CASING AND TUBING STRESSED AT 100 PERCENT OF THE GRADE MINIMUM YIELD STRENGTH

	API Grade	Heat- Treatment	Wall (Inches)	Hardness RC	Specimens failed/ Specimens tested	Comments
Casing A	P-110	Q&T	0.46	29	2/2	as received
Casing B	P-110	Q&T	0.34	29	2/2	as received
Casing C	N-80	N	0.36	19	0/1	as received
Casing D	L-80	Q&T	0.28	21	0/1	as received
Casing E	N-80	Q&T	0.27	23	2/2	as received
		a	0.27	22	0/2	retempered
Casing F	K-55	HR	0.26	19	0/2	as received
Tubing G	J-55	N	0.19	19	0/2	as received
Tubing H	N-80	N	0.17	20	0/2	as received
Tubing I	N-80	Q&T	0.18	25	0/2	as received
		b	0.18	25	2/2	embrittling temper
Tubing J	P-105	Q&T	0.16	32	2/2	as received
		c	0.16	30	1/2	retempered
Casing K	P-110	Q&T	0.50	30	2/2	as received
		d	0.50	23	0/1	retempered
		e	0.50	23	1/1	embrittling temper
Tubing L	N-80	N&T	0.48	21	0/2	as received
Tubing M	C-80	Q&T	0.40	21	0/2	as received
Tubing N	C-90	bore Q&T ^f	0.42	20	0/2	as received

Q&T = Quench and Temper exterior only

N = Normalized

N&T = Normalized and Tempered

HR = Hot Rolled

^a 1200 F - 1 hr, water quench

^b Step cooled 1125 F-950°F, 25°F - 1/2 hr increments

^c Rapid air cool from 1200°F

^d 1200°F - one hour water quench

^e 1200°F - one hour slow cooled

^f Bore quenched

Source: Troiano and Hehemann 1981a

TABLE 3.1-10b. COMPOSITION OF C-RING SPECIMENS TESTED FOR SSC

Steel	C	Mn	P	S	Si	Cr	Mo	V
A	0.26	1.47	0.013	0.015	0.20	--	--	--
B	0.24	1.53	0.011	0.018	0.19	--	--	--
C	0.35	1.58	0.009	0.015	0.18	--	--	--
D	0.24	1.62	0.011	0.012	0.22	--	0.30	--
E	0.25	1.40	0.010	0.014	0.19	--	--	--
F	0.43	1.24	0.013	0.017	0.19	--	--	--
G	0.43	1.16	0.015	0.016	0.21	--	--	--
H	0.37	1.58	0.017	0.014	0.20	--	0.14	0.06
I	0.26	1.42	0.008	0.017	0.08	--	--	--
J	0.23	1.61	0.015	0.011	0.14	--	0.33	0.06
K	0.26	1.54	0.013	0.019	0.18	--	--	--
L	0.13	0.45	0.010	0.007	0.51	9.0	0.95	--
M	0.32	0.54	0.008	0.014	0.29	0.97	0.22	--
N	0.32	0.53	0.008	0.023	0.27	1.1	0.29	--

-- data not reported

Source: Troiano and Hehemann 1981a

This study also illustrated the importance of hardenability on SSC resistance. High hardenability promotes the attainment of the fine microstructures and uniformly distributed carbides (tempered martensite) most resistant to SSC. Steel D with 0.30 percent Mo--which strongly promotes hardenability--resisted SSC at HR 21, while steel E, the same composition but lacking Mo, failed at HRC 23. Steels M and N, essentially AISI 4130 analyses, as well as steel L (9 Cr-1 Mo) did not fail despite their high wall thickness. Metallographic examination revealed these steels to have the improved microstructure obtainable by alloy addition for improved hardenability and/or efficient quenching [Troiano and Hehemann 1981a].

Several of the steels in the C-ring study were retempered to test for the possibility of temper embrittlement. These steels are indicated in Table 3.1-10a; the laboratory heat treatments are described in the footnotes of that table. Steel E, an N-80, failed the C-ring SSC test as received. Retempering to relieve any temper embrittlement allowed this steel to pass. Hardness was also reduced from HRC 23 to HRC 22. Steel I passed the test at HRC 25 as received. It was one of the two steels to pass at HRC greater than 22. After receiving an embrittling temper, it failed at HRC 25. Both samples of steel J, a P-105 with as-received hardness of HRC 32, failed. Retempering to relieve any temper embrittlement allowed one of two samples to pass at HRC 30. Steel K, a P-110 which failed as-received with HRC 30, was given two heat treatments, one to relieve any temper embrittlement, and one an embrittling treatment. Both produced hardnesses of HRC 23. The embrittling treatment caused failure while the other treatment did not. These findings illustrate the need for exacting quality control during fabrication of tubulars for geothermal service.

Republic Steel Company has published results of an effort to develop a higher strength SSC resistant low alloy steel [Waid and Stigletz 1979]. This experimental steel has the following composition: 0.22C, 0.50Mn, 0.27Si, 0.040P, 0.040S, 1.90Cr, .65Mo, 0.22V, and 0.04Al. It is being developed under the designation RS-115. This steel has a much higher temper resistance than the steels currently used for L-80 and C-90 casing steels. For example, 4130,

commonly used in the above grades, requires a temper temperature of 1000°F to reach a hardness of HRC 30. RS-115 requires 1250°F to obtain the same hardness. RS-115 also has enhanced hardenability. The combined factors of higher temper temperatures and higher hardenability make a fine microstructure of tempered martensite (with uniform carbide distributions) feasible on a commercial scale. This microstructure is most resistant to SSC, as stated previously.

Figure 3.1-2 shows the median survival stress (defined in Table 3.1-8) of RS-115 compared to those of L-80 and C-95 as a function of yield strength and hardness. Examination of the figures gives an estimated minimum yield strength breakpoint for RS-115 of at least 125 ksi. Figure 3.1-2 shows that RS-115 offers SSC resistance equivalent to L-80 or C-90 at 25 to 35 percent greater yield strengths.

3.1.3 Identification of Casing Steels with Improved Localized Corrosion Resistance

Several environmental factors contribute to the severe downhole metal-loss corrosion at the Salton Sea resource. Temperatures below the flash zone are on the order of 500°-600°F. Chloride concentrations range from around 85,000 ppm to at least 155,000 ppm. The reservoir contains at least 5000 ppm total carbon dioxide, some present as carbon dioxide and some as bicarbonate. The distribution between these two species changes as the fluid rises up the well and flashes into two-phase fluid. One of the major effects of the bore flashing is to partition some of the carbon dioxide into the vapor phase, raising the pH of the liquid phase.

Cooled samples of the liquid phase at the well-head typically have a pH of 5-6, depending on separation pressure. The calculated pH of the reservoir fluid--and that of the produced fluid below the flash zone--is 4.5. The estimated fugacity of the carbon dioxide in the reservoir is 37.5 psia. The reservoir fluid also contains around 35 ppm hydrogen sulfide, as well as an abundance of heavy metal ions. The lead concentration is around 70 ppm and

Figure 3.1-2. Comparison of the Median Survival Stress of RS-115 and API Grade L-80 and C-90 Casing Steels in NACE Solution [Waid and Stiglitz 1979]

the combined concentration of arsenic, antimony, copper, and noble metals is 20-50 ppm [McCright 1981]. Downhole, all surfaces become coated with a heterogeneous scale of silica and heavy metal sulfides. Many heavy metal sulfides are semiconductors and may serve as fixed cathodes, causing accelerated localized corrosion at defects in the scale.

Using refreshed autoclaves, Shannon [1977] investigated the effect of chloride concentration on metal loss corrosion of carbon steels. Figure 3.1-3 shows the results of corrosion rate tests of ten carbon steels over a wide range of temperatures (112°-482°F) in synthetic brines containing 6070 ppm chloride and 123,200 ppm chloride. The brines were deaerated and maintained at a total pressure of 1000 psig, including a carbon dioxide partial pressure sufficient to produce a pH of 5.0. There was no hydrogen sulfide, and the results were expressed as uniform corrosion--calculated from weight loss by assuming that metal is removed evenly from the entire surface and that no pitting occurs. Nonetheless, the results are qualitatively comparable to field experience at Wairakei (1500 ppm chloride, pH 6.3, 489 ppm carbon dioxide) and the Salton Sea.

This experiment showed a decrease in weight-loss corrosion with increasing temperature for carbon steel in 6070 ppm chloride synthetic brine. The decrease was attributed to a transition from ferrous carbonate films at 122°F to magnetite films at higher temperatures. In the 133,500 ppm brine, the ten steels showed a decrease in corrosion rate from 122°F to 300°F. Above 300°F, some samples showed a continued slight decrease in metal-loss rate up to the maximum test temperature of 482°F. Other samples showed a dramatic increase in the corrosion rate over this range [Shannon 1977]. This wide variation between similar test specimens may indicate a borderline passivity. In some cases the magnetite film is resistant to the high chlorides at temperatures above 300°F and in other cases the film ruptures and rapid acceleration of corrosion occurs.

Figure 3.1-3. Corrosion of Carbon and Low-Alloy Steels in Low and High Chloride Synthetic Brines with pH = 5.0.

Shaded regions plotted from data provided by Shannon [1977]. Broken line plotted from data provided by Posey, Palko, and Barcarello [1977]

The broken curve in Figure 3.1-3 is data replotted from a study of corrosion of ASTM A212B carbon steel in 123,200 ppm sodium chloride without carbon dioxide or other dissolved gases [Posey, Palko, and Bacarello 1977]. Comparison of this curve with results for specimens in brine containing carbon dioxide shows that laboratory tests without dissolved corrosive gases are probably invalid for evaluating downhole corrosion resistance. Also, because most of the carbon dioxide is lost from the geofluid upon flashing, materials test results above ground may indicate less severe corrosion than actually occurs downhole, as was discussed in Section 2.2.

Four in-situ downhole corrosion tests of low-alloy steels have been performed at the Salton Sea KGRA. The general conditions of these tests are summarized in Table 3.1-11.

In the Shell Development company coupon test [Treseder and Weiland 1976], the only low-alloy material exposed was J-55 casing. The test also contained several highly alloyed metals. Results for these materials are discussed in Section 4.1.1. The findings for the J-55 tubing and a J-55 weight-loss coupon at a 4260 ft. depth in the State No. 1 well are summarized in Table 3.1-12. In this test, the casing had been used previously for a few days in another Salton Sea well and therefore did not have a new surface. The J-55 coupon was electrically coupled to a Monel 400 sample holder, and may have received a degree of cathodic activation. The weight-loss corrosion rate expressed as uniform corrosion was 380 mpy, but the coupon was pitted. The worst pit was 43.8 mils deep after the 16 day exposure, giving an annual linearized penetration rate of 1000 mpy. The depth ratio--the ratio of pitting to uniform corrosion rate--was 2.6.

The corrosion pattern for the J-55 string supporting the test rack showed pitting of typically 100-200 mpy above 3290 ft. with generally discrete pits. Below this depth--probably the flash zone--pit penetration rates were typically 500-1600 mpy with either large discrete pits or large patches of rapid penetration--mesa and canyon attack [Treseder and Weiland 1976].

TABLE 3.1-11. TEST CONDITIONS DURING THE FOUR DOWNHOLE CORROSION TESTS AT THE SALTON SEA KGRA

Test Identification	Shell Development Co. Downhole Corrosion Test	LLL 3-Mo. Coupon Test	LLL 3-Mo. Tubing Test	LLL 6-Mo. Tubing Test
Well Name	State No. 1	Magmamax 1	Woolsey 1	Magmamax 1
Total exposure (hrs)	386	2280	1656	6 Mo ^a
with brine flow (hrs)	--	1500	904	4 Mo
without brine flow (hrs)	--	780	752	2 Mo
Brine flow rate (gpm)	800 - 1200	400 - 500	500	--
Temperature				
Bottom Hole (°F)	608		500	
Wellhead (°F)	--	500 410	366	values presumed similar to LLL
Pressure (psia)	--	630 (at 1800 ft.)	166 (surface)	
Brine Chemistry				
pH (surface)	--	5.6 - 6.0	5.8	
pH (reservoir)	4.5	4.5	4.5	3-Mo
Cl ⁻ (ppm)	127,000	135,900	85,700	Coupon
SO ₄ ⁻² (ppm)	1.2	110	108	Test
Total CO ₂ (ppm)	5,000	4,472	--	
Total H ₂ S (ppm)	30	35	--	

-- Data not reported.

^aAbout 490 ft. of the test string fell to the bottom of the well and was not recovered for an additional two months.

Sources: Treseder and Weiland 1976; McCright 1981; Cosner and Apps 1978.

TABLE 3.1-12. RESULTS OF 16-DAY DOWNHOLE CORROSION TEST IN SALTON SEA KGRA WELL STATE NO. 1

J-55 tubing Joint No.	Approximate Depth (ft.)	Pitting Rate ^a		Crevice Corrosion at Coupling (mpy)	Comments
		Maximum (mpy)	Average ^b (mpy)		
15	450	140	90	none	Shallow etch, light pitting
51	1530	320	155	320	Few shallow pits
63	1890	270	185	410	General pitting
80	2400	480	320	--	General pitting
108	3240	450	190	730	General pitting
109	3290	340	200	480	General pitting
116 Top	3380	750	515	910	Deep large diameter pits
116 Bottom	--	1500	650	1200	Deep large diameter pits
133	3390	1200	740	1800	Large areas corroded deeply
137	4100	1600	1000	1500	Large areas corroded deeply
142	4260	1300	950	2200	Large areas corroded deeply
142 Coupling	--	1600	1400 ^d	1600	Severe crevice corrosion adjacent to end
143 ^c	4260	2000	1600 ^d	2000	Severe general corrosion
J-55 Coupon	4260	1000	--	500	Corrosion rate by weight loss was 380 mpy. Coupled to Monel 400 tool. Possibly cathodically activated.

-- No data available.

^a Calculated from maximum observed penetration after 16 days exposure extrapolated to one year exposure

^b Average of eight deepest pits

^c Perforated pup joint specimen holder

^d Average of four deepest pits

Source: Treseder and Weiland 1976

Lawrence Livermore National Laboratories (LLNL) placed a 1728 ft. string of J-55 tubing in Salton Sea well Woolsey No. 1 for 1656 hours [Quong and Owen 1980]. The well was produced at about 500 gpm for about 55 percent of the exposure period. The general conditions of this test were summarized in Table 3.1-11. In addition to the J-55, a few joints of N-80 and C-75 were also included in the string. The J-55 was exposed in two heat treatments, producing two microstructures. The chemical analyses and microstructures are described in Table 3.1-13. The researchers felt that the most important corrosion parameter was maximum pit penetration rate on the hypothesis that total failure of the casing would occur not long after perforation, and this parameter was measured.

After the 69 day exposure, the string was removed and inspected. The worst pit in the central region of each joint and the worst pit in the upset area at the joint end were located visually and the depth was measured. The results from selected joints of J-55 are given in Table 3.1-14 along with all of the results from the N-80 and C-75. The normalized J-55 showed worst pits ranging from 6 mils (32 mpy) to 109 mils (577 mpy) with an average of 40 mils (213 mpy). The coarse-grained, annealed, J-55 showed worst pits ranging from 2 mils (11 mpy) to 46 mils (243 mpy) with an average of 35 mils (185 mpy). There is no statistically significant difference in the reported results of these two heat treatments of J-55.

The N-80 and C-95 casings showed worst pit depths of less than 0.5 mil after 69 days exposure, for an extrapolated penetration rate of less than 3 mpy.

Coupons of four commercially obtained low alloy steels and six low alloy steels supplied by the United States Bureau of Mines (BOM) were also exposed for 95 days at a depth of 1800 ft. in Salton Sea well Magnamax 1 [McCright 1981]. The well was in production for 1500 hrs. of the 2280 hrs of the test. The test conditions were summarized in Table 3.1-11.

TABLE 3.1-13. COMPOSITION AND MICROSTRUCTURE OF CASING STEELS USED IN TUBING CORROSION TEST IN SALTON SEA WELL WOOLSEY NO. 1

Casing Grade API	Composition	Heat Treatment	Microstructure
J-55	0.31C, 1.43Mn, 0.11P, 0.12S, 0.06Si, 0.13 Mo	Normalized	Normalized ferritic/pearlitic structure with ferrite surrounding prior austenite grain boundaries. Fine grained: 9-10 ASTM grain size. Slight decarburization up to 3 mils deep
J-55	0.31C, 1.43Mn, 0.11P, 0.12S, 0.06Si, 0.13Mo	Annealed	Ferritic/pearlitic structure with ferrite surrounding prior austenite grain boundaries. Coarse grained: 2-3 ASTM grain size. Slight decarburization up to 3 mils deep.
C-75 Type 1	0.44C, 1.60 Mn, 0.016P 0.018S, 0.20Mo, 0.23Si	API specs require quench and temper	Very fine structured tempered martensite. Slight decarburization up to 3 mils deep.
N-80	0.44C, 1.60Mn, 0.016P 0.018S, 0.20Mo, 0.023 Si (prepared from same heat of steel as C-75 Type 1, treated to N-80 specifications)	Not specified	Very fine structured tempered martensite. Slight decarburization up to 3 mils deep.

Source: Quong and Owen 1980

TABLE 3.1-14. RESULTS OF 69-DAY TEST OF J-55, C-75, AND N-80 TUBING IN SALTON SEA KGRA WELL WOOLSEY NO. 1.

API Grade	Joint No.	Approximate Depth (ft.)	Maximum Rate of Penetration (mpy)	Heat Treatment
J-55	42B ^a	332	11	Annealed
J-55	40B	411	32	Normalized
C-75	39	445	<3	Quench and Temper
J-55	37	513	<3	Not reported
J-55	34B	616	32	Normalized
J-55	29B	782	74	Normalized
J-55	27B	848	32	Normalized
C-75	21	1055	3	Quench and Temper
N-80	19	1119	3	Not reported
J-55	18B	1152	53	Normalized
J-55	16B	1221	95	Annealed
J-55	13B	1324	95	Normalized
J-55	12B	1358	116	Normalized
J-55	11B	1393	116	Annealed
J-55	10B	1427	159	Normalized
J-55	9B ^b	1461	492	Annealed
J-55	9A ^b	1461	492	Normalized
J-55	8A	1495	577	Normalized
J-55	7B	1529	116	Annealed
J-55	7A	1529	323	Normalized
J-55	6B	1564	222	Annealed
J-55	6A	1564	344	Normalized
J-55	5A	1595	222	Normalized
C-75	4A	1629	2.8	Quench and Temper
C-75	4B	1629	2.1	Quench and Temper
J-55	3B	1662	243	Annealed
J-55	3A	1662	428	Normalized
N-80	2A	1694	3.0	Not reported
N-80	2B	1694	2.8	Not reported

^aB=Section near upset end of joint.

^bA=Section near center of joint.

Source: Quong and Owen 1980

The specimens were cylindrical, about 0.25 inch in diameter and about five inches long. They were ground to a 400 paper finish, preweighed, and installed in the test rack. The specimens were electrically insulated from each other and the mounting rack by Teflon spacers. The assembly was inserted in a perforated Teflon sleeve at the end of the supporting tubing string. The test depth (1800 ft) was far below the flash zone, and the specimens were exposed to carbon dioxide-rich, single-phase brine. The perforated structures around the coupons allowed circulation of the geothermal fluid.

After exposure, the coupons were cleaned by glass bead blasting--shown not to cause significant metal loss. The results of this test are shown in Table 3.1-15. One of the carbon steels (AISI 1018) was totally destroyed; the other, ASTM A106B, had an average weight loss corrosion rate of 17 mpy. It had pits 50 mils deep for an annualized pitting rate of 264 mpy, which agrees with the J-55 experience in the Woolsey No. 1 tubing test.

The two commercially acquired low-alloy steels ASTM A387 grade 5 (5.5Cr-0.5Mo) and A387 grade 9 (9Cr-1Mo-1Si) and the BOM-supplied 2.25 Cr-1Mo all had about one-fourth the weight loss of the 106 carbon steel. The A387 grade 5 and A387 grade 9 also had pitting less than one-sixth as deep as the carbon steel. The best alloy was the 2.25 Cr-1Mo [McCrigh 1981a].

Examination of the tubing "string" which supported the corrosion experiment fixture and instrument package indicated severe more-or-less localized corrosion. The tubing was made of API J-55. Many sections of the tubing string were attacked and perforated through the wall thickness of about 145 mils (annualized corrosion rate greater than 560 mpy). Yet, there were always large areas of virtually unattacked metal adjacent to the perforated areas.

In some cases, the perforations were elongated along the tube axis, perhaps indicative of attack initiated by sulfide inclusion stringers. In other cases, however, the attacked area was more or less circular or followed the circumference of the tube, so that no simple generalization on the cause

TABLE 3.1-15. CORROSIONS OF LOW ALLOY STEELS EXPOSED FOR THREE MONTHS AT A DEPTH OF 1800 FEET IN SALTON SEA KGRA WELL WOOLSEY NO. 1

Alloy Designation or Composition	Weight Loss Corrosion ^a		Observations on Attacked Surface
	Average ^b (mpy)	Range (mpy)	
<u>Commercial Steels</u>			
AISI 1018 (0.18C)		Indeterminate	Both 0.1 in thick specimens corroded away.
ASTM A106B (0.30C)	17.0	16.6 - 18.5	Deep pits (50 mils). Attack very severe near one end of specimens.
ASTM A387 Grade 5 (5.5Cr-0.5Mo-0.15C-0.5Si)	4.5	4.1 - 4.6	Small shallow pits (5-8 mils deep) over much of the surface area.
ASTM A387 Grade 9 (9Cr-1Mo-0.15C-1Si)	4.6	4.4 - 4.9	Small pits (5-8 mils deep) over surface. Similar to A387 grade 5
<u>Bureau of Mines Steels</u>			
0.5Mo	--	24.7 - 40.5	Very heavy attack on entire specimen area.
5.0Mo	--	14.9 - 15.0	Heavy attack. Large pits evenly distributed.
10.0Mo	--	4.1 - 4.2	Some pits. Much improved resistance compared to 0.5Mo and 5Mo.
2.25Cr-1Mo	--	1.0 - 2.9	Abundant shallow pits uniformly distributed.
2.25Cr-2Mo	--	3.8 - 4.1	Similar to 2.25Cr-1Mo.
2.25Cr-1Mo-1Si	--	33.1 - 33.9	Wide pits; generalized attack.
2.25Cr-1Mo-1Si	--	24.4 - 29.7	Wide deep pits. Heavy attack.

-- Data not reported.

^aExpressed as though metal were lost uniformly

^bThree or four coupons

Sources: Lawrence Livermore Laboratory 1979; McCright 1981.

of the local attack was possible. The string of J-55 tubing was comprised of material from different sources. As the specification for this grade of steel allows considerable compositional and microstructural latitude, some of the differences in the corrosion behavior from one section to another may be attributed to these metallurgical factors [McCright 1981a].

A string of intermixed joints of ten compositionally controlled low-alloy steels, commercially acquired J-55, N-80, and C-75 casing, and four special heat treatments of the J-55 and N-80, was also installed downhole in the Magmamax No. 1 well late in federal fiscal year 1980. The 1800 foot long, 74-joint string was assembled so that each material would be exposed in the upper, middle and lower sections of the well. The flash zone moved up and down in the upper two sections according to operating conditions, while the lower section was probably always exposed to single phase liquid.

The tubing was installed in well Magmamax No. 1 for six months with the well in production for about 65% of that time. When the string was retrieved, it was found that a joint of J-55 had corroded through--parted--at about 1308 feet, dropping the bottom 497 feet of string to the bottom of the well; 377 feet of this bottom section were recovered two months later. Unfortunately, the results of this test have not been formally published. The above account of the experiment and Table 3.1-16 were assembled from informal communications with R.D. McCright, of LLNL [1981b].

From Table 3.1-16, it is readily apparent that the compositionally controlled steels--with their tight restrictions on composition and purity--are much superior to the property-controlled (API) steels. The specifications for the property-controlled steels allow much wider ranges of composition. For example, API Specification 5A for N-80 and J-55 sets limits for sulfur and phosphorous only.

The AISI 1018 carbon steel gave dramatically better performance than did any of the API grades, but the ASTM A106B carbon steel and A204 (0.5Mo steel) did not do much better than did N-80, which gave the best performance

TABLE 3.1-16. RESULTS OF TUBING CORROSION TEST IN SALTON SEA WELL MAGMAMAX NO. 1

	Upper and Middle Section 6 Mo. Exposure	Lower Section 8 Mo. Exposure	Ranking Key (Based on visual inspection)
<u>Composition Controlled Alloys</u>			
AISI 1018 (carbon steel)	B	B	A: Best performance Less than 20 mils penetration of tube wall. No perforations.
ASTM A106B (carbon steel)	C	E	
ASTM A204 (0.5Mo)	E	C	
ASTM A387gr 2(0.75Cr-0.5Mo)	B	B	B: Fair performance Corrosion pustules and ruptured scale, but no visually significant localized penetration into tube wall.
ASTM A387gr 11(1.25Cr-0.5Mo)	B	B	
ASTM A387gr 22(2.25Cr-1Mo)	B	A	
ASTM A387gr 5(5Cr-0.5Mo)	D	A	
ASTM A387gr 7(7Cr-0.5Mo)	A	lost	
ASTM A387gr 9(9Cr-1Mo)	A	lost	C: Poor performance Patches of considerable corrosion with penetration greater than 20 mils into tube wall. No perforations of the tube wall.
<u>Property Controlled Alloys</u>			
API J-55 as received	E	E	D: Bad performance Considerable corrosion with readily apparent penetration into the tube wall. One to five perforations of the 145 mil thick tube wall per 20 feet of tubing.
API C-75 as received	E	E	
API N-80 as received	D	D	
API N-80 Q+T ^a	C	--	
API N-80 air cooled ^b	C	--	
API N-80 furnace cooled ^d ^c	C	--	E: Worst performance Extensive corrosion patches with more than 20 mils penetration. More than five perforations of the 145 mil thick tube wall per 20 feet of tubing.
API N-80 spheriodized ^d	C	--	
API J-55 Q+T	C	--	
API J-55 air cooled	D	--	
API J-55 furnace cooled	D	--	
API J-55 spheriodized	D	--	

-- No data available.

^aAustenized (heat above A₃ temperature), oil quenched, then tempered to grade specifications.

^bAustenized, then air cooled (normalized).

^cAustenized, then furnace cooled.

^dSpheriodized (24 hours just below A₃ temperature).

Source: Personal communication with Daniel McCright, Lawrence Livermore Laboratories.

of the API grades. The 0.75Cr-0.5Mo, 1.25Mo, and 2.25-1Mo steels gave fair-to-best performances, indicating that relatively minor alloying with chromium and molybdenum can significantly improve downhole corrosion resistance. The 7 Cr-0.5 Mo and 9Cr-1Mo gave the best performance, as one would expect from their higher chromium content.

Recent work at Case Western Reserve University [Roy, et al. 1980; Troiano and Hehemann 1981b], in corrosive media which do not simulate geothermal conditions, has shown that impurities and inclusions in low-alloy steel play a major role in pit initiation. The tighter compositional controls of the ASTM and AISI grades result in reduced inclusions; this may in turn account for the improved corrosion resistance of these alloys. As was discussed in section 3.1.2, minor alloying, minimization of sulfur content, and shape control of sulfur inclusions also increase resistance to sulfide stress cracking, always a factor in geothermal operations.

The results of these four downhole corrosion tests do not solve the problem of downhole localized corrosion in hypersaline resources. The data do suggest, however, that commonly available API casing is a poor risk in this application. A moderate alloy steel such as A387 grade 2, grade 7, or grade 9 heat treated to API specifications for C-90 or C-95 may offer the best combination of localized corrosion and SSC resistance of any low alloy steel.

3.2 Drillstem

API 5A grade D and E tubings are frequently used in geothermal drilling. The corrosion problems experienced with drillstem are in many regards the same problems encountered in sour oil drilling. The principal problems are wear and erosion; corrosion, usually in the form of pitting; and corrosion-fatigue resulting in twist-offs. All of the above corrosion phenomena decrease the strength-related properties required by the extremely high mechanical loads and transient shocks encountered in geothermal drilling. The degradation of strength-related properties is all the more severe because most geothermal drilling occurs in the presence of hydrogen sulfide

once the reservoir is penetrated. The presence of hydrogen sulfide limits the yield strength of the drillstring materials. In many cases, the reservoir is underpressured, and drilling mud cannot be used to prevent the influx of geothermal fluid, lest irreversible damage to the formation results. Instead, air or foam is often used, leading to severe pitting.

For example, the Hot Dry Rock Geothermal Project at Fenton Hill, NM, experienced numerous "twist-offs" while drilling at depths greater than 10,000 feet in granite. Three failures of API Grade E, 5-inch drill pipe were investigated. One piece parted at 4549 feet, one at 7000 feet, and one at 7270 feet during normal drilling operations. The failures occurred as separate events a few weeks apart. The formation temperature at the respective depths were 234°F, 294°F, and 306°F. However, the hole was much cooler. Fresh water--with a pH of 8.9 and containing 166 ppm chloride and 1250 ppm sulfate--was used as drilling fluid. The return temperature was less than boiling (about 198°F at Fenton Hill). The drill pipe had between 750 and 900 rotating hours of service at the time of failure.

In each case, failure analysis showed that the drill pipe was heavily pitted on the internal surface and that corrosion-fatigue cracks had originated in the pits and propagated to failure. The pipe had been bought "used" and was not inspected prior to use at Fenton Hill [Anliker 1981]. Inspection prior to use might well have prevented the failures.

As indicated above and by much other experience [Salzbrenner 1980], corrosion-fatigue and pitting are probably the predominant drillstem killers. The two are frequently linked, because pits serve as stress concentrators and because the micro-environment in the pit may be far more corrosive than in the bulk drilling fluid. The pH may be 1-3 in the bottom of a pit, regardless of the bulk pH of the drill fluid. Bearing this connection in mind, the two failure modes are discussed separately in the following two sections.

3.2.1 Corrosion-Fatigue

Metals under cyclic loading can fail at stresses far below those stresses that characterize their static mechanical properties. When this phenomenon occurs in "inert" environments (i.e., air), it is called fatigue. When the applied stress is plotted against the logarithm of the number of cycles to failure (S/N plot), the cycle-to-fail curve becomes asymptotic to a limiting value of stress. Below this stress there will be no failure, whatever the test length. This is the "fatigue limit" or "fatigue strength" [Gilbert 1956; Wescott 1938].

When the metal is exposed to a corrosive environment while under cyclic stress, the S/N graph never becomes asymptotic to a limiting stress. The fatigue endurance limit (FEL) is the greatest unit stress which may be applied under given conditions of stress, rate of stress application, temperature, and corrosive environment without causing failure in a given number of cycles of stress [Westcott 1938]. The values for corrosion-fatigue limits are useless, except for comparison within one set of tests, unless the number of cycles and cycle rate are given.

Almost no fatigue studies have been reported in geothermal environments, and those which have been reported are all in steam [Ellis and Conover 1981]. No such tests under downhole-like conditions have been performed. However, tests in geothermal steam clearly show that the acid gases present in geothermal operations cause serious exacerbation of corrosion-fatigue. For example, fatigue tests of 2.5Ni-Cr-Mo-V rotor alloy in geothermal steam at Otake, Japan, indicate a reduction in FEL of 41.4 percent at 100 million cycles of stress. These specimens were cyclically loaded during exposure to the environment. In boiler-quality steam, the reduction in FEL for 2.5Ni-Cr-Mo-V was 16.1 percent at 10 million cycles of stress and 17.2 percent at 100 million cycles of stress. Similar results were obtained at Cerro Prieto and The Geysers, California [Ellis and Conover 1981].

Corrosion-fatigue tests were done in a solution containing 35,400 ppm chloride with additions of carbon dioxide, hydrogen sulfide, and oxygen. AISI 1035 specimens were stressed 10 million cycles at 10 Hz [Mehdizadeh, McGlasson, and Landers 1966]. Chloride had no significant effect on the fatigue endurance of low-alloy steels. In a neutral, air-free (less than 0.1 ppm oxygen) solution, the FEL (compared to the FEL in air) increased slightly. Addition of 3000 ppm hydrogen sulfide to the chloride solution lowered the pH to 4.5. The endurance limit decreased 20 percent and cracking and hydrogen blistering occurred. The effect of hydrogen sulfide on harder materials may be much more severe. These materials are cold-worked under cyclic stress and may become susceptible to SSC as well as to corrosion fatigue.

Addition of 700 to 800 ppm carbon dioxide and 250 to 300 ppm bicarbonate to the chloride solution reduced the pH to 5.5 and reduced the FEL 41 percent. Many cracks were observed. Although carbon dioxide does not cause SCC of statically loaded materials, it appears to be an effective cracking agent when combined with cyclic stress.

The synergistic effect of carbon dioxide and hydrogen sulfide is worse than the sum of their actions. In a chloride solution containing 700 to 800 ppm carbon dioxide and 60 to 70 ppm hydrogen sulfide, FEL decreased 62 percent. Both pitting and surface cracking were observed.

The addition of less than ten ppm oxygen drastically reduced the FEL in the chloride solution (65 percent reduction). Addition of three ppm oxygen doubled the reduction in FEL in the chloride/hydrogen sulfide solution, but caused little, if any, increase in damage in the chloride/carbon dioxide solution.

Tests on carbon steels and low- and middle-alloy steels in fresh, salt, and seawater show that endurance limits in a moderately corrosive medium (i.e., saltwater) are practically independent of the chemical composition of the steel [Mehdizadeh, McGlasson, and Landers 1966]. However, the same metallurgical features which lead to improved resistance to sulfide stress

cracking in casing also lead to improved toughness and corrosion fatigue resistance [Salzbrenner 1980]. Recent development of such steels was presented in Section 3.1.2.

3.2.2 Pitting and Metal-loss Corrosion

Another major problem encountered in geothermal drilling is oxygen damage when air drilling. At The Geysers, mud drilling is used down to the impermeable cap over the geothermal steam reservoir. Below this depth, air drilling is required to prevent formation damage. Air flow rates of 3000 cu.ft./min. are common. The return air is mixed with geothermal steam containing rock cuttings and corrosive gases. This combination of conditions produces serious erosion and pitting damage to the API grade E drill pipe. As indicated above, pitting also promotes corrosion-fatigue. Thus, mitigation of pitting should also reduce fatigue failures and twist-offs.

Use of a Corrosion Inhibitor

In the early 1970's, Union Oil Company discarded one foot of drill pipe for each two feet of hole when air drilling at The Geysers. In addition, an average of two to three fishing jobs were performed per month per well.

Union developed an amine-based inhibitor, sold commercially under the trade name Unisteam. This inhibitor is a water-soluble monomer at temperatures below 250°F. At higher temperatures, it forms a resinous gum which coats the drill pipe as well as the abrasive rock chips. The resinous coating protects against erosion, while the amine functional group inhibits corrosion. The inhibitor dosage is at least 200 ppm in the steam produced while drilling. Dosages of one to six gallons/hour are typical. The inhibitor is mixed with 10 bbl of water and injected into the air stream at one gpm. The maximum amount of Unisteam injected is limited to 140 gallons per day to avoid resin plugging of the drill bit.

Using Unisteam in the above method at The Geysers allows seven feet of hole to be made for each foot of drill pipe scrapped, a 72 percent reduction in the cost of drill pipe. The use of Unisteam, in conjunction with a vigorous program of inspection, has nearly eliminated fishing operations [Fisher and Pyle 1977; 1978].

In many cases, mud cannot be used at liquid-dominated resources because the reservoirs are also underpressured, or because the mud sets at high temperatures [Fisher and Pyle, 1977; Baron and Ungemach 1981]. Air-water drilling with 400 gpm water mixed in 800-1000 cu.ft./min. of air is often used under such conditions. The air-water drilling fluid is mixed downhole with typically acidic geothermal fluid containing chlorides and other corrosive species. The combination of air, corrosive ions, and high temperature--often above 450°F--causes severe corrosion.

Union reported that in such operations corrosion rates were in excess of 25 lb/sq. ft./yr, which is equivalent to 575 mpy expressed as uniform corrosion. A string of grade 1 drill pipe was destroyed in 10 days [Fisher and Pyle 1978]. Addition of Unisteam amine resin corrosion inhibitor, coupled with maintenance of a pH of 9.5-11 with ammonium or sodium hydroxide, reduced the corrosion loss to less than 2 lb/sq.ft./yr. (50 mpy expressed as uniform corrosion); a 92 percent reduction in the metal loss rate [Fisher and Pyle 1977; 1978; Pye 1981].

Other corrosion inhibitors may also be valuable in these operations. However, considerable caution is required. Many inhibitors used at lower temperatures, for example the inhibitors used with acidizing solutions, break down at high geothermal temperatures. They may become ineffective, yield undesired byproducts, or may even be corrosive.

Use of an Inert Gas

Another approach to air/water drillstem corrosion control, developed by Sandia National Laboratories, is replacement of the air by an inert gas. Either cryogenically distilled nitrogen or specially combusted diesel exhaust may be used [Caskey and Copass 1981; Hinkebein and Snyder 1981].

In drilling tests at the Baca, New Mexico, geothermal resource, eight drillstem corrosion rings were included in the tool joints during 1315 feet of drilling using aerated water/air mist with pH 10-12. These rings showed weight-loss corrosion ranging from 73 mpy to 450 mpy (expressed as uniform corrosion). The average weight-loss corrosion rate for these rings was equal to 200 mpy. Most of the rings showed numerous deep pits [Caskey and Copass 1981].

A second drilling run was made using cryogenically distilled nitrogen rather than air, and water with pH 8-9. The four corrosion rings exposed showed weight-loss corrosion rates equivalent to 4.4 mpy to 30 mpy, with an average of 12 mpy. Most showed little if any pitting. These data indicate that use of inert gas/water drilling fluid can drastically reduce pipe corrosion, especially pitting.

The use of diesel exhaust as an inert gas source has also been studied. This evaluation concluded that pitting corrosion of drillstem steel will be suppressed if the dissolved oxygen concentration in the water film coating the steel is kept below 0.05 ppm. The dissolved oxygen concentration is a complex function of temperature, pressure, ionic strength of the water, and gas/water ratio. In the specific case where bottom hole temperature is 347°F, pressure is 250 psig, sodium chloride equals 1000 ppm, and inert gas/water ratio is 3.33 SCF/gal, the maximum allowable oxygen content in the inert gas was calculated to be 50 ppm (the algorithm for this calculation is given in Hinkebein and Snyder [1981]).

It was concluded that this oxygen concentration could be obtained by reacting diesel exhaust with a stoichiometric amount of fuel in a catalytic converter. Acids formed by the reaction of nitrogen oxides, sulfur oxides, and carbon dioxide with water require neutralization by addition of caustic to the drilling water. It was concluded that inert gas/water drilling using treated diesel exhaust is an economically viable option [Hinkebein and Snyder 1981].

3.3 Casing Materials for Low-Temperature Geothermal Production Well Operations

Low-temperature geothermal production wells present much less severe problems than do their high-temperature counterparts. For example, thermal stress, which can approach or exceed the yield strength of casing steels in high-temperature geothermal wells, is trivial in low temperature operations. Likewise, there should be little risk of casing collapse due to expansion of pockets of trapped water or mud in an incomplete cementing job. Conventional water well drilling, completion, and cementing practices seem adequate for low-temperature production wells.

3.3.1 Steel Casing

The general characteristics of low-temperature geothermal resources were summarized in Tables 2.2-9 and 2.2-10; chemistries of 21 low-temperature resources were given in Table 2.2-4. A recent statistical evaluation [Ellis 1982] of thirty-six carbon steel corrosion/geothermal environment data sets showed that there is a strong statistical association of variations in pH and total alkalinity with weight-loss corrosion rate. Variations in chloride, sulfate, and hydrogen sulfide (over the range 0.02 ppm to more than 5ppm) were not shown to correlate significantly with changes in the weight-loss corrosion rate. The Ryznar Index, commonly used to predict corrosiveness of domestic water supplies, was shown to not be predictive in low-temperature geothermal operations.

Low-temperature resources have been divided into two classes, as shown in Tables 2.2-9 and 2.2-10. Class Vb resources have pH 7.8 to 9.85 and total alkalinities less than 217 ppm (as calcium carbonate). The median weight-loss (uniform) corrosion rate of carbon steel in these resources is 0.12 mpy with a probable upper limit (95 percent probability) of 1.65 mpy [Ellis 1982].

Pitting of carbon steel is not particularly severe in Class Vb resources either. Of the resources studied, 28 percent had no detectable pitting and an additional 40 percent had pitting less than 5 mpy. The highest pitting rate was about 20 mpy. Carbon steel or low-alloy steel casings will probably give good service lives in Class Vb low-temperature geothermal production wells.

The Class Va resources are a different story. The resources have pH of 6.7-7.6 and total alkalinities of more than 207 ppm (as calcium carbonate). The weight-loss corrosion rate of carbon steel in these resources is 5 mpy to 20 mpy (95 percent probability limits) with a median of 12.5 mpy. Furthermore, the corrosion is characterized in most cases by severe pitting. Of eleven cases studied, one showed no pitting and 8 mpy uniform corrosion. Nine cases were reported to have heavy pitting: though the depth was not quantified, pits were numerous and certainly more than 5 mpy. One case had localized corrosion of 83 mpy. In this case, the 0.300-inch wall of the three-inch schedule 40 well-head pipe was 78 percent penetrated in about two years [Ellis 1982; Anliker and Ellis 1981]. Clearly, significant problems may occur with carbon steel casing used in Class Va resources. Whether or not low-alloy composition-controlled steel casing would give improved performance is not known.

3.3.2 Nonmetallic Casing

A number of thermoset and thermoplastic resin systems have been investigated by the National Water Well Association (NWWA) as alternatives to steel casing for low- to intermediate-temperature geothermal wells. The following thermoplastic systems were judged to be suitable, within limits, for casing applications:

ABS (Polymerized acrylonitrile-butadiene-styrene monomer)

PVC (Polyvinyl chloride)

CPVC (Chlorinated polyvinyl chloride)

SBR (Styrene-butadiene copolymer resin)

Epoxy resin, polyester resin, and vinylester resin thermosetting systems are also suitable. These are usually offered in composite or fiber-reinforced materials. All of these systems are essentially inert to the corrosive species in geothermal fluids, including dissolved oxygen. Polyimide resin systems, though resistant to very high temperatures, are susceptible to catastrophic hydrolysis and cannot be used in contact with geothermal fluid [Gass, Purdin and Armitage 1979].

The principal limitations on use of non-metallic casings, as compared to steel casing, are related to mechanical properties and resistance to temperature. Table 3.3-1 summarizes some of the mechanical properties of the basic resin systems examined by the NWWA. API K-55 steel casing is included for comparison. The values presented in this table should be taken as a general guideline only. Within each family of compounds, differences in grade, formulation, and curing process can result in considerable variation in mechanical properties and thermal resistance. Variations among commercial products of the same type and grade may also occur.

The strength of the thermoplastics is largely a function of the basic polymer system; detailed formulation, including additives; and curing process. In general, the smaller the quantity of compounding additives, the better the resistance. Crosslinking can also improve mechanical properties.

TABLE 3.3-1. APPROXIMATE MECHANICAL PROPERTIES AND LIMITATIONS ON NON-METALLIC CASING MATERIALS

Material	SpGr (68°F)	Tensile Strength (at 68°F) (ksi)	Tensile Modulus (at 68°F) ^a (ksi)	Ceiling Temperature (°F)	Tensile Modulus at Ceiling Temperature (ksi)	Thermal Expansion (10 ⁻³ in/in °F)	Depth Limit (ft)
Thermoplastics							
ABS	1.04	4.5	299.9	180	220.4	3.05	1000
CPVC	1.55	8.4	422.4	180	--	3.78	1000
PVC	1.40	8.0	419.6	150	284.4	2.78	1000
SBR	1.06	3.8	320.0	140	284.4	4.17	1000
Thermosets							
Epoxy	1.89	9.5	1351.1	266	--	1.28	--
Polyester	1.80	8.2	1378.1	150	--	1.22	--
Vinylester	1.53	15.2	1041.1	199	--	1.22	--
Fiber-Reinforced Plastics							
Epoxy (continuous wound)	--	--	2190.2	266	1393.8	--	6562
Epoxy (fiber mat)	--	--	1329.8	150	938.7	--	--
Vinylester	--	--	938.7	199	739.6	--	1200
Reinforced Plastic Mortar (RPM)	1.95	27.0	2999.5	140	--	0.50	--
Casing Steel^b							
API K-55	7.84	75.0	39593.6	1800	--	0.63	--

-- No data available.

^aksi = thousand pounds per square inch^bIncluded for comparison purposes.**Abbreviations**

ABS - polymerized acrylonitrile, butadiene, and styrene monomers

CPVC - chlorinated polyvinyl chloride

PVC - polyvinyl chloride

SBR - styrene butadiene copolymer resin

Source: Gas, Purdin and Armitage 1979

Of the thermosetting plastics, the epoxy-type resins have greater thermal resistance than do vinyl ester resins, which have greater resistance than do polyester resins. Numerous formulations using different monomer molecular structures and hardeners are in use; however, a detailed discussion of variations due to these factors is beyond the scope of this document.

The thermosets are often offered in composite (fiber-reinforced plastic--FRP) forms. Due to the fiber reinforcement, these materials retain much of their ambient temperature strength up to their ceiling temperature. In general, strength and stiffness increase with increasing glass fiber content up to about 30 to 40 percent fiber weight. Above this level, strength decreases. Continuous-wound glass fiber gives higher strength than do other fiber arrangements. In fiber-reinforced plastic mortar (RPM), a layer of resin and sand is sandwiched between layers of fiber and resin for increased strength and rigidity.

The mechanical properties of all the nonmetallics in Table 3.3-1 decrease with increasing temperature. Comparison of ambient and ceiling temperature tensile moduli shows an 11 to 36 percent decrease at the ceiling temperature. Above the ceiling temperature these properties degrade rapidly.

The mechanical properties of these materials also deteriorate with prolonged exposure at elevated temperatures, but most of the regression occurs during the first three months. The long-term strength of the casing will be one-half to one-third of the short-term values stated in Table 3.3-1, while the long-term tensile modulus will be one-fourth to one-fifth of one short-term value. However, as the continuous loading on installed casing is relatively low (on the order of 0.08 psi), long-term strength and tensile modulus are not normally design or performance concerns [Cass, Purdin and Armitage 1979].

The depth limits in Table 3.3-1 are only general guidelines based on the experience of well drillers and manufacturer's recommendations. These depth limits are primarily a function of joint strength rather than tensile strength of the casing [Gass, Purdin and Armitage 1979].

In Pakistan and the United States, eight- to ten-inch diameter 200 mil-wall epoxy FRP has been used to depths of 295 feet in water wells, but it is reported that this thin-walled pipe has a tendency to collapse under normal well development stresses. Increasing the wall thickness-diameter ratio increases resistance to collapse: 240 mil-wall vinylester FRP has been used in a 1200 ft. well producing 200°F water. In France, seven-inch diameter 500 mil-wall epoxy FRP casing has been installed to a depth of 6562 ft. to produce 140°F water which is very corrosive to steel [Gass, Purdin and Armitage 1979].

The factors which determine the correct design of a well using non-metallic casing, and whether such casing is economical over steel casing, are quite complex and are beyond the scope of this document. The design of wells with nonmetallic casing is considered in detail in Gass, Purdin and Armitage (1979 Vol. 2).

3.4 Tubular Goods for Geothermal Injection Wells

At this time, only a few geothermal power plants--Otake and Hatchobaru, Japan; Ahuachapan, El Salvador; Larderello, Italy; and The Geysers and Magma Power, CA--are disposing of geothermal waste by injection. It is anticipated, however, that in the future most U.S. geothermal power plants will dispose of their spent brine by injection, both to solve the problem of waste disposal, as well as to conserve the resource and prevent subsidence.

Little if any specific investigation has been done of the corrosivity of spent geothermal brine on injection well tubulars. [Defferding 1980; Reid, et al. 1974; Bachman 1979; Jordan 1978]. Some major similarities and differences between geothermal injection and oilfield injection are presented in this section. No consideration is given to treatment requirements for scale control or particulate (suspended solids) removal.

The first major difference between geothermal injection and oilfield injection is the extremely large volume of water produced by geothermal power operations [Defferding 1980]. Table 3.4-1 gives the disposal volumes of a number of geothermal power plants in barrels per day per MWe (net). The 50 MWe (net) Heber Binary plant, for example, will discharge on the order of 785,500 bpd of spent brine.

In the case of geothermal injection, the spent brine could be injected into the producing formation or another hot formation, or it could be injected into a cool formation. This is in contrast to oilfield brine disposal which is usually into relatively cool formations.

To date, geothermal injection wells have been designed much like production wells (see section 3.1). The spent geothermal brine is injected into the production casing which is cemented from the injection zone back to the surface. This practice is in direct contrast to the oilfield practice--in many cases mandated by regulation--of injecting brine via an injection tube packed off at the top of the injection zone. In the latter practice, the annulus between the wall casing and injection tube is filled with oil or treated water. Annular pressure is monitored to detect leaks of the injection tube. Like oilfield systems, geothermal injection systems can be either open or closed.

3.4.1 Open Disposal Systems

In open systems, the geothermal waste is ponded, or otherwise exposed to air, prior to injection. Injection activities at The Geysers (about 234,000 bpd steam condensate) are open. Introduction of dissolved oxygen to

TABLE 3.4-1. WATER PRODUCTION FROM A SAMPLING OF GEOTHERMAL POWER PLANTS

Power Plant	Reservoir Temperature (°F)	Power Cycle	Waste Water Production		
			Brine	bpd/MWe (net) ^a Condensate ^b	Total
Cerro Prieto, Mexico	518	Flash-steam	4760	200	4960
East Mesa, California ^c	375	Binary LBNL-500	13200	None	13200
The Geysers, California	392	Rankine	None	260	260
Hatchobaru, Japan	554	Flash-steam	3020	120	3140
Heber, California (planned)	380	Binary	10500	None	10500
Larderello, Italy	428	Rankine	None	200	200
Raft River, Idaho	300	Binary	13800	None	13800
Wairakei, New Zealand	500	Flash-steam	6760	270	7030

^aSpecific gravity assumed equal to unity.

^bVaries with weather conditions.

^cFrom Nichols and Olander 1980.

Source: Defferding 1980 except as noted.

the geothermal waste drastically increases the corrosion rate. Hinkebein and Snyder (1981) offer the following equation as a first order predictor of "uniform" corrosion of carbon steel:

$$\text{mpy} = 13.7 (\text{ppb } \text{O}_2) \exp \frac{-2440}{^\circ\text{F}+460} + \exp [4(4-\text{pH})] + 4.9 (\%\text{NaCl})$$

This equation indicates that brine with one percent sodium chloride, pH 6.5, and no dissolved oxygen would cause a carbon steel corrosion rate of about 5 mpy in 150°F brine. This estimate is in good agreement with geothermal experience (Ellis and Conover 1981). At the same temperature, the same brine would have a dissolved oxygen content of 3-4 ppm if saturated with air. The estimated corrosion rate is 750-1000 mpy. This corrosion would be in the form of severe pitting: steel corrosion in brine occurs primarily as pitting at oxygen concentrations above 50 ppb [Hinkebein and Snyder 1981].

Clearly, if an open brine handling system is used, it is imperative that the brine be deaerated prior to injection. This could be achieved by mechanical means such as vacuum degassing, chemical treatment with excess sulfite, or by a combination of both methods. Condensate at The Geysers is deaerated prior to injection, but the volume is rather small (about 234,000 bpd for 15 stations). By contrast, a single 50 MWe (net) flashed-steam power plant may produce 235,000-530,000 bpd of water. Binary plants of the same size may produce as much as one million bpd of waste. These large volumes would make deaeration extremely costly. Treatment with inhibitors, as opposed to deaeration, is not likely to be viable, because such treatments do not prevent pitting [Ostroff 1979].

3.4.2 Closed Disposal System

In closed systems, the geothermal fluid is not exposed to air at any point during its processing. The Raft River 5 MWe (net) Binary Power Plant (at Raft River, ID) uses a closed system. The 50 (net) Heber Binary Power Plant will also use a closed system. The geothermal fluid is produced by

downhole pumps under a wellhead pressure of several hundred pounds per square inch. The pressurized brine first passes through the working fluid vaporizers where its temperature is decreased, then goes to the injection wells. The primary benefit of the closed system is that the carbon dioxide in the brine remains dissolved, thus there is no rise in pH and no precipitation of calcium carbonate. If a closed system is used, perhaps in conjunction with an inert gas blanket if the system pressure approaches atmospheric, there should be no need for costly deaeration of the spent fluid. The elevated carbon dioxide content may make the cooler brine more corrosive than the hot brine, as was discussed.

It is quite difficult to maintain a truly closed system, and it is recommended that the redox potential of the spent brine be monitored. Provisions to automatically inject an oxygen scavenger are also advisable. Though some consumption of oxygen scavenger may occur, it should be much less than would occur if the brine were aerated.

Severe thermal shock to pipes and injection wells is a major consideration with closed system injection. When the power plant is tripped off-line (upset), the injection wells will be slugged with production temperature brine which must continue to be produced for some time. A 150°F difference in normal versus upset injection temperature would produce compressive stresses of over 30 ksi in constrained (cemented) injection well casing.

A fairly common practice in nongeothermal waste water injection is to construct the well with a fiber reinforced epoxy (FRP) injection tube packed-off at the top of the injection formation. Due to the temperature limitations on nonmetallic casing, this approach will probably not be viable for closed systems, or for open systems if injection is into a hot formation where temperatures can be high when injection operations are interrupted. A similar limitation also probably applies to nonmetallic coatings on steel casing.

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4.0 STAINLESS STEELS AND NON-FERROUS METALS FOR HIGH-TEMPERATURE DOWNHOLE SERVICE

SUMMARY

This summary is quick reference to the material presented in Section 4. Please refer to the section for caveats, qualifications, and references cited for the material presented here.

Highly corrosion-resistant alloys are required for tubular goods and for many specialized purposes in almost any geothermal operation. This section presents a general discussion of the expected downhole performance of a number of alloys. Because such information is quite limited, only general guidelines for material selection are given. The suitability of these alloys for use in specific downhole tools is discussed in later sections.

A summary of the characteristics of the various alloy families is given as Table 4.0-1. The division into families generally follows the NACE Standard MR-01-75 (1980 rev.).

INTRODUCTION

As was shown in Section 3.1.1, severe localized corrosion of common casing metals materials may occur downhole. At one major U.S. geothermal resource, the Salton Sea KGRA, CA, this downhole corrosion may be so severe that it curtails development of the resource. Section 3.1.3.3 indicates that low-alloy additions to steels may not adequately mitigate this problem. Highly alloyed metals may be needed for the casing itself or to clad the casing used in this resource.

In addition to possible use as tubular goods, highly corrosion-resistant alloys will be required for specialized purposes in almost any geothermal operation. For example, high-strength corrosion-resistant metals will be required for parts such as springs, snap-rings and the like, even for tools

TABLE 4.0-1. SUMMARY OF THE ALLOY FAMILIES

Alloy Type	Examples	Recommendations and Cautions
Stainless Steels		Subject to intergranular corrosion if incorrectly heat treated
Martensitic Ferritic Stainless Steels (up to 17% chromium, 2% molybdenum, no nickel)	Types 410, 422, 430, 440A	Do not have adequate corrosion resistance for downhole use in Class I, III, or IV geothermal resources. Intergranular corrosion sensitization of ferritic steels at about 1700°F.
Highly Alloyed Ferritic Stainless Steels	E-Brite 26-1 (26Cr-1Mo)(XM27) Titanium-stabilized E-Brite 26-1S (XM33) Allegheny-Ludlum (A-L) 29-4 (29Cr-4Mo) A-L 29-4-2 (29Cr-4Mo-2Ni) SeaCure 26-3 (26Cr-3Mo)	E-Brite 26-1 (XM27 and XM33) are accepted under NACE Standard MR-01-75 (1980 rev.) if hardness $\leq$ HRC 22. Seacure 26-3, A-L 29-4 and A-L 29-4-2 may need similar hardness restriction. SCC threshold temperature in aerated 151,550 ppm chloride solution with no hydrogen sulfide is 375°F $\pm$ 25°F for E-Brite 26-1 and A-L 29-4-2 and 425°F $\pm$ for A-L 29-4.
Austenitic (300 Series) Stainless Steels (16-24% chromium, 8-19% nickel, 0-4% molybdenum)	Types 304, 316 Low-carbon 304, 316 Stabilized 304, 310, 317	May not have markedly better pitting resistance than do some low-alloy steels at high temperature. Risk SCC if cold worked or if subjected to tensile stress. Subject to intergranular corrosion if heated to 905°-1450°F range (perhaps to 1650°F), then cooled slowly.
Highly Alloyed Austenitic Stainless Steels	Carpenter 20Cb3 Avesta 254-SLC Type 904L A-L 6X Haynes 20 Mod Sanicro 28 Hastelloy M-532	Only A-L 6X has been tested downhole. It showed no detectable uniform or localized corrosion at Raft River. Some alloys have Stress Corrosion Cracking (SCC) threshold $\geq$ 300°F in 151,550 ppm chloride, but fail the boiling 45% magnesium chloride test which contains dissolved oxygen. Some have higher SCC resistance in the air-free hydrogen sulfide-rich environment.
Precipitation (Age) Hardening Stainless Steels (Hardness to HRC 30-35 if special heat treatment used)	A-286 17-4PH 15-5PH PH 15-7 MO	Because of chromium and molybdenum contents, these alloys probably have localized corrosion resistances similar to those of the austenitic stainless steels. 17-4PH and 15-5PH are susceptible to SCC in boiling 45% magnesium chloride; PH 13-8MO is resistant to SCC in this test.
Duplex Stainless Steels (austenite, ferrite matrix, hardness $\leq$ HRC 28)	Sandvik 2205 AF 22	Some are susceptible to SCC in NACE solution at room temperature. All those studied failed by SCC in NACE solution at 350°F. At lower sulfide, higher pH levels, there is either a greater SCC resistance or an increase in incubation time.

(Continued)

TABLE 4.0-1. SUMMARY OF THE ALLOY FAMILIES (Continued)

Alloy Type	Examples	Recommendations and Cautions
<u>Nickel-Based Alloys</u>		Generally resistant to SCC in the boiling 45% magnesium chloride tests and in NACE solution if not coupled to steel or otherwise cathodically charged. Many are subject to hydrogen embrittlement when cathodically charged.
Ni-Cu Alloys	Monel 400, K500	Subject to rapid corrosion at elevated temperatures in the presence of even a trace (<1 ppm) of hydrogen sulfide. Monel K500 (140 ksi yield strength) is resistant to SCC in NACE solution at 77°, 325°, and 425°F.
Ni-Fe-Cr + Ni-Fe-Cr-Mo Alloys (Analogous of Type 304 and Type 316 stainless steels - more than 40% nickel replaces much of the iron)	Incoloy 800, 825	No downhole experience. Incoloy 800 and 825 have SCC threshold temperature 325 +25°F in aerated 151,550 ppm chloride. Incoloy 825 resistant to SCC in NACE solution at 77° and 350°F. Subject to hydrogen embrittlement when coupled to steel.
Ni-Cr Alloys (chromium alloys of nickel, little iron, no molybdenum; maximum hardness HRC 35)	Inconel 600, X-750	Susceptible to hydrogen embrittlement if coupled to large areas of rapidly corroding steel. Inconel 600 and X-750 resistant to SCC in aerated 151,500 ppm chloride at 450°F.
Ni-Cr-Mo Alloys	Inconel 625 Inconel 718 Pyromet 31 Hastelloy C-4, C276, G, G-3, X Haynes 8700	Inconel 625 and Hastelloy C-276 were very resistant under severe downhole conditions; others may give similar performance. In-situ aging may significantly reduce SCC threshold stress when coupled to steel. The alloys do not appear susceptible to SCC when uncoupled: they are resistant to SCC in boiling 45% magnesium chloride at 310°F, some have SCC threshold temperatures >450°F. These alloys are susceptible to sensitization by improper heat treatment or welding practice.
<u>Cobalt-based Alloys</u>	MP35N Haynes Alloy 6B	MP35N considered extensively for high-strength tubular goods in deep sour service and as logging cable armor. MP35N generally immune to SCC at strength levels up to 250 ksi unless coupled to steel at ambient temperature and exposed to hydrogen sulfide. In-situ aging reduces transverse threshold stress of MP35N at low temperatures. MP35N is resistant to SCC in boiling 45% magnesium chloride at 310°F. Haynes Alloy 6B was tested at Raft River with similar results.
<u>Titanium and Titanium Alloys</u>	Ti-0.2 Pd TiCode 12	Cathodic to steel and most other alloys. Can become hydrogen-embrittled if coupled to large areas of rapidly corroding steel. Titanium showed no detectable corrosion and no localized attack in Raft River test.
<u>Copper-based Alloys</u>	Cupronickel	Copper-based alloys will probably be of little use in contact with geothermal fluid, except possibly leaded red bronze used as bearings.
<u>Aluminum and Aluminum Alloys</u>		Not recommended for geothermal service: have failed, often catastrophically, in virtually every attempted geothermal application except aerial transmission lines.

with carbon steel or low alloy steel bodies. Bearings may require materials with virtually no corrosion potential. Instruments and logging sondes will require an envelope which is resistant to a wide range of corrosive and thermal environments. Cable armor will also be required.

This section presents a general discussion of the expected downhole corrosion performance of a number of highly alloyed ferrous, nickelous, and cobaltous alloys as well as titanium and two of its alloys. Copper and aluminum alloys are also briefly mentioned. Information on the downhole performance of these materials is quite limited, therefore only general guidelines for material selection are presented. The suitability of these alloys for application in specific downhole tools is discussed in later sections.

4.1 Downhole Corrosion Test Experience

Two downhole materials tests of highly alloyed materials have been executed in wells of the Salton Sea KGRA (Class I resource). A single field test was also performed using a well of the Raft River KGRA, ID (Class IV). Though this test was done above ground, the geofluid was produced by a downhole pump at sufficient pressure to prevent any flashing or loss of carbon dioxide or other gases. Therefore, results are probably representative of actual downhole corrosion of this resource. In addition, a single laboratory study using synthetic Salton Sea brine and carbon dioxide gas was performed (Section 3.1.3 illustrated the critical importance of dissolved gases in downhole corrosion studies).

The two Salton Sea wells represent probably the most severe downhole environment encountered anywhere in the world. The Raft River test results reflect downhole corrosion in what may be the least corrosive Class IV geothermal resource encountered to date. The autoclave test was performed using synthetic Salton Sea brine containing only 250 ppm dissolved carbon dioxide compared to the 4472 ppm to 5000 ppm in the reservoir. The autoclave also contained no hydrogen sulfide and was at a lower temperature than the reservoir. These factors, taken together, made this test much less severe than the

downhole Salton Sea tests. The test was significant because even at these less hostile conditions, Type 316L and Type 430 stainless steels failed by stress corrosion cracking.

Table 4.1-1 summarizes the conditions for each of these tests. Table 4.1-2 is a matrix showing the stainless steel and nickel-, cobalt-, and titanium-based alloys tested and the test location. In Table 4.1-2, the alloys are grouped into families which tend to have similar uniform and localized corrosion resistance in many environments. The results obtained in each of these tests are presented in Tables 4.1-3 through 4.1-6.

4.2 Non-geothermal Stress Corrosion Cracking Tests

Highly alloyed, corrosion resistant metals are potentially susceptible to stress corrosion cracking (SCC) by at least three processes --- chloride-SCC, SSC, and a chloride-sulfide-SCC --- in hydrogen sulfide-bearing chloride solutions. Austenitic alloys containing less than about 45 percent nickel are generally recognized as being susceptible to chloride-SCC (an anodic active path mechanism) in the boiling 45 percent magnesium chloride test (156,900 ppm chloride solution at 310°F). Some nickel alloys with even higher nickel content are susceptible to chloride-SCC in solutions of comparable chloride content at higher temperatures [Koltz 1981].

Many alloys, especially the nickel- and cobalt-based alloys, are resistant to sulfide stress cracking (SSC)--a form of hydrogen embrittlement--when stressed for thirty days at 100 percent of their yield strength in NACE solution (5 percent sodium chloride, 0.5 percent acetic acid, saturated with about 3000 ppm hydrogen sulfide). However, these same alloys are susceptible to hydrogen embrittlement if cathodically charged or if coupled to steel [Uhlig and Asphahani 1979; Troiano 1979; Asphahani 1980; Kane, et al. 1977; Harris and Lemke 1982].

Low-alloy steels are active metals in geothermal environments and have corrosion rates controlled by the proton reduction reaction rate. How-

TABLE 4.1-1. SUMMARY OF CONDITIONS FOR DOWNHOLE HIGH-ALLOY CORROSION TESTS

	Salton Sea Well State No. 1 (Class I)	Salton Sea Well Magmamax No. 1 (Class I)	BuMines Autoclave Test	Raft River Well RRGE No. 1 (Class IV)
<u>Physical Conditions</u>				
Sample Location	At depth of 4260 ft.	At depth of 1800 ft.	Autoclave	Above ground
Fluid phase	Single phase liquid. No loss of dissolved gases.	Single phase liquid. No loss of dissolved gases.	Single phase synthetic Salton Sea brine with no hydrogen sulfide or ammonia.	Pumped (pressurized) single phase liquid with no loss of dissolved gases.
Temperature (°F)	608	500	450	271
Pressure (psia)	--	630	--	42
Exposure period (days)	16	95	15	109
<u>Corrosive Chemistry</u>				
pH	4.5	4.5	5.0-6.4	7.2
Cl ⁻ ppm	127,000	135,900	140,200	776
CO ₂ (Total as CO ₂) ppm	5,000	4,472	250	--
HCO ₃ ⁻ ppm	--	--	-- ^a	64
SO ₄ ⁼ ppm	1.2	<10	none	60
H ₂ S (Total) ppm	30	35	none	0.1-0.2
NH ₃ Total ppm	--	570	none	--

-- No data available

^aNone added as bicarbonate

Sources: McCright 1981; Cosner and Apps 1978; Ellis and Conover 1981; Treseder and Weiland 1976.

TABLE 4.1-2. MATRIX OF MATERIALS TESTED DOWNHOLE VERSUS THE TEST LOCATION (COPPER AND ALUMINUM ALLOYS EXCLUDED)

Alloy Family Specific Alloy	Saltion Sea		Raft River	BuMines
	Well State No. 1 (coupled to steel)	Magnamax No. 1 (electrically isolated)	Well RRGE No. 1 (electrically isolated)	Autoclave (electrically isolated)
<u>Austenitic Stainless Steels</u>				
Type 304			X	
Type 316			X	
Type 316L	X			X
Type 216			X	
<u>Highly Alloyed Austenitic Stainless Steel</u>				
Allegheny-Ludlum 6X			X	
<u>Ferritic or Martensitic Stainless Steels</u>				
Type 410	X		X	
Type 422		X		
Type 430		X		X
Type 440A			X	
<u>Highly Alloyed Ferritic Stainless Steels</u>				
E-Brite 26-1		X		X
Allegheny-Ludlum 29-4			X	
Allegheny-Ludlum 29-4-2			X	
<u>Ni-Cu Alloys</u>				
Monel 400	X		X	X
Monel K500	X			
<u>Ni-Cr Alloys</u>				
Inconel 600	X	X		
Inconel X-750	X			
<u>Ni-Cr-Mo</u>				
Inconel 625			X	X
Hastelloy C-276		X		X
Hastelloy G			X	
<u>Ni-Mo</u>				
Hastelloy B		X		
<u>Cobalt Alloys</u>				
MP35N		X		
Haynes 6B			X	
<u>Titanium Alloys</u>				
Titanium		X	X	X
Ti-012Pd				X
TiCode 12				X

TABLE 4.1-3. CORROSION OF STAINLESS STEELS AND OTHER ALLOYS COUPLED TO LARGE AREA OF CARBON STEEL, EXPOSED DOWNHOLE IN SALTON SEA WELL STATE NO. 1 FOR 16 DAYS

Alloy	Weight-Loss "Uniform" Corrosion (mpy)	Localized Corrosion	Mode	SCC Test ^a Results Depth (mils)
<u>Stainless Steels</u>				
Type 316L	2	None detected.		Not detected.
Type 410	50	No pitting, but crevice corrosion 28 mils deep (6.40 mpy)	TG	50
<u>Nickel Alloys</u>				
Monel 400	25	No pitting. Crevice corrosion 3.9 mils deep (90 mpy)	IG	1
Monel K500	--	--	TG	0.8
Inconel 600	2	None detected.		Not detected.
Inconel X-750	--	--	TG	3

-- No data available

TG = Transgranular attack

IG = Intergranular attack

^aU-bend specimens fabricated from annealed stock

Source: Treseder and Weiland 1976

TABLE 4.1-4. CORROSION OF STAINLESS STEELS AND NON-FERROUS ALLOYS EXPOSED DOWNHOLE IN SALTON SEA WELL MAGMAMAX NO. 1 (CLASS I RESOURCE) FOR 95 DAYS

Alloy	Weight-Loss "Uniform" Corrosion ^a (mpy)		Localized Corrosion
	Average ^b	Range	
<u>Stainless Steels</u>			
Type 430	17.8	16.5-21.8	Large patches of heavy localized attack
Type 422	4.5	2.7-6.0	Light to moderate localized attack on entire surface
E-Brite 26-1	0.9	0.8-1.2	Few tiny pits
Allegheny-Ludlum 29-4	<0.5	<0.5	Not detected
<u>Nickel Alloys</u>			
Inconel 600	1.4	1.3-1.5	Not detected
Hastelloy B	1.2	1.1-1.5	Not detected
Hastelloy C-276	<0.5	<0.5	Not detected
<u>Cobalt Alloy</u>			
MP35N	<0.5	<0.5	Not detected
<u>Titanium Alloy</u>			
Titanium	2.1	1.5-3.2	Not detected

Note: The samples were electrically isolated with Teflon spacers. No test for SCC was performed.

^aCorrosion rate calculated from weight loss assuming even distribution of metal loss.

^bAverage for 3 or 4 specimens.

Source: McCright 1981

TABLE 4.1-5. RESULTS OF CORROSION TESTS IN PUMPED, PRESSURIZED RAFT RIVER (CLASS IV) GEOTHERMAL FLUID

Alloy	Uniform Corrosion (mpy)	Pitting ^a (mpy)	Crevice ^a Corrosion (mpy)	Comments
<u>Stainless Steels</u>				
Type 304	0.02	30.3	D	Numerous pits.
Type 316	0.11	8.7	D	Less pitting than Type 304.
Type 410	0.22	39.5	41.0	Numerous narrow deep pits. Severe crevice corrosion.
Type 440A	0.28	76.5	100	Scattered deep pits. Severe crevice corrosion.
Allegheny-Ludlum 216	0.38	47.9	D	
Alleghney-Ludlum 6X	<0.005	ND	ND	
Alleghney-Ludlum 29-4	<0.005	ND	ND	
Alleghney-Ludlum 29-4-2	<0.005	ND	ND	
<u>Nickel Alloys</u>				
Monel 400	79.7	--	--	14 day Test.
Inconel 625	<0.005	ND	ND	No evidence of corrosion.
Hastelloy G	<0.005	D	ND	Few scattered pits.
<u>Titanium Alloy</u>				
Titanium	<0.005	ND	ND	
<u>Cobalt Alloy</u>				
Haynes 6B	0.017	ND	ND	
<u>Copper Alloys</u>				
7Al-bronze	3.9	ND	ND	Dealloying.
9Al-bronze	7.5	7.5	7.9	Dealloying.
9Al-4.5Ni-bronze	9.8	122	9.3	Dealloying.
61Cu-39Zn	20	D	D	Small pits, dealloying. 14 day test.
90-10 Cupronickel	275	ND	D	
70-30 Cupronickel	164	ND	D	
<u>Aluminum Alloys</u>				
1100	The aluminum alloys showed extreme corrosion with as much as 25% weight-loss in their 77 day exposure.			
5052				
6061				

-- No data available

D=Detected but not quantified

ND=Not detected

Note: 109 day exposure except as indicated by comments. No test for SCC was performed.

^a Calculated from maximum measured depth of penetration measured to ± 0.039 mil

Source: Miller 1977

TABLE 4.1-6. AUTOCLAVE TEST RESULTS IN SYNTHETIC SALTON SEA BRINE CONTAINING 250 PPM CARBON DIOXIDE^a

Alloy	Uniform Corrosion (mpy)	Pitting (mpy)		Crevice Corrosion (mpy)	SCC (U-bend test)
		Max	Ave		
<u>Stainless Steels</u>					
Type 316L	0.2	ND		ND	F ^d
Type 430	--	<13.0 ^b		--	F
E-Brite 26-1	0.2	27.2	26.0	ND	ND
<u>Nickel Alloys</u>					
Monel 400	--	<13.0		ND	--
Inconel 625	0.1	ND		ND	ND
Hastelloy C-276	--	ND		--	ND
<u>Titanium Alloys</u>					
Titanium	ND	ND		ND	ND
Ti-012Pd	ND	ND		<1	ND
TiCode 12	--	ND		ND	--
<u>Copper Alloy</u>					
70-30 Cupronickel	1.0	47.2	24.0	ND	--

-- No data available.

F = Failure occurred.

ND = Not detected.

^aThis synthetic downhole environment was a 140,100 ppm chloride brine with no hydrogen sulfide, and an initial charge of 250 ppm dissolved carbon dioxide-- 5 percent of the concentration in the Salton Sea reservoir. The carbon dioxide concentration doubtlessly decreased during the 15 day test. This simulation is much less severe than the actual downhole environment.

^bPenetration depth less than 0.5 mils after 15 days.

Source: Cramer and Carter 1980

ever, highly alloyed metals are passivated and the corrosion rate is controlled by the very slow (passivated) anodic reaction. This means that the rate of atomic hydrogen formation is slow and embrittlement, if it occurs at all, requires extremely long exposures. When these metals are coupled to steel, the cathodic proton reduction reaction becomes rate controlling and cathodic hydrogen embrittlement often occurs.

Conventionally, one expects chloride-SCC to occur at high temperatures and SSC to occur at near ambient temperatures. Often, tests in hot concentrated chloride solutions are used to assess chloride-SCC resistance, while NACE solution at ambient temperature is used as an accelerated test for SSC resistance.

However, studies of nickel alloys in high chloride (151,500 ppm) solution containing hydrogen sulfide and elemental sulfur at temperatures above 350°F showed that cracking occurred by an active path anodic mechanism involving sulfidation of the nickel in the alloy [Kane *et al.* 1979]. This chloride-sulfide SCC is a different process than either SSC or chloride-SCC. Therefore, accelerated laboratory tests using NACE solutions at high temperatures, or similar solutions, may give the most meaningful results. Also, due to the difficulty of determining the mechanism of stress corrosion cracking in chloride/sulfide environments, the term stress corrosion cracking (SCC) will be used generically in the rest of this section.

Tables 4.1-7 and 4.1-8 summarize the restrictions on stainless steels and nickel- and cobalt-based alloys under NACE Standard MR-01-75 (1980 rev.). Table 4.1-9 gives SCC behavior data on various stainless steel- and nickel-based alloys in sulfide-free hypersaline solutions. Tables 4.1-10 and 4.1-11 present SCC data on stainless steels in sulfide/chloride environments. The Ni-Fe-Cr-Mo alloy Incoloy 825 is included in Table 4.1-11. Table 4.1-12 details SCC resistance of the Ni-Cr-Mo family of alloys in sulfide/chloride environments. Table 4.1-13 addresses SCC resistances of cobalt-based alloys in NACE solutions.

TABLE 4.1-7. RESTRICTIONS FOR STAINLESS STEELS EXPOSED TO HYDROGEN SULFIDE UNDER NACE STANDARD MR-01-75 (1980 REV.)

Alloy Family	Specific Examples of Alloys	Restrictions for Specific Alloys	Restrictions for Family of Alloys
Austenitic Stainless Steels	T302; 304; 304L; 308; 309; 310; 316; 316L; 317; 321; 347 A-182; A-193 gr B8, B8M, B8MA, B8R, B8RA; A-194 gr 8A, 8MA, 8R, 8RA; A-320 gr B8, B8M; A-351 gr CF8M B-463, B-473 Carpenter 20CB3	CF8 and CF8M seal rings restricted to HRC 83	<ul style="list-style-type: none"> o Acceptable as cast or wrought at HRC 22 maximum in annealed condition free of cold work designed to enhance mechanical properties. o Risk of chloride-SCC at elevated temperatures
Ferritic Stainless Steels	T405; 430 A-268Tp405; 430 E-Brite 26-1 (26Cr-1Mo) E-Brite 26-1-Ti		<ul style="list-style-type: none"> o Acceptable at HRC 22 maximum in annealed condition.
Martensitic Stainless Steels	T410; 501 A-217 gr CA15; A-268 Tp 410; #296 gr CA15M; A-487 gr CA15M		<ul style="list-style-type: none"> o Hardness HRC 22 maximum o Required Heat Treatment: <ul style="list-style-type: none"> - normalize or austenize and quench, followed by - double temper at 1150°F minimum with second temper temperature lower than first temper temperature o Weldments stress relieved at 1150°F minimum for HRC 22 maximum. o Stress relief at 1150°F minimum after cold deformation for HRC 22 maximum
Precipitation (Age) Hardening Stainless Steels	17-4PH A-286 PH 15-7Mo	HRC 33 maximum with special heat treatment ^a HRC 35 maximum. Solution annealed or double aged condition Snap rings with special heat treatment ^a acceptable to HRC 30-32	<ul style="list-style-type: none"> o Some may be susceptible to chloride SCC at elevated temperatures
Duplex Stainless Steels	Sandvik SAF2205 Mannesmann AF22 and Similar		<ul style="list-style-type: none"> o Chloride-SCC possible at elevated temperature o HRC 28 maximum

^aRefer to referenced standard.

Source: NACE Standard MR-01-75(1980 rev.)

TABLE 4.1-8. RESTRICTIONS ON NICKEL- AND COBALT-BASED ALLOYS UNDER NACE STANDARD MR-01-75 (1980 REV.)

Alloy Family	Specific Example Alloys	Specific Restrictions	General Restrictions (applicable to all groups)
<u>Ni-Cu</u>	Monel 400 and similar		<ul style="list-style-type: none"> o Maximum hardness HRC 35 except as noted. o Some of these materials may be susceptible to chloride-SCC at elevated temperature
Ni-Cu-Al	Monel K500 and similar	HRC 35 maximum in hot rolled and annealed, solution annealed, or solution annealed and age hardened condition.	
<u>Ni-Fe-Cr</u>	Incoloy 800 and similar		<ul style="list-style-type: none"> o Some of these materials may be susceptible to hydrogen embrittlement when strengthened by cold work. o Plastic deformation in service may increase risk of chloride-SCC.
<u>Ni-Fe-Cr-Mo</u>	Incoloy 825 and similar		
<u>Ni-Cr</u>	Inconel 600 and similar		
Ni-Cr-Al	Inconel X-750 and similar	Solution annealed, or solution annealed and aged, or hot rolled, or hot rolled and aged.	
<u>Ni-Cr-Mo-Al</u>	Inconel 625, Hastelloy C, Hastelloy C-26, Hastelloy G, Hastelloy X and similar		
	Inconel 718 and similar	Solution annealed, solution annealed and aged, hot rolled, hot rolled and aged.	
	Pyromot 31	HRC 35 maximum, solution annealed.	
<u>Co-Ni-Cr-Mo</u>	MP35N, Elgiloy, Havar, Nimonic 50, similar	MP35N allowable to HRC 48 with special heat treatment. ^a	
<u>Co-Ni-Cr-W</u>	Cyclops L605, Haynes 25, similar		
<u>Co-Cr-W</u>	"Stellites"	As cast	

^aRefer to NACE MR-01-75 (1980 rev.)

Source: NACE MR-01-75 (1980 rev.)

TABLE 4.1-9. STRESS CORROSION CRACKING BEHAVIOR OF STAINLESS STEELS AND NICKEL-BASED ALLOYS IN HYDROGEN SULFIDE-FREE HYPERSALINE MEDIA

Alloy Family	Threshold Temperature for SCC in 151,550 ppm Chloride (°F+25°F) ^a		Boiling 45% Magnesium Chloride ^b (310°F, 156,925 ppm Chloride)
	Sodium Chloride	Magnesium Chloride	
<u>Austenitic Stainless Steels</u>			
304	<190 ^c	--	F ^d
316	--	--	F ^d
<u>High Alloy Austenitic SS</u>			
Carpenter 20Cb3	325	325	F
Avesta 254-SLX	--	--	F
Allegheny-Ludlum 904 L	375	375	F
Haynes 20 Mod	--	--	F
Sanicro 28	375	325	--
Hastelloy M-532	325	375	--
<u>High Alloy Ferritic SS</u>			
E-Brite 26-1	375	325	--
A-L 29-4	425	375	--
A-L 29-4-2	375	325	--
<u>Precipitation Hardening SS</u>			
17-4 PH	--	--	F ^d
15-5 PH	--	--	F ^d
PH 13-8 Mo	--	--	NF ^e
<u>Duplex Stainless Steels</u>			
Uranus 50	--	--	F
Sandvik 3RE60	--	--	F
AF-22	--	--	F
Ferralium 225	375	325	F
<u>Ni</u>			
Alloy 200	>450 ^f	>450	--
<u>Ni-Cu</u>			
Monel K-500	--	--	NF ^e
<u>Ni-Fe-Cr</u>			
Incoloy 800	325	325	--
<u>Ni-Fe-Cr-Mo</u>			
Incoloy 825	325	325	F
<u>Ni-Cr</u>			
Inconel 600	>450	>450	NF ^e
Inconel X-750	--	--	NF ^e
<u>Ni-Cr-Mo</u>			
Inconel 625	--	--	NF
Hastelloy G	--	--	NF
Hastelloy G-3	425	425	NF ^e
Hastelloy C-4	>450	425	NF ^e
Hastelloy C-276	450	425	NF ^e
Hastelloy X	--	--	--
Inconel 718	325	375	--
Haynes 8700	--	--	NF
<u>Ni-Mo</u>			
Hastelloy B	>450	>450	--
Hastelloy B-2	>450	>450	--

F: Failed.

NF: Did not fail.

-- No data reported.

^a 7-day test, all specimens stressed slightly above yield [Koltz 1982, except as noted].

^b 10-day test, all specimens stressed slightly above yield [Asphahani 1980, except as noted].

^c Goldberg, 1976.

^d 14-day test specimen stressed 30 percent of yield [Watkins and Greer 1976].

^e 14-day test, specimen stressed 80 percent of yield [Watkins and Greer 1976].

^f No failures at 450°F, the highest temperature tested.

Sources: Sources indicated in footnotes.

TABLE 4.1-10. STRESS CORROSION CRACKING PERFORMANCE OF AUSTENITIC AND AGE (PRECIPITATION)
HARDENING STAINLESS STEEL ALLOY FAMILIES IN HYDROGEN SULFIDE-RICH CHLORIDE SOLUTIONS

Alloy	Cold Work %	Test Temperature °F	Modified NACE Solution			0.15 psia Hydrogen Sulfide (ca 440 ppm)		
			0% NaCl	1% NaCl	5% NaCl	20% NaCl	5% NaCl	25% NaCl
Austenitic SS								
Type 304	0	77	F	--	--	--	--	--
	30	77	F	NF	F	F	--	--
	30	215	--	F	--	F	--	--
	30	325	--	F	--	--	--	--
	30	425	--	--	--	F	--	--
Type 310	30	77	--	NF	NF	F	--	--
	30	215	--	F	--	F	--	--
	30	325	--	F	--	F	--	--
	30	425	--	F	--	--	--	--
Type 316	0	77	--	--	--	--	--	--
	0	195	--	--	--	--	--	--
	0	350	--	--	F	--	--	--
	0	390	--	--	--	--	--	--
	20	77	--	--	F	--	--	--
	20	195	--	--	--	--	F	--
	20	350	--	--	F	--	--	--
	20	390	--	--	--	--	--	F
	50	77	--	--	F	--	--	--
	50	195	--	--	--	--	F	--
	50	350	--	--	F	--	--	--
	50	395	--	--	--	--	--	NF
	Age Hardening SS							
A-286								
Aged 16 hrs. at 1200 °F YS = 190 ksi	215	--	--	NF	--	--	--	
	325	--	--	F	--	--	--	
	425	--	--	--	F	--	--	
Aged 16 hrs. at 1300 °F YS = 155 ksi	325	--	--	F	--	--	--	
	425	--	--	--	F	--	--	
Aged 1 hr. at 1150 °F YS = 165 ksi	425	--	--	--	F	--	--	
Aged 1 hr. at 1200 °F YS = 170 ksi	425	--	--	--	F	--	--	
Aged 4 hrs. at 1200 °F YS = 175 ksi	425	--	--	--	F	--	--	

F: Failed (cracked).

NF: Did not fail.

-- No data available.

Source: Troiano 1979 except data for Type 316 from Asphahani 1980.

TABLE 4.1-11. STRESS CORROSION CRACKING PERFORMANCE OF THE DUPLEX STAINLESS STEEL, HIGHLY ALLOYED AUSTENITIC STAINLESS STEEL, AND Ni-Fe-Cr-Mo ALLOY FAMILIES IN SULFIDE/CHLORIDE ENVIRONMENTS

Alloy Family	Cold Work (%)	Rockwell Hardness	NACE Solution ^a		450ppm ^b Hydrogen Sulfide	
			Solution ^a		5% NaCl	25% NaCl
			77°F	350°F	195°F	390°F
<u>Duplex Stainless Steel</u>						
Uranus 50	0	B88	F	F	--	--
	20	C31	F	F	--	--
	50	C30	F	F	NF	NF
Sandvik 3RE-60	0	B95	F	F	--	--
	20	C39	F	F	F	--
	50	C39	F	F	NF	--
AF22	0	B94	NF	F	--	--
	20	C33	F	F	--	--
	50	C33	F	F	NF	NF
Ferralium 225	0	B96	--	F	--	--
	20	C33	F	F	--	--
	50	C33	F	F	NF	NF
<u>Highly Alloyed Austenitic S.S.</u>						
Carpenter 20Cb3	0	B76	--	NF	--	--
	20	C26	NF	NF	--	--
	50	C25	NF	F	NF	NF
Avesta 254-SLX	0	B73	--	NF	--	--
	20	C26	NF	NF	--	--
	50	C27	NF	F	NF	NF
A-L 904L	0	B67	--	F	--	--
	20	C14	NF	NF	--	--
	50	C22	NF	F	NF	NF
Haynes 20 Med	0	B69	--	F	--	--
	20	C26	F	F	--	--
	50	C28	F	F	NF	NF
<u>Ni-Fe-Cr-Mo</u>						
Incoloy 825	0	B77	--	NF	--	--
	20	C28	NF	NF	--	--
	50	C29	NF	NF	NF	NF

Note: 1000 hr exposure period. All specimens stressed to 107% of their yield strength.

-- No data available

F: Failed.

NF: Did not fail.

^a 5 percent sodium chloride (30,310 ppm chloride), 0.5 percent acetic acid, saturated with hydrogen sulfide.

^b concentration estimated from 0.15 psi partial pressure

Source: Asphahani 1980

TABLE 4.1-12. STRESS CORROSION CRACKING RESISTANCE OF Ni-Cr-Mo FAMILY ALLOY C-RINGS IN NACE SOLUTION^a AT AMBIENT AND ELEVATED TEMPERATURES (700 hr or longer exposures)

Alloy	Code Reduction (%)	Rockwell Hardness	Yield Strength ^b (ksi)	Pre-aging (hrs @ °F)	Coupled to Steel	Test Temperature (°F)	Threshold Stress Ratio (R) ^c (Threshold stress/YS)
Hastelloy G ^d	0-50	B77-C35	--	none	no	77	R>1.0
	0-50	B77-C35	--	none	no	350	R>1.0
Hastelloy G-3 ^d	0-50	B82-C37	--	none	no	77	R>1.0
	0-50	B82-C37	--	none	no	350	R>1.0
Haynes 8700 ^d	0-50	B76-C36	--	none	no	77	R>1.0
	0-50	B76-C36	--	none	no	350	R>1.0
Inconel 625	59	--	187	none	yes	77	0.73<R<0.82
	59	--	--	250 400	yes	77	0.57<R<0.73
	59	--	--	287 700	yes	77	R<0.57
	59	--	--	255 600	no	77	R>0.82
Hastelloy C-4	48	--	182	none	yes	77	0.76<R<0.85
	59	--	201	none	yes	77	0.41<R<0.57
	59	--	--	1 1000	yes	77	R<0.82
Hastelloy C-276	37	--	154	none	yes	77	R>0.88
	48	--	176	none	yes	77	R>0.85
	59	--	190	none	yes	77	R>0.82
	37	--	--	10min 900	yes	77	R<0.88
	48	--	--	10min 900	yes	77	R<0.85
	59	--	--	10min 900	yes	77	R<0.82
	48	--	--	339 300	yes	77	R<0.85
	59	--	--	252 400	yes	77	R<0.82
	37	--	--	535 600	no	77	R>0.88
	48	--	--	535 600	no	77	R>0.85
	59	--	--	50 800-1000	no	77	R>0.82
	59	--	204	100 932	yes	150	R<0.57
	59	--	201	none	yes	225	R>0.82
	59	--	204	100 932	yes	225	0.74<R<0.82
	59	--	201	none	yes	300	R>0.82
	59	--	204	100 932	yes	300	R<0.82

-- No data available.

^a 5% sodium chloride (30,310 ppm chloride), 0.5% acetic acid, saturated with hydrogen sulfide

^b longitudinal yield strength. The transverse yield strength is related to the longitudinal yield strength by:

$$YS(trans)/YS(long) = 1 - 0.003(\%CW)$$

^c > means that no failure occurred at the highest stress tested

^d < means that failure occurred at the lowest stress tested

^d Asphahani 1980

Source: Kane, et al. 1977 except as noted.

TABLE 4.1-13. STRESS CORROSION CRACKING RESISTANCE OF SOME COBALT-BASED ALLOYS IN THE NACE SOLUTION^a AT AMBIENT AND ELEVATED TEMPERATURES

Alloy	Cold Reduction %	Yield Strength ^b (ksi)	Pre-Aging (hrs. @ °F)	Coupled to Steel	Test Temperature (°F)	Threshold Stress Ratio (R) ^c (Threshold Stress/Y.S.)
<u>C-rings</u>						
MP35N	35	160	none	yes	77	R>0.88
	35	173	4 1100	yes	77	0.62<R<0.79
	59	224	none	yes	77	R>0.82
	51	205	4 1100	yes	77	R<0.36
	59	--	5 700	yes	77	R<0.82
	59	--	252 700	yes	77	R<0.57
	59	--	252 400	yes	77	0.57<R<0.74
	59	--	50 800-1000	no	77	R>0.82
	59	--	266 600	no	77	R>0.82
	59	224	none	yes	225	R>0.82
	59	235	4 1100	yes	225	R>0.82
	59	224	none	yes	300	R>0.82
	59	224	4 1100	yes	300	R>0.82
<u>Tensile</u>						
MP35N	51	205	4 1100	yes	77	R>1.1
	51	205	4 1100	no	77	R>1.0
MP35N ^d	unspecified	291	unspecified	no	77	R>1.0
MP159 ^d	unspecified	219	unspecified	no	77	R>1.0
Haynes 25 ^d	unspecified	249	none	no	77	R>1.0
<u>Unspecified</u>						
Elgiloy ^e	42	--	-- 896	no	77	R>1.0
Haynes 25 ^e	20	--	-- 400	no	77	R<1.0
	20	--	-- 400	no	400	R<1.0
	20	--	-- 400	yes	77	R<1.0
	20	--	-- 932	no	77	R<1.0
	20	--	-- 932	no	400	R<1.0
	20	--	-- 932	yes	77	R<1.0
	40	--	none	no	77	R>0.0
	40	--	none	no	400	R<1.0
Haynes 118 ^e	60	--	none	no	77	R>1.0
	60	--	none	no	400	R>1.0
	40	--	-- 400	no	77	R>1.0
	40	--	-- 400	no	400	R>1.0
	40	--	-- 400	yes	77	R<1.0
	40	--	-- 1100	no	77	R>1.0
	40	--	-- 1100	no	400	R>0.0
	40	--	-- 1100	yes	77	R<1.0
	48	--	-- 1400	no	77	R>1.0
	48	--	-- 1400	no	400	R<1.0
	48	--	-- 1400	yes	77	R>1.0

-- No Data Available

^a5 percent sodium chloride (30,310 ppm chloride), 0.5 percent acetic acid, saturated with hydrogen sulfide

^bLongitudinal yield strength. The transverse yield strength is given by:
Y.S. (trans)/Y.S. (long) = 1 - 0.003(%CW)

^c>indicates no failure at the highest stress tested

^d<indicates failure at the lowest stress tested

^eFrom Watkins and Greer, 1976

^eFrom Uhlig and Asphahani, 1979

Source: Kane, et al. 1977 except as noted

4.3 Evaluation of Test Data

In the following discussion, the materials considered are divided into groups or alloy families, generally along the lines used in NACE Standard MR-01-75 (1980 rev.). This discussion is based on information presented in Sections 4.1 and 4.2 except as noted.

4.3.1 Stainless Steels

Most of the stainless steels discussed above are subject to intergranular corrosion if incorrectly heat treated. Intergranular corrosion is severe localized corrosion at or adjacent to grain boundaries, with little or no attack on the bodies of the grains. The alloy disintegrates (grains fall out) and/or loses its strength. Stress is not required for intergranular corrosion.

Intergranular corrosion occurs in austenitic stainless steels when they are sensitized (i.e., heated in the 905° to 1450°F range) and cooled slowly [Fontana and Greene 1967]. The range may extend to 1650°F [Cihal 1974]. In this temperature range, chromium carbides form at the grain boundaries, and the metal adjacent to the carbides is depleted of chromium. Chromium levels may drop to less than two percent at the grain boundaries. Galvanic corrosion between the body of the grain and the grain boundary causes rapid corrosion of the boundary. When stainless steels are welded, a zone called the heat-affected zone (HAZ) along each side of the weld is heated into the sensitizing range. The HAZ is a site of intergranular attack, often called weld decay.

Intergranular corrosion of austenitic stainless steels can be controlled in three ways. First, the material can be quench-annealed or solution-annealed (heated to a high temperature, typically 1950° to 2050°F, and water quenched). At this annealing temperature, the chromium carbides are redissolved in the grain. The quenching is important because if the alloy is al-

lowed to cool slowly, the entire structure will be sensitized. Stainless goods are usually supplied in quench-annealed form. If they are welded during fabrication, they must be re-treated [Fontana and Green 1967].

HAZ intergranular corrosion can be controlled by lowering the carbon content below 0.03 percent. These low carbon alloys do not require quench-annealing after welding and can be welded on-site. These alloys have a great propensity for picking up carbon when welded. The surfaces around the weld must be kept completely grease- and oil-free, or sensitization will occur.

HAZ intergranular attack can also be prevented by the addition of strong carbide formers (stabilizers) to combine with the carbon. Niobium (or niobium plus tantalum) and titanium are used to stabilize stainless steels [Fontana and Greene 1967].

Ferritic stainless steels are also subject to intergranular corrosion and weld decay. The same mechanism, chromium depletion, is responsible. The range of sensitizing temperatures is not established, but sensitization of nickel-free ferritic steels begins at about 1700°F. Addition of two percent nickel raises the sensitization temperature to 1900°F. Molybdenum content has little effect on intergranular corrosion of ferritic stainless steels. A one-hour treatment at 1510°F followed by water quenching prevents intergranular corrosion, and weld decay of one to two percent nickel alloys. Lower nickel alloys require four hours at 1510°F [Bond and Lizlovs 1969].

Addition of more than 0.4 percent titanium to 18Cr-2Mo alloys completely prevents intergranular corrosion in the Strauss test after all sensitizing treatments. Alloys containing more than 1.2 percent titanium are embrittled after annealing from 1510°F. This embrittlement can be removed by water quenching from 1900°F. Additions of 0.61 percent niobium prevent intergranular corrosion of post-weld specimens in the Strauss test [Bond and Lizlovs 1969].

The Martensitic and Ferritic Stainless Steel Family

This family includes stainless steels containing up to about 17 percent chromium, two percent molybdenum and no nickel. As indicated by the group name, they are martensitic or ferritic alloys. Examples of this family which have been tested downhole are Type 410, Type 422, Type 430, and Type 440A. In the downhole test in Magmamax No. 1, the Type 430 had heavy localized attack and a weight loss equal to 17.8 mpy corrosion. Type 422 fared a little better, probably due to its molybdenum content. In the State No. 1 well test--coupled to steel--Type 410 showed crevice corrosion rates of 640 mpy and transgranular SCC 50 mils (1140 mpy) deep after 16 days. In the Raft River test, Types 410 and 440A had low weight-loss corrosion rates, but developed penetrating pits and crevice corrosion, with about 40-100 mpy penetration rates. The above experience indicates that these materials do not have adequate corrosion resistance for downhole service in Class I, III, or IV geothermal resources.

The Highly Alloyed Ferritic Stainless Steel Family

The principal alloys of this family are E-Brite 26-1 (26Cr-1Mo) (XM27), titanium stabilized E-Brite 26-1S (XM33), Allegheny-Ludlum (A-L) 29-4 (29Cr-4Mo), A-L 29-4-2 (29Cr-4Mo-2Ni), and SeaCure 26-3 (26Cr-3Mo).

In the 109-day Raft River test (Table 4.1-5), A-L 29-4 and 29-4-2 showed less than 0.005 mpy corrosion rate with no localized corrosion detected. In the 95-day Magmamax No. 1 test, E-Brite 26-1 showed a weight-loss corrosion rate of 0.8 - 1.2 mpy with a few tiny pits, while A-L 29-4 showed less than 0.5 mpy corrosion with no detected localized attack. E-Brite 26-1 (XM27 and XM33) are accepted under NACE Standard MR-01-75 (1980 rev.) provided their hardness does not exceed HRC 22. SeaCure 26-3, A-L 29-4, and A-L 29-4-2 are not yet included, but similar hardness restrictions seem prudent. The SCC threshold temperature--above which SCC can occur--in aerated 151,550 ppm chloride solution without hydrogen sulfide is 375°F for E-Brite 26-1 and A-L

29-4-2, and 425°F for A-L 29-4. The threshold values, measured in sodium chloride, are plus or minus 25°F (Table 4.1-9).

The Austenitic (300 Series) Stainless Steel Family

These stainless steels contain 16-24 percent chromium, 8-19 percent nickel, and zero-4 percent molybdenum. Included are Type 304 and Type 316, the low carbon (L) versions of Type 304 and Type 316, the stabilized versions of Type 304, as well as Type 310 and Type 317.

Under NACE Standard MR-01-75 (1980 rev.), these alloys and their cast counterparts are acceptable for hydrogen sulfide service at ambient temperatures in the annealed condition free of cold work designed to enhance their mechanical properties. Cold work greatly increases the risk of SCC, as shown in Table 4.1-10. For example, annealed Type 316 failed by SCC in NACE solution (30,310 ppm chloride solution with no oxygen and about 3000 ppm hydrogen sulfide) at 350°F. With 20 percent cold work, failure in this solution occurred at 77°F. In a similar solution, failure occurred at 195°F.

Since it contains no molybdenum, (as compared to the 2 to 3 percent Mo in Type 316), Type 304 and its analogs, Types 304L, Type 321, and Type 347, can be expected to have even less SCC resistance than Type 316. Type 310, with about the highest alloy content of this family, failed by SCC in a modified NACE solution containing one percent sodium chloride (6062 ppm chloride) at 215°F but not at 77°F. In modified NACE solution with 20 percent sodium chloride (132,000 ppm chloride), it failed at 77°F (Table 4.1-10).

In the 16-day downhole test in Salton Sea well State No. 1, Type 316 showed no localized corrosion or SCC and only a 2 mpy corrosion rate. However, Type 316 did fail by SCC in the 15-day autoclave tests. As was discussed in Section 4.1.1, conditions of this test are much less severe than actual downhole conditions at Salton Sea. SCC resistance was not tested at

Raft River, but in this long-term test Type 304 had numerous pits with a maximum annualized rate of 30.3 mpy. Type 316 had fewer pits with an annualized rate of 8.7 mpy.

In short, these alloys may not have markedly better pitting resistance than do some of the low-alloy steels (Section 3.1.3) in many high temperature environments. They risk SCC if cold worked or if subjected to tensile stress.

The Highly Alloyed Austenitic Stainless Steel Family

Considered in this group are Carpenter 20Cb3, Avesta 254-SLX, Type 904L, A-L 6X, Haynes 20 Mod, Sanicro 28, Hastelloy M-532, and similar alloys. Only A-L 6X has been tested in downhole environments (Table 4.1-5) at Raft River. It showed essentially no detectable uniform or localized corrosion. A number of these alloys show SCC thresholds of at least 300°F (Table 4.1-9) in 151,550 ppm chloride (as sodium chloride), though they fail the boiling 45 percent magnesium chloride (156,925 ppm chloride) test. The above environments contain dissolved oxygen, which promotes SCC.

As shown in Table 4.1-11, some of these alloys have higher SCC resistance in air-free hydrogen sulfide-rich environments. Carpenter 20Cb3, Avesta 254-SLX, Type 904L, and Haynes 20 Mod--all 50 percent cold worked--showed no SCC in 30,000 ppm chloride/450 ppm hydrogen sulfide solution at 105°F, or in 151,550 ppm chloride/450 ppm hydrogen sulfide solution at 390°F. Haynes 20 Mod failed in NACE solution at 77°F.

The Precipitation (Age) Hardening Stainless Steel Family

NACE Standard MR-01-75 (1980 rev.) accepts A-286, 17-4PH, PH 157 Mo, and similar alloys with hardnesses up to HRC 30 to 35 provided special heat treatments (set forth in the Standard) are used. However, 17-4PH and 155PH are susceptible to SCC in boiling 45 percent magnesium chloride (156,925 ppm chloride, 310°F). PH 13-8Mo is resistant to SCC in this environment. Because

of their chromium and molybdenum contents, members of this alloy family probably have localized corrosion resistances similar to those of the austenitic stainless steels.

The Duplex Stainless Steel Family

Duplex (austenite/ferrite matrix) stainless steels were developed to obtain the SSC resistance of austenitic stainless steels combined with the chloride-SCC resistance of ferritic stainless steels. Sandvik 2205, AF 22 and similar alloys are allowed at hardnesses of up to HRC 28 under NACE Standard MR-01-75 (1980 rev.), though Table 4.1-11 shows that some are susceptible to SCC in NACE solution at room temperature at much lower hardnesses. All those reviewed in this study failed by SCC in NACE solution at 350°F. For the 1000-hour exposure period, these alloys were resistant to SCC in 6062 ppm chloride/450 ppm hydrogen sulfide solution at 195°F and in 151,550 chloride/450 ppm hydrogen sulfide solution at 390°F. Whether these results signify resistance to SCC at lower sulfide, higher pH levels, or only an increase in incubation time, is not known.

4.3.2 Nickel-Based Alloys

The nickel-based alloys are generally resistant to SCC in the boiling 45 percent magnesium chloride test (156,925 ppm chloride, 310°F), as well as in NACE solution, provided they are not coupled to steel or otherwise cathodically charged. A wide variety of these alloys are subject to hydrogen embrittlement when cathodically charged, however.

The Ni-Cu Alloy Family

This family includes Monel 400, Monel K500 and similar alloys. When exposed for 16 days in Salton Sea well State No. 1, Monel 400 had a weight-loss corrosion rate equivalent to 25 mpy uniform corrosion. It also showed crevice corrosion at an annualized rate of 90 mpy. In this test it was

coupled to a large area of steel. The Monel 400 showed intergranular SCC about 1 mil deep. Monel K500 showed similar SCC (Table 4.1-3). At Raft River, Monel 400 had a weight-loss corrosion rate equivalent to almost 80 mpy. Like the cupronickels, the Ni-Cu alloys appear to be subject to rapid corrosion at elevated temperatures in the presence of even trace (less than 1 ppm) amounts of hydrogen sulfide. Monel K500 (140 ksi yield strength) is resistant to SCC in NACE solution at 77°, 325°, and 425°F [Troiano and Hehemann 1979].

The Ni-Fe-Cr and Ni-Fe-Cr-Mo Alloy Families

The alloys in these families are analogs of the Type 304 and Type 316 stainless steels. They contain more than 40 percent nickel in place of much of the iron commonly found in stainless steels. Incoloy 800 is representative of the Ni-Fe-Cr family, while Incoloy 825 is representative of the Ni-Fe-Cr-Mo family. No reports of these alloys in downhole geothermal environments have been found. In aerated 151,550 ppm chloride, both Incoloy 800 and Incoloy 825 had SCC threshold temperatures of $325^{\circ} \pm 25^{\circ}\text{F}$ (Table 4.1-9). When not coupled to steel, Incoloy 825 was resistant to SCC in NACE solution at 77°F and 350°F as shown in Table 4.1-11. It is subject to some degree of hydrogen embrittlement when coupled to steel.

The Ni-Cr Alloy Family

This family includes such alloys as Inconel 600, Inconel X-750, and similar alloys. All are chromium alloys of nickel, containing little iron and no molybdenum. Some may contain minor amounts of aluminum or other precipitation hardening elements. In the 95-day downhole test at the Salton Sea well, Magmamax No. 1, Inconel 600 showed a uniform corrosion rate of 1.3-1.5 mpy with no detected localized corrosion. Similar corrosion rate results were obtained in the 16-day State No. 1 test, and no SCC was observed in this test. In the State No. 1 test, Inconel X-750 showed SCC 3 mils deep after 16 days. Inconel 600 and Inconel X-750 are resistant to SCC in aerated 151,550 ppm chloride solutions at 450°F.

Under NACE Standard MR-01-75 (1980 rev.), these alloys are acceptable at a maximum hardness of HRC 35. The age hardenable varieties, such as Inconel X-750, are allowed in the solution-annealed, solution-annealed and aged, hot rolled, or hot rolled and aged conditions. These alloys are susceptible to hydrogen embrittlement if coupled to large areas of rapidly corroding steel.

The Ni-Cr-Mo Alloy Family

Some representatives of this family are Inconel 625, Inconel 718, Pyromet 31, Hastelloy C-4, Hastelloy C-276, Hastelloy G, Hastelloy G-3, Hastelloy X, and Haynes 8700. Only Inconel 625, Hastelloy C-276, and Hastelloy G have been tested under downhole high-temperature conditions. At Raft River, Inconel 625 showed a uniform corrosion rate of less than 0.005 mpy and no detectable localized corrosion. Hastelloy G had comparable uniform corrosion, but a few scattered pits of unquantified depth (Table 4.1-5). In the 95-day Magmamax No. 1 test, Hastelloy C-276 had a uniform corrosion rate of less than 0.5 mpy (detection limit) with no localized attack. In short, these alloys, Inconel 625 and Hastelloy C-276, appear very resistant under severe downhole conditions. Other alloys of this family may give comparable performance.

A major concern in the high-temperature geothermal use of some or all of these alloys may be the effect of in-situ aging on SCC resistance. For example C-rings of Inconel 625, cold reduced 59 percent to give a yield strength of 187 ksi, had a threshold stress between 0.73 and 0.82 of the longitudinal yield strength when coupled to steel in 77°F NACE solution. Similar Inconel 625 C-rings, aged for 250 hours at 400°F had a threshold stress of between 0.57 and 0.73 of the longitudinal yield strength under the same test conditions. Aging the Inconel 625 C-rings at 700°F for 287 hours reduced the threshold stress to less than 0.57 of the longitudinal yield strength in 77°F NACE solution when the C-rings were coupled to steel. Hastelloy C-276

also showed a decay in threshold stress upon aging even at temperatures as low as 300°F (Table 4.1-12), though the magnitude of the decrease is not quantified.

The decline in threshold stress is not as severe at elevated temperatures. C-rings of Hastelloy C-276, 59 percent cold reduced and aged 100 hours at 932°F (204 ksi longitudinal yield strength), had a threshold stress of less than 0.57 of the longitudinal yield stress at 150°F. At 225°F, the threshold stress was 0.74 to 0.82 of the longitudinal yield stress, and at 300°F the threshold stress was greater than 0.82 of the longitudinal yield stress.

All of the above threshold stress values are for Ni-Cr-Mo alloy C-rings (transverse stress) coupled to steel. These alloys do not appear susceptible to SCC in the uncoupled condition. Table 4.1-9 shows that as a group they are resistant to SCC in boiling 45 percent magnesium chloride (at 310°F). Some have SCC threshold temperatures above 450°F.

The Ni-Cr-Mo alloys are susceptible to sensitization by improper heat treatment or welding practice. The mechanism of sensitization, and resultant intergranular corrosion, is different from that of stainless steels. At carbon contents above 0.004 percent, a molybdenum-rich carbide phase forms in the temperature range of 1200°F to 2200°F. This depletes the molybdenum at the grain boundaries. The molybdenum-depleted zones are attacked by reducing acids [Streicher 1976] and could be affected by high-temperature geothermal fluids.

4.3.3 Cobalt-Based Alloys

The cobalt-based alloys, especially MP35N, have been considered extensively for high-strength tubular goods for deep sour service. MP35N is also of major interest as logging cable armor.

Until recently, MP35N was considered to be immune to SCC at strength levels up to 250 ksi. However, it can be susceptible to SCC when coupled to steel at ambient temperatures in a hydrogen sulfide-rich environment [Troiano and Hehemann 1979].

MP35N is normally extensively cold worked to acquire high strength. The cold work produces anisotropy in the mechanical properties of the metal: the yield strength in the longitudinal direction is greater than that in the long transverse direction. The difference between these yield strengths increases with increasing percentage of cold reduction. The resistance of MP35N to hydrogen embrittlement when coupled to steel is also anisotropic, with C-rings (transverse stress) being more susceptible than tensile (longitudinal stress) samples. For example, a tensile sample of MP35N, cold reduced 51 percent, aged 4 hours at 1100°F, with a longitudinal yield strength of 205 ksi, was resistant to SCC in 77°F NACE solution when stressed at 100 percent of its longitudinal yield strength. A C-ring of the same metal, with the same thermal history and mechanical properties, had a threshold stress of less than 0.36 of the longitudinal yield strength under the same test conditions.

In-situ aging may be a major factor in the long-term performance of this metal. Unaged MP35N C-rings, 59 percent cold reduced (longitudinal yield strength 224 ksi) had a threshold stress of more than 0.82 of the longitudinal yield strength in 77°F NACE solution, even when coupled to steel. Aging the same material for 252 hours at 400°F reduced the threshold stress of steel coupled C-rings to between 0.57 and 0.74 of the longitudinal yield strength. Aging at 700°F for the same period of time reduced the threshold stress of steel coupled C-rings to less than 0.57 of the longitudinal yield strength, as shown in Table 4.1-13.

The anisotropic decay in transverse threshold stress is apparently significant only at low temperatures, as shown in Table 4.1-13. Steel coupled C-rings of 51 percent cold reduced MP35N, aged for 4 hours at 1100°F, had a transverse threshold stress of less than 0.36 of the longitudinal yield strength in NACE solution at 77°F. With the same aging, 59 percent cold re-

duced material had transverse yield stresses of more than 0.82 of the longitudinal yield stress at 215°F and 300°F. These stresses are comparable to that of unaged material.

MP35N is resistant to SCC in boiling 45 percent magnesium chloride at 310°F [Uhlig and Asphahani 1979]. It was exposed in the Magmamax No. 1 test. Its corrosion rate was less than 0.5 mpy (detection limit) with no detectable localized corrosion. Haynes Alloy 6B, another cobalt alloy, was tested at Raft River with similar results (Tables 4.1-4 and 4.1-5).

4.3.4 Titanium and Titanium Alloys

Titanium was tested in the Magmamax No. 1 test (Table 4.1-4), the Raft River Test (Table 4.1-5), and the Bureau of Mines autoclave test (Table 4.1-6). The conditions of these tests were summarized in Table 4.1-1. In the Magmamax test, titanium showed 1.5-3.2 mpy uniform corrosion with no detectable localized attack. In the much less hostile Raft River test, it had no detectable corrosion (less than 0.005 mpy) and no localized attack. The same results were obtained in the autoclave tests. This last test also included Ti-0.2Pd and Ticode 12, which showed no detectable corrosion except for incipient crevice corrosion of the Ti-0.2Pd.

Titanium and its alloys are cathodic to steel and most other alloys. If coupled to large areas of rapidly corroding steel, titanium and its alloys can become hydrogen embrittled [Covington 1977; George, Manning and Schrieber 1975]. Whether or not this would be a major problem in downhole geothermal applications is not known.

4.3.5 Copper-Based Alloys

Both 70-30 cupronickel and 90-10 cupronickel showed more than 100 mpy weight-loss corrosion in the Raft River test (Table 4.1-5). This corrosion rate is consistent with the performance of cupronickels in sulfide bearing environments. The other copper-based alloys tested at Raft River all

showed dealloying. As the Raft River resource probably represents the least hostile of high-temperature resources, the copper-based alloys as a class will probably have little usefulness in contact with geothermal fluid. This estimate is supported by the poor performance of these alloys in a large number of geothermal process streams at many geothermal power plants [Ellis and Conover 1981]. One possible exception is leaded red bronze used as bearings.

4.3.6 Aluminum and Aluminum Alloys

Aluminum and its alloys are not recommended for geothermal service. They have failed, often catastrophically, in virtually every attempted geothermal application except aerial electric transmission lines [Ellis and Conover 1981]. At Raft River, three aluminum alloys were tested--1100, 5052, and 6061. The coupons lost as much as 25 percent of their weight during the 77 days they were exposed. No "uniform" corrosion rate was calculated [Miller 1977].

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SUMMARY

Section 5 considers cements for completing high-temperature geothermal wells. It summarizes the U.S. Department of Energy/Brookhaven National Laboratory research program and follow-up downhole testing of candidate cement slurries by the National Bureau of Standards. Additional studies by Union Oil Company in conjunction with Halliburton Services and with Dowell Division of Dow Chemical Company are also included. This summary is a quick reference to that material. Please refer to the section for caveats, qualifications and references cited for the material presented here.

Cementing of the annular space between the steel casing and the formation wall secures the casing in the well, isolates the producing zone, and prevents fluid migration between zones. There have been emplacement problems such as incomplete bonding between cement and casing, empty pockets in the cement, and premature set-up in the hot hole; and long-term problems such as strength regression, stress cracking, and separation of the cement from either the borehole or the casing.

At least 26 separate cement formulations were evaluated in a DOE-sponsored test program. Sixteen cements which met minimum standards set forth by the National Bureau of Standards were field-tested downhole for one year in flowing brine at 417°F to verify their properties. Both precured and in situ cured specimens were tested. The results of these tests are considered preliminary.

Union Oil and Halliburton Services tested a number of oil field cements and additives downhole at Baca and Imperial Valley for up to one year. In situ curing was the same as for the DOE-sponsored tests. Union Oil and Dowell researchers compared cements in above-ground autoclaves designed to simulate the dry-steam conditions at the Geysers - 464°F and 485.6 psi.

Exposure time ranged up to two years. Because the steam was dry, it contained no liquid, salts, or dissolved solids; it did contain 5000 ppm carbon dioxide. Compressive strength and permeability were used to determine the suitability of the cements for the geothermal environment. X-ray diffraction was used in the Union Oil studies to determine the dominant binding phases. Table 5.0.1 lists the compositions of the cements determined by the above tests to be the most suited for the geothermal environment. The table is not a ranking of the cements. As a general statement, a cement with 100 parts by weight API Class G cement and 35-40 parts by weight silica flour or sand is probably worthy of consideration for geothermal applications.

INTRODUCTION

Section 5.1 presents a brief discussion of typical problems encountered in cementing geothermal wells and summarizes the U.S. Department of Energy/ Brookhaven National Laboratory research program to develop improved cements for this application. The minimum standards which must be met by acceptable cements are also given in this section.

Sections 5.2.1.1 and 5.2.1.2 present a summary of the results of the DOE cement development program, including discussion of the efforts of various subcontractors in their individual research and laboratory test programs. Section 5.2.1.3 discusses the follow-up downhole testing of candidate cement slurries by the National Bureau of Standards. The information and evaluations presented in this Section and in Section 5.2.1.4 will probably be most applicable to actual well completion needs. Section 5.2.2 describes a similar research program undertaken privately by Union Oil Company and Halliburton Services on cements for use in liquid-dominated wells. Section 5.2.3 is a comparative evaluation of their test results with the DOE program. Section 5.3 describes another Union Oil study, this time with the Dowell Division of Dow Chemical Company, on cements for use in dry steam wells. Here again, comparisons are made to cements tested by the National Bureau of Standards, where applicable.

TABLE 5.0-1. CEMENTS WHICH APPEAR MOST SUITABLE
FOR THE GEOTHERMAL ENVIRONMENT

Cement ID	Source	Components	Concentration parts by weight	Slurry Density lbm/cu.ft.
NBS A	Dowell	API Class G cement	100	119
		silica flour	35	
		water	54	
		lignin-sugar retarder	1	
NBS B	Dowell	API Class J cement	100	115
		water	44	
		lignin-sugar retarder	0.4	
NBS D	INEL	cement	100	113
		water	45	
		retarder	0.7	
NBS X	Halliburton	API Class G cement	100	116
		silica flour (SSA-1)	40	
		water	60.3	
		dispersant (CFR-2)	0.75	
		retarder (HR-7)	0.4	
		fluid loss additive (HALAD-22A)	0.75	
D 3	Dowell	API Class G cement	100	113
		needles fly ash	75	
		silica flour	35	
		retarder	1	
		water	93	
D 5	Dowell	API Class G cement	100	120
		silica flour	35	
		sodium chloride	20	
		retarder	1	
		water	54	
D 6	Dowell	API Class G cement	100	120
		silica flour	35	
		sodium chloride	5.4	
		retarder	1	
		water	54	
D 10	Dowell	API Class G cement	100	109
		silica flour	35	
		powdered coal	27	
		retarder	1	
		water	63	
UH 1	Union Oil Halliburton	API Class G cement	100	116
		silica flour	40	
		dispersant	0.75	
		retarder	0.4	
		low water-loss material	0.75	
UH 4	Union Oil Halliburton	API Class G cement	100	129
		silica sand	40	
		dispersant	0.75	
		retarder	0.4	
		water		
UH 5	Union Oil Halliburton	API Class G cement	100	133
		silica sand	100	
		retarder	0.3	
		water		
UD 2	Union Oil/ Dowell	API Class G cement	100	117.3
		silica flour	35	
		water	56	
UD 7		1:1 fly ash and API Class G cement	100	111.7
		silica flour	35	
		water	96.4	

NBS = National Bureau of Standards

D = Dowell

U-H = Union Oil - Halliburton

Most of the cements developed are variations of standard oil-well cements (usually API Classes G, J, or A) with silica additives and various retarders effective at high temperatures. One such cement features the addition of glass spheres as a means of lessening slurry density. In addition, some of the experimental cements developed utilized more unorthodox bonding mechanisms, including furan, epoxy, polystyrene, and polyurethane polymers; mixtures of styrene-acrylonitrile-acrylamide monomers; semi-organic systems with polymeric organosiloxane; phosphate-bonded glass cements; and aluminum hydroxide- and zinc oxide-based hydrothermal cements.

5.1 Geothermal Cementing Problems

Cementing of the annular space between the steel casing and the formation wall is one of the most critical steps in the completion of a geothermal well. The cement not only secures the casing in the well but also isolates the producing zone and prevents fluid migration between zones. An inadequate cementing job--one which leaves cement-free voids in the annulus--can cause numerous difficulties in conventional oil or gas wells; however, such difficulties are magnified in geothermal wells because of the high temperatures and pressures and the corrosive species present. These difficulties occur both at the time of cement emplacement and over the long-term. They may be briefly listed as follows [Varnado 1979]:

Emplacement Problems

- o Thick drilling muds, made necessary by the high bottom-hole temperatures, are difficult to displace in the annulus. Thus, cements may tend to bypass pockets of mud and form an incomplete bond with the casing. Mud displacement is even more difficult if the casing is off-center in the borehole or against one wall.
- o Cement slurries often set up prematurely without retardation in hot boreholes, yet excessive use of retarders can degrade cement strength properties. Also, retarders in current use can exhibit erratic behavior above 400°F.

- o Unstable boreholes, where formation swelling or sloughing is occurring, can cause thin or uneven sheaths.
- o Geothermal well formations are usually rather fragile, suggesting or requiring the use of lightweight cement slurries. These, however, have inferior strength properties compared to heavier slurries.
- o In the case of borehole washouts, the washed-out area or the adjacent sections of the borehole may not be properly filled with cement. (This, of course, would be a potential problem with any cement. However, accelerated set-up rates in hot holes increase the risk that voids will remain unfilled with cement.)

Long-term Problems

Problems which affect a cement's performance over the longer term may be difficult to anticipate adequately in static design conditions. For instance, thermal shocks from bringing the well into production or from subsequent operation may break down the cement system, causing strength regression, stress cracking, or separation of the cement from either the casing or the borehole. This can lead to migration of the fluid behind the casing, and to subsequent casing corrosion and cement erosion or leaching. Thermal shocks of several hundred degrees may be frequent and cement failure may occur within two or three years of operation. Also, pipe expansion and longitudinal movement from elongation and shrinkage of the metal can cause cement cracking. Thus, pipe-to-cement bonding strength is very important, as it is likely to be tested severely by the temperature cycling which results from drilling, testing, shutting in, and producing a well.

Geothermal formations are also inherently fragile because of their fluid nature. In one study, the operators felt that lightweight cements, on the order of 12.0 lb/gal (90 lb/cu.ft.) or less, were needed to prevent formation damage and lost circulation [Nelson 1980]. This study also showed that cement costs average about two percent of total well costs, or about \$17,000 to \$50,000. One operator indicated that a 10 percent increase in the cement cost could be accepted if performance improvements were demonstrated.

5.2 Cement Development and Testing Programs for Geothermal Wells
Producing from Liquid-Dominated Resources

5.2.1 DOE-Sponsored Geothermal Cement Development Program

A series of DOE-sponsored programs under the direction of Brookhaven National Laboratories (BNL) was conducted to develop cements specifically for geothermal applications. In addition to BNL, organizations participating in this phase were Battelle Columbus Laboratories, Colorado School of Mines, Dowell Division of Dow Chemical U.S.A., Pennsylvania State University, Southwest Research Institute, and the University of Rhode Island.

The DOE/BNL program for cement development for wells producing from high temperature liquid-dominated resources had several phases. Phase 1 was problem definition and establishment of minimum acceptable properties. A BNL advisory panel, in affiliation with the American Petroleum Institute (API), established the following criteria for geothermal cements [Kukacka 1980].

- o Compressive strength greater than 1000 psi within 24 hours of placement.
- o Permeability to water of less than 0.1 millidarcy.
- o Bond strength to steel casing greater than 10 psi.
- o No significant strength regression or increase in permeability after prolonged exposure at 750°F to 25 percent sodium chloride brine solutions, flashing brine, or dry steam.
- o Capability of three- to four-hour retardation at expected placement temperatures.
- o Compatibility with drilling mud.
- o Noncorrosivity to steel well casing.

The problem definition was followed by development of individual candidate cementing compositions (Phase 2). Most of these candidate cements

were then tested by the National Bureau of Standards (Phase 3) to verify that they met the minimum standards set forth above. The verified cements were then field-tested downhole for one year in flowing brine at 417°F in a well of the Cerro Prieto geothermal field, Mexico (Phase 4).

Cement Development Tests

At least 26 separate cement formulations were evaluated in Phase 2. The compositions of these candidate slurries are summarized in Table 5.2-1 along with several currently used cements which were also subjected to Phase 3 testing. Included were adaptations of two polymer cement compositions that had been developed earlier for surface applications but which met the criteria for acceptable geothermal cements [Zeldin and Kukacka 1980]. One was based on organic binders -- a mixture of styrene-acrylonitrile-acrylamide with divinyl benzene as a cross-linking agent (cement C in Table 5.2-1). The other was based on semi-inorganic polymers, such as organosiloxane, which could be used together with a mixture of sand flour and cement in 9:1 ratios for high-temperature applications of up to 570°F (cement P in Table 5.2-1).

The performance of the candidate cements in BNL's tests is reported, together with the testing conditions, in Table 5.2-2. Cement C was not advanced to Phase 3 and Phase 4 laboratory and downhole tests because of indications that it would not meet strength and pumpability criteria at temperatures above 460°F. However, other research has shown it to be excellent for surface applications, such as a lining material for carbon steel pipes to handle wellhead geofluids and as concrete piping for condensate and cooling water. For further information on its performance and cost effectiveness in such applications, see Fontana and Zeldin [1980], and Ellis and Conover [1981].

Battelle Columbus Laboratories (BCL) investigated a number of cementing materials for geothermal well use [Kalyoncu and Snyder 1981]. These included Portland cement types I, III, and V; oil well cement classes G, H, and J; and additives such as silica flour, blast furnace slags, pozzolan,

TABLE 5.2-1. FORMULATIONS OF THE MORE PROMISING CEMENT SLURRIES IN THE GOVERNMENT-SPONSORED GEOTHERMAL CEMENT DEVELOPMENT PROGRAM

Cement ID	Source ^a	Components	Concentration parts by weight	Slurry Density lbm/cu.ft.
A	Dowell	API Class G cement	100	119
		silica flour	35	
		water	54	
		lignin-sugar retarder	1	
B	Dowell	API Class J cement	100	115
		water	44	
		lignin-sugar retarder	0.4	
C	BNL	solid aggregate	100	147
		liquid organic monomers ^b	22	
D	INEL	cement	100	113
		water	45	
		retarder	0.7	
E	CSM	modified Class J cement	100	n.a.
		perlite	4.5	
		bentonite	1.1	
		water	85	
F	BCL	API Class J cement	30	103
		pozzolan	40	
		blast furnace slag	30	
		water	60	
		carboxymethyl cellulose	0.5	
G	DSIR	API Class G cement	30	n.a.
		silica flour	40	
		pozzolan	30	
		water	60	
		carboxymethyl cellulose	0.5	
H ^c	SwRI	hydrothermal cement	100	125
		water	20.8	
I	Ube	cement	100	113
		water	50	
		retarder	0.3	
J	DSIR	portland cement	100	n.a.
		water	50	

(Footnotes appear on the last page of this table.)

(Continued)

TABLE 5.2-1. FORMULATIONS OF THE MORE PROMISING CEMENT SLURRIES IN THE GOVERNMENT-SPONSORED GEOTHERMAL CEMENT DEVELOPMENT PROGRAM (Continued)

Cement ID	Source ^a	Components	Concentration parts by weight	Slurry Density lbm/cu.ft.
K	Dowell	API Class G cement	100	101
		silica flour	35	
		bentonite	2	
		perlite	8.5	
		water	116	
		retarder	1	
L	Dowell	API Class G cement	100	105
		silica flour	35	
		diatomaceous earth	10	
		water	91	
		retarder	1	
M	PSU	API Class J cement	80	110
		calcined chrysotile	20	
		water	47.5	
		D-28 Dowell retarder	0.25	
N	PSU	calcium oxide-aluminum oxide system cement	100	111
		5 m quartz flour	100	
		water	89.1	
		100 XR Pizzolithe	0.9	
O	PSU	API Class J cement	60	n.a.
		calcined chrysotile	40	
		water	47.5	
		retarder	0.375	
P	BNL	API Class C cement	10	147
		silica flour	90	
		liquid siloxane monomer	50	
R	Dowell	API Class B cement	100	119
		silica flour	35	
		sodium chloride	20	
		water	54	
		lignin-sugar retarder	1	

(Footnotes appear on the last page of this table.)

(Continued)

TABLE 5.2-1. FORMULATIONS OF THE MORE PROMISING CEMENT SLURRIES IN THE GOVERNMENT-SPONSORED GEOTHERMAL CEMENT DEVELOPMENT PROGRAM
(Continued)

Cement ID	Source ^a	Components	Concentration parts by weight	Slurry Density lbm/cu.ft.
S	Dowell	API Class G cement	100	n.a.
		silica flour	100	
		sodium silicate	2	
		sodium hydroxide	1	
		water	135	
		lignin-sugar retarder	1	
T	BCL	API Class J cement	30	n.a.
		silica flour	30	
		blast furnace slag	40	
		water	50	
		carboxymethyl cellulose	0.5	
U	BCL	API Class J cement	30	n.a.
		pozzolan	30	
		blast furnace slag	40	
		water	50	
		carboxymethyl cellulose	0.5	
W	Ube	Ube lightweight cement	100	97
		water	68	
		retarder	0.2	
X	Halliburton	API Class G cement	100	116
		silica flour (SSA-1)	40	
		water	60.3	
		dispersant (CFR-2)	0.75	
		retarder (HR-7)	0.4	
		fluid loss additive (HALAD-22A)	0.75	
Y	Halliburton	API Class G cement	100	133
		silica sand (SSA-2)	100	
		water	44.5	
		retarder	0.3	
Y1	Halliburton	API Class G cement	100	114
		silica flour (SSA-1)	100	
		water	85.1	
		retarder (HR-12)	0.3	

(Footnotes appear on the last page of this table.)

(Continued)

TABLE 5.2-1. FORMULATIONS OF THE MORE PROMISING CEMENT SLURRIES IN THE
GOVERNMENT-SPONSORED GEOTHERMAL CEMENT DEVELOPMENT PROGRAM
(Continued)

Cement ID	Source ^a	Components	Concentration parts by weight	Slurry Density lbm/cu.ft.
Z	Halliburton	API Class G cement silica flour (SSA-1) water retarder (HR-12) fluid loss additive (HALAD-22A)	100 80 77 0.3 0.5	115
AA	Dowell	API Class A cement silica flour glass spheres water retarder	100 25 40 115 0.6	67
BB	IIE	API Class G cement (Mexico) silica flour water retarder	100 40 59.2 1	118
3	Dowell	API Class G cement needles fly ash silica flour retarder water	100 75 35 1 93	113
5	Dowell	API Class G cement silica flour sodium chloride retarder water	100 35 20 1 54	120
6	Dowell	API Class G cement silica flour sodium chloride retarder water	100 35 5.4 1 54	120

(Footnotes appear on the last page of this table.)

(Continued)

TABLE 5.2-1. FORMULATIONS OF THE MORE PROMISING CEMENT SLURRIES IN THE GOVERNMENT-SPONSORED GEOTHERMAL CEMENT DEVELOPMENT PROGRAM (Continued)

Cement ID	Source ^a	Components	Concentration parts by weight	Slurry Density lbm/cu.ft.
10	Dowell	API Class G cement silica flour powdered coal retarder water	100 35 27 1 63	109
49	Dowell	API Class B cement sand retarder water	100 35 1.2 56	119

^aKey to Slurry Sources:

Dowell - Dowell Division of Dow Chemical Co., USA
 BNL - Brookhaven National Laboratory
 INEL - Italian National Energy Agency
 CSM - Colorado School of Mines
 BCL - Battelle Columbus Laboratories
 DSIR - Department of Scientific and Industrial Research (New Zealand)
 SwRI - Southwest Research Institute
 Ube - Ube Industries (Japan)
 PSU - Pennsylvania State University
 Halliburton - Halliburton Services, USA
 IIE - Instituto de Investigaciones Electricas (Mexico)

^bMonomer formulation is 50 percent styrene, 35 percent acrylonitrile, 5 percent acrylamide, 10 percent divinylbenzene

^cCement H has varied in composition during the NBS test program. In the preliminary laboratory testing at SwRI, the No. 60 series was judged the best performer. Its composition was 50 parts by weight silica flour, 10 parts britesil, 10 parts anhydrous sodium silicate, 0.5 parts bentonite, 7 parts aluminum hydroxide, and 23 parts water. The final report states that this mixture was sent to NBS [Curtice and Mallow 1979]. However, NBS' preliminary lab tests used SwRI series No. 1 and No. 2 with different amounts of water [Curtice and Mallow 1979; Krause and Fuller 1979]. These formulations contained 50 parts silica sand, 25 parts silica flour, 10 parts britesil, 10 anhydrous sodium silicate, 18 parts water, and either 5 parts zinc oxide or 7 parts aluminum hydroxide. However, the formulation of cement H used in the final NBS laboratory tests and downhole testing seems closest to the No. 100 series: 50 parts silica sand, 25 parts silica flour, 10 parts britesil, 5 anhydrous sodium silicate, 3 parts bentonite, 8 parts aluminum hydroxide or titanium oxide, and 20 parts water [Curtice and Mallow 1979].

Source: Kukacka 1980; and Krause 1981a.

hydrated lime, perlite, and aluminum phosphate. Several formulations, which used Class J cement, pozzolan, blast furnace slags, and silica flour, were developed and seemed suitable for geothermal use. Of these, cements T and U in Table 5.2-1 possessed the best long-term compressive strengths and thickening times (see Table 5.2-2).

Researchers at the Colorado School of Mines (CSM) studied Class G Portland cement and the dicalcium silicate-silica cement, Class J, together with various extenders and retarders at temperatures of 300°- 660°F and saturated steam pressure [Kalousek 1979]. X-ray diffraction techniques were used to determine the dominant binding phases after exposure to elevated temperature for periods of one and seven days. Normal Portland cements could be used successfully to about 247°F. Above that, it was found that Class J cement had superior compressive strengths at 300°- 345°F; however, Class G cements with additional silica had higher strengths at temperatures of 480°- 660°F. At the conclusion of the project, a modified Class J cement with bentonite and perlite extenders was selected for further study (cement E in Table 5.2-1).

The Dowell Division of Dow Chemical Company (Dowell) conducted a detailed series of tests on a wide variety of potential geothermal cements [Nelson 1980]. An initial screening program was conducted on more than 60 candidate cements. These included: Portland cements (API types B, G, and H), non-Portland cement (API Class J), modified Portland lightweight cements, synthetic silicate and/or aluminate systems, organic-based polymer systems, lignosulfonate and modified sugar retarders, and various extenders (bentonite, perlite, fly ash, diatomaceous earth, coal, gilsonite, and sodium silicate).

The screening tests surveyed performance in the following areas: thickening time (the slurry must remain pumpable for at least three hours at 300°F and 5220 psi), compressive strength after curing at 437°F and 617°F for 24 hours and seven days, water permeability, cement-to-steel bonding strength after 28 days of curing under water at 400°F and 2538 psi, expansion during curing at 400°F and 2538 psi, and erosion under exposure to simulated dynamic steam and brine contact for periods of up to 15 months.

TABLE 5.2-2. TEST PERFORMANCE AND TESTING CONDITIONS OF CANDIDATE CEMENTS IN INDIVIDUAL LABORATORY DEVELOPMENT PROGRAMS

Cement/Source		Compressive Strength (psi)		Permeability (millidarcies)	Pumpability (hr)	
C	BNL	24,000 (1 day, 25% sodium chloride solution @ 460°F)		33,000 (365 days, @ 460°F, 25% sodium chloride solution)	0.002 after 150 days, 460°F 25% sodium chloride solution	3 @ 158°F
P	BNL	8700-11,600 (120 days, 25% sodium chloride @ 570°F)			0 after 120 days, 25% sodium chloride at 570°F	4 @ 399°F
T	BCL	1650 (1 day , @ 400°F) with sat. steam)	2850 (7 days, @ 400°F with sat. steam)	1300 (28 days, @ 400°F with sat. steam)	--	2.6 @ 400°F
U	BCL	1450 (1 day, @ 400°F) with sat. steam)	2200 (7 days, @ 400°F with sat. steam)	3100 (28 days, @ 400°F with sat. steam)	--	2 @ 400°F
A	Dowell	3590 (1 day, @ 440°F) ^a	7110 (7 days, @ 440°F) ^a	2750 (28 days, @ 440°F) ^a	<0.01 after 3 days @ 440 F	>6 @ 300°F
B	Dowell	4400 (1 day, @ 440°F) ^a	4300 (7 days, @ 440°F) ^a	3230 (28 days, @ 440°F) ^a	--	6 @ 300°F
R	Dowell	5350 (1 day, @ 440°F) ^a	5860 (7 days, @ 440°F) ^a	1350 (28 days, @ 440°F) ^a	<0.001 after 3 days @ 440°F	>6 @ 300°F
K	Dowell	2060 (1 day, @ 400°F) ^a	--	1560 (28 days, 400°F) ^a	<0.09 after 3 days @ 400°F	>6 @ 300°F
L	Dowell	2250 (1 day, @ 400°F) ^a	--	2000 (28 days, @ 400°F) ^a	<0.10 after 3 days @ 400°F	>5 @ 300°F
S	Dowell	2560 (1 day, @ 400°F) ^a	--	940 (28 days, 400°F) ^a	0.04 after 3 days @ 400°F	>6 @ 300°F
AA	Dowell	975 (1 mo., @ 600°F) ^a	--	875 (3 mos., @ 600°F) ^a	0.42 after 1 month @ 600°F	--

-- No data available.

^aThese samples may have been cured in "hot water," steam, or dry air. Report does not specify which samples were subjected to what conditions.
Source: Zeldin and Kukacka 1980; Nelson 1980

The cements that survived these screening tests were then tested at two geothermal sites, a moderately saline one at East Mesa and a highly saline one at the Salton Sea KGRA, California. At East Mesa, two-inch cement cubes (precured under water at 400°F, 2500 psi for 28 days) were exposed in a chamber at the wellhead to brine at about 300°F for periods of 1, 3, 7, and 17 months. At the Salton Sea, the samples were placed in wire baskets inside one of the well flashers. Because of the extreme salinity of the geofluid, scaling was a chronic problem and the well had to be shut down periodically to restore circulation. Thus this test was particularly severe, given the geofluid salinity and the repeated thermal shocks.

On the basis of these tests, the Dowell researchers recommended six cements for further testing -- three of normal weight slurries and three of lightweight slurries. These are listed in Table 5.2-1 as cements A, B, and R (normal weight) and K, L, and S (lightweight slurries). Polymeric cements of furfuryl alcohol and powdered coal, and epoxy, polystyrene, and polyurethane were found to be unsuitable for downhole use, principally due to problems with creep and severe strength regression at temperatures above 390°F, although this does not rule out their use above ground in such applications as piping and linings [Nelson 1980].

Table 5.2-2 includes Dowell's results for their six candidate cements from the initial screening tests (A, B, R, K, L and S). In the wellhead tests, however, other cements actually performed better than Dowell's three normal weight candidates. Five of these are shown in Tables 5.2-3 and 5.2-4 with their results and those of the normal-weight candidate slurries. These additional slurries might also be considered for use, particularly in wells where thermal shock or direct contact with geofluids will be encountered.

To produce lightweight slurries suitable for use in the more fragile geothermal formations, Dowell researchers experimented with Portland cements (API Classes A and G) mixed with glass balloons. These were found to yield excellent lightweight cements under most conditions. However, their cost is

TABLE 5.2-3. COMPRESSIVE STRENGTH TEST RESULTS FOR SELECTED CEMENT SLURRIES EXPOSED TO SIMULATED AND ACTUAL GEOTHERMAL WELLHEAD CONDITIONS

Cement ID ^d	Compressive Strength After Simulated Geothermal Conditions ^a		Compressive Strength After Exposure to Actual Geofluids ^b		
			East Mesa ^b		Salton Sea ^c
	28 days	15 months	28 days	17 months	76 days
A	10,380	2,250	1,500	600	3,380
#3	4,230	2,180	2,250	1,050	2,000
#5	4,250	1,280	880	340	4,870
#6	7,200	--	1,250	1,110	2,270
#10	4,500	--	1,730	1,000	1,630
B	3,750	2,250	2,700	1,020	2,630
R	5,900	5,050	2,030	420	3,440
#49	2,580	5,190	2,500	1,430	2,750

^a Simulated brine (15,850 mg/l chloride, 200 mg/l carbon dioxide, 27,050 mg/l TDS) at 300°F, pressure not specified

^b 1,600-26,300 mg/l TDS (total dissolved solids) in brine at 300°F and 100 psi

^c 214,400 mg/l TDS in brine at 347°F and 115 psi

^d Compositions given in Table 5.2-1.

Source: Nelson 1980

TABLE 5.2-4. WATER PERMEABILITY TEST RESULTS FOR SELECTED CEMENT SLURRIES EXPOSED TO SIMULATED AND ACTUAL GEOTHERMAL WELLHEAD CONDITIONS

Cement ID ^d	Water Permeability (microdarcies) after Exposure to Simulated Geothermal Conditions ^a		Water Permeability (microdarcies) after Exposure to Actual Geofluids		
	28 days	15 months	East Mesa ^b		Salton Sea ^c
			28 days	17 months	76 days
A	0.009	0.011	0.01	0.08	Cracked
#3	0.035	0.024	0.02	0.08	Cracked
#5	0.062	0.11	0.06	0.05	0.001
#6	0.002 (14 days)	--	0.05	0.03	0.362
#10	0.005 (14 days)	--	0.08	0.08	Cracked
B	0.041	0.35	0.18	0.35	Cracked
R	0.012	0.016	--	0.03	Cracked
#49	0.027	0.13	0.01	0.02	Cracked

^aSimulated brine (15,850 mg/l chloride, 200 mg/l carbon dioxide, 27,050 mg/l TDS) at 300°F, pressure not specified

^b1,600-26,300 mg/l TDS (total dissolved solids) in brine at 300°F and 100 psi

^c214,400 mg/l TDS in brine at 347°F and 115 psi

^dCompositions given in Table 5.2-1.

Source: Nelson 1980

considerably higher and, under exposure to high geothermal temperatures, they may tend to become reactive, resulting in high permeability. Thus their use was judged to be limited. Nevertheless, if slurry density is of crucial importance and the cement will not be in direct contact with high temperature geofluids, they may be useful. Cement AA in Table 5.2-1 is such a slurry; Dowell's testing results for it are given in Table 5.2-2 [Nelson 1980].

Researchers at the Pennsylvania State University investigated two types of cementing materials for use in geothermal wells [Roy, et al. 1980a; 1980b]. One contained magnesia-containing mixtures and was prepared by mixing a Class J cement with various sources of magnesia, such as calcined chrysotile or magnesium oxide, along with calcium oxide and silica fine quartz powder. The other cement system was formulated from high-alumina (brand S) cements, which were mixed with different silica sources. The variations developed from these two groups were then tested, after curing at various temperatures and pressures, for compressive strength, water permeability, cement/steel and cement/rock bond strengths, 96-day stability in hydrothermal water or 20 percent brine, and maintenance of pumpability at temperatures up to 350°F for four hours. At the end of the project, the researchers referred magnesia-containing cements M and O (Table 5.2-1) and aluminous cement N for further study.

Southwest Research Institute workers developed a family of hydrothermal cements which differ from Portland-type cements in that they contain no calcium silicates and, rather than forming a crystalline hydrate, cure by an endothermic conversion of totally inorganic reagents into amorphous polymers of silicon oxide and polysilicic acids [Curtice and Mallow, 1979]. Test slurries were exposed, without precure, to environments of saturated steam and artificial brine (450-15,870 mg/l chloride, 20-200 mg/l sulfate, 125-700 mg/l bicarbonate) at temperatures of 600°F and 725°F and pressures up to 5kpsi. During their studies, the researchers found cements that seemed to work well at 500°-600°F and an aluminum hydroxide-based cement that worked well at temperatures of over 600°F. A later variation of this cement is designated as entry H in Table 5.2-1.

Scientists at the University of Rhode Island studied phosphate cements formed by mixing glass frits of various silica compositions with phosphoric acid [Rockett 1979]. In these reactions, the glass supplies calcium and aluminum ions which react with phosphate groups to form the cement. Difficulty was encountered in finding a formulation which would give adequate compressive strengths, however. Because of this, no data was developed on pumpability or permeability to water, and only a little information was produced on the strength of cement/steel bonding and on long-term geothermal stability. At the end of the study, no cement compositions were referred for further study.

Property Verification Testing

Test procedures for measuring compressive strength, tensile splitting strength, shear bond at the cement-steel interface, and cement permeability to water were compiled by NBS and approved by the API Task Group on Geothermal Cements [Krause and Fuller 1979]. Also, a fluid handling facility was constructed which enabled set (precured) cements to be exposed to simulated geothermal fluids at pressures up to 8700 psi and temperatures up to 750°F. Two of the pressure vessels were equipped for measuring the shear-bond strength or the permeability to water at elevated temperatures and pressures.

The cements developed in each of the individual research programs just discussed which showed the most promise of meeting or exceeding the API Task Force physical property requirements were submitted to the National Bureau of Standards (NBS) for Phase 3 verification testing. In addition, several cements currently in use in the U.S. and foreign countries were included in this phase. Sources of these materials were the Italian National Energy Agency (INEL), the New Zealand Department of Scientific and Industrial Research (DSIR), Ube Industries (Japan), Halliburton Services, and the Instituto de Investigaciones Electricas (Mexico). These cements are also listed in Table 5.2-1.

Of the 26 cements submitted as candidates for downhole testing, 20 were laboratory tested. Six were not tested because of time constraints or late submission. In most cases, the NBS tested two slurry formulations from each supplier, choosing candidates according to the supplier's recommendation if more than two were originally submitted. The cements were tested as follows. First, slurries were prepared according to API recommended practice. The test specimens were set-cured under water in brass molds at elevated temperature and pressure (392°F and 3045 psi) for two days. Then they were exposed to distilled water or 20 percent sodium chloride in water for periods of one week or one month before being tested at room temperature and pressure for a given strength parameter. Tables 5.2-5 through 5.2-8 present test results for the ten cements that performed best in the tests. (These cements, plus some other later additions, were the sample population for the phase four downhole tests.)

Compressive strengths, presented in Table 5.2-5, exceeded the 1000 psi minimum for all of these selected cements and showed no significant regression over time. Five of the cements produced higher strength values after exposure to the higher temperature brine solution than in pure water (B, L, P, Y, and Z). The same trends are apparent in the tensile strength values given in Table 5.2-6. Shear bond strengths (between the cement and sandblasted steel surfaces) greatly exceeded the minimum value of 10 psi (see Table 5.2-7); however, the values at 572°F were significantly lower for all but cements B and I than they were at 392°F. Considerable scatter is evident in the water permeability data given in Table 5.2-8. Most of the cements were well below the 100 microdarcy maximum permeability level; however, there is a clear tendency towards greater permeability with higher temperatures and longer exposure.

Cement Y was noteworthy for its consistently excellent performance in all tests. Most of the rest were good in some tests and significantly poorer in others. Cement P is a good example: very good compressive and tensile strengths and poorer (although still acceptable) shear strength and permeability levels. Cement W may be of interest because of its low slurry

TABLE 5.2-5. CEMENT COMPRESSIVE STRENGTH AFTER EXPOSURE TO VARIOUS LABORATORY TEST FLUIDS AT 2900 PSI (1000 psi minimum acceptable level)

Cement ID	Compressive strength, psi				
	Set-cure 392°F for 2 days	Exposure to pure water at 392°F for		Exposure to 20 percent sodium chloride brine at 572°F for	
		7 days	28 days	7 days	28 days
A	9280 $\pm$ 1300	5800 $\pm$ 1450	4200 $\pm$ 720	2170 $\pm$ 140	2460 $\pm$ 140
B	7540 $\pm$ 1010	2900 $\pm$ 430	3480 $\pm$ 290	4200 $\pm$ 430	4640 $\pm$ 290
D	7540 $\pm$ 290	7100 $\pm$ 580	6810 $\pm$ 870	4780 $\pm$ 1160 (3300 $\pm$ 1160) ^a	6670 $\pm$ 2030
I	5650 $\pm$ 290	5360 $\pm$ 870	7540 $\pm$ 140	4600 $\pm$ 290 ^a	6235 $\pm$ 1700 ^a
L	3910 $\pm$ 140	4060 $\pm$ 430	3770 $\pm$ 430	5070 $\pm$ 1300	7540 $\pm$ 120
M	5800 $\pm$ 720	3200 $\pm$ 150 ^a	3900 $\pm$ 150 ^a	3700 $\pm$ 140 (4400 $\pm$ 440) ^a	4100 $\pm$ 70 ^a
P	8700 $\pm$ 580	10,000 $\pm$ 140	10,730 $\pm$ 580	12,180 $\pm$ 1450	14,200 $\pm$ 1000 ^a
W	3620 $\pm$ 90	3480 $\pm$ 290	3330 $\pm$ 140	2900 $\pm$ 290	2610 $\pm$ 290
Y	--	7300 $\pm$ 1900 ^a	7500 $\pm$ 1500 ^a	9900 $\pm$ 900 ^a	9600 $\pm$ 900 ^a
Z	10,300 $\pm$ 290	4930 $\pm$ 40	4350 $\pm$ 580	5800 $\pm$ 140	4930 $\pm$ 290

-- No data available

^aData derived from bar graphs (Krause 1981a). Two ranges given only when the sources differ significantly.

Source: Kukacka 1980; Krause 1981a

TABLE 5.2-6. CEMENT TENSILE SPLITTING STRENGTH^a AFTER EXPOSURE TO VARIOUS LABORATORY TEST FLUIDS AT 2900 PSI

Cement ID	Tensile Splitting Strength (psi)				
	Set-cure 392°F for 2 days	Exposure to pure water at 392°F for		Exposure to 20 percent sodium chloride brine at 572°F for	
		7 days	28 days	7 days	28 days
A	1070±130	1070±100	670±70	320±40	290±30
B	870±60	450±30	500±70	710±90	740±70
D	840±260	770±220	540±40	500±120	960±260
I	590±90	600±100	830±100	490±30 ^b	640±70 ^b
L	520±130	600±40	580±70	940±100	960±60
M	570±40	300±30 ^b	490±40 ^b	570±30	550±90 ^b
P	540±140	720±160	960±120	1330±220	960±200 ^b
W	350±70	430±30	400±30	400±60	390±30
Y	--	840±190 ^b	870±260 ^b	1330±150 ^b	1170±100 ^b
Z	1120±130	780±60	770±60	880±70	830±10

-- No data available

^aNo minimum acceptable level for geothermal cement tensile strength was set by the API committee. However, since the tensile strength of a cement is usually around one-tenth to one-eighth of its compressive strength, a possible minimum threshold for tensile strength might be 100-125 psi. Because all the cements tested greatly exceeded that value in the laboratory tests, measures of tensile strength were dropped in subsequent phases of the NBS program. (Krause 1982)

^bData derived from bar graphs (Krause 1981a)

Source: Kukacka 1980; Krause 1981a

TABLE 5.2-7. CEMENT SHEAR-BOND STRENGTH AT SANDBLASTED STEEL INTERFACE AFTER EXPOSURE TO VARIOUS LABORATORY TEST FLUIDS AT 2990 PSI (10 psi minimum acceptable level)

Cement ID	Shear-bond strength (psi)			
	Exposure to pure water		Exposure to 20% sodium	
	at 392°F for		chloride brine at 572°F for	
	7 days	28 days	7 days	28 days
A	2860	1800	930	1400
B	2640	2800	2000	3130
D	3610	3520	--	2610
I	2480	2900	1460	3040
L	2290	2170	1490	1190
M	2230	2220	1290	620
P	230	260	40	40
W	2020	1840	970	950
Y	6900 ^a	7100 ^a	6000 ^a	5100 ^a
Z	2000	1770	860	1320

-- No data available

^aData derived from bar graphs (Krause 1981a).

Source: Kukacka 1980; Krause 1981a

TABLE 5.2-8. CEMENT PERMEABILITY TO WATER AT 77°F AFTER EXPOSURE TO VARIOUS LABORATORY TEST FLUIDS AT 2990 PSI (100 μ D maximum acceptable level)

Cement ID	Permeability Values in Microdarcies (μ D) ^a			
	Exposure to Water at		Exposure to 20% Salt Water	
	390°F for		at 570°F for	
	7 Days	28 Days	7 Days	28 Days
A	0.71	5.3	0.033	29
B	4.9	11	9.1	10
D	4.8	12	9.4	21
I	11	15	40	69
L	48	110	48	51
M	2.1	1.2	1.9	2.1
P	13 (6) ^a	--	--	15 (8) ^a
W	14	16	43	88
Y	0.1 ^a	3.5 ^a	0.1 ^a	0.1 ^a
Z	2.5	2.0	5.4	4.0

-- No data available

^aData derived from bar graphs. Two values given only when the sources disagree significantly.

Source: Kukacka 1980; Krause 1981a.

density--its performances were consistently acceptable, although they were not as good as those posted by the best heavy slurries. This is to be expected for such lightweight slurry. Another lightweight slurry, L, performed slightly better in these tests than did W.

Downhole Testing in a Flowing Geothermal Well

The most important part of the test program was to be the downhole testing phase, since it was to most closely resemble actual performance conditions. This phase was made possible by the cooperation of the Instituto de Investigaciones Electricas (IIE), the Comision Federal de Electricidad (both of Mexico), and BNL and NBS of the United States. Through this cooperation, well Q-757 in the Cerro Prieto geothermal field was made available for downhole and aboveground testing.

The verified cements were field-tested downhole in flowing brine at 417°F for one year. The field testing has been completed, but laboratory analyses are not finished. A series of tests at a more meaningful temperature of 660°F was also planned. Unfortunately, the latter tests were cancelled because of budgetary restraints.

In the low-temperature testing, two types of samples were used for each test exposure: pre-cured and in situ-cured specimens. The pre-cured samples were two-inch cubes which were set-cured for one day in brass molds immersed in water at 392°F and 2900 psi. For this operation, laboratory autoclaves were used. The in situ-cured series was prepared by filling hollow Berea sandstone molds with the respective cement slurry prepared from dry ingredients at the wellhead, closing the molds with steel discs, placing them downwell, and then allowing curing to take place with exposure to the geofluid.

Sixteen cements were selected by NBS for testing. For each cement, 16 cube specimens and eight sandstone cup specimens were prepared for each exposure (downhole or autoclave). After exposure times of 1 day (control

group), 3 months, 6 months and 12 months, 4 cubes and 2 sandstone molded samples of each cement were withdrawn and evenly divided between the NBS and IIE laboratories for testing. In addition to the compressive strength and permeability tests, examination by scanning electron microscopy and X-ray diffractometry will be conducted on the test samples.

Testing conditions for the downhole series were: temperature 417°F, pressure 1334 psi, pH 6.8, chloride content 6,395 ppm, silicon dioxide content 347 ppm, carbon dioxide 2,200 ppm and sulfate 2 ppm [Kukacka 1980; Ellis and Conover 1981]. These tests were to be conducted at a depth of about 2,300 feet (total well depth is about 3,040 feet) with the samples placed in wire cages which allowed direct contact between the cement and the geofluid.

The autoclave tests were conducted in six pressurized vessels connected to the well with two-inch (ID) steel pipe. Pressure valves at the entrance and exit to each chamber were used to control the pressure within the vessels as they were heated by the flowing two-phase geofluid. Separate pressure gauges indicated the wellhead pressure, which was continuously recorded, and the pressure within each vessel. Vessel pressure was maintained as close to the 80-120 psi wellhead pressure as possible. The operating temperature of one vessel (the only one equipped with a thermometer) was 248°F-284°F [Krause 1981b].

Because of the limited amount of space available for samples, only two tests were conducted -- compressive strength and water permeability. The samples will be examined later by scanning electron microscopy and X-ray diffractometry. The decision to conduct only two tests was made by the API Geothermal Cement Advisory Committee on the basis of the results of the laboratory tests and other studies. Tensile strength for a given cement was shown by the laboratory tests to be about one-tenth of the compressive strength. Cement-to-steel bonding strengths are mostly determined by the surface condition of the steel, which in actual well completion activities is largely determined by the ability of the cement to displace drilling mud in the annulus. (The laboratory test results reported in Table 5.2-7 showed that the

bonding strengths of the best candidate cements to cleaned steel were well above required levels.) Although it was clearly impossible to do displacement testing of this sort in the NBS downhole program, laboratory tests performed by Dowell shed light on the situation.

Dowell Researchers found that a typical cement slurry with a density of 13 lb/gal (97 lbm/cu.ft.) would not thoroughly displace a representative drilling mud of density 9 lb/gal (67 lbm/cu.ft.), although the mud would not cause pumping difficulties. To achieve satisfactory mud removal, and hence adequate cement-steel bond strengths, spacers and washers compatible with both the mud and the cement should be used [Nelson 1980]. This finding is applicable to all light- and medium-weight slurries.

Results from Downhole and Autoclave Testing

The downhole tests at well Q-757 were completed in April and the autoclave tests in July, 1982. Test results are presented in Figures 5.2-1 through 5.2-6. It is to be stressed, however, that these data and the conclusions that are presented are preliminary results only. Formal presentation of the complete test results will be made by NBS-IIE when all of the evaluations are completed.

For these tests, the top surface of each cube was ground flat to provide a uniform surface for compressive strength measurements. In the case of the sandstone core samples, rod specimens were obtained by drilling with a diamond core drill. The rods were then cut into three sections with a diamond saw to give two compressive strength samples and one permeability sample, each one-inch in diameter and one-inch long.

Two cube and two rod compressive strength samples and one rod permeability sample of each type of cement (for example, three months autoclave or three months downhole) were sent to each testing laboratory. The lack of available testing space downhole or in the autoclave chambers prevented a statistically significant sample population. In addition, test instrument

Figure 5.2-1. Room-Temperature Compressive Strengths of 2-Inch Cube Specimens of Various Cements Precured (392°F, 3900 psi, 1 day) and Exposed in Flowing Geothermal Fluid at 417°F Downhole 2297 Feet in Cerro Prieto Well Q-757 (1 MPa = 144.9 psi) [Krause 1982a]

Figure 5.2-2. Room-Temperature Compressive Strengths of Sandstone-Molded Cements Exposed in Flowing Geothermal Fluid at 417°F Downhole 2297 Feet in Cerro Prieto Well Q-757 (1 MPa - 144.9 psi) [Krause 1982a]

Figure 5.2-3. Room-Temperature Water Permeability of Sandstone-Molded Cements Exposed in Flowing Geothermal Fluid at 417°F Downhole 2297 Feet in Cerro Prieto Well Q-757 (1 nm² = 0.001013 millidarcy) [Krause 1982a]

Figure 5.2-4. Room-Temperature Compressive Strengths of 2-inch Cube Specimens of Various Cements Precured (One Day at 392°F and 3900 psi) Then Exposed in Autoclaves with Flowing Geothermal Fluid from Cerro Prieto Well Q-757 (1 MPa = 144.9 psi) [Krause 1982a]

SANDSTONE-MOLDED CEMENTS, TREATED ABOVEGROUND

Figure 5.2-5. Room-Temperature Compressive Strengths of Sandstone-Molded Cements Exposed in Autoclaves with Flowing Geothermal Brine from Cerro Prieto Well Q-757 (1 nm² = 0.001013 millidarcy) [Krause 1982b]

SANDSTONE-MOLDED CEMENTS, TREATED ABOVEGROUND

Figure 5.2-6. Room-Temperature Water Permeability of Sandstone-Molded Slurries Exposed in Autoclaves with Flowing Geothermal Fluid from Cerro Prieto Well Q-757 ($1 \text{ nm}^2 = 0.001013$ millidarcy) [Krause 1982b]

variation, coupled with the inherently heterogenous structure of cement, meant that a certain spread would be expected in the test results, as can be seen in the figures.

Since the results presented are preliminary, as discussed above, and no attempt has yet been made to quantify the spread in the test results, it would be inappropriate at this time to attempt to draw rigidly quantitative conclusions about the performance of the cements. However, some qualitative observations may be made.

Qualitative Evaluation of Current Downhole Test Results

This test was intended primarily to develop experimental techniques for the 662°F series. Though most conventional concretes passed at the relatively low temperature of 417°F, some of the DOE materials, formulated specifically for $\geq 572^\circ\text{F}$, may improve at higher temperatures.

Table 5.2-9 presents a ranking of the cements as Very Good, Good, and Not Acceptable. These rankings, based on the NBS/IIIE data, are preliminary and somewhat arbitrary. A more accurate assessment can be made when all test data are available.

After exposure at 417°F for one year, Cement A appears to be a very successful geothermal cement. Its compressive strength values are well above the 1000 psi minimum and the results are comparable in both the autoclave and downhole tests. The pronounced strength regression noted in the precured cubes from the one-day to the six-month levels is typical in these tests and reflects the severe exposure of the cement located directly in the flowing geofluid, and probably some thermal shock from the initial sample emplacement as well. The sandstone core (in situ-cured) samples are probably more reflective of the actual cement exposure and curing conditions in a well. For cement A, the sandstone core samples show a general increase in compressive strength over time. Permeability levels are very low as well.

TABLE 5.2-9. PRELIMINARY QUALITATIVE PERFORMANCE RANKING OF CANDIDATE CEMENTS IN THE 417°F DOWNHOLE TESTING PROGRAM AT CERRO PRIETO

Overall Performance ^a	Cement ^b
Very Good	A ^c B D P (some question - see text) W (lightweight) X
Good	I K (lightweight) L (lightweight) M Y1 Z BB
Not Acceptable	F H N (OK for above ground)

Notes:

^a Considers NBS/IEE results through 6 months of downhole testing. Most weight is given to the performance of the in situ-cured sandstone core samples (exposed downhole) in compressive strength and permeability testing.

^b No attempt is made to rank cements in order of desirable performance within each category.

^c See also Dowell cements 3,5,6,10 in Tables 5.2-3 and 5.2-4.

As was mentioned above, Dowell (the supplier of cement A) also tested other cements of similar composition. Those that performed even better than cement A (Dowell cements 3, 5, 6, and 10) in Dowell's wellhead tests are listed with their results and compositions in Tables 5.2-3 and 5.2-4. These cements might also be considered for commercial use, depending on the particular well conditions.

Cement B also seems to be a good candidate for low-temperature geothermal applications. As with cement A, the precured cube compressive strengths show pronounced regression; however, the in-situ cured sandstone sample compressive strengths are very high. Permeabilities are also higher, but are still quite acceptable (the very high one-day result from IIE would seem to be due to incomplete curing). Overall, cement B was by far the best performing Class J cement tested.

Cement D is also excellent for geothermal applications, and may have been widely used in the Italian fields. Although the precured cubes exhibited significant strength regression for six months, the in situ-cured sandstone cores show considerably higher strengths and low permeabilities (again, the high one-day IIE result is likely the result of an insufficiently cured sample).

Cement F seems unsuitable for low temperature downhole use. The longer-term compressive strengths are lower, especially downhole, and the permeabilities at six months exposure were too high to meet the recommended API guidelines.

Cement H also seems to be unsuitable for geothermal use at 417°F. Compressive strengths are low and permeabilities are much too high. Several different formulations of these hydrothermal cements have been tested in these trials and previous laboratory tests conducted by NBS (see note a to Table 5.2-1). They have yielded consistently low results throughout. Since this cement was formulated for use at 750°F, improvement in properties might be expected at higher temperatures.

Cement I is another mixture with good compressive strength values, but permeability values which are fairly high. Permeability is generally within acceptable limits, however.

Cements K and L seem less suitable because their compressive strengths are lower than those of some other cement and permeabilities are high. However, these are lightweight formulations and would be expected to have somewhat lower strengths and higher permeabilities. If they were to be used in circumstances where slurry density was of prime concern and contact with geofluids was minimized, they would probably serve very well. Their strength values do show very little regression over time and are more than adequate, according to the API recommendations (greater than 1000 psi). Cement L seems to be a slightly better performer than K, as was seen in Dowell's testing (see Table 5.2-2).

Cement M is an API Class J cement and shows behavior similar to another Class J cement, F. Compressive strengths of the precured cubes are low; however, values for the in situ-cured sandstone specimens are higher and the permeability values are good. Thus, this cement would probably be quite adequate for geothermal applications, especially those involving less prolonged exposure to geofluids.

Cement N, an experimental aluminum oxide cement, seems unsatisfactory for geothermal applications. Its downhole compressive strengths are very low for both sample types, and permeability values are unsatisfactorily high after prolonged exposure to geofluids. However, the aboveground compressive strengths are high, possibly indicating that its service would be satisfactory in environments of restricted exposure or lower temperature.

The results from cement P are erratic because of the low temperatures. The cement was formulated for use above 572°F; below this temperature unreacted monomers cause strength reductions and permeability. For example downhole sandstone core compressive strengths are very high; however, those from above ground are quite low. Cube strengths average about the same in

either testing location (4300 psi) because they were cured in autoclaves at a similar temperature. The cement seems to have compressive strengths and permeabilities that are at least adequate, and possibly excellent, for geothermal application. The cement is an experimental blend of API Class C cement with silica flour and liquid siloxane monomer, and whether its performance would merit any increased costs incurred by the addition of the siloxane has not been proven. BNL scientists have estimated that cement P would cost about \$800/cu.ft. on a commercial basis. Thus its use would probably be restricted only to certain critical areas.

Cement W is a lightweight cement from Japan. Of the three lightweights tested by NBS/IIIE in this program (K, L, and W), cement L appears to be the best performer. Permeability is fairly high, as one would expect for a lightweight slurry, but certainly is within acceptable limits. Overall, the slurry performs about as well as most of the regular weight mixtures, but has the advantage of its lower density. For best results in field use, slurry W should be used in conjunction with compatible washers and spacers, as was discussed in Section 5.2.1.4 above.

Cement X appears to be a very good performer of normal weight. Its compressive strengths are very good for all samples, and its permeability is also good and shows no signs of deterioration over time. Next to slurry A, X appears to be the best API Class G candidate.

For cement Y, two different slurry formulations were used, as is shown in Table 5.2-1. Slurry Y1 was used for the downhole testing, and slurry Y was used in the aboveground tests, as well as in the prior laboratory tests, where it was clearly the best performer. As the tables show, Y produced very high compressive strengths in the autoclave testing chambers, but then those tests were generally less rigorous. Y1 gave fair results downhole, with the in situ-cured sandstone cup specimens performing significantly better than the precured cubes. Y1 permeabilities were low. An additional consideration might be slurry density, because Y is a very heavy slurry. More testing in

identical conditions is necessary, however, before definite conclusions can be stated about their relative performance. (For comparison with independent testing results on slurry Y, see section 5.2.2).

Cement Z uses similar components to Y1, although in different proportions and with the addition of a fluid loss additive. Z has good compressive strengths, with some regression noticeable in the first three months of exposure, and permeabilities of consistently acceptable levels.

Cement BB is another API Class G slurry of normal weight. Its initial strengths and aboveground sandstone core strengths are particularly high. However, the downhole tests show substantial strength regression, as do the aboveground cube samples.

Comparing only the six-month downhole sandstone core sample compressive strengths and the six-month permeability levels, the API Class G cements tested by NBS/IIIE (A, K, L, X, Y, Y1, Z, and BB) have a good-to-less good performance order of: A, X, Y1, BB, Z, L, K (the last two are listed in order of compressive strength; their order of permeability performance is K, L). However, slurries K and L are lightweights, as was noted above. Thus other considerations may influence their use.

5.2.2 Results of Industry-Sponsored Cement Testing for Liquid-Dominated Wells

An independent program similar to the NBS/IIIE downhole testing in the DOE program was conducted by Union Oil Company and Halliburton Services in Baca, New Mexico, and Imperial Valley, California, geothermal wells [Gallus et al. 1979a]. In this program, a variety of oil field cements and additives were tested downhole for periods of time ranging up to one year. Researchers in this program originated the sandstone core testing technique, subsequently approved by the API Task Force and used by NBS, to better simulate the actual cement exposure conditions than is possible with the usual precured two-inch cube test technique.

The specific testing procedure involved saturating the sandstone cylinders with well production fluid, filling the three-inch axially drilled specimen chamber of each cylinder with drilling fluid, applying 25 psi pressure for 30 minutes to produce filter cake and filtrate invasion, mixing the cement slurry according to API procedures, pouring the slurry into the mold, and then capping the cylinder with a metal lid. These procedures, simulated the well conditions, with the cement confined by field brine-saturated and filtrate-invaded formation rock, mud filter cake, and steel. To prevent slurry boiling, the cylinders were lowered into the wells at predetermined rates based on well-pressure and temperature data. (Conditions at Baca: pH 7.2 and 2500 mg/l chloride, 180 mg/l bicarbonate, 5500 mg/l TDS; in the Imperial Valley: pH 5.2, 55,000 mg/l chloride, 70 mg/l bicarbonate, and 98, 150 mg/l TDS.)

After exposure to the geofluids for predetermined test periods (one day, one month, two months, three months, six months, and one year), the samples were removed from the wells and laboratory tested for compressive strength and air and water permeability. They were also examined by X-ray diffraction to determine the dominant binding phases present. The required minimum compressive strength was selected as 1000 psi, as in the NBS study. However, the maximum allowable permeability was an order of magnitude larger than in the DOE-NBS study (1 millidarcy as opposed to 0.1 millidarcy for NBS).

Table 5.2-10 lists the most successful cement formations and their compositions. The majority have API Class G cement as their basic constituent, with the addition of various silica sources and other additives. Compositions 1 - 3 are Class G with varying amounts of silica flour (325 mesh). Compositions 4 - 6 are Class G with varying grinds and amounts of silica sand (60-170 or 20-40 mesh). Compositions 8 - 10 contain varying amounts of expanded perlite. Compositions 11 - 12 contain varying amounts of fly ash with or without silica.

TABLE 5.2-10. CEMENT SLURRY FORMULATIONS OF PROVEN DOWNHOLE PERFORMANCE IN INDUSTRY-SPONSORED TESTING PROGRAM

Cement	Components of Slurry	Concentration (parts by weight except as indicated)	Slurry Density (lbm/cu.ft.)
1	API Class G cement silica flour dispersant retarder low water-loss material water	100 40 0.75 0.4 0.75 60	116
2	API Class G cement silica flour retarder low water-loss material water	100 80 0.3 0.5 77	115
3	API Class G cement silica flour retarder low water-loss material water	100 100 0.3 0.6 82	116
4	API Class G cement silica sand dispersant retarder water	100 40 0.75 0.4 36	129
5	API Class G cement silica sand retarder water	100 100 0.3 44	113
6	API Class G cement perlite 20-40 mesh sand retarder water	100 1 cu. ft. 100 0.4 70	120
7	API Class J cement HEC water	100 0.5 44	115
8	API Class G cement perlite silica flour gel dispersant retarder water	100 1 cu. ft. 40 2 0.5 0.2 97	103
9	API Class G cement perlite silica flour gel dispersant retarder water	100 1 cu. ft. 80 3 0.5 0.3 100	108
10	API Class G cement perlite silica flour bentonite retarder low water-loss material water	100 2 cu. ft. 40 2 0.3 0.75 143	95
11	API Class G cement fly ash dispersant retarder low water-loss material water	100 100 1.5 0.4 39	108
12	API Class G cement silica flour bentonite retarder low water-loss material water	100 100 80 4 0.4 2 66	108

Source: Gallus, et al. 1979a.

To summarize the findings of this study [Gallus, et al. 1979a], slurries 4 and 5 gave the best compressive strength values after six months exposure downhole. Significantly, these are the compositions which contain silica sand, although slurry 4 (40 lb sand/100 lb cement) did somewhat better, with compressive strengths of 9000 to 20,000 psi, than did slurry 5 (100 lb sand/100 lb cement, 7800 psi compressive strength). Permeabilities for both were very low, on the order of zero to 0.05 mD.

Next came slurry 1, with 40 lb silica flour/100 lb cement, which had strengths of 4900 and 3250 psi after six months exposure. The permeability of this mixture was only slightly higher (0.1 mD). Higher silica flour contents in slurries 2 and 3 did not result in an increase in strength (each measured about 2600 psi). In fact, these large excesses of silica caused the Class G cement to behave like slurry 5, a Class J cement, which gave the same strength values.

Extenders, such as perlite and fly ash, seemed to lower the compressive strength of the cement appreciably, unless sufficient silica was added to complete the xonotilite-to-truscottite reaction, thus giving thermal stability to the cement. This was especially evident in slurry 8, which contained 40 lb silica flour/100 lb cement, but was extended with 1 cu.ft. of perlite. It had 2000 psi compressive strength at six months but zero at 12 months. Slurry 10, also with 40 lb silica flour/100 lb cement, had mixed performances at six months: 400 psi and 1500 psi. However, slurry 9, with 80 lb silica flour/100 lb cement had consistently higher strengths: 1400 psi and 1800 psi after six months, and 1300 psi after 12 months. Similarly, slurry 11, with fly ash extender, gave mixed values of 900 psi and 3200 psi after six months, as well as unacceptably high permeabilities (1.6 mD). However, slurry 12, with fly ash plus 80 lb silica flour and 2 lb bentonite/100 lb cement performed much better (2500 psi and 0 mD). Also discussed in the report [Gallus et al. 1979a] are two lightweight slurries. These are not included in Table 5.2-10: their performances did not meet API specifications for either compressive strength or permeability.

5.2.3 Comparison of Industry and DOE Test Results

In a comparison of the test slurries used by NBS in the DOE program, as listed in Table 5.2-1, with those studied by Union Oil/Halliburton Services (Table 5.2-10), it can be seen that some of the cements are very similar, and others identical. The following table (5.2-11) compares the equivalent, or nearly equivalent slurries in terms of their compressive strengths and permeability performances after twelve months exposure downhole in the respective test wells (exceptions to this time period are noted).

The highest strength performer in the Union Oil/Halliburton tests was their slurry U-H No. 4. Although no NBS candidate resembles it very closely, one of Dowell Corporation's slurries (D-1), based on Class G cement, contained a similar percentage of silica sand (35 lb/100 lb cement) and retarder (1.2 lb/100 lb cement). Its strength and permeability values after seven months downhole at East Mesa are included here for comparison.

The next highest Union Oil/Halliburton performer was slurry 5. It seems to be exactly the same as the Halliburton NBS candidate Y slurry. No six-month downhole data for it have been yet released by NBS, so the three-month autoclave values determined by NBS and IIE are given. Since the autoclave test was generally less rigorous than the downhole exposure, these values probably represent fairly good agreement with those reported by Union Oil.

It is worth noting that the high strength performance of both slurries 4 and 5 would not necessarily be predicted from the literature about cements. Both contain high percentages of silica sand, which has been stated as resulting in lower strength and poorer permeability performance than does finer grind silica flour [Eilers and Nelson 1979]. NBS' slurry A, their best performer, does contain silica flour, but no downhole test results have been generated in the NBS study for sand-containing cements, such as NBS slurry Y.

TABLE 5.2-11. COMPARISON OF INDUSTRY AND GOVERNMENT CEMENT TEST RESULTS

<u>Industry Samples</u> Government Samples	Slurry Weight lbm/cu.ft.	6-Month Sandstone Core Compressive Strength (ksi)	6-Month Sandstone Core Permeability (mD)
U-H #4	129	9-20	0.05
Dowell #1 (G+35% sand)	119	2.8 (7 mo. E. Mesa)	0.03
U-H #5 =	133	7.8	0
NBS Y	133	8.4-12.3 (3 mo. above grd) ^a	0.0009
U-H #1 =	116	3.3-4.9	0.1
NBS X	116	5.8-6.4	0.009 - 0.01
NBS A	119	6.2-8.8	0.004 - 0.008
U-H #6	120	3.2	0.04
U-H #3 =	116	2.6	0
NBS Y1	114	5.4-5.8	0.001 - 0.005
U-H #2 =	115	2.6	0
NBS Z	115	3.3-5.5	0.0012 - 0.0019
U-H #12	108	2.5	0
Dowell #3	112	1.5 (7 mo. E. Mesa)	0.02
U-H #8	103	2.0	0.08-0.25
NBS K	101	1.6-2.3	0.1-0.6

U-H: Union Oil Company - Halliburton Services

NBS: cement from NBS Property Verification Study

Dowell: cement from DOE funded Dowell Testing

^aSix-month aboveground test data received from NBS too late for general incorporation into this document give even higher compressive strengths for NBS slurry Y: 10.8-15.5 ksi (Krause 1982).

Note: 12-month data for the NBS samples can be derived from Figures 5.2-1 through 5.2-6.

Sources: Gallus, et al. 1979a

In a separate laboratory study which accompanied the field work, the Union Oil/Halliburton researchers tested Class G cements with the addition of 60 lb silica/100 lb cement, either as flour or sand, after one year of treatment at 800°F and 6000 psi in fresh water. The compressive strength of the cement with sand was 7210 psi; that with silica flour, 5250 psi. However, when the flour mixture was thickened with 0.75 lb dispersant/100 lb cement the resulting strength was 9260 psi. More research is desirable.

The Union Oil/Halliburton third-ranked slurry (U-H No. 1) seems to be of equivalent composition to NBS X, another Halliburton submission. As can be seen, its results are somewhat better in the NBS study, although certainly all are very acceptable. Another similar cement is NBS A, a Dowell cement. It is slightly more dense and has thus far produced superior results in the NBS study. Its results are somewhat better than those of the other two cements in its category.

Union Oil/Halliburton slurry 6, another sand-containing cement with perlite, has no comparable formulation in the NBS program. It may be worth noting that, although its compressive strength at six months is at a very satisfactory level, nevertheless it shows a very steep decline from the three months value of 9000 psi. This extreme strength regression, due to the presence of extenders such as perlite, was noted previously in the discussion of U-H slurries 8, 9, 10, and 11. Probably, as in the cases of U-H slurries 9 and 10, which contained significant amounts of silica flour, the sand in U-H slurry 6 boosts the strength, but the longevity of the boost is apparently short.

Three slurries roughly tied for fifth place in performance in the Union Oil/Halliburton study. Two of these are equivalent to NBS candidates: U-H slurry 3 equals NBS Y1, and U-H 2 equals NBS Z. Both NBS Y1 and Z are also Halliburton candidate slurries. Their performances were better in the NBS program, however, especially in the case of NBS Y1. U-H slurry 12 is

fairly similar to Dowell slurry 3 (discussed above and in Table 5.2-3), which contains 79 lb fly ash and 35 lb silica flour/100 lb cement. The Union Oil/Halliburton candidate seems to be a somewhat better, although lighter weight, performer.

In sixth place in the Union Oil study was U-H slurry 8. It is fairly similar to the lightweight NBS slurry K, and their performances are very comparable. It is worth noting, however, that NBS slurries L, and particularly W, have posted better strengths and permeabilities as lightweight cements.

5.3 Results of Industry-Sponsored Cement Testing in Dry Steam Wells

The previous sections have all involved cement tests conducted in liquid-dominated geothermal wells. To see what cement formulations would behave satisfactorily in dry steam wells, tests were conducted by Union Oil and Dowell researchers in The Geysers geothermal field in northern California [Gallus, et al. 1979b]. Specimens of various cement formulations were exposed to steam in Berea sandstone molds, as in the above program, for periods of time ranging from 90 days to two years. At the end of each exposure period, compressive strength and permeability tests were conducted, as in the above test programs, and X-ray diffraction studies were used to determine the dominant binding phases present.

Aboveground autoclaves were used for the actual exposures because, by piping wellhead steam into the autoclaves and then controlling the interior pressure, downhole conditions could be closely simulated with better sample accessibility. Exposure conditions were 464°F and 485.6 psi. The steam was dry and contained only traces of entrained solids. However, it did contain about 5000 ppm carbon dioxide and 220 ppm hydrogen sulfide. As in the Union Oil/Halliburton tests in liquid-dominated wells, described in the previous section, acceptable compressive strength and permeability thresholds were 1000 psi and 1.0 millidarcy (the latter an order of magnitude more lenient than the current API permeability threshold).

The cements tested, their densities, and the test results are listed in Table 5.3-1. As in the previous section, similarities exist between the cements tested and other cements considered previously in this chapter. These will be mentioned in the course of the summary discussion of the tabulated results.

The most satisfactory cement for use in dry steam wells appears to be U-D slurry 2, an API Class G cement fortified with 35 lb silica flour/100 lb cement. This slurry is very similar to NBS candidate A, which, not surprisingly, was submitted by Dowell Division, and has been discussed previously as the best performer so far in the NBS downhole tests. In dry steam environments, it has very good compressive strength and permeability values, and thus would seem to be an excellent choice in either application.

The second-best performer, and really the only other clearly acceptable selection, is U-D slurry 7, composed of API Class G cement extended 1:1 with fly ash and fortified with 70 lb silica flour/100 lb cement. Its strength and permeability levels are certainly satisfactory for use, although they do show some regression over the two-year test period. U-D slurry 7 is very similar to Dowell slurry 3, cited above (see especially Table 5.2-2) for its good performances in Dowell's own downhole test program in flowing wells.

U-D slurry 3, a Class J cement very similar to NBS slurry B, showed adequate strength and barely adequate permeability values, but the X-ray diffraction examination revealed scawtite and other low-strength binding phases to be the dominant components present. These phases unfortunately seem to be favored in the curing process instead of the higher strength binders, xonotilite and truscottite, when high concentrations of carbon dioxide are present. This is the case at The Geysers, where the steam contains about 5000 ppm carbon dioxide. Thus it is probably advisable to avoid using Class J

TABLE 5.3-1. CEMENT COMPOSITIONS AND TEST RESULTS FROM THE INDUSTRY-SPONSORED DRY STEAM TEST PROGRAM AT THE GEYSERS

Union Oil/Dowell Cement System ^a	Slurry Density (lbm/cu. ft.)	Compressive Strength (psi above) and Permeability (mD, below) at Time (days)			
		90	180	365	730
1. API Class G cement, 36% water	124.2	2552 6.4	1899.5 2.4	1799 2.0	2249 1.4
2. API Class G cement 35% silica flour, 56% water	117.3	6497 3.9×10^{-2}	4973.5 3.9×10^{-2}	5472 5.9×10^{-2}	7897 1.5×10^{-2}
3. API Class J 43.5% water	114.8	2374 0.19	2674 3.9×10^{-2}	2674 9.9×10^{-2}	2899 7.9×10^{-2}
4. API Class J cement, 8% perlite, 63.6% water	93.0	1975 0.35	1899.5 0.39	1675 0.25	1475 0.16
5. 1:1 Natural Pozzolan and API Class G cement, 35% silica flour, 4% bentonite, 113% water	104.2	1174.5 0.56	1374 0.42	2324 2.5×10^{-2}	1799 1.6×10^{-2}
6. API Class G cement, 8% perlite, 35% silica flour, 4% bentonite, 110% water	91.8	1599 6.9	1299 2.1	1449 1.9	1449 1.7
7. 1:1 Fly Ash and API Class G cement, 35% silica flour, 96.4% water	111.7	5198 1.9×10^{-2}	5348 1.9×10^{-2}	-- --	2923 2.1×10^{-2}

-- No data available

^aPercents indicate pounds of additive per 100 lb of cement.

Source: Gallus, et al. 1979b

cements in such locations. U-D slurry 4 (the same cement with the addition of 8 lb perlite/100 lb cement showed similar behavior but somewhat lower, although still acceptable, strengths. Its permeabilities are acceptable according to the Union Oil/Dowell standards but not to those of the API.

U-D slurry 5 yielded somewhat higher strengths than did U-D slurry 4; however, its permeabilities fall on either side of the API standard. Since the latter values are below the API limit, and well below that of Union Oil/Dowell Division, the cement might be cautiously recommended for use--especially in situations where a lighter weight slurry is needed.

U-D slurries 1 and 6 seem not to be adequate for dry steam well use because of excessively high permeabilities. U-D slurry 6 is somewhat similar to NBS slurry K, another Dowell submission, but has a lower density. Apparently, even the addition of 35 lb silica flour/100 lb cement could not compensate for the deleterious effect of the perlite and bentonite extenders, as was the case with U-H slurry 8 in the Union Oil/Halliburton program. U-D slurry 1 shows that Class G cement is not capable of developing adequately low permeabilities without additional silica. This observation from dry steam testing is usually accepted for brine wells also. However, cements in which the silica source is silica sand were not tested in this program, so no comparative conclusions can be made about their use in dry steam wells without further testing.

5.4 References

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6.0 HIGH-TEMPERATURE ELASTOMERS

SUMMARY

This summary is a quick reference to the material discussed in Section 6. Please refer to the section for caveats, qualifications and references cited for the data presented here.

Elastomers in moderate depth/temperature geothermal service often fail because of the high temperatures and the hydrolytic reducing environments. Static seals often fail from thermochemical degradation; dynamic seals from abrasive wear or mechanical stress at high temperature and pressure.

In hot (500°F) oxidative environments, most rubber compounds harden by oxidative reactions. In reducing aqueous geothermal environments many soften and weaken by hydrolysis. High-temperature aerospace elastomers are often unsuitable for geothermal applications.

Most geothermal elastomer research has focused on packer seals, O-rings, and drill bit seals as typical applications. Major stresses on the packer seal are caused by "packing off" (compression during installation) and differential pressure. The most critical factors that determine elastomer performance are tensile strength, ultimate elongation, Shore A hardness and extrusion resistance.

L'Garde, Inc., has conducted the most extensive search for new elastomers. Their Y267 EPDM (Ethylene Propylene Diene Monomer) has performed satisfactorily in a number of laboratory and field tests under various harsh conditions, often without significant deformation or deterioration. It does, however, appear to be electrically conductive and subject to degradation by a high-oxygen environment.

A summary of the most significant performances of Y267 EPDM and other elastomers tested is given in Table 6.0-1.

TABLE 6.0-1. SUMMARY OF SIGNIFICANT ELASTOMER PERFORMANCES

Elastomer	Fluid	Temperature °F	ΔP psi	Comments
Y267 EPDM	Brine	400	3,000	O-rings sealed for 6 months.
	Isobutane	400	3,000	O-rings sealed for 6 months, some permanent set and cracking.
	Oil	400	3,000	O-rings sealed for 6 months, some swell and ribbing.
	Brine	510	3,000	O-rings sealed for 46 hour test, no significant damage.
	Isobutane	510	3,000	O-rings sealed for 46 hour test, no significant damage.
	Oil	510	3,000	O-rings sealed for 46 hour test, no significant damage.
	Sour crude	450	20,000	Packed seal sealed 4.5 days + 3 days at 10,000 psi, slight swell and softening.
	Sweet crude	450	15,000	Packed seal sealed 6 days, slight swell and softening.
	Water, crude	400	--	Packed seal showed not deterior- ation after 5 months contin- uous operation.
	Water	525	7,500	O-ring performed 56 hours in test, no obvious deterior- ation.
	Oil	633	7,500	O-ring subjected to cycling for 4 days, some swelling and permanent deformation.
	Brine	356	--	Seal performed successfully for more than 8 months.
	(Water debris grease)	550	--	Drill bit seal subjected to 90 rpm, 5 mils wobble and stroke
Parker E692-75	Brine	400	3,000	Test fixture failed, seal assumed to approximate Y267 performance.
	Isobutane	400	3,000	O-ring failed at 90 days.
	Oil	400	3,000	O-ring survived 6 months, some swell and ribbing.
	Brine	510	3,000	O-ring sealed for 46 hours test, no significant damage.
	Isobutane	510	3,000	O-ring failed.
	Oil	510	3,000	O-ring sealed for 46 hour test, no significant damage.
	Brine	500	4,100	O-ring was nibbed after 22 hours

(Continued)

TABLE 6.0-1. SUMMARY OF SIGNIFICANT ELASTOMER PERFORMANCES (Continued)

Elastomer	Fluid	Temperature °F	ΔP psi	Comments
Viton 501	Brine	400	3,000	O-ring brittle, failed.
	Isobutane	400	3,000	O-ring failed at 41 days.
	Oil	400	3,000	O-ring showed severe set, slight nibbing after 6 months.
	Brine	510	3,000	O-ring failed 46 hour test.
	Isobutane	510	3,000	O-ring failed 46 hour test.
	Oil	510	3,000	O-ring severely damaged in 46 hour test.
Viton G	{ 38% water 38% oil 12% carbon dioxide 12% hydrogen sulfide }	300	1,750	Lost much tensile strenght and elongated after 10 days.
Viton B	{ 38% water 38% oil 12% carbon dioxide 12% hydrogen sulfide }	300	1,750	Retained properties relatively well for 10 days.
Viton 4205	{ Water debris grease }	550	--	Drill bit seal subjected to 90 rpm, 5 mils wobble and stroke, sealed 107 hours.
Viton, Teflon, Coated	{ Water debris grease }	550	--	Drill bit seal subjected to 90 rpm, 5 mils wobble and stroke, sealed 107 hours.
HTCR	{ Water debris grease }	550	--	Drill bit seal subjected to 90 rpm, 5 mils wobble and stroke, sealed 107 hours.
	Pacer DHT-906 lubricant	250-500	1,000	Drilling motor bearing seal survived 412 rpm rotations for 200 hours with little degradation.
Variseal	Pacer DHT-906 lubricant	250-500	1,000	Drilling motor bearing seal survived 412 rpm rotations for 164 hours.

-- No data available.

The coating of an elastomer with a thin film to enhance its resistance to hostile environments and to enhance its lubricity has been the subject of several studies. A coating of polymerized tetrafluoroethylene (PTFE) was shown to significantly prolong the life of Viton 4205 and Parker EPDM. When PTFE was applied to ethylene-propylene rubber, however, the benefit was pronounced, but lasted only until the coating evaporated (about 48 hours).

DOE has received a patent on a process for curing a packer seal after it is in place and packed off. This procedure virtually eliminates the stress caused by compression during pack-off; therefore, very high modulus extrusion-resistant compounds can be used that would crack during ordinary compression settling procedures.

INTRODUCTION

Elastomers are widely used in moderate depth/temperature oil and gas wells. Typical applications include packer seals for the cased hole, O-rings, cablehead components, drill bit journal seals, and logging cable jackets and insulation. Elastomeric seals are preferred over metal seals when conditions are in their capability range because they are reliable and economical, tolerant of particulate matter and of variances in the sealing surfaces, can be reusable and can be installed by unskilled workmen in the field. The challenge has been to develop high-temperature elastomers which will extend these significant advantages to higher temperatures.

This section is a generalized survey of the use of elastomers in geothermal wells. The applications mentioned here are considered representative of other applications as well. Elastomers for specific applications are also discussed in the appropriate sections.

6.1 Materials Problems

Elastomeric seals which perform well in moderate depth/temperature oil field applications cannot tolerate the high temperatures sometimes encountered in a geothermal well. And high-temperature elastomers developed for the oxidizing aerospace industry environment are not suited for the hydrolytic, reducing environment of a geothermal well. Static seals often fail because of thermochemical degradation from the combined effects of steam and sour gas at elevated temperatures. Dynamic seals often fail because of abrasive wear even at low temperature or because of mechanical stresses at high temperature and pressure [Arnold, et al. undated]

Adverse conditions in high-temperature geothermal boreholes include temperatures of 432° to 633°F, pressures of up to 7000 psi and corrosive well fluids which can include water, steam, brine, carbon dioxide and hydrogen sulfide [Arnold, Bieg, and Coquat 1980].

At 500°F in oxygen, most rubber compounds harden by thermal cleaving of double bonds and formation of cross-links which create three-dimensional matrices with little elasticity. In water or steam at high temperatures, cross-links are broken and most elastomers become soft and weak. At high temperatures, sulfur also rapidly cleaves double bonds and forms cross-links to make the rubber hard and brittle. When the elastomer loses its elasticity, it can no longer function as a seal.

6.2 Evaluations of Alternative Elastomers

Most research on geothermal elastomers has focused on packer seals, O-rings, and drill bit seals. It has been assumed that materials which could function in these capacities would be suited for other uses as well. Other specific applications of elastomers are included in other sections of this report.

Major mechanical stresses of compaction on the packer seal are caused by "packing off" (compression of the seal during installation) and then by the additionally applied differential pressure. Dynamic O-rings and drill bit seals suffer abrasive wear both from moving parts and from debris. The most critical characteristics which determine elastomer performance as a seal or O-ring are tensile strength, ultimate elongation, Shore A hardness, and extrusion resistance.

Two areas of research have been relatively successful: compound development of elastomers which can withstand the adverse conditions and application of a coating which can protect an elastomer from its environment. The coating might also enhance lubricity, thus lessening the stress on dynamic seals. A third approach, of special significance with packer seals, is the possibility of curing seals only after they are in their final compressed configuration.

Several facts must be considered when test results are compared, especially when these results are from different laboratories. First, seemingly minor variations in test conditions can drastically affect results: for example, the clearance that a seal must bridge can be the predominant independent variable over polymer type or compound. [Hirasuna 1981a].

Another problem is that there are so many elastomeric compounds identified by the same polymer designations. In general, an elastomer compound is made up of about 50 percent polymer and 50 percent other ingredients. It is not unusual for a very minor ingredient to markedly change the characteristics of the compound. When requirements demand the ultimate capability of a polymer, very specific tailoring of the recipe for the application may be required. Even if it is determined, for example, which of the many ethylene propylene diene monomer (EPDM) polymers is referred to, the exact recipe may still not be known. And much of the time the designation is simply "EPDM".

6.2.1 Development of Four GEM (Geothermal Elastomeric Materials) Elastomers

In 1976, the Department of Energy contracted with L'Garde, Inc., to develop elastomer compounds which could withstand the conditions of the typical geothermal environment [Hirasuna, et al. 1979; Hirasuna 1981b; Hirasuna and Stephens 1981]. Of particular concern was the 500°F temperature requirement. The resulting developments yielded compounds from four polymer systems which successfully exceeded contract requirements.

A synthetic brine, consisting of 300 ppm hydrogen sulfide, 1000 ppm carbon dioxide, and 25,000 ppm sodium chloride in water, was formulated to simulate downhole chemistry. The intent was to represent as fairly as possible the conditions of the majority of potential geothermal wells, not necessarily the worst conditions that might be encountered.

Preliminary screening studies were performed on 129 candidate elastomer compounds. Consideration was given especially to elastomers with saturated backbones to avoid having sites which might be reactive to the environment. The most pertinent parameters measured were ultimate tensile strength, ultimate elongation, Shore A hardness, and extrusion resistance. These tests were performed both on virgin samples and on samples which had been aged in the brine. This screening limited more expensive evaluation to a fraction of the 129 candidates. The four most promising compounds using each of the four polymer types are listed in Table 6.2-1.

Several specific elastomers of each type were then tested in a laboratory evaluation test designed and fabricated to subject a full-scale 4-inch packer seal to simulated downhole environments. In this test the seal was simultaneously subjected to the chemistry, temperature, mechanical forces, pressure forces, and limited surface exposure of the seal just as it would be on an operational packer. This test provided the full spectrum of interactive operational environments, the combination of which is important when evaluating materials being stressed to their ultimate capacity. After an extended

TABLE 6.2-1. ELASTOMER SYSTEMS SELECTED FOR THE GEM STUDIES

Common Chemical Designation	Trade Name	Manufacturer
Fluoroelastomer (FKM)	Viton "F" type	DuPont
Ethylene Propylene Diene Monomer (EPDM)	Nordel	DuPont
Propylene-Tetrafluoroethylene	AFLAS	Asahi Glass
EPDM/Viton Blend	Nordel/Viton	

Source: Hirasuna, et al. 1979.

effort, successful compounds of each of the four polymers were formulated. Table 6.2-2 gives the percent of the four critical parameters retained by the four GEM elastomers after aging in brine for 22 hours at room temperature or at 500°F. These elastomers performed satisfactorily in a laboratory-simulated packer immersed in synthetic brine at 500°F for 46 hours at a differential pressure of 3100 to 4100 psi and a diametral gap of 50 mil [Hirasuna 1981a].

In addition to the packer seal tests, these compounds were compared to commercially available compounds in static O-ring simulation tests. A 2-329 O-ring groove of standard commercial dimensions (approximately 2-inch diameter, 0.25-inch cross-sectional diameter) was used with no back-up. The measured diametral clearance was 9 mils. The O-rings were subjected to synthetic brine at 500°F for up to 22 hours at pressure differentials of up to 4100 psi. The GEM compounds had the distinct advantage of being formulated especially for these conditions [Hirasuna, et al. 1979]. Results of the O-ring tests are summarized in Table 6.2-3. In general, a reduction of differential pressure from 4100 to 3100 psi could increase the life of the seal by a factor of from 2 to 4 [Cassidy, 1979].

TABLE 6.2-2. HYDROTHERMOCHEMICAL STABILITY OF GEOTHERMAL ELASTOMERS AFTER SOAKING IN SYNTHETIC BRINE^a FOR 22 HOURS

Elastomer	Percent of Property Retained ^b			
	Ultimate Tensile @ Room Temp.	Ultimate Elong. @ Room Temp.	Shore A Hard @ 500°F	Extrusion Resistance @ 500°F
EPDM-267	97	105	100	103
Viton-255	72	101	100	55
EPDM/Viton-266	96	84	101	96
AFLAS-291	93	118	100	87

^a25,000 ppm sodium chloride, 1,000 ppm carbon dioxide, 300 ppm hydrogen sulfide.

^bCharacteristics of virgin specimens and specimens aged in brine were compared. Percentage number is the percent of the original value retained by the aged specimen. Specimens not packed off.

Source: Hirasuna, et al. 1979.

TABLE 6.2-3. SUMMARY OF O-RING SIM TEST DATA^a

Compound Designation	P, psi	Time, h	Comment
L'Garde GEM Viton-255	3, 100	22.0	Nibbled Slightly
Parker Fluoroelastomer V-709	2, 100	10.5	Broke
Parker Fluoroelastomer V-747	2, 100	5.25	Broke
L'Garde GEM Nordel-267	4, 100	22.0	Excellent Condition
Parker EPDM E 692-75	4, 100	22.0	Nibbled, 1-1/2 - 2"
L'Garde GEM Nordel/Viton Blend-266	4, 100	22.0	Excellent Condition
L'Garde GEM AFLAS-291	4, 100	22.0	Minor Extrusion 1" Nibbled
DuPont Perfluoroelastomer Kalrez-3074	2, 100	22.0	Nibbled 2"

^aSize 2-329 O-ring with no backups, measured clearance 9 mils. Temperature 500°F. Synthetic brine containing 25,000 ppm sodium chloride, 1,000 ppm carbon dioxide and 300 ppm hydrogen sulfide.

Source: Hirasuna, et al. 1979.

After the four GEM compounds were proven successful at these test conditions, they were tested for extended periods of time as packer seals, with all other factors the same as before. Results of these tests are given in Table 6.2-4. Though compound development was halted when the required performance at 500°F was achieved, the four GEM compounds were also tested at 600°F, both in the virgin state and after aging in synthetic brine for 22 hours. The Nordel-267 and the AFLAS-280 survived with reasonable retention of properties; the Viton was destroyed and the Viton/Nordel blend significantly degraded [Hirasuna, et al. 1979.]

6.2.2 Laboratory and Field Experience with Y267 EPDM Technology

After development of the GEM compounds, L'Garde tested the compounds further and furnished test slabs, O-rings, and packer seals to other organizations for additional testing. Molded parts based on Y267 technology are available in commercial quantities from BJ-Hughes Rubber, Parker Seal, and Precision Rubber. Y267 EPDM technology is available directly from L'Garde. It should be noted that Y267 EPDM is apparently an improved version of the Nordel 267.

In a direct test of the success of the technology, L'Garde tested O-rings from BJ-Hughes (N-22-1), Precision Rubber (42679) and Parker Seal (E962-85). The O-rings were tested in 500°F synthetic brine at 4100 psi for 13-day periods, during which the temperature and pressure were varied. The diametral gap was 6 mils; no back-up rings were used.

Though the Precision Rubber elastomer tested out to be equivalent to L'Garde's Y267, the test results as a whole indicate a possible problem with consistency of product. Therefore, L'Garde recommends that parts from more than one manufacturer be tried whenever this technology is tested in a critical application [Hirasuna 1982a].

TABLE 6.2-4. SUMMARY OF EXTENDED-TIME PACKER SEAL SIM TESTS^a

Designation	Run Time, Hrs.	Differential Pressure, psi	Comments Relative to 22-Hour Run
AFLAS-291	46	3,530	Very slightly more extrusion.
Nordel-267	94	4,240	Slightly more extrusion.
Nordel/Viton-266	46	4,220	Slightly more extrusion at both ends.
Nordel/Viton-275	46	3,310	Very slightly more permanent deterioration.
Viton-255	94	4,030	Extrusion on both ends, some breakage at chamfer.

^aSynthetic brine at 500°F with 25,000 ppm sodium chloride, 1000 ppm carbon dioxide, and 300 ppm hydrogen sulfide.

Source: Hirasuna, et al. 1979.

As of this writing there have been numerous successful applications of the Y267 EPDM technology. It has been shown to withstand both the high temperature and, in most part, the harsh environment of geothermal applications, often without significant deformation or deterioration. Apparent limitations at this time to its use are its vulnerability to a high-oxygen atmosphere and its conductivity, which limits its use as an electrical insulator [Hirasuna, 1982b; Pettitt, 1982].

Table 6.2-5 summarized the most important experiences with Y2367 EPDM. Laboratory tests which were preliminary to field tests are grouped beside them. All tests except three laboratory tests were performed by organizations independent of the fabricators. The Y267 was considered to perform acceptably well or better in each case.

Some of the tests listed here are described later in more detail because they also included tests of other elastomers. They are included here for completeness. The later descriptions give comparisons of the Y267 EPDM with the other available elastomers.

6.2.3 Testing of Commercially Available O-Rings

Eleven commercially available O-ring compounds were exposed for 24 hours at 525°F and approximately 5000 psi to a brine which contained 15,800 ppm sodium chloride, but no hydrogen sulfide [Arnold, Bieg, and Coquat 1980]. A fixture which simulated the cablehead of a geothermal logging sonde with a diametral gap of 30 mils was then used to determine sealing efficiency of the O-rings. Tensile strength measurements were made on samples that had been completely immersed in brine, and thus had a higher exposure to the brine than did O-rings in the fixture. The extent of degradation was determined by measuring mechanical and thermomechanical properties such as tensile strength, compression set and glass transition temperature. A material was considered to have passed the sealing test even if a small amount of water leaked through. Some of the elastomers were also tested with a 1.25 mil coating of polychloro-p-xylene. Coated elastomers are discussed in a later subsection.

TABLE 6.2-5. SUMMARY OF Y267 EPDM LABORATORY & FIELD TESTS

LABORATORY TESTS					SUBSEQUENT FIELD TESTS				
TEST	FLUID	Temp. °F	P psi	Time Days	TEST	FLUID	Temp. °F	P psi	Time Days
L'GARDE ECT IMMERSION	Brine, C ₄ H ₁₀ , Oil	375		180	BAKERSFIELD STIM	Steam + Crude	400	250	150
L'GARDE ECT O-RINGS	Brine, C ₄ H ₁₀ , Oil	510	3000	5	BACA GEOTHER FRACT (2x)	H ₂ O + Fract Fluid	320	3080	0.5
OTIS PACKER	H ₂ O	575	3000	5	BACA GEOTHER DST (3x)	H ₂ O	340	600	0.8
OTIS PACKER	Swt. & Sour Crude	450	20,000	5	FENTON GEO FRACT (4x) ^d	H ₂ O, CO ₂ , H ₂ S	450	7200	7.5
LANL, CEMENT WIPER	H ₂ O	552	4310	.9	FENTON HILL CEMENT	Cement/H ₂ O	525	0	0.02
LANL, FLOAT VALVE ^e	H ₂ O	536	0	1.3	FENTON HILL DRILLING ^e	H ₂ O	?	2000	1.7
LANL O-RING TESTS	H ₂ O, Mobil 1	525	7500	1.7	FENTON HILL LOGGING ^a	H ₂ O, CO ₂ , H ₂ S	603	6000	0.4
BATTELLE RICHLAND	H ₂ O	400	600	4	BACA LOGGING ^a	H ₂ O	575	1700	0.3
UNION/PI EXPLOSIVE	Explosive	475	1000	1	MAGMA CORROSION PROBE	Brine	356	N/A	240+
WKM VALVE CHANGER ^b	Steam	500	700	0.04	GEYSERS EXPLOSION EXPT	Steam	500	665	2
BAKER SERVICE SETTING TOOL	Steam, Oil	600	30,000	1	GEYSERS VALVE CHANGER (3x) ^a	Steam	500	400	0.03
CUSTOMER NO. 1 (2x) ^c	Steam	575	?	?	GULF COAST GAS WELLS	Gas Wells	?	?	?
CUSTOMER NO. 2 ^c	Steam	575	?	?	GEOTHERMAL COMPLETION ^a	?	575	?	?
OTIS SLICK JT ^d	H ₂ O	525	3000	10	GULF COAST, 27/28 SEALS TO GO	Gas Wells	?	?	?
TERRATEK DRILL BIT SEAL	Grease Debris H ₂ O	550	0/200	4.3	SEVEN STAB-INS, GEO-THERMAL	H ₂ O	450	7200	7.5
PARKER	Amines, NACE A	212	N/A	7					
SPERRY VICKERS	Hydrazine	425	N/A	85					

Source: Hirasuna 1982b

NOTE: The Y267 performed acceptably well or better in each case.

^aThe same set of seals was used more than once.^bPrecision Rubber Associations^cParker Seals Associations^dBJ-Hughes Associations^eEPDM formulation unknown, degradation in testing apparent.

Results of the exposure tests and seal efficiency tests are given in Table 6.2-6. The data indicate a correlation between the thermochemical stability of an elastomer and its sealing ability. Results indicated that the coating could protect the elastomer from thermochemical degradation, but could not prevent the breakdown of elastomers from the heat itself.

6.2.4 Testing of Elastomers in Hot Brine, Oil and Isobutane

Thirty-four elastomer compounds were screened for compatability with hot brine in anticipation of requirements for downhole pumps and binary power requirements [Friese 1981; Hirasuna, Friese and Stephens 1981]. Eight elastomers were chosen for further studies on the basis of hardness, ultimate tensile strength, ultimate elongation, weight, volume, and resistance of the compounds before and after immersion in brine, 99.5 pure isobutane, ASTM No. 1 oil, Pacer DHT - 185M oil, and Chevron Cylinder 460X oil, each separately for 120 hours (5 days). The brine was the same as that used in the development of the GEM elastomers (25,000 ppm sodium chloride, 1000 ppm carbon dioxide, 300 ppm hydrogen sulfide).

Table 6.2-7 shows the results of the screening tests and the compounds chosen for further study. The chosen compounds were considered to be the best, but are not necessarily the only compounds which could survive further testing. Viton-255 was also considered good, but was not tested further because the polymer is no longer being made. Results for the chosen compounds are shown in Table 6.2-8.

Each chosen compound was tested as an O-ring in each of the three fluids for 46 hours at 375°F, 450°F and 510°F with a differential pressure of 3000 psi. The radial gap behind the O-rings was 3 mils. Four of these compounds were then tested in the three fluids for 6 months at 400°F and 3000 psi differential pressure. The fixture permitted slow sliding, up to one cycle per day. Results of the O-ring tests are shown in Table 6.2-9.

TABLE 6.2-6. DEGRADATION OF UNCOATED ELASTOMERS IN THE PRESENCE OF SYNTHETIC GEOTHERMAL BRINE^a

Compound Designation	Change in Tensile Strength, (%)	Change in Elongation (%)	Change in T _g ^c	Seal Efficiency Test ^d
EPR-540	-62	+30	+2	pass
Fluorosilicone-449	b	b	+100	fail
Kalrez 1050	-24	- 6	0	pass
Kalrez 3074	no test	no test	0	pass
N-552 (Nitrile Rubber)	b	b	+69	fail
Parker EPDM-692	-70	+23	0	pass
Silicone-609	b	b	+100	fail
Viton-709	b	b	+12	fail
Viton-752	-52	-68	+2	pass
Viton-747	b	b	+140	fail

^a15,000 ppm sodium chloride with no dissolved gases at 525°F, 5000 PSI, 24 hours

^bToo brittle for measurement of tensile properties.

^cT_g = glass transition temperature.

^dAn elastomer was considered to have passed the sealing test even if a small amount of water leaked through.

Source: Arnold, Bieg and Coquat 1980.

TABLE 6.2-7. ELASTOMER SCREEN TESTED BY IMMERSION IN
BRINE, ISOBUTANE, AND OIL FOR 120 HOURS
(5 days)

	Passed Approach 1 ^a	Passed Approach 2 ^b	Chosen for Further Study ^c
Borg Warner EPDM CL81	Yes	No	No
DuPont Kalrez 1018	Yes	Yes	Yes
Kalrez 3065	No	No	No
Firestone PNF R227819	No	No	No
PNF R227945	No	No	No
L'Garde EPDM Y267	No	No	Yes
Viton 255	Yes	Yes	No
Viton 501	Yes	Yes	Yes
Blend 275	No	No	No
Blend 301	No	No	No
Blend 266	No	No	No
AFLAS 291	Yes	Yes	Yes
B.J. Huges XD273	Yes	No	No
F.H. Maloney 484-NBR	No	No	No
488-NBR	No	No	No
588-(F)	No	No	No
National O-Ring V-14	No	No	No
Oil States Std OSR	No	No	No
PARCO Viton E60-C-75	Yes	No	Yes
Viton E60-C-90	No	No	No
Viton VTR5362-70	No	No	No
Parker V747-75	No	Yes	No
E692-75	No	No	No
Precision Fluoroelastomer 16959	No	Yes	Yes
Viton 19999	No	No	No
Seals E. AFLAS 7170 x 14	Yes	Yes	Yes
3M Fluorel L4733	No	No	No
Fluorel L4774	No	No	No
Fluorel L4775	Yes	No	No
Fluorel L4776	No	No	No
Utex RD-215-80	No	Yes	No
RD-245-90	No	No	No
Vernay Fluoroelastomer VL 150 3M3	Yes	Yes	Yes
Fluoroelastomer VL 1503 T17	No	Yes	No

^aCompounds failed Approach 1 if, after testing in any of the fluids, they had a Shore A hardness change of 10 units or more, were brittle, or had a post-test elongation of less than 100%.

^bCompounds failed Approach 2 if, after testing in at least two fluids, they were brittle, and if the sum of their figures of merit for oil, brine and isobutane were not in the top ten. The figure of merit is the sum of the absolute percent change values for weight, volume, ultimate strength, elongation and hardness.

^cCompounds were chosen for further study if they passed Approach 1 and Approach 2, except Viton 255 which is no longer marketed. Parker 16959, Kalrez 1018, EPDM 267, and Parker E692-75 were selected for their excellent performances in individual fluids.

Source: Friese 1981

TABLE 6.2-8. SCREENING TEST RESULTS FOR EIGHT ELASTOMERS IN BRINE, ISOBUTANE, AND OIL

Compound	Screening Test Results ^a		
	<u>Brine</u>	<u>Isobutane</u>	<u>Oil</u>
L'Garde EPDM Y267	b	b	c
Parker EPDM E692-75	b	b	c
L'Garde Viton 501	b	b	b
Vernay Fluoroelastomer VL1503M3	b	b	b
Precision Fluoroelastomer 16959	d	b	b
Seals Eastern AFLAS 7170X14	b	b	b
L'Garde AFLAS 291	b	b	b
DuPont Kalrez 1018	b	e	b

^aElastomers immersed for 120 hours (5 days).

^bCompound performed well.

^cHardness changed by ten units or more.

^dElastomer became brittle.

^eFigure of merit more than 100 (see Table 3.3-7)

^fIn some cases there was little difference between best and worst; for instance, all compounds did well in oil.

Source: Friese 1981

TABLE 6.2-9a. LONG-TERM PERFORMANCE OF FOUR BEST O-RINGS IN BRINE, ISOBUTANE AND OIL

	<u>46</u>	<u>hour,</u>	<u>3000</u>	<u>psi</u>	
	375°F	450°F	510°F		6 months, 400°F, 3000 psi
<hr/>					
L'Garde					
EPDM Y267					
Brine	A	A	A	A -satisfactory	
Isobutane	A	A	A	B -slight permanent set, 10%	
Oil	A	A	A	cracked, but intact	
				C ^a -some swell, moderate nibbling	
Parker					
EPDM E692-75					
Brine	A	A	A	-test fixture failed ^b	
Isobutane	A	A	C	C -failed at 90 days	
Oil	A	A	A	C ^a -some swell, moderate	
L'Garde					
Viton 501					
Brine	B	B	C	C -brittle, failed	
Isobutane	B	C	C	C -failed at 41 days	
Oil	A	A	A	B -severe set, slight nibbling	
Vernay					
Fluoroelastomer					
VL1503M3					
Brine	A	C	C	C -brittle, failed	
Isobutane	B	B	B	B -moderate permanent set but survived	
Oil	A	A	B	C -failed, brittle, slight nibbling	

A: Damage limited to moderate set and swelling.

B: Severe set, cracks or splits, signs of extrusion.

C: Nibbling or catastrophic failure.

^aThough there was moderate nibbling, the seal did survive.

^bBased on previous data, the elastomer would be expected to perform as well as the Y267 at this temperature.

Source: Hirasuna 1982

TABLE 6.2-9b. SHORT-TERM PERFORMANCE OF FOUR BEST O-RINGS IN BRINE, ISOBUTANE AND OIL

	<u>46 hour, 3000 psi</u>		
	<u>375°F</u>	<u>450°F</u>	<u>510°F</u>
Precision Fluoroelastomer 16959			
Brine	B	C	C
Isobutane	A	B	B
Oil	A	B	C
Seals Eastern AFLAS 7170X14			
Brine	B	B	C
Isobutane	C	C	C
Oil	B	B	B
L'Garde AFLAS 291			
Brine	B	B	B
Isobutane	B	C	C
Oil	B	B	B
DuPont Kalrez 1018			
Brine	A	B	C
Isobutane	C	C	C
Oil	B	B	B

A: Damage limited to moderate set and swelling.
 B: Severe set, cracks or splits, signs of extrusion.
 C: Nibbling or catastrophic failure.

Source: Hirasuna 1982

Significant failures were AFLAS and Kalrez in isobutane at all temperatures and Parker E 692-75 EPDM in 510°F isobutane. The Y267 EPDM performed reliably at 510°F in all three media.

The fact that the EPDM's performed well as O-rings in oil, but failed the screening test of immersion in oil indicates a possible inherent fallibility in such immersion tests. It suggests that emphasis should be placed on tests which more accurately simulate the proposed environment.

6.2.5 Testing of Fluoroelastomers

DuPont compared some properties of three Viton fluoroelastomers and Nordel [Moran 1979]. Nordel was discussed previously (as Y267). Comparisons of tensile strength, elongation and compression set resistance of the Viton compounds as they age in 400°F steam are given in Figures 6.2-1, 6.2-2 and 6.2-3. The "G" type Viton is peroxide cured; the E-60 and B-910 are dihydroxy cured.

In another evaluation, Viton B-910 and Viton "G" were tested in a mixture of 38 percent water, 38 percent oil, 12 percent carbon dioxide and 12 percent hydrogen sulfide. After ten days at 300°F and 1750 psi, the "G" type had lost much of its tensile strength and elongation while the "B" type retained its properties relatively well. Both elastomers were reported to be affected by exposure to the mixture at 400°F and 2200 psi.

6.2.6 Testing of Drill Bit Seals

TerraTek tested a number of elastomers for use as the rotating journal seal of a tricone bit [Hendrickson, Winzenried and Jones 1980]. On each revolution, longitudinal and radial jogs are superimposed on the rotational motion. Figure 6.2-4 is an illustration of the test procedure used on the more promising candidates to simulate as closely as possible the actual downhole conditions. A new seal and a successively higher temperature was used until an ultimate soak temperature was determined for each elastomer.

Figure 6.2-1. Comparison of Tensile Strengths of Three Viton Compounds [Moran 1979]

Figure 6.2-2. Comparison of Elongations of Three Viton Compounds [Moran 1979]

Figure 6.2-3. Comparison of Compression Set Resistance of Three Viton Compounds [Moran 1979]

Figure 6.2-4. Mission Profile for the TerraTek Trip-In Simulation Seal Test [Hendrickson, Winzenried and Jones 1980]

The lubricant used was a high-temperature elastomer-compatible journal grease developed for the program. Table 6.2-10 gives the test results for the most successful compounds. Four compounds successfully met the test goals of 550°F and 100 hours. For more details of the TerraTek study, see Section 7.1.1.2.

6.2.7 Testing of Downhole Drilling Motor Bearing Seals

The thrust bearings in downhole mud motors have caused severe problems because the bearings operate directly in the abrasive drilling mud and because the rubber friction bearings and the ball bearings used have low load capacities. Development is underway for a bearing-seal package which can operate for at least 200 hours at bit pressure drops of 1000 psi and a circulating temperature of 250°F. It must be able to soak at 500°F for short times and at 350°F for many hours [Hendrickson, Winzenried and Jones 1980].

TerraTek devised a seal test machine to evaluate potential seals. The chamber was kept at 250°F throughout the test and the shaft of the machine rotated at 412 rpm. A differential pressure of 1000 psi was maintained. Seal failure was defined as the leakage of one gallon of lubricant past the seal.

Only one of the six seals tested, the HTCR (High Temperature Corrosion Resistant) SF, survived the full 200 hours. This seal, manufactured by Utex Industries, is composed of AFLAS base material reinforced with fibers of alternating plies of synthetic aramid and glass fabric. Though seal temperature exceeded 500°F during the test, there was little degradation of the seal material [Sandia 1981].

The Variseal, manufactured by American Variseal Corporation, survived for 164.8 hours. This seal has a modified PTFE body filled with a proprietary material which is loaded by an alloy spring. Four other seals, all manufactured by Utex Industries, did not fare as well. Testing is continuing on the Variseal.

TABLE 6.2-10. DRILL BIT ELASTOMERIC SEAL TEST RESULTS

Elastomer Designation	Manufacturer	Base Polymer(s)	Test Type ^g	Soak Temp. °F	Run Temp. °F	life, Hours ^h
DD-227	Utex Ind. Inc.	Proprietary	Trip-In	550	302	94+
DD-231	Utex Ind. Inc.	Proprietary	Trip-In	550	302	92+
HTCR ^a	Utex Ind. Inc.	Proprietary	Trip-In	550	302	120
Kalrez No. 3062	DuPont, Inc.	Kalrez ^d	Constant Temp	--	455	63
Kalrez No. 3072	DuPont, Inc.	Kalrez ^d	Constant Temp	--	393	86+
RD-176	Utex Ind. Inc.	Viton ^e	Constant Temp	--	392	70+
Teflon coated ^b	Sandia Laboratories	Viton ^e	Trip-In	482	302	107
Viton No. 4205	Parker Seal, Inc.	Viton ^e	Trip-In	500	302	107
266-IV-15 ^c	L'Garde, Inc.	EPDM ^f /Viton ^e	Constant Temp	--	392	47+
267-11-35 ^c	L'Garde, Inc.	EPDM ^f	Trip-In	550	302	104+

^aHigh temperature corrosion resistant

^bCapacitive Discharge method

^cThe L'Garde seals were originally intended for static seal applications.

^dPerfluoromethylvinyl ether-tetrafluoroethylene copolymer

^eFluorocarbon elastomer

^fEthylene-propylene-diene monomer terpolymer

^gAll tests run at 90 RPM with abrasives present, 5 mils wobble and stroke. All seals were subjected to trip-in tests at 550°F, but only successful tests at the highest attainable soak temperatures are shown.

^hLife tests were frequently terminated for scheduling reasons. These are denoted by a plus sign.

Source: Hendrickson, Winzenried and Jones 1980

For maximum performance of these two seals, they should be used with Pacer DHT-90G lubricant, the maximum diametral clearance between the sleeve and backing ring should be 5 mils, and the sleeve should have a hardness of at least HRC 60 and a surface finish of 4-8 μ in.

6.3 Coated Elastomers

Several studies have been performed on the feasibility of coating an elastomer to enhance its resistance to hostile environments and to enhance its lubricity. Two methods for coating elastomers are capacitive discharge and glow discharge. In the capacitive discharge method, a plasma-polymerized film is deposited on the elastomer in a vacuum. In the glow discharge method, the elastomer is exposed to ultraviolet radiation to create free radicals on the surface, then subjected to a proprietary process (used also for military purposes) [Hendrickson, Winzenried and Jones 1980].

Early research by TerraTek indicated a problem with the coating detaching from the elastomer. The glow discharge method appears to have relieved that problem somewhat. Table 6.2-11 summarizes the results of tests run on uncoated and coated Viton 4205 and Parker EPDM seals. The coating used was polymerized tetrafluoroethylene (PTFE) applied by the glow discharge method. These tests indicated that the coating can have a beneficial effect on the life of the seal [Hendrickson, Winzenried and Jones 1980].

Tests by Sandia indicate that when PTFE is applied to ethylene-propylene rubber the beneficial effect is pronounced, but short-lived, lasting only until the coating evaporates, about 48 hours. No similar improvement was obtained with coated fluoroelastomers.

Sandia also tested a 1.25 mil coating of Parylene C (polychloroxylylene) on O-rings of Vitron V-709-80 and Vitron V-747-75. The coating was applied by means of a Union Carbide pyrolytic vapor phase technique. The

TABLE 6.2-11. EFFECT OF PTFE COATING ON THE LIFE OF AN ELASTOMERIC SEAL

Seal Type	Temperature	Seal Life
Viton 4205		
Uncoated	500°F	107 hours
Coated	550°F	53 hours ^a
Parker EPDM		
Uncoated	550°F	9-1/2 hours
Coated	550°F	34 hours

^aAccording to Hendrickson, seal life would probably have been around 100 hours at a slightly lower temperature.

Source: Hendrickson, Winzenried and Jones, 1980.

O-rings were contained in a simulated cablehead at 525°F and 4500 psi. The V-709-80 seal held while the V-747-75 seal failed. Uncoated O-rings of both materials failed to seal. However, these results were judged inconclusive [Arnold, Coquat and Baker 1978].

The life of a dynamic seal increases with lubricity. In the Sandia tests, the coefficient of friction of ethylene-propylene rubber was improved by the coating, but the improvement was short-lived. The effect on nitrile rubber, however, was much longer-lived. Nitrile rubber, however, is not suited for use at temperatures about 500°F [Arnold, et al. undated].

6.4 Cure-in-Place Elastomers

DOE received domestic patent 4,244,908 on a process for curing a packer seal only after it is in place and packed off [Hirasuna, et al. 1979]. With this process the stress caused by the compression during pack-off is virtually eliminated; therefore, very high-modulus extrusion-resistant compounds can be used which would crack during ordinary compression setting procedures. The process can be used for geothermal applications and inherently lends itself to enhanced oil recovery wells which are cool until steam is injected. For geothermal applications, the seal needs to be kept cool until packed off. The ultimate practicality and applicability of the concept have not yet been fully demonstrated.

A L'Garde elastomer, Compound 248, successfully cured in place and sealed at 500°F for 22 hours at 4000 psi with a 150 mil diametral gap. This diametral gap is three times that used in most other tests of packer seals. The larger gap placed the seal under significantly greater stress than was experienced with seals tested with smaller gaps.

6.5 References

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SUMMARY

Section 7 considers drill bits, downhole drilling motors, and other selected downhole tools used in the drilling and completion of a geothermal well. This summary provides a quick reference to that material. Please refer to the section for caveats, qualifications, and references cited for the material presented below.

Drill Bits

Most geothermal well drilling is done with roller cone drill bits, but diamond bits are also used. A roller cone bit may have sealed or unsealed bearings; a sealed bit can drill about two to four times the footage of an unsealed bit if the seal can be kept intact. The cutting surface consists of hardened steel teeth, diamonds, or tungsten carbide inserts. Diamonds may be natural or synthetic.

Most materials problems of roller cone bits used in the geothermal environment involve components of the bearing system. This system can be damaged by high temperatures and by abrasive particles. Drilling fluids used to cool the bit and to carry cuttings to the surface are not always effective. The high rotational speeds of downhole motors and, in sealed bits, cutter "wobble" also contribute to premature bearing failure.

Tests have been conducted on both mechanical and elastomeric drill bit seals. No mechanical seals have been considered for further development because of warpage and excessive wear from abrasion. Elastomeric seal development, discussed in more detail in Section 6, resulted in the choice of L'Garde 267-II-35 EPDM for fluid drilling and Utex HTCR for air drilling. The HTCR seals were then subjected to further laboratory tests and to testing with a compatible Pacer lubricant in TeraTek's Drilling Research Laboratory hot-air

drilling facility where it demonstrated a longer bit life than did the commercial bits or a bit manufacturer's proprietary bearing/seal/lubricant system.

TeraTek, with government sponsorship, conducted a study to produce a hardened version of a standard unsealed roller cone bit for air drilling at The Geysers and in similar formations. Hot toughness, fracture toughness, and hardenability were tested for a number of metals. Conventional Reed Y736JA bits were then modified by substituting alternative materials to make two prototypes of hardened geothermal bits, the Mark IIIA and the Mark IIIB. Bit geometries were identical. A comparison of the materials used in the construction of these bits is given in Table 7.0-1.

TABLE 7.0-1. COMPARISON OF MATERIALS SELECTIONS IN CONVENTIONAL AND HARDENED GEOTHERMAL (MARK III) BITS

	Conventional	Prototype	
	Reed Y736JA	Mark IIIA	Mark IIIB
Cones	AISI 4820	Same	Same
Gage row inserts	Carboloy 231	Carboloy 90	Carboloy 90
Lug (spindle)	AISI 8620	Timken CBS-600	Timken CBS-600
Friction Pin Assembly			
Pin	lug*	lug*	lug*
Hardfacing	Cabot No. 1 Mod	Cabot No. 1 Mod	Cabot No. 1 Mod
Pilot bushing	AISI 430	AISI M-50	Carboloy 248
Thrust button	AISI M-2	Same	Same
Rollers and Balls	AISI 8-2	AISI M-50	AISI M-50

*The pin is an integral part of the lug.

During field testing at The Geysers, considered a worst-case wear test, the improved bits demonstrated 30 percent more bit life and 70 percent more in-gage hole drilled per bit than did the conventional bit. Wear in the ball and roller races was reduced by 56 percent, wear on the rollers was reduced by about 67 percent, and total radial wear on the friction (pilot) pin system was reduced by about 55 percent.

Diamond bit research has been focused on design improvement rather than materials development. Testing with polycrystalline diamond compact (PDC) cutter bits indicates that bits with PDC cutter blanks bonded to tungsten carbide or steel support posts by brazing or diffusion bonding processes may be applicable only for softer formations.

Downhole Drilling Motors

Downhole drilling motors may be positive displacement motors (PDMs) or turbodrills. The PDM has a metallic rotor and an elastomeric stator; both the rotor and the stator of the turbodrill are metallic. All currently used downhole drilling motors have open (drilling water lubricated) bearings. Materials development in this area has centered on development of improved stator elastomers and development of a sealed bearing system.

Elastomers are discussed in Section 6. Though they were not designed for this purpose, some of the elastomers discussed in Section 6.2 might extend the present temperature limit of 340°-380°F for PDMs to more than 450°F. Because it has no elastomeric parts, the turbodrill has a ceiling temperature above 600°F.

The bearings determine the life of the turbodrill. Open bearings have a life of more than 5 hours in granite at 430°F, 300-400 rpm, 20,000 lb(f) weight on bit, with no shock absorber tools. Sealed, oil-filled bearings for both PPMs and turbodrills are being developed. In tests by TeraTek, a double-spring Variseal (carbon-filled TFE body loaded with two alloy springs) with an SAE660 bronze backup ring lasted 164.8 hours at 1500 psi differential pressure; a Utex HTRC SF (AFLAS) elastomer reinforced with synthetic aramid and glass fabric) did not fail after 200 hours and 7200 psi. These seals were tested with Pacer DHT 90G lubricant, 0.005 inch backup ring clearance, HRC 60 shaft, 250°F circulating fluid, and 412 rpm shaft speed. Other Utex configurations lasted up to 72 hours under similar conditions.

A bearing seal package is also being developed, but none have survived more than 54 hours at 500 psi differential pressure.

Packers

The packer seal has historically been an elastomer which suffered severely from the high temperatures encountered in geothermal applications. It has been necessary to precool the well with water before setting the packer.

The use of elastomers as packer seals is discussed in Section 6. L'Garde's elastomer Y267 EPDM has performed successfully as a packer seal at temperatures above 575°F. Several L'Garde elastomers are supposed to perform satisfactorily when packed hot in a laboratory-simulated packer immersed in synthetic brine at 500°F for 46 hours at a differential pressure of 3100 to 4100 psi and a diametral gap of 50 mils. Elastomers are also being developed which can be cured in place. These are discussed in Section 6.

Seals of Y267 EPDM, of reinforced Teflon, and of knitted wire mesh reinforcement filled with Grafoil have sealed for several days at 400°F and 7000 psi differential pressure with no failure or partial extrusion.

Downhole Shock Absorbers and Jars

Commercially available shock absorber tools can be used at temperatures to 300°F; a metal high-temperature version is usable to 400°F. A specially modified (modifications unspecified) high-temperature shock absorber offered by Houston Engineering, Inc., was tested downhole to more than 500°F. Elastomers appeared to be the major materials problem, though the elastomers used by the vendor were not specified. It is suggested that L'Garde's Y267 EPDM elastomers, discussed in Section 6, be considered for this use.

Commercially available axially responsive HYDRA-JAR hydraulic drilling jars modified by Houston Engineering, Inc., successfully operated above 600°F. The modifications were not disclosed.

Type J rotary mechanical jars by Bowers Tools, Inc., were successful in major fishing operations above 400°F. They suffered premature failure due to failure of internal seals.

Percussion Drills

Commercially available percussion drill motors (hammers) contain O-rings and other elastomeric seals, valve tubes, and mountings which are vulnerable to thermal failure above 300°F.

In a laboratory test, a custom-machined aluminum (6061-T6) valve tube allowed 52 minutes of air-drilling at 350°F before fatigue failure. A hammer with silicone rubber replacements for elastomeric parts and a DuPont Vespal polyimide valve tube air-drilled for 4 hours at 350°F, 9 hours at 400°F, and 2 hours at 450°F.

It was concluded that commercially available percussion drills with minor modifications can operate at geothermal temperatures. It was noted, however, that the polyimide used in the above test is susceptible to catastrophic hydrolysis if exposed to water at a high temperature.

INTRODUCTION

This section describes the materials-related problems which affect the reliability and performance of selected downhole equipment used during the drilling and completion of geothermal wells. The majority of the discussion of problems and research efforts underway to solve these problems relates to tools used in drilling the borehole. This discussion is limited primarily to conventional drill bits and downhole drilling motors. However, other selected

tools used during drilling and completion operations are also discussed. Some downhole equipment or materials -- such as tubular goods and cements -- used during these operations are discussed in other sections of this reference.

Drilling and completion of high-temperature geothermal wells employs the same basic methods, equipment, and materials developed for the oil and gas industry. However, the high temperatures associated with most developed geothermal formations and the corrosive, erosive nature of produced fluids, acid gases and drilling fluids, can cause rapid degradation of materials used in the construction of conventional equipment. In addition, most of the developed geothermal resources exist in hard, abrasive, and highly fractured formations. Drilling in these formations is slow and difficult, and resulting wear of penetrating equipment is great.

Any one or a combination of these adverse downhole conditions can lead to early materials failure and performance problems. These failures require removal of downhole equipment for replacement or repair of the affected component. Due to the high cost of rig time, any situation which results in additional tripping or remedial well work greatly increases the cost of the well.

These equipment problems are not so serious in low-temperature geothermal drilling and completion. For such operations in low-temperature, mostly sedimentary, geothermal formations, water-well technology has proved to be quite adequate.

In many of the research efforts discussed, a change in material or the development of a new material for use in construction of the component may not be the only consideration. Redesign of the equipment or component may be just as important in satisfying the performance requirements for geothermal use. Much of the research performed has resulted in improved performance through tool redesign as well as new materials applications or development.

Discussion of the improvement due to equipment design, not directly related to materials, is beyond the scope of this section. For further information about these design considerations, the reader is referred to the cited references.

7.1 Drill Bits

Most geothermal well drilling is done with roller cone bits. Roller cone bits may have sealed or unsealed bearing systems, depending on the drilling fluid used and the expected downhole temperature. Cutting structures for roller cone bits consist of hardened steel teeth or tungsten carbide inserts. Where hard, abrasive formations are encountered, more wear-resistant grades of carbide inserts are used than are used in oil and gas drilling.

Diamond bits with natural or synthetic diamonds as the cutting surface are also used. There are the following bit types [Varnado, ed. 1979a]: (1) conventional diamond bits using natural industrial diamonds set in a cast matrix covering the bit surface; (2) polycrystalline diamond compact (PDC) cutter bits using synthetic diamond cutters joined with tool posts which are then attached to the bit body; and (3) impregnated diamond bits using synthetic and natural diamond grits in powder metal "inserts" which are arranged on the bit surface.

Conventional sealed roller cone bits are rated at 280-325°F, this rating based on the temperature limitations of the elastomeric seal material. The bits can demonstrate bit lives of 2 to 3 days in normal depth (not deep) oil and gas wells [Chadwick 1981]. Long bit life can be obtained in such wells, even at high static bottom-hole temperatures, as long as the cooling effect of the drilling fluid can maintain the circulating bottom-hole temperature within these limits. Where circulating downhole temperatures allow it, the use of sealed bits is preferred over unsealed bits because the relative bit life is higher. Sealed bits with roller-bearings or journal-bearings can drill approximately two or four times, respectively, the footage that a similar unsealed bit can at the same downhole conditions [Hendrickson, et al. 1977].

Where sealed bits cannot be used due to high bottom-hole temperatures, unsealed bits are often used. These bits have open bearing systems which are cooled and cleaned directly by the drilling fluid. Although unsealed bits allow drilling into higher temperature geothermal formations than do sealed bits, problems with shortened bit life due to degradation and wear of the metal bit components do arise, especially when air rather than mud or water is used as the drilling fluid.

The materials problems with conventional roller cone bits used in the geothermal environment involve components for sealed and unsealed bearing systems, and, to some degree, components for cutting structures. Problems with diamond bits concern mainly the diamond cutting structures since there are no moving parts in these bits.

Drilling fluids, including water- and oil-based muds, water, air, and foams, cool the bit and carry cuttings to the surface. Depending on the downhole temperature and the type of formation being drilled, the cooling and lubricating effect provided by a selected drilling fluid helps to optimize bit performance and bit life by keeping the bit components within their designed operating temperature limits. Water or muds are particularly effective for this cooling function where downhole temperature conditions allow it.

In some geothermal formations, formation characteristics, drilling problems and future production considerations may dictate drilling fluids, such as air, which do not adequately cool the bit. Under these conditions, the temperature limits of bit components may be exceeded, leading to premature failure of the bit. In addition, the type of geothermal formation being drilled and the fluids encountered by the bit downhole can lead to other problems with bit components, such as abrasive wear of bit component surfaces, mechanical problems caused by drilling in hard formations, and thermochemical degradation.

An additional consideration for conventional bits is that improvements are needed so that they will be more compatible with the load and speed characteristics of downhole drilling motors. The use of these motors for drilling multiple wells from a single well site and for correcting well deviations in hard formations has considerable utility in geothermal exploration. However, most commercial downhole motors operate at much higher rotational speeds than the rated operating speeds of conventional roller cone bits, these higher speeds contribute to premature bearing failure and shortened bit life [Maurer 1976]. Use of conventional diamond bits can partially solve this problem. However, the rate of penetration may be low in hard formations at the higher speeds and lower bit weights [Newsom, et al. 1978].

7.1.1 Roller Cone Bits

Materials Problems Affecting Roller Cone Bit Performance

Sealed Bits

The seals which protect the lubricated bit bearings from direct exposure to the drilling fluid, well cuttings, and formation fluids are the most prominent materials problem for sealed roller cone bits. In many geothermal wells, formation temperatures are high, typically in excess of 300°F and ranging to 700°F [Barker, et al. 1976; Hendrickson, et al. 1977]. Under these conditions, cooling of the bit by the drilling fluid may be ineffective, resulting in higher bottom-hole temperatures than can be tolerated by the seals. Additional heat is also generated in the bit by friction in the bit bearings and at the seal interface. This heat cannot be dissipated. Use of air -- frequently used as the drilling fluid in geothermal reservoirs -- is particularly ineffective in protecting sealed bits from this frictional heat. Bits may also be exposed directly to the full formation temperature during tripping to change the bit or during periods when the rig is not operating.

Exposure of conventional sealed bits to any of these high-temperature environments can result in failure of the seals, leading eventually to bit bearing failure through loss of bearing lubricant. Temperature-related seal failures include the following: (1) softening or thermal degradation due to broken cross-links in the seal material; (2) brittle failure caused by hardening of the material due to the formation of unwanted cross-links; and (3) compressive deformation of the seal and loss of sealing effect during successive periods of heating and cooling [Hendrickson, et al. 1977].

Although temperature effects may be considered the primary problem with sealed bits, other factors also contribute to short seal life [Hendrickson, et al. 1977]. In sealed roller cone bits there is a certain amount of cutter "wobble" due to bit design. This movement causes varying pressure loads on the seals and varying size gaps in the interface to be sealed. Where "wobble" amplitude is high, the seal does not perform properly: lubricant is lost and the bearings are contaminated by the drilling fluid and cuttings. In geothermal wells, drilling and formation fluids may contain abrasive cuttings and hydrogen sulfide. Abrasion can result in mechanical wear of the seal while exposure to hydrogen sulfide can cause embrittlement of the elastomeric material.

Unsealed Bits

The life of an unsealed bit depends largely on the cooling effect that the drilling fluids have on the downhole environment. As with sealed bits, mud or water may effectively moderate the temperature of the unsealed bit, resulting in prolonged bit life. However, bit life can be shortened during geothermal air drilling, more than in air drilling of oil and gas wells, because of the higher temperatures associated with geothermal formations.

Specific problems with the effect of unsealed bit materials on bit life during air drilling in geothermal formations have been discussed primarily in relation to drilling experiences at The Geysers, California [Barker,

et al. 1976]. At The Geysers, air drilling with unsealed bits is conducted in hard, abrasive and highly fractured rock which produces 500 psi steam at 465°F. Although air drilling allows for increased penetration rates and reduces the chances for plugging of steam production zones, the air does not adequately cool and clean the metal bit components. As a result, the bit is exposed to bottomhole temperatures approximately equal to the drawing temperature (400-450°F) of the steels used in conventional bit bearings. Exposure to these downhole temperatures as well as to peak temperatures of up to 1100°F -- generated by friction within the unlubricated bearings [Leslie 1976] -- leads to annealing of the steels used in the races, cones and bearings. The resulting reduction in bit component hardness is illustrated in Table 7.1-1.

TABLE 7.1-1. CONVENTIONAL BIT COMPONENT HOT HARDNESS VERSUS TEMPERATURE AFTER ONE HOUR AT TEMPERATURE

Component	Hardness (Rc)				
	68°F	500°F	600°F	800°F	1040°F
Cutter cone roller race	57	49	42	26	--
Lug roller race	59	53	47	28	--
Roller bearing	58	51	47	28	--
Friction pin hard facing	59	--	--	55	51

-- data not available

Source: Barker, et al. 1976

Reduction in Rockwell C hardness (HRC) of conventional bearing steels from 58 to 50 has been reported by bearing suppliers to decrease bearing life by a factor of 5 because of increased wear [Nielsen, Barker and Carwile 1977].

At The Geysers, the predominant modes of conventional bit failure are bearing wear due to prolonged exposure to high downhole temperatures and to loss of bit gage (or diameter) due to the erosion of the gage-cutting area of the cones by the abrasive rock cuttings. Lighter bit weightings are used at The Geysers to extend bit bearing life, but these cause more abrasive particles to be generated per foot of depth; these particles then contribute

to gage wear. The combination of these two interrelated problems -- bearing wear and gage wear -- results in bit life ranging from 10 to 20 hours at The Geysers (using low bit weights), compared to 30 to 60 hours in conventional petroleum drilling at twice the bit weight. The life of conventional unsealed bits used at The Geysers has been reported to be 20 to 25 percent of the life expected during non-geothermal drilling [Barker, et al. 1976].

Results of Alternate Materials Selection on Roller Bit Performance

Research in this area under DOE funding was initiated in 1975 and has continued under several programs. The major objectives of the research have been: (1) to develop for sealed bits seals and compatible lubricants capable of operating in the geothermal environment; and (2) to substitute steels with improved hot-hardness and fracture toughness for use as components in unsealed bits. Discussion of developed lubricants is beyond the scope of this reference; the reader should consult the references cited for this information.

Sealed Bits

A sealed bit program was conducted to develop seals and lubricants which would provide 100 hour bit seal life for fluid drilling at 662°F and capabilities for foam or air drilling at 572°F [Hendrickson and Winzenreid 1980]. To date, several elastomeric compounds have been shown to seal effectively to 550°F in the laboratory. Development work has been performed on mechanical seals for downhole temperatures in excess of 550°F.

Screening tests were performed on a number of elastomeric materials including fluorocarbon elastomers (Viton or Fluorel), fluorosilicone rubbers, Buna-N (nitrile), modified Buna-N, perfluoroelastomers (Kalrez), fluorinated polyphosphazene rubber (PNF-200), peroxide cured Viton, ethylenepropylenediene monomer terpolymer (EPDM), tetrafluoroethylenepropylene copolymer (Aflas), and various EPDM/Viton compounds [Hendrickson, et al., 1978a; Hendrickson, Winzenreid and Jones 1979; 1980]. Some seals were tested with a coating of

Parylene-C (a Teflon-like material). Testing was performed at the nominal conditions indicated in Table 7.1-2 with some variations in lubricants used and amount of abrasives present. During screening tests of elastomeric materials, development and design of mechanical and mechanical/elastomeric seals for higher temperature applications were also conducted. These seals included radial lip seals, disc spring seals, and spring-loaded face seals. A seal was said to pass if it leaked less than 1 ml of grease or lost less than 150 psi differential pressure in the lubricant reservoir over a 15-minute period.

TABLE 7.1-2. SEAL TESTER CAPABILITIES AND STANDARD CONSTANT TEMPERATURE. TEST DETAILS

Parameter	Maximum Capabilities	Screening Test Conditions (Nominal)
Temperature	800°F	392°F
Pressure	3,000 psi	2,150±50 psi
Rotational Velocity	500 rpm	90 rpm
Radial Motion	±0.017 in.	±0.005 in.
Axial Motion	±0.025 in.	±0.005 in.
Abrasives	Any	The Geysers Franciscan Graywacke and Feldspar Sand Mixture
Fluid	Liquid	Water

Source: Hendrickson, Winzenreid and Jones 1979

The most promising elastomeric seal candidates, based on the longest seal lifetime in a series of screening tests on each material, were subjected to additional trip-in tests which more closely simulated actual downhole conditions. A compatible lubricant developed during the program was used. These trip-in tests helped in determining the ultimate soak temperature for each seal material. This test procedure was discussed in Section 6.2.5 and illustrated in Figure 6.2-4. A list of the most promising elastomeric seal materials from both the constant temperature screening tests and the trip-in tests was shown in Table 6.2-8. Direct comparisons concerning seal life should not be made between the two different types of tests due to the different test conditions.

During the trip-in tests, versions of the radial lip seal and metal bellows face seal were evaluated. The disc spring seal was not included in the trip-in testing due to sealing problems. The radial lip seals held pressure at ambient temperature, but leaked at soak temperatures of 482°F to 550°F, due to shrinkage of the polytetrafluoroethylene seal body at temperatures greater than 392°F. Abrasive wear was minimal [Hendrickson, Winzenreid, and Jones, 1980]. For the metal bellows face seal, leakage was a problem above 212°F because stresses induced during manufacturing caused warpage of the primary seal ring. Also, wear of the carburized steel (CBS-600) mating ring was excessive when abrasives were used [Hendrickson, Winzenreid and Jones 1980]. No further development for mechanical drill bit seals was considered following these tests, although design improvements could be made for longer seal life.

Based on the results of the trip-in tests, two elastomeric seals were selected: one for use in fluid drilling, L'Garde 267-II-35 EPDM, and one for air drilling, Utex HTCR [Finger 1981a]. The HTCR seals were then proofed in laboratory drill bit tests.

Finally, the HTCR seals and a compatible lubricant by Pacer were substituted in three commercial 7-7/8 inch bits and run against cast iron targets in TerraTek's Drilling Research Laboratory hot-air drilling facility. Three other similar bits were tested: an unmodified commercial sealed bit and two bits containing the bit manufacturer's proprietary bearing/seal/lubricant system. Each bit was instrumented to measure journal temperatures and lubricant reservoir pressures. One of the research bits with HTCR seals ran for over 12 hours at a bit weight of 25,000 pounds and an air temperature of 340°F. Average bearing temperatures were over 450°F. There were no bearing failures. The second HTCR sealed research bit did not fail after 12 hours with bearing temperatures over 400°F. The third research bit with HTCR seals failed after 4 hours of drilling. One bearing was running over 600°F but a different bearing failed. The commercial bits with proprietary sealed bearing

components were tested at comparable loads and temperatures and failed in less than 8 hours. The unmodified commercial bit failed as well. The run life was not reported [Sandia National Laboratories 1981a].

Although the improved seals and lubricants tested did demonstrate longer bit life than did commercial bits in air drilling lab tests, it was noted that temperature differences of up to 200F° were recorded for lugs on the same research bit. Such temperature differences were greater than those observed for the commercial bit. However, the effect of these temperature differences on bit life has yet to be resolved [Finger 1982].

Unsealed Bits

A study was undertaken by TerraTek, with government sponsorship, to produce a hardened version of a standard unsealed roller cone bit for air drilling at The Geysers and in similar formations.

Figures 7.1-1 and 7.1-2 summarize results of hot toughness studies. The solid horizontal line at HRC 55 in Figure 7.1-1 represents the minimum desired hardness for good wear resistance. The selected metals also require high fracture toughness -- the energy required to cause a crack to propagate. High fracture toughness often requires reduced hardness; therefore, trade-offs between wear resistance and toughness are required. Figures 7.1-3, 7.1-4, and 7.1-5 summarize the results of the fracture toughness-versus-temperature relationships for a number of candidate hardened drill steel alloys. Fracture toughness shown in these figures is a quantitative measure of fracture resistance; it is independent of specimen size. Figure 7.1-6 displays Charpy Test results for some additional metals. Charpy results depend on specimen size and cannot be translated into fracture toughness. The Charpy Test can be used for ranking purposes.

Figure 7.1-1. Hardness vs. Temperature for Bit Lug Metals [Hendrickson, et al. 1978a]

NOTE: The horizontal line at HRC 55 is the minimum desired hardness for wear resistance.

Figure 7.1-2. Hardness of Additional Drill Bit Steels to 800°F [Cutler, et al. 1980]

Figure 7.1-3. Fracture Toughness of Drill Bit Steels to 800°F [Hendrickson, et al. 1978b]

Figure 7.1-4. Fracture Toughness of Roller Bearing Steels as a Function of Temperature [Hendrickson, et al. 1978a]

Figure 7.1-5. Fracture Toughness of Timken CBS-600 as a Function of Temperature [Hendrickson, et al. 1978a]

Figure 7.1-6. Charpy Impact Test Results of Three Drill Bit Metals as a Function of Temperature [Hendrickson, et al. 1978a]

Figure 7.1-7 explores the temperature/fracture toughness relationships of the gage inserts. Carboloy 90 and 231 are sintered 90 percent tungsten carbide and 10 percent cobalt with room temperature hardnesses of HRA 89.0 and HRA 87.8, respectively. Carboloy 248 is sintered 89 percent tungsten carbide and 11 percent cobalt with HRA 88.6.

Another important factor in improved high-temperature bit metal selection is high hardenability -- uniform through-section hardness as a result of quenching. Figure 7.1-8 shows Jominy End Quench Test results for four steels. The hardenability is best for those steels which have the least change in hardness with distance from the quenched end.

After a series of preliminary laboratory tests in which improvements in materials selection for a series of bits were made, conventional Reed Y736JA bits were modified by substituting alternative materials to make Mark III prototype bits. The materials selections for the standard and Mark III bits are compared in Table 7.1-3. The geometries of the bits are identical.

TABLE 7.1-3. COMPARISON OF MATERIALS SELECTIONS IN CONVENTIONAL AND HARDENED GEOTHERMAL (MARK III) BITS.

	Conventional	Prototype	
	Reed Y736JA	Mark IIIA	Mark IIIB
Cones	AISI 4820	Same	Same
Gage row inserts	Carboloy 231	Carboloy 90	Carboloy 90
Lug (spindle)	AISI 8620	Timken CBS-600	Timken CBS-600
Friction pin Assembly			
Pin	lug*	lug	lug
Hardfacing	Cabot No. 1 Mod	Cabot No. 1 Mod	Reed "tube metal"
Pilot bushing	AISI 430	AISI M-50	Carboloy 248
Thrust button	AISI M-2	Same	Same
Rollers and Balls	AISI 8-2	AISI M-50	AISI M-50

* the pin is an integral part of the lug

Sources: Maish 1979; Vanardo 1979; Hendrickson, et al. 1980.

Figure 7.1-7. Fracture Toughness of Tungsten Carbide Inserts as a Function of Temperature [Hendrickson, et al. 1978a]

Figure 7.1-8. Hardenability of AISI 4820 and Timken CBS-600 [Hendrickson, et al. 1978a]

Field tests of the Mark III were conducted at The Geysers in August and September, 1978 [Hendrickson, et al. 1980; Maish 1979]. The test took place during drilling of two legs of Union Geothermal's CMHC No. 6 well. The well was drilled with mud to the top of the geothermal reservoir. Air drilling was used during the rest of the drilling and the bits were tested during this latter stage. The drilled formation is Franciscan graywacke and micro-graywacke sandstone. The combination of abrasiveness (quartzite and feld spar phenocrysts), strength, and ductility makes this formation a worst-case wear test. The formation temperature in the test interval was 400°-475°F. Weight on bit was 20-35 ksi and speed was 40-70 rpm. The drilling was done using 2400 CFM of air with Unisteam inhibitor (see Section 3) to protect the drill string. Drillers and bit manufacturers do not think that Unisteam affects bit life [Hendrickson, et al. 1980].

During the test, Mark III bits were alternated with Reed Y73JA bits, as well as with other conventional bits. Figure 7.1-9 summarizes the results from Leg 1 of the drilling, while Figure 7.1-10 summarizes the results from Leg 2. In these figures, "M-50" designates the Mark IIIA bit with M-50 steel bushings; "WC" indicates the Mark IIIB bit with Carboloy 248 bushings.

Since the bit geometries and loadings were identical, no significant difference in penetration rate was expected or observed. Bit performance was compared by the equivalent time (hours drilling plus 2.5 times the hours reaming) elapsed before the reduction in gage made further drilling with the bit uneconomical. This "economic break-even" loss of gage is set at 0.20 inch at The Geysers. Figure 7.1-11 compares the performance of the Mark III prototype bit with conventional bits. This figure shows that the Mark III bit allows an additional 5 hours of drilling or 2 hours of reaming. This represents a 30 percent improvement.

Figure 7.1-9. Performance of Mark III Geothermal Bits and Conventional Bits During Drilling of Leg 1 of Well CMHC No. 6 at The Geysers [Hendrickson, et al. 1980]

Figure 7.1-10. Performance of Mark III Geothermal Bits and Conventional Bits During Drilling of Leg 2 of Well CMHC No. 6 at The Geysers [Hendrickson, et al. 1980]

$$H_{\text{hole}} = H_{\text{drill}} + 2.5 H_{\text{ream}}$$

Figure 7.1-11. Comparison of Conventional and Mark III Hardened Geothermal Prototype Bit Performance in Field Tests at The Geysers [Hendrickson, et al. 1980]

NOTE: BHA is the "Bottom Hole Assembly."

The bits were also compared in terms of the amount of in-gage hole drilled per bit. This value was determined by the point when the next bit in the hole began reaming. On this basis, the Mark III drilled an average of 70 percent more hole than did the conventional bits [Hendrickson, et al. 1980].

Post-test examination of experimental and conventional bits lead to the following observations [Hendrickson, et al. 1980; Vanardo 1979b]. First, wear in the ball and roller races was reduced by 56 percent by using Timken CBS-600 steel lugs instead of the AISI 8620 lugs of the conventional bit. Microhardness traces showed that surface temperatures exceeded 750°F on the roller and ball traces and 1100°F under the hardfacing on the end of the friction pins. The friction pins of both conventional and Mark III bits showed deformation. The deformation was less severe in the Mark III because of the high hardenability of the Timken CBS-600.

Second, the M-50 rollers (HRC 56) showed only about 3 mils wear, one-third the wear of the S2 rollers. Wear was uniform, with little variation in taper or diameter. This degree of wear was considered acceptable. The balls of the ball bearings of both the conventional and Mark III bits wore excessively and non-uniformly as a result of excessive reaming -- which utilizes reverse loading of the ball bearing systems to support the cones. According to roller performance, much better performance is anticipated in the absence of excessive reaming, but a steel with higher hardness and fracture toughness may be required for the bearing balls.

Finally, the friction (pilot) pin systems of the Mark III bits reduced total radial wear to about 45 percent that of conventional bits. The underlying Timken CBS-600 lug material supported the hardfacing better than did the conventional AISI 8620 lug material. The Mark III bits tested had two different friction pin systems. The AISI M-50/Cabot No. 1 Mod system (Mark

IIIA) wore slightly better than the Carboloy No. 248/"tube metal" system (Mark IIIB). Additionally, two of the nine examined Carboloy bushings were broken or disintegrated. The Mark IIIA system was deemed preferable to the Mark IIIB both in terms of durability and cost.

The Mark III bit demonstrated a significant improvement over its conventional counterpart. The 30-70 percent longer drilling life would significantly reduce well costs at The Geysers due to the reduced number of trips required. This cost savings would more than offset the 10-30 percent increase in bit cost [Hendrickson, et al. 1980]. Despite the demonstrated improvement, however, no commercial bit vendor appears to be offering the Mark III modifications.

7.1.2 Diamond Bits

Materials Problems Affecting Diamond Bit Performance

Conventional diamond drag bits, with natural diamonds, are particularly effective in drilling medium hard to hard rock formations if the bit can be effectively cleaned and cooled by mud or water. However, in geothermal drilling, use of such fluids may be precluded due to harmful plugging effects on the production zone. Depending on the bottomhole temperature, natural diamonds can actually burn up when the bit cannot be cooled effectively [Hibbs and Flam 1976].

The diamonds in a conventional diamond drag bit are susceptible to cleavage and fracture if impacted in the proper direction, particularly when drilling hard, fractured rock. The bonding mechanism that holds the natural diamonds is also a problem when drilling in such formations.

Development of Polycrystalline Diamond Compact (PDC) Bits

Because the use of natural diamond drag bits is limited in geothermal applications, research efforts have aimed at development of polycrystalline diamond compact (PDC) cutter bits. These PCD bits are less susceptible to directional wear problems and have abrasion and wear resistance properties approaching those of natural diamonds. The vast majority of research into drag bits with PDC's has involved laboratory testing of individual cutter performance in various hardness rock formations, improved bit hydraulics, cutter placement, and laboratory and field testing of bits using these cutters in a variety of bit configurations [Huff and Varnado 1980; Hoover and Middleton 1981]. This research has resulted in improvement of the bit design which incorporates PDC materials rather than in specific materials development. These design developments are beyond the scope of this report. However, important conclusions concerning application of PDC bits in geothermal drilling are included here.

Rotary and downhole motor drilling in sedimentary geothermal formations similar to those encountered during petroleum drilling have resulted in penetration rates two to three times greater than are experienced with conventional rock bits at rotary speeds [Sandia 1981b; 1982]. However, when downhole motors are used at higher rotational speeds for drilling of hard, highly fractured formations, these same bits do not perform well because of extreme wear of the PDC material and loss of PDC drill blanks at the point where they are bonded to the stud materials.

In the past several years, research into PDC bit improvement has indicated that bits with PDC cutter blanks bonded to tungsten carbide or steel support posts by brazing or diffusion bonding processes may be applicable only for the softer formations such as shales, siltstones, and some sandstones. Therefore, use may be limited to resources such as the Imperial Valley [Hoover and Middleton 1981; Sandia 1981c].

7.2 Downhole Drilling Motors

7.2.1 Performance of Available Motors

Downhole drilling motors are of two basic types: positive displacement motors (PDM) and turbodrills. Positive displacement motors consist basically of a helical metal shaft (the rotor) which turns in an elastomeric stator--usually nitrile or Buna-N rubber. PDM's are constant displacement devices and have the advantage that motor speed is controlled directly by the drilling fluid flow rate.

Turbodrills are driven by a multi-stage mud or water turbine rather than by a positive displacement system. Both the rotor and stator are metallic, eliminating the elastomeric stator of PDM's. Turbodrill speed is not entirely controlled by the drilling fluid flow rate, and control of drill motor speed requires a tachometer. Several tachometer designs are available.

A number of downhole drilling motors were used at the Fenton Hill Hot Dry Rock Project and a hardened turbodrill was developed [Williams, et al. 1981]. The Fenton Hill experience indicates that the major materials limitation on PDM's is the thermochemical breakdown of the elastomeric stator at temperatures above 310°-350°F. Three kinds of PDM's were used at Fenton Hill; their practical temperature limit was around 340°-380°F, as shown in Table 7.2-1. Though not designed for this purpose, some of the elastomers in Section 6.2 might extend the temperature ceiling to more than 450°F. Because of many factors not relating to the motors themselves, the rate-of-penetration numbers in this table should not be used to rank the PDM's.

The Maurer turbodrill is a specially designed and hardened motor for high-temperature granite (hard rock) drilling. Design modifications include slow speed, 150-800 rpm, and special--though undisclosed--metals selection. In most of the tests at Fenton Hill, the turbodrills had open (drilling water lubricated) metallic roller bearings. Table 7.2-1 indicates that the hardened

TABLE 7.2-1. LIMITATIONS ON DOWNHOLE DRILLMOTORS USED AT
FENTON HILL, NEW MEXICO.

Motor	Temperature Rating (°F)	Practical Limit (°F)	Average Rate of Penetration (ft/hr) ^e
<u>Positive Displacement</u>			
BST ^a motor	350	340-380	11
DynaDrill ^b	310	340-380	13
CDT ^c motor	310	340-380	16
<u>Turbodrill</u>			
MEI ^d	610	600	21

^aBaker Service Tools, Houston, TX

^bSmith International, Irvine, CA

^cChristensen Downhole Tools, Oklahoma City, OK

^dMaurer Engineering, Inc., Houston, TX

^eDo not use this column to rank PDM's,

Source: Williams, et al. 1981; Pettitt and Carden 1981

turbodrill has a ceiling temperature above 600°F. This high ceiling temperature is due primarily to the lack of elastomeric components. The bearings determine the life of the turbodrill: these have a rotating life of more than five hours in granite at 430°F when operated without shock absorber tools at 300-400 rpm and 20,000 lb(f) weight on bit. The penetration rate under these conditions was 26 ft/hr with a Smith Tool Company Q9JL (12.25 inch diameter) bit.

Open-bearing turbodrills have also been used in other geothermal and hot oil field drilling. A brief summary of four such experiences is given in Table 7.2-2.

7.2.2 Development of Sealed Motor Bearings

The motors discussed above use open bearings lubricated by the drilling fluid. Such bearings wear rapidly as a result of erosion by drilling debris. Sealed, oil-filled bearings could easily extend the life of the motor to 200 hours or more if such bearings could withstand the high geothermal temperatures and desired high differential pressures.

TerraTek has been working for several years with DOE sponsorship to select suitable seals to meet the following objectives:

- o Operating life of at least 200 hours with a circulating drilling fluid temperature of 250°F and a pressure differential of at least 1000 psi.
- o Resistance to "soaking" at 350°F for many hours, and at 500°F for short times.

Fifty-five tests of different combinations of seals, back-up rings, shaft coatings, and lubricants were tested in this program. In many cases, several factors were varied between tests, making data analysis difficult. The test environmental conditions were:

TABLE 7.2-2. HIGH-TEMPERATURE PERFORMANCE OF DIRECTIONAL TURBODRILLS WITH OPEN BEARINGS

Location	Geothermal			Hot Oilfield
	The Geysers CA	East Brawley CA	Salton Sea CA	Brazos Area Bek #A69 Offshore, TX
Formation	graywacke, greenstone	siltstone	sandstone siltstone claystone	sand shale
Hole diameter (inches)	12.25	8.5	12.25	8.5
Temperature (°F)	380	520-575	400-520	350
Depth (ft)	2,800	9,000	5,965	13,600
Bent Sub (degrees)	1.5	2.0	2.0	2.0
Rate of Penetration (ft/hr)	22	12	12-25	30

Sii Turbodrill with open (drilling fluid-lubricated) ball bearings.
Source: Herbert 1981

Circulating Fluid Temperature:	250°F
Forward Pressure:	2500 psi
Back Pressure:	1000 psi
Differential Pressure:	1500 psi
Speed:	420 rpm
Shaft finish:	4-18 μ inch RMS

Table 7.2-3 summarizes the test results by seal material type. Almost all of the tests were performed with chromium plating on the shaft, but it was eventually decided to use a harder HRC 60 shaft. Also, in the last few tests, the lubricant was changed from Texaco Multigear Lubricant EP-SAE85W-90 to a modified Pacer lubricant designated DHT-90G. The back-up ring clearance was reduced to 0.005 inches. These changes resulted in the 164.8 hour run with the Variseal and the greater than 200 hour endurance of the UTEX HTCR-SF seals. The seal face in the last test showed almost no wear, even though the interfacial temperature exceeded 500°F.

TerraTek also began testing of downhole motor bearing seal packages (BSP's) in 1981. Only sketchy results are available to date [Kelsey, 1981b; Sandia 1981d]. No seal package tested (through December 1981) survived for more than 54 hours despite a reduction of the differential pressure to 500 psi, only 50 percent of the minimum target differential pressure.

7.3 Packers

Packers are used downhole to isolate intervals of the well for stimulation and/or testing of production zones. Isolation of the various zones in the borehole facilitates flow control through the fracture.

The packer seal has historically been an elastomer which suffered severely from the high temperatures encountered in geothermal applications. It has been necessary to precool the well with water before setting the packer. Also, the failure rate for the seal has been high.

TABLE 7.2-3. PERFORMANCE OF DOWNHOLE MOTOR BEARING SEAL SYSTEMS IN SIMULATION TESTING

Seal: Description	Backup Ring Material	P (psia)	Endurance (hrs)	No of Trials	Comments
UTEX 701: cotton reinforced Buna-N Chevron design	Brass	1500	1.15-18.20	5	
UTEX 42D: same as 701 except graphite filled Buna-N	Buna-N	1500	3.10	1	
UTEX 125-RD181: Viton and cotton reinforced Viton	Brass	1500	8.64-11.25	2	
UTEX Grafoil-BeCu: BeCu with thin layers of grafoil	Brass	1500	9.88-17.50	2	
	Al-bronze		5.90	1	
	P-bronze		40.9		
UTEX Graphite Metal Matrix: graphite with copper wire reinforcement	Al-bronze	1500	4.55-13.05	2	
	TFE + P-bronze		1.98	1	
	P-bronze		23.5	1	
	Sintered graphite		0-0.8	2	backup rings failed
	SAE660 bronze		0	1	
UTEX Graphite-Glass Matrix: Similar to above, but with glass matrix	SAE660 bronze	1500	2.0	1	
Johns-Manville Uneevac: asbestos reinforced neoprene	Al-bronze	1500	10.62-26.55	2	
Canted UTEX 701: See UTEX 701	Al-bronze	1500	0	1	
Canted UTEX 42D: See UTEX 42D	Al-bronze	1500	0-.72	3	
UTEX Grafoil-brass: Brass with thin grafoil layers	SAE 660 bronze	1500	2.92-3.17	2	
UTEX Grafoil-phosphor bronze: similar to other grafoil designs	System A: brass system with flexible leaves - zero clearance	1700/1500	3.48	1	
	Same, thinner leaves - System A		3.7-32.5	2	
UTEX HTRC SF: Aflas elastomer reinforced with synthetic arimid and glass fabric	SAE 660 bronze	1500	53.3-71.8	2	16 mil clearance. Estimated shaft/seal interfacial temp. >700°F
	not reported	7200	>200	1	Pacer DBT 90G lubricant. Shaft AISI 8620 Steel HRC 60, Did not fail.
Canted HTRC: Same as HTRC SF canted design	SAE 660	1500	0	1	
Variseal (double spring): carbon filled TFE body loaded with two alloy springs	SAE 660 bronze	1500	10.3-164.8	2	Pacer DBT 90G lubricant
Hybrid Assembly V: Aflas and Grafoil	System A (see above)	1500	3.8	1	
Hybrid Assembly SF: Aflas and HTRC SF	SAE 660	1500	6.7-8.0	2	

Note: Circulating fluid temperature at 250°F and shaft speed 412 rpm. The endurance is defined as the time required for one gallon of lubricant to escape.

Sources: Kelsey 1981a; 1981b; DeLaFosse, *et al.* 1981; DeLaFosse, Tibbitts, and Black 1979; Tibbitts *et al.* 1980a, 1980b, TerraTek 1979a; 1979b.

Elastomer Y267 EPDM has been successful as a packer seal material at temperatures as high as 575°F. This elastomer is discussed in detail in Section 6.0. Otis has laboratory-tested the Y267 EPDM, reinforced Teflon (rated for 625°F), and a knitted mesh wire reinforcement filled with Grafoil (rated for 700°F). Each of these has survived 400°F and a pressure differential of 7000 psi for several days without failure or partial extrusion [Taylor 1981].

Otis packers have been run successfully in several field installations. One packer survived 5 months at 350°F and 300 psi differential, one survived 14 hours at 390°F and 4,800 psi differential, and another survived 30 hours at 415°F and 900 psi differential. Which of the three seal materials were used in these tests is not known [Taylor 1981].

Lynes Services, Inc. has designed an inflatable packer which consists of a bladder of an EPDM-based elastomer reinforced by underlying metal leaves. These packers have been tested at 525°F and 5000 psi differential pressure. The lifetime for the inflated packer is calculated to be 72 hours [Cremer, et al., ed. 1980].

Dresser/Guiberson has devised a sealing element which consists of a plastic core of asbestos fiber (rated to 1200°F) treated with various fillers, including graphite suspended in glycerin. The core is formed in a die by compression of about 50 percent, and is then wrapped with a biased asbestos cloth to retain and protect it. Sets of special 16-gauge steel expanding plates are added to create a retaining bridge between the packer and the I.D. of the hole [Cremer, et al., ed. 1980]. This packer has been successfully static-tested by the manufacturer at 575°F and 5000 psi differential pressure for eight hours. It is expected to be successful at 750°F and possibly at 1200°F [Pettitt 1982].

Neither the Lynes nor the Guiberson packer has been tested at actual downhole conditions. They are to be tested by Los Alamos National Laboratory in the near future [Pettitt 1982].

7.4 Downhole Shock Absorbers and Jars

Laboratory testing by the Drilling Research Laboratory, Inc., (DRL) in support of the Fenton Hill Hot Dry Rock (HDR) geothermal project indicated that properly designed high-temperature shock absorbers would be needed to prevent damage to drills and drillstem by extreme vibration while drilling through granite at Fenton Hill. Commercially available shock absorber tools such as Sii Drilco's low-temperature rated (rubber) shock tools were used to drill at temperatures up to 300°F while a metal high-temperature version is usable to 400°F. A specially modified (modifications unspecified) high temperature shock absorber offered by Houston Engineering, Inc. was tested downhole to more than 500°F [Rowley 1982; Williams, et al. 1981]. The major materials problem seems to be elastomeric seals, however elastomers used by the shock absorber vendors are not disclosed. It is suggested that the GEM Y267 EPDM elastomer discussed in Section 6.2.1 may be useful in this application.

Drilling jars were also used extensively at the HDR project to assist in unsticking of drillpipe in the sharply deviated hole. Commercially available axially responsive HYDRA-JAR hydraulic drilling jars were modified by Houston Engineering, Inc. The modifications were not disclosed. These hydraulic jars successfully operated above 600°F.

Major fishing operations at temperatures above 400°F were successfully conducted using Type J rotary mechanical jars (Bowen Tools, Inc.). These jars performed reliably but suffered premature failure due to thermal failure of internal seals [Williams, et al. 1981].

7.5 Percussion Drills

Percussion drills use a stationary hydraulic or pneumatic drive unit to transmit rotation, static thrust, and cyclic impact to the bit. Percussion drilling has the following potential advantages over conventional rotary drilling:

- o High penetration rates through hard brittle rock such as is found in many geothermal formations,
- o Light weight on bit, resulting in a straighter hole, and
- o Compatability with air and foam drilling.

Percussion drill motors (hammers) are not normally designed to operate at geothermal temperatures: commercially available hammers contain O-rings and other elastomeric seals, valve tubes, and mountings which are vulnerable to thermal failure above 300°F.

In a laboratory test, commercially available tools drilled for three minutes with air at 350°F before the delrin valve tubes failed. Replacement of a valve tube with a custom-machined aluminum (6061-T6) tube allowed 52 minutes operation at 350°F before fatigue failure of the valve tube [Finger 1981b].

A hammer was modified by replacing the stock elastomeric parts with silicone rubber duplicates and replacing the valve tube with a polyimide (DuPont Vespal) counterpart. As in previous tests, the hammer was driven by compressed air. It operated for four hours at 350°F, followed by nine hours at 400°F. After an additional two hours at 450°F, the motor stopped. Examination showed that the retaining rim in the bit had been eroded by silica and alumina particles entrained in the air supply. It was concluded that with minor modifications, commercially available percussion drilling motors can operate at geothermal temperatures [Finger 1981b]. It should be noted however, that polyimides, used in the above laboratory test, are subject to catastrophic hydrolysis if exposed to water at elevated temperatures. Other materials for the valve tube would be required.

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8.0 LOGGING TOOLS

SUMMARY

This summary is a quick reference to the material discussed in Section 8. Please refer to the Section for caveats, qualifications, and references cited for the data presented below.

Logging tools are used to determine the thermal and hydrologic characteristics of a geothermal reservoir. They generally consist of electrical equipment encased in a waterproof and perhaps insulated housing attached by a cablehead to an electromechanical cable. This section considers only the cable, the cablehead, and the sealed package. Electrical instruments and electronic components are not considered. The goal is performance at 570°F for 1000 hours and at 435°F for 10,000 hours. Suggested materials for the various components of a geothermal tool are given in Table 8.0-1.

INTRODUCTION

A good understanding of the thermal and hydrologic characteristics of a geothermal reservoir is essential for the development of that source. Temperature, pressure, flow, and caliper measurements are considered the most important. These measurements can then be used in the estimation of other parameters such as porosity, permeability, geometry, continuity, etc.

A typical logging tool consists of electrical equipment encased in a waterproof and perhaps insulated housing attached to an electromechanical cable by a cablehead. Signals are usually sent from the instrument through the cable to the well surface.

To insure reliable data acquisition, all electrical components and conductors must be protected from the harsh environment. This protection includes a sheath on the cable, a sealed cablehead, and a sealed housing around the electrical instrument. This section considers only materials for

TABLE 8.0-1. SUMMARY OF SUGGESTED MATERIALS FOR GEOTHERMAL LOGGING TOOL COMPONENTS

Component	Suggested Material	Temperature Limit	Comments
<u>Cable</u>			
Conductors	Stranded Copper Silver-Coated		More conductive than nickel-coated, but more susceptible to high temperature and hydrogen sulfide
	Nickel-Coated		
Insulation	PFA Teflon	575°F	Water-permeable at high pressure, high electrical volume resistivity
	TFE Teflon	630°F	Available only as a powder, high electrical volume resistivity
	Tefzel Teflon	<500°F	
	FEP Teflon	<500°F	
Filler	PFA Teflon	500°F	Can be extruded
	TFE Teflon	600°F	Must be sintered
<u>Armor</u>			
Stranded Armor	Galvanized improved plow steel		Not satisfactory in hydrogen sulfide environment
	MP35N		Five times the resistivity of galvanized improved plow steel, not affected by hydrogen sulfide, costly
	Type 304 Stainless Steel		Fair resistance to hydrogen sulfide, extremely susceptible to chloride stress corrosion cracking if cold worked
Metal Sheath	Inconel - 625		Easy to work with
	Allegheny-Ludlum 29-4C		
	Ticodex 12		Extremely susceptible to chloride stress corrosion cracking if cold worked
	Type 304 Stainless Steel		
Outer Jacket	Polyetheretherketone (PEEK)		Impervious to water, under development
<u>Cablehead</u>			
Metals	Monel K-500	930°F	
	Inconel 625		
	Hastelloy (C, C-4, or C-276)		
Sandia NL Cablehead Grease	DuPont Krytox AD 143		Protects electrical terminations from brine

(Continued)

TABLE 8.0-1. SUMMARY OF SUGGESTED MATERIALS FOR GEOTHERMAL LOGGING TOOL COMPONENTS (Continued)

Component	Suggested Material	Temperature Limit	Comments
Lawrence Berkeley NL Cablehead Pressure Seal	Shell 826 Epoxy or equivalent	600°F	
Grease	Dow Corning Silicone Vacuum Grease		
Los Alamos NL Cablehead Epoxy	See above		
Grease	See above		
Elastomeric Parts	L'Garde Y267 EPDM	600°F	Graphite filler conducts electricity
Bulkhead Protector for Ceramic Connection	Viton		Nonconductive
Instrument Package			
Metals	TiCode 12	572°F	Uniform corrosion <0.5 mpy in 15,000 ppm chloride at 450°F. Resistant to pitting, crevice corrosion, stress corrosion cracking, intergranular corrosion, and weld corrosion.
	Ti-0.2 Pd	590°	
	AISI 310 - Annealed	590°-806°F	
	Allegheny Ludlum 6X, 29-4, 20-4-2		
	Hastelloy C-276	450°F	
	Inconel-625 TZM		
Adhesives	Ablebond 70-1		Conductive epoxy with 25 mΩ change at 572°F with long-term use
	Ablebond 70-2		Nonconductive
	Ablebond 71-1	660°F Continuous 930°F Intermittent	Silver-filled epoxy, volume resistivity 0.001Ω-cm at 660°F
	AbleFilm 506	300°F Continuous	Glass fabric, flexible epoxy for bonding materials with mismatched coefficients of expansion
	AbleFilm ECF 506		Silver-filled conductive epoxy, electrical resistance 0.005Ω, same usage as 506

(Continued)

TABLE 8.0-1. SUMMARY OF SUGGESTED MATERIALS FOR GEOTHERMAL LOGGING TOOL COMPONENTS (Continued)

Component	Suggested Material	Temperature Limit	Comments
Insulating Materials	Ablebond 71-2		High-temperature epoxy
	8254	525°F	Thick-film sealing glass
	Epotek H20E		Silver conductive adhesive for high temperature
	EA6	525°F	
	Shell 826	600°F	
	Asbestos Fibers		
	Calcium Silicate		
	Cellular Glass		
	Diatomaceous Silica		
	Expanded Perlite		
Insulating Packages	Glass Fibers		
	Mineral Fiber		
	Silica/Alumina Fibers		
Cylindrical Dewar Flask	Evacuated aluminum layers with glass fiber spacers	600°F	1/2" to 5" diameter, up to 12 feet long, heat sink used, by Vacuum Barrier Corp.
Dewar		500°F	By Southern Cryogenics
Thermoelectric Cooler		390°F	Maximum temperature differential 300°F at $Q_c = 0$

these protective components which contact the geothermal liquid or steam. Electrical instruments and electronic components are not considered. Listings of high temperature components and instruments are given by O'Rourke and Ransom [1979] and Baker [1975].

8.1 Materials Problems

A logging instrument for a high-temperature geothermal well may be expected to withstand temperatures of from 300° to 680°F, pressures of up to 7000 psi and corrosive well fluids which can include water, steam, brine, carbon dioxide, and hydrogen sulfide [Arnold, Bieg and Coquat 1980]. An instrument may be exposed to this environment for only a few minutes or indefinitely.

Electrical components are now being developed which can withstand 525°F for 100 hours and 435°F for 1000 hours. A subsequent goal is performance at 570°F for 1000 hours and at 435°F for 10,000 hours [Veneruso 1981a].

The electrical instrument itself may be shielded from the high pressure with the use of a tubular housing which can also withstand the corrosive environment. Special insulated flasks may protect the instrument from the intense heat. However, the cable and cablehead are sensitive to the effects of heat, pressure and hostile environment.

A logging cable consists of one or several conductors each surrounded by insulation. The conductor(s) are then encased in a metal armor. In a standard seven-conductor cable, the seven conductors are individually insulated; a wrap of insulation around this core of insulated conductors also serves as a bedding for the armor. In a coaxial cable, a center core of conductor fibers is wrapped with insulation and covered with a conducting shield, an outer jacket of insulation, and the armor wire.

The insulation should have good high temperature properties, a dielectric constant less than 30, reasonable mechanical properties, good processing characteristics, and resistance to water, steam, hydrocarbons, and other chemicals. It should have a 1 megahertz dissipation factor of less than 0.001 [Garne 1979].

The armor is usually several layers of high-strength wire. It must be able not only to support the weight of the downhole instrument and package, but also to withstand additional pulling if the instrument gets stuck in the well. Recent research indicates that a solid metal sheath may be used as armor instead of strands of wire.

Fillers and binders make the cable a more solid unit less susceptible to radial compression. Compression can lead to unacceptable elongation. These fillers should normally have good high-temperature properties. However, in some cables they are useful only during manufacture and can even be made of cotton.

The cablehead serves several functions. It (1) provides an interface for the high-strength mechanical connection as well as the electrical conduction path to the instrument, (2) seals the instrument from the high-pressure corrosive well fluids, (3) serves as a breaking point of calibrated tensile strength in case the instrument gets stuck in the well, and (4) provides "handles" for gripping the instrument package to get it out of the well if it does get stuck.

Identified materials problems with cableheads in geothermal wells are (1) corrosion of metals in contact with geothermal brine, (2) thermal degradation of the electrical termination and insulation system, and (3) thermal breakdown of elastomeric seals.

8.2 Evaluation of Available Materials and Components

The following is a summary of successful materials for the various components of a geothermal logging tool and, in cases where no successful material has been developed, a summary of relevant research.

8.2.1 Cable

Conductors

The conductors in a cable are almost always stranded copper. These copper strands are normally coated with nickel or silver to protect them from the high temperature corrosive environment. Silver-coated copper is more conductive than is nickel-coated, but is less able to withstand the high temperature [Kerr 1979]. Corrosion by hydrogen sulfide permeating through the insulation may be a significant problem with silver-coated conductors.

Insulation

Perfluoralkoxyethylene (PFA) and Tetrafluoroethylene (TFE) Teflons, both by DuPont, appear to be the best insulations commercially available for geothermal logging cable. TFE retains some of its strength even above its softening point of 620°F. Tefzel (ETFE - a copolymer of ethylene and tetrafluoroethylene) and FEP (fluorinated ethylene propylene) Teflons, also by DuPont, may also be used in some applications, but lose insulation resistance and/or deformation resistance at temperatures above 500°F [Garne 1979].

PFA is melt extrudable; TFE is available only as a powder. Therefore, the TFE can be applied only in a paste extrusion or as a film laminate. PFA is usable to 575°F, TFE to 630°F. These upper limits may be extended slightly at pressures above approximately 10,000 psi. PFA tends to cold flow more than does TFE, particularly near the upper temperature limit [Wagoner 1979]. Insulated Wire, a cable manufacturer in New York, has apparently developed a proprietary process for sintering Teflon [Dennis 1982].

PFA and TFE are attacked chemically by molten alkali and fluorinated hydrocarbons, neither of which is present in nature. They are immune to sodium chloride, calcium chloride, hydrogen sulfide, calcium carbonate and magnesium carbonate [Wagoner 1979].

The electrical volume resistivity for PFA and TFE is very high: greater than 10^{18} ohm-cm at 60°F. There is some evidence that PFA may deteriorate in the presence of water at high temperature and pressure. Under high pressure, water fills all the voids in the material and actually passes through it to the conductors. This water does not generally affect the electrical properties of the cable, but it can affect the cable terminals [Wagoner 1979]. An outer jacket to eliminate water infiltration is discussed later in this section. A summary of the characteristics of PFA, TFE, Tefzel and FEP is given as Table 8.2-1.

TABLE 8.2-1. MATERIALS FOR ELECTRICAL INSULATION FOR CABLES

	Teflon PFA	Teflon TFE	Tefzel	Teflon FEP
Melting Point, °F	572	617	520	525
Dielectric Constant	2.1	2.1	2.6	2.1
Dissipation Factor at 1 MHz	0.0004	0.0002	0.005	0.0007
Cost, \$/lb (1979)	15.00	9.00	10.00	7.50
Deformation at 500°F	Good	Fair	Good	Poor
Chemical Resistance	Excellent	Excellent	Excellent	Excellent
Processibility	Good	Needs Special Equipment	Good	Good

Source: Veneruso 1981b.

A TFE-insulated cable by Vector Cable Company was successfully field-tested for 20 hours at a peak temperature of 535°F and a typical temperature of 480°F [Coquat 1979a]. In laboratory tests, a TFE-insulated cable maintained an insulation resistance of at least 150 megohms per foot in a nine-hour test at 600°F, 10,000 psig, and 1350 lb tension in a 5 percent sodium chloride solution. The TFE lost its insulating capability at 630°F. A PFA-insulated cable withstood 500°F [Rose 1979].

A seven-conductor cable with PFA teflon coating on the conductors and TFE braids as armor bedding and filler has been tested by Los Alamos National Laboratory. The cable works at 600°F for a short time, then loses insulation resistance. It is considered satisfactory to 475°F [Dennis 1982].

In a U.S. Geological Survey experiment at 509°F, a cable insulated with PFA showed acceptable high temperature leak resistance, while a Tefzel - insulated cable did not [Hess 1979].

Insulated Wire has developed a coaxial cable which can function to 660°F and 2500 psi with no failure. This cable features a nickel-plated copper conductor and braid shield, TFE insulation and a jacket of cigarette-wrapped (lapped) sintered Teflon [Dennis 1982].

Filler

PFA and TFE Teflon are also used as filler material in the cable. TFE, which is available as tape, braid, matrix filler, etc., must be sintered in place. PFA can be extruded. TFE is apparently usable to 600°F, PFA to 500°F [Veneruso 1981b].

Armor

In most oil field applications galvanized improved plow steel is the material of choice for the standard stranded armor. This steel has a galvanizing weight of 0.5 oz./sq.ft. Galvanized steel is not satisfactory in a

hydrogen sulfide environment. However, MP35N (discussed in Section 4), a completely iron-free alloy, can be used [Wagoner 1979]. MP35N exhibits five times the resistivity of galvanized steel, but is much more costly [Garne 1979]. A summary of the characteristics of these armor materials and those of 304 stainless steel, a material which has fair resistance to hydrogen sulfide, is given as Table 8.2-2. Type 304 stainless steel, along with most other austenitic grades, is extremely susceptible to chloride stress corrosion cracking--even in dilute chlorides--if it is cold worked.

TABLE 8.2-2. MATERIALS FOR CABLE ARMOR

Material	Tensile Strength (psi)	Cost \$/lb (1979)	Resistivity $\mu\Omega/\text{cm}$	H ₂ S Resistance	Chloride Resistance
Galvanized Improved Plow Steel (GIPS)	270,000	0.50	20.1	Poor	Fair
MP35N	290,000	50.00	101	Excellent	Excellent
304 SS	280,000	2.50	72	Fair	Variable

^aHighly susceptible to chloride-scc in cold worked condition.
Source: Veneruso 1981b.

The use of a metal sheath as insulation for geothermal cable is being investigated by Halpen Engineering, Inc. Inconel-625 is considered the easiest to work with of the suitable materials. Others considered are Allegheny Ludlum 29-4C, Ticode 12, and 304 stainless steel, though Type 304 would have considerable risk of chloride-SCC. Four outer sheaths are formed, welded, and drawn in succession. Splices in the sheath are butt welded. A pin is used to make a mechanical joint in the copper core; an insulating sleeve assures alignment.

Short samples of metal sheath cable with several splices have shown no leakage at 10,000 psi, 600°F, and with a 100 psi tensile load [Veneruso 1981a].

Aerospace Research Corporation tested three 8-foot sections of the metal-sheath cable. One had four sheaths of Allegheny Ludlum 29-4C, another had 4 sheaths of Inconel-625, and the other had two sheaths of Inconel-625 and two of 304 SS. These cables were exposed to a 650°F, 5000 psig, 5 percent sodium chloride solution for nine hours, plus one hour warm-up. The samples were subjected to 1000 lb tension and one ampere load current continuously throughout the test. A helium leak test showed no leakage in any of the cables. The largest drop in insulated resistance was for the Inconel 625 sample, which went from 3.0×10^{11} ohms to 1.7×10^8 ohms [Aerospace 1980].

Tests by Sandia National Laboratories indicate that at 525°F the metal-sheath cable can withstand repeated flexures in passing over sheaths of 50-inch diameter as long as the cable tension does not exceed 1500 lb. Preliminary designs have been made of a "tractor puller" well entry system to largely eliminate tension on the cable as it tranverses the sheaves [Veneruso 1981c].

Outer Jacket

Insulated Wire has developed a material to keep moisture out of the cable. The material, polyetheretherketone (PEEK), has shown promise and will undergo further tests [Dennis 1982].

8.2.2 Cablehead

The metal parts of a cablehead should be made of corrosion-resistant materials. Metals which have been proposed for this use are Monel K-500, Inconel 625 and Hastelloy (grade not specified, most likely Hastelloy C, C-4, or C-276). The Monel K-500 can withstand temperatures up to 930°F in brine

solutions [Coquat 1979b]. More information on the corrosion of these alloys is given in Section 4. The use of other materials in a cablehead depends on its specific design.

Sandia National Laboratories Cablehead

In a design proposed by Sandia National Laboratories [Coquat 1979b], the electrical conductor is terminated to a metal/ceramic feed-through. The cavity surrounding the termination assembly is filled with Dupont Krytox AD143. This fluid has five important properties at 550°F: (1) electrical insulation, (2) chemical stability, (3) low water absorption, (4) strong wetting characteristics for all termination parts, and (5) density greater than that of water. The cavity filled with this fluid cannot be totally sealed from the geothermal brine, but since this insulating fluid is heavier than the geothermal brine and it wets the cavity parts, the brine cannot affect the electrical terminations.

Elastomeric seals or metal seals have been used to seal the cablehead to the tool. Elastomeric seals are discussed in Section 6.0. Metal seals require more careful handling, but a stainless-steel Conoseal can seal indefinitely at 930°F and 20,000 psi.

A 2-inch O.D. cablehead of the above design and with metal seals was developed by Sandia and Gearhart-Owen Industries, Inc. It was field-tested by Sandia to a peak temperature of 570°F with no leakage problems. No specific test data were available.

Lawrence Berkeley National Laboratory Cablehead

Lawrence Berkeley National Laboratories (LBNL) has designed an inexpensive 1.5-inch O.D. multiconductor cablehead to operate at temperatures up to 300°F [Solbau, Goranson and Benson 1981]. The body is machined from stainless steel. For low to moderate temperature applications, the cablehead

incorporates a pressure seal of Shell 826 Epoxy or its equivalent. If necessary, the seal can be removed with an electric drill, the cable reheaded and a new seal poured, even under field conditions.

The epoxy is said to have excellent corrosion, chemical and solvent resistance. The epoxy seal is adaptable to single- and multiconductor cables. Epoxy with an operating temperature of up to 600°F is available; high temperature epoxies are listed in Section 8.2.3.

The cablehead also incorporates a grease barrier. A high-temperature grease fills all the voids in the cablehead assembly to prevent the adverse effect of the brine on the support connections of the cable. Dow Corning Silicone Vacuum Grease or the equivalent is recommended for this use, with regreasing before each use. Dupont Krytox AD143 might also be attractive for this application.

According to LBNL, this cablehead has been successfully tested under a variety of operating conditions. No test results were available.

Los Alamos National Laboratory Cablehead

A cablehead by Los Alamos National Laboratory has been downhole for 80 days at 390°F and for several hours at 600°F with no leakage [Dennis 1982]. In this cablehead design, the cavity surrounding the termination assembly is partially filled with epoxy and the remainder is filled with DuPont Krytox oil to allow for expansion.

All elastomeric parts are L'Garde Y267 EPDM, considered good to 600°F, except the bulkhead protector for the ceramic connection. Viton was used for this protector because the graphite filler in the EPDM conducts electricity. Research is underway by L'Garde to develop a nonconductive EPDM.

8.2.3 Instrument Package

Metals

Several metals have already been suggested for use as cable armor and the body of the cablehead. The following is a more general discussion of metals which can withstand the downhole conditions in a geothermal well.

A list of metals suitable for use in downhole instrument packaging is given as Table 8.2-3. These metals survived testing at 450°F in 155,000 ppm chloride with uniform corrosion less than 0.5 mpy year. Resistance to pitting, crevice corrosion, stress corrosion cracking, intergranular corrosion, and good weld corrosion resistance were also considered. The test results indicated that TiCode 12 may be used up to 572°F, Ti-0.2Pd to 590°F, and annealed AISI 310 from 590°F to 806°F in a chloride environment [Ellis and Conover 1979]. In addition, MP35N and many other Ni-Cr-Mo alloys are viable candidates. These metals are discussed in Section 4.

TABLE 8.2-3. METALS SUGGESTED FOR GEOTHERMAL INSTRUMENTATION PACKAGE APPLICATIONS

AISI 310 (Annealed)
Allegheny Ludlum 6X, 29-4, 29-4-2
Hastelloy C-276
Inconel-625
TZM
Ti-0.2 Pd
TiCode 12

*Tests performed at 450°F in 155,000 ppm chloride. The above materials exhibited uniform corrosion less than 0.5 mpy. The materials exhibited resistance to pitting, crevice corrosion, stress corrosion cracking, intergranular corrosion, as well as good weld corrosion resistance.

Source: Veneruso 1981b.

Adhesives

Adhesives are used in the construction of downhole instruments and cableheads. Table 8.2-4 is a listing of adhesives with potential for downhole use. No test data was available; the characteristics given are from manufacturers' specifications.

Insulated Packages

Several insulating packages are available to protect the electronics in the instrument from the downhole temperatures. Table 8.2-5 is a listing of fibers which have been proposed for use as insulating material in such packages. Table 8.2-6 presents commercially available insulating packages. The information given in this table is from manufacturers' specifications. No use data on the packages are available, except for the Vacuum Barrier flask. Los Alamos has had one last for 12 hours at 525°F; the interior temperature reached 185°F. Heat sinks were used to maintain this interior temperature [Dennis 1982].

TABLE 8.2-5. THERMAL CONDUCTIVITIES OF SOME INSULATING MATERIALS AVAILABLE FOR GEOTHERMAL DOWNHOLE APPLICATIONS

Material	k at 600°F, Btu/hr·Ft·°F
Asbestos Fibers	0.042 to 0.055
Calcium Silicate	0.042 to 0.051
Cellular Glass	0.063
Diatomaceous Silica	0.039 to 0.068
Expanded Perlite	0.045
Glass Fibers	0.034
Mineral Fiber	0.038 to 0.056
Silica/Alumina Fibers	0.029 to 0.050

Source: Veneruso 1981b. Investigated by Woodward-Clyde Consultants.

TABLE 8.2-4. ADHESIVES SUGGESTED FOR GEOTHERMAL DOWNHOLE APPLICATIONS*

Manufacturer	Material	Comments
Ablestik Adhesive Co.	ABLEBOND 70-1	Conductive epoxy with a 25-m change at 572°F with long-term use
	ABLEBOND 70-2	Nonconductive adhesive tested for 200 hours at 570°F with a 11-lb force applied
	ABLEBOND 71-1	Silver-filled conductive epoxy for continuous use at 660°F and intermittent use at 930°F Volume Resistivity: 0.0001 -cm at 660°F
	ABLEFILM 506	Glass fabric, flexible epoxy for bonding materials with mismatched coefficients of expansion; for continuous usage at 300°F
	ABLEFILM ECF 506	Same usage as 506; silver-filled, conductive epoxy; for continuous operation at 300°F Electrical Resistance: 0.005
	ABLEBOND 71-2	High-temperature epoxy
DuPont	8254	Thick-film sealing glass for 525°F use
Epoxy Technology, Inc.	Epotek H20E	Silver conductive adhesive used for high-temperature applications
Hysol Division Dexter Corp.	EA6	Adhesive used in temperatures up to 525°F

*Characteristics taken from Manufacturers' specifications. No test data was available.

Source: Veneruso 1981b.

TABLE 8.2-6. INSULATING PACKAGES AVAILABLE FOR GEOTHERMAL DOWNHOLE APPLICATIONS

Manufacturer	Product	Specifications*
Vacuum Barrier Corp.	Insulating Package Cylindrical Dewar Flask	Insulation: Evacuated aluminum layers with glass fiber spacers External Temperature, Maximum: 600°F Length: Up to 12 feet Diameter: 1/2 inch to 5 inches Heat sink used
Southland Cryogenics	Dewars	Product: High-temperature Dewars built to cost requirements Sizes: Standard sizes in stock Temperature Range: Typically up to 500°F
Borg-Warner Thermoelectric	950 Series Thermoelectric Cooler	Temperature Range: Up to 390°F: for operation below 300°F, contact Borg-Warner engineers. Maximum Temperature Differential, T : 300°F at $Q_c = 0$ Maximum Heat Pumped by Module, Q_c : 17 to 174 Btu/hr for $T = 0$ Maximum Current: 6 amps Maximum Voltage: 1.5 to 15 volts Nominal Resistance: 0.15 to 1.20 Size, inches: 0.38 x 0.38 x 0.15 to 1.20 x 1.20 x 0.15

*These are manufacturers' specifications. No test data was available.

Source: Veneruso 1981b.

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SUMMARY

This summary is a quick reference to the material discussed in Section 9. Please refer to the Section for caveats, qualifications, and references cited for the data presented here.

Downhole production pumps allow production of pressurized, unflashed, single-phase liquid with minimal temperature drop compared to the reservoir. They also greatly reduce the number of wells required to supply the geothermal plant. The high cost of pulling a downhole pump, plus the expense of standby wells, dictate an acceptably long pump life.

Currently used downhole production pumps are either lineshaft pumps or electric submersible pumps. Downhole pumps in geothermal use may have to survive brine temperatures of at least 400°F with varying amounts of entrained matter. No pump has yet established a reputation for reliable performance.

A lineshaft pump is suspended in the well and is connected to its motor--at the wellhead--by the lineshaft, which is supported in a production tube by 150-200 lineshaft bearings. These bearings may be exposed to the geothermal fluid or they may be enclosed and lubricated with oil or treated, filtered water from the surface. These bearings are the biggest materials problem with lineshaft pumps. Currently, lineshaft pumps are limited to about 1000 feet.

An electric submersible pump is not restricted to the 1000-foot limit. The pump is connected to the motor by a seal section and to the surface by a power cable. The vulnerability of this cable to mechanical damage during pump installation and the potential failure of seals which protect the motor and electrical connections from intrusion of geothermal fluid are the most serious limitations of the submersible pump.

A third pump type, the downhole turbo pump, is in the development stages. If successful, it will combine the best features of the lineshaft and submersible pumps: the motor will be above-ground, yet there will be no lineshaft.

This section discusses both pump performance and component performance. Pump performance is summarized in Table 9.0-1; component performance in Table 9.0-2.

INTRODUCTION

High-capacity downhole production pumps have three major functions in geothermal power plant operations:

- o They allow production of pressurized, unflashed, single-phase liquid,
- o They allow production of geofluid with minimal temperature drop compared to the reservoir.
- o They may greatly reduce the number of wells required to supply the geothermal plant.

Preventing flashing in the wellbore prevents the formation of calcium carbonate plugs. In fact, binary plant designs call for maintaining pressure throughout the plant. Minimum temperature drop is also important in binary power plant design, though not so important for flashed-steam plants. The number of wells has a drastic effect on total plant cost, and may determine the economic viability of a geothermal project.

In the case of all planned binary power plants, and in the case of pumped flashed-steam plants, plant availability and capacity factors are critically dependent on reliable high-capacity downhole pumps with long

TABLE 9.0-1. SUMMARY OF TESTS OF DOWNHOLE PUMPS

Manufacturer	Type	Estimated Ambient Temperature (°F)	Setting Depth (ft)	Endurance (Hours)	Comments
Peerless	Lineshaft, enclosed bearings	325-360	500-900	600-4000	Bearing failures, pump which survived 4000 hours did not fail
Vertiline	Lineshaft, enclosed bearings	190	550	to 24000 total	
Centrilift	Electrical Submersible	275-300	1860-2021	to 114 Operating	Seal failures, damage to cablehead
REDA	Electric Submersible	275-360	620-1098	7900	Failure due to erosion of impeller. Degradation of cable insulation a secondary problem.

TABLE 9.0-2. SUMMARY OF TESTS OF DOWNHOLE PUMP COMPONENTS

Component	Suggested Material	Comments
Bowl and Impeller	Class 20 Cast iron	Works well in low-temperature applications
	Nickel-aluminum bronze	
Lineshaft Bearings	Carbon steel	Some serious corrosion problems
	Leaded red bronze (CA 836, CA 838, SAE 660 and similar alloys)	Susceptible to precipitation of scales which clog bearing clearances and to long-term hydrogen sulfide corrosion. Hardness approximately $RH_A 21$
	Graphite-impregnated Teflon	May lose strength above 325°F
	Type 316 Stainless Steel	
		Hardness (RH_A) Linear Coefficient of Thermal Expansion (10^{-6} in/in °C)
TiB ₂		86 9.7
Alumina (A-47)		87 9.8
TC-30		87 7.6
Si ₃ N ₄ (SN-501)		87 3.5
WC (55-A)		88.2 6.0
Shaft	Type 416 Stainless Steel	Initial hardness HRC 19-22, plasma-sprayed Tribaloy 700 increases hardness to HRC 47, nickel-chromium-boron-silicon alloy coating increases hardness to HRC 44.5 - 67.5
Packing	Grafoil ribbon (tight wrap)	Performs excellently at lower temperatures
	Graphite Filament yarn	Good in conjunction with grafoil
	TFE Molded Packing Sets	Performs excellently at lower temperatures if properly adjusted
Seals (see Section 6 for elastomers)	Nitinol (nickel-titanium alloy)	Mechanical memory: when heated to above transition temperature, it attempts to return to original shape; susceptible to crevice corrosion, pitting, and stress corrosion cracking

service lives. In addition, the high cost of pulling downhole pumps, plus the cost of standby wells to assure continuous brine supply, dictate an acceptably long pump life.

Although other technologies are being developed, lineshaft and submersible pumping systems are the only technologies for high-temperature geothermal brines that are at least semi-proven. Each type has its own advantages and limitations; the two types are likely to share the market on a reasonably equal basis in the near future.

The lineshaft pump consists of a downhole pump suspended in the well by the production tube. The pump is connected to its motor--located at the wellhead--by the lineshaft. The lineshaft is supported in the production tube by lineshaft bearings at five to ten foot intervals. The practical setting depth limit for lineshaft pumps is about 1000 feet.

The lineshaft bearings may be open--exposed to the geothermal fluid. More commonly they are enclosed and do not contact the geothermal fluid. Enclosed bearings may be lubricated with treated, filtered water pumped from the surface, or they may be oil lubricated.

The geothermal submersible electric pump consists of three modules suspended from the production tube in the geothermal well. The bottom most module is the electric motor, which is connected directly to the seal section (second module). The seal section connects the motor to the pump. The submersible electric pump's great advantage is that the motor is located close to the pump and no long lineshaft--with its failure-prone bearings--is required. Submersible electric pumps are therefore not restricted to the 1000 foot setting depth limitation of lineshaft pumps.

To date, Lineshaft systems have better consistency of performance, but, in addition to the depth limitation, are characteristically more difficult to install and repair.

Currently available downhole pump experience from geothermal operations is fragmentary and limited. Almost all downhole geothermal pump experience has been incidental to other project aims, and most experience is poorly documented. In addition, the downhole pump industry is extremely competitive, and closely restricts dissemination of information on details of pump design, and especially of pump failures.

Though there have been a few isolated successes and there are apparent solutions for the major "first generation" problems concerned with temperature and experience with installing and operating the pumps, no pump has established a reputation for reliable performance. And "second generation" problems, which would become apparent after an extended run time and which would be attributable primarily to the aggressive nature of the brine, have not yet been a concern.

Available domestic experience is insufficient for establishing a statistically valid geothermal pumping reliability (run life). Consequently, near-term reliability must be estimated by using considered engineering judgement in light of recent accomplishments toward solving first generation problems. Using this process, it is not unreasonable to expect that near-term lineshaft and submersible pumping systems will most likely provide average run lives of six to twelve months in applications up to about 365°F (185°C). Anticipating performance above this temperature is highly speculative, especially for submersible pumps where consistent performance for elastomerics and motor and cable insulation is critical.

9.1 Limiting Materials Problems

Table 9.1-1 summarizes the pertinent physical and chemical stresses likely to be encountered in high-temperature downwell pumping operations. Data on TSS were not available. If these data are representative of geothermal sources to be developed in the future, then half of all

TABLE 9.1-1. RANGE OF CONDITIONS LIKELY TO BE ENCOUNTERED BY EXISTING
AND NEAR-TERM DOWNWELL PUMPS

Parameter	Anticipated Range of Downwell Pump Conditions		
<u>Chemical Factors</u>			
pH	Most resources probably pH 5.5-6.5 below flash zone		
Cl	16-24,468 ppm (four resources above 10,000 ppm)	median ~1,230 ppm	mean ~3,754 ppm
CO ₂ (total)	36-5,000 ppm	median ~500 ppm	mean ~1,000 ppm
H ₂ S (total)	0.1-467 ppm (two resources above 100 ppm)	median ~2 ppm	mean ~30 ppm
NH ₃	<0.1-46 ppm	median ~0.9 ppm	mean ~7 ppm
SO ₄	8-12,222 ppm (only one resource above 325 ppm)	median ~73 ppm	mean = 105 ppm
TKS	80-38,000 ppm (four resources above 10,000 ppm)	median ~1,815 ppm	mean = 4,860
<u>Physical Factors</u>			
Temperature	Near-term pumps not expected for >400°F service. Most pumped high temperature resources anticipated to be less than 360°F.		
Depth	U.S. experience to date is ~350-2,020 feet settling depths.		

high-temperature pumps will handle fluids containing less than 1230 ppm chloride, 73 ppm sulfate, 500 ppm carbon dioxide, 2 ppm hydrogen sulfide, 0.9 ppm ammonia, and 1815 ppm TKS.

Lineshaft Pumps

Only those lineshaft pumps operating in resources at <320°F and 1500 ppm TKS have avoided serious problems. The lineshaft bearings are the most important single factor in the lifespan of a lineshaft pump: lineshaft bearing wear has been implicated as a failure/distress mode in every lineshaft pump which has failed in field trials.

The water with which these bearings are normally lubricated loses viscosity and therefore lubricating properties with increasing temperature. In the case of open bearing pumps, the lubricating brine may contain large amounts of dissolved solids. However, bearing scaling problems occur even when the bearings are enclosed and lubricated with filtered treated brine from the surface. Some pumps have enclosed bearings lubricated with oil from the surface, but this oil may foul heat exchangers and could damage injection formations.

Currently used bearings are either graphite impregnated Teflon or leaded red bronze. The Teflon bearings allow some compliance to lateral loading, but cannot survive at much above 320°F. The leaded red bronze bearings are susceptible to scaling, and any abrasive particles in the lubricating fluid will severely damage this medium-hard bearing material. A lineshaft pump typically requires 150 - 200 bearings to support the lineshaft. With currently used technology, high vibration, excessive bearing wear, and shaft failure are likely to occur in less than 1500 hours in high temperature pumping operations [Concoran 1981]. A good bearing material should have a hard surface to resist scoring by sand particles, it should have good frictional and wear properties, and it should be corrosion resistant.

Pump manufacturers have also expressed a real need for improved seals for geothermal application, especially for 1 3/8 to 9 inch diameter static flange seals. Rotating shaft seals may also be a problem. Other specific materials problems are wearing of the shaft and leaking of the shaft packing in the bearing housing.

Submersible Electric Pump

Electric submersible pumps are critically vulnerable to electrical failures. One obvious weak link is the power cable which extends from the wellhead to the motor. This cable is at high risk of mechanical damage during pump installation. Improved assembly and installation techniques have alleviated some of the cable problems, but not completely eliminated them. These problems seem to relate more to high temperature than to geothermal brine chemistry [Werner 1982].

Any intrusion of water into the pump motor can be expected to cause prompt failure; therefore, the motor-section seals are a major weak point. One set of seals is located in the pothead--where the power cable is connected to the motor. Repeated problems with this part have been reported.

The other vulnerable set of seals is in the seal section. The pump motor is filled with oil and normally operates at a temperature about 150°F higher than the surrounding well water. The principal function of the seal section is to allow the large volumetric expansion of the oil as the motor heats up from ambient temperature to more than 400°F, as well as the lesser expansions and contractions when the pump is cycled off and on. The seal section must accommodate oil expansion while preventing any water from entering the motor itself. Experience has shown this to be difficult in high temperature operations.

9.2 Pump Testing and Development

A number of field trials of geothermal pumps in high-temperature wells have occurred over the years, though these tests have been incidental to other projects. Results are summarized in Tables 9.2-1 and 9.2-2; a more detailed discussion of some trials is presented below.

The significant results of the pumping experience of each manufacturer can best be appreciated by considering all of that manufacturer's experiences as a case history. Pump experience within each case history can then be studied to identify the discoveries and modifications that were made to cope with the problems encountered. The significant discoveries and modifications are summarized in Table 9-2.3. Tables 9.2-1, 9.2-2, and 9.2-3 together demonstrate that problems have been encountered in the installation and/or operation of virtually every major component of the pumping systems.

The Department of Energy funded the construction of a skid-mounted Geothermal Pump Test Facility (GPTF) by LANL. This GPTF is designed to simulate the temperatures and pressures of a geothermal well, but does not simulate the chemistry of typical geothermal wells. The facility has been used by a number of downhole pump manufacturers, including Centrilift, TRW-REDA, Peerless Pumps, Kobe, and Sperry-Vickers. The results of these tests are covered by proprietary agreements.

A comprehensive study of the geothermal pump problem, State-of-the-Art Assessment of Geothermal Pump Reliability, is to be released by EPRI in Spring, 1983. This study considers fifty field trials, some of which are included here.

Lineshaft Pumps

A Peerless lineshaft pump performed successfully for more than 4,000 hours at Brady Hot Springs, Nevada in 1975. The pump delivered 100 gpm brine from 500 feet at 325°F and 135 psi. Total dissolved solids at the site were

TABLE 9.2-1. SAMPLING OF GEOTHERMAL LINESHAFT PUMP PERFORMANCES

Pump Description	Lineshaft Bearing Configuration	Resource	Estimated Ambient Temperature (°F)	Setting Depth (ft)	Endurance (hrs)	Cause of Failure
Peerless 100 gpm	Enclosed* Teflon-water Lubricated	Brady Hot Springs, NV	320	500	4000 (operating)	Did not Fail
Peerless 100 gpm	Enclosed* Teflon-Water Lubricated	Easte Mesa, CA	335	600-900	600-840 hrs (Several pumps)	Bearings Failed By Creep
Peerless 250 hp	--	Raft River, ID	355	802	1060 (operating)	Did not Fail But Tailshaft Bearing Worn Thin
Peerless 1100 gpm	Enclosed* Graphite Impregnated Teflon-Water Lubricated	East Mesa, CA	355	--	--	Bearings Scaled-Up
Peerless	Enclosed* SAE660 Bronze- Water Lubricated	East Mesa, CA	360	600-900	Ave. 1400	Bearings Scaled-Up
Peerless	Open- Unspecified Material	Heber, CA	360-390	--	Brief	Bearings Scaled Up
Worthington 200 hp	Open-CA836 Bronze	Warm Springs, MT	170	830	50	Shaft Unscrewed Bearing Damage Result of Above
Vertiline Model 10RL 100 hp	Enclosed* CA838 Bronze-Oil Lubricated	Klamath Falls, OR	190	550	24000 hrs total 4900 hrs rotating 97600 Start-Stop	Impeller Locking Keys Fell Out Minor Corrosion

--Data not available

*Bearings are lubricated from the surface and do not contact geothermal brine.

Data Sources: Nichols and Malgieri 1978; Stiger 1980; McAlpin 1981; Anliker and Ellis 1981; Shannon 1981.

TABLE 9.2-2. SAMPLING OF GEOTHERMAL ELECTRIC SUBMERSIBLE PUMP PERFORMANCES

Pump Description	Resource	Estimated Ambient Temperature (°F)	Setting Depth (ft)	Endurance (hrs)	Cause of Failure
Centrilift Type 10-JB1300 1 400 hp motor 1 250 hp motor	Raft River, ID	275-300	2021	114 (operating) 2880 (total)	Seal Failure Nitrile Bushing Failure
Centrilift Type 11JA1100 1 400 hp motor 1 100 hp motor	Raft River, ID	275-300	1860	Zero	Damaged Cable Head
Centrilift Type 10JB1300 1 400 hp motor 1 250 hp motor	Raft River, ID	275-300	2021	8.5 (operating)	Upper Seal Failed
REDA 80 hp	East Mesa, CA Well 6-2	326	----	4150 (operating) Continuous	Burned Connection In 2 Motor
REDA 80 hp	East Mesa, CA Well 6-2	350-360	----	<2100	Cable Head Failures
REDA (custom)* 80 hp	East Mesa, CA Well 6-2	350-360	----	7900	Eroded Impellers
REDA Type 8M675 2 160 hp motors	Raft River, ID	275-300	1000	568 (operating) 5700 (total)	Did Not Fail
REDA Type 8M675 2 160 hp motors	Raft River, ID	275-300	773	1359 (operating) 8100 (total)	Power Cable Shorted
REDA Type 4n1500 2 160 hp motors	Raft River, ID	275-300	620	112 (operating) 4400 (total)	Did Not Fail
REDA Type 8M675 2 160 hp motors	Raft River, ID	275-300	1098	85 (operating) 2570 (total)	Motors "Burnt" Cable Shorted

*Pressurized with oil from the surface

Sources: LBNL 1981; Nichols, Olander, and Lobach 1980; Nichols and
Malgieri 1978; Stiger 1980; Werner 1981; Whitbeck 1981.

TABLE 9.2-3. SIGNIFICANT HIGH-TEMPERATURE GEOTHERMAL PUMPING EXPERIENCES

Pump Manufacturer	Resource	Problems, Improvements, Modifications, and Other Significant Events
Peerless (Lineshaft)	Brady Hot Springs and Mammoth Lake	<ul style="list-style-type: none"> o Identified maximum temperature threshold for teflon/graphite bearings to be approximately 320°F. o Selected enclosed lineshaft lubrication system.
	East Mesa	<ul style="list-style-type: none"> o Experienced problems with enclosed brine lubrication: changed to enclosed water lubrication with water soluble oil dosages.
	East Mesa	<ul style="list-style-type: none"> o Experienced repeated lineshaft bearing failure due to excessive vibration: modified lineshaft bearing alloy, increased lineshaft diameter, and reduced lineshaft bearing spacing. These corrections apparently successful in reducing lineshaft vibration.
	Raft River	<ul style="list-style-type: none"> o Identified that enclosed, treated brine lube apparently adequate for lineshaft lubrication at this resource. Confirmed ~320°F ceiling temperature for teflon/graphite bearings.
	Heber	<ul style="list-style-type: none"> o Experienced lineshaft vibration with significant localized shaft wear.
Centrilift-Hughes (Submersible)	Raft River	<ul style="list-style-type: none"> o Corrected use of unsuitable material for lower end pump bushing. o Identified need for more extensive quality control and inspection for pumps to be placed in geothermal service. o Recognized need for increased care in handling and installation. o Developed technique to correct failures caused by deposition of motor epoxy (insulation) particles into rotating motor members.
	Pump Test Facility	<ul style="list-style-type: none"> o Experienced repeated water intrusion due to pothead leaks: improved pothead design. o Identified and corrected inadequate pothead insulation material. o Selected lubrication oil with suitable lubricity at elevated temperatures.
	Pump Test Facility	<ul style="list-style-type: none"> o Experienced seal assembly problems: modified elastomers to correct. o Corrected inadequate thrust bearing runner material.
	Pump Test Facility	

Sources: Jacobson and Ishii 1981; Nichols and Malgieri 1978; and personal communication with Barber - Nichols Engineering, Centrilift - Hughes, Inc., Chevron Resources Co., EG&G Idaho, Inc., Kobe, Inc., Magma Power Co., Peerless Pump Co., Republic Geothermal, Inc., and TRW - Reda Pumps.

3,200 ppm. The composition of this brine was detailed in Table 3.1-5. Enclosed Teflon bearings were lubricated with filtered brine from the surface. The same pump design failed due to extrusion of the Teflon bearings when operated in an East Mesa well producing 335°-355°F brine [Nichols and Malgieri 1978]. This indicates that 325°F is about the upper temperature limit for Teflon lineshaft bearings.

Two 250 hp Peerless pumps are currently operational at 980 and 996 feet at Raft River, ID (see Table 4.1-1 for brine composition), but have not been run since June, 1982. They have logged 1340 and 1485 hours. A third pump at 980 feet ran without failure for 1643 hours before being pulled for other reasons. No inspection report was available.

Peerless emphasizes that the cleaner and cooler the water which lubricates the bearing the longer they will wear. An auxiliary pump can be used to provide this cleaner, cooler water. An auxiliary pump would lubricate only the top bearing of the upper bowl in the tail-end pump assembly, leaving the other bearings in the bowl, including the tail bearing, to be lubricated by hot brine. Peerless' experience shows, however, that the bulk of the bearing wear is in the upper-end bearing [Marshall and Van Treek 1981].

A Vertiline centrifugal pump, Model 10RL, operated for 24000 hours in 190°F geothermal fluid at Klamath Falls, OR. Table 2.2-4 gives the fluid chemistry. The 14-stage pump was powered by a 100 hp motor and was set at 550 feet. The rated capacity of the pump was 500 gpm, but actual production did not exceed 350 gpm.

The pump apparently failed for purely mechanical (design) reasons and the materials used were judged to be suitable for the application. The materials of construction were as follows:

Pump bowls	Gray cast iron (ASTM A48 Class 20)
Bowl bearing	Leaded red bronze (ASTM E584 Alloy C83800)
Impellers	Leaded red bronze (ASTM B584 Alloy C83800)
Impeller collet	Type 316 stainless steel

The leaded red bronze showed some pitting; the Type 316 did not. Because of the performance of the collets, Type 316 stainless steel was recommended as an alternate bearing material. Another alternative would be a nickel-free aluminum bronze such as ASTM B148 Alloy C95200 or ASTM B148 Alloy C95800 [Anliker and Ellis 1981].

A 200 hp Worthington lineshaft pump operated for 50 hours in a Warm Springs, MT, geothermal well. The pump was set at 830 feet and produced 170°F water containing 5 ppm chloride, 2 ppm bicarbonate, 0.5 ppm hydrogen sulfide, and 162 ppm sulfate. The fluid pH was 6.3.

Unlike the other pumps in Table 9.1-1, this pump had open bearings. After 50 hours of operation, the pump developed severe vibration and was pulled. There was serious damage to the leaded red bronze lineshaft bearings, but this damage resulted from the failure, rather than causing it. The pump vendor attributed failure to unscrewing of the lineshaft [McAlpin 1981].

Submersible Pumps

The REDA submersible pump is a multistage centrifugal pump driven by a special high slenderness ratio hermetically sealed electric motor running in oil. The pump has K-Monel shafting, Ni-resist impellers and diffusers, and a carbon-steel housing. Journal bearings are used only at the top and bottom of the pump shaft; these bearings are made of bronze and are lubricated by the

geothermal fluid. The motors are of standard construction. The power cable has solid copper conductors, EPDM coating on the conductors, lead sheathing, and a galvanized steel armor [Scott 1982].

Several 160 hp REDA pumps have been tested at the Raft River 5MW Geothermal Binary Project. The brine at Raft River has a TDS of 1,400 to 2,700 ppm; downhole temperature is approximately 275°-300°F. The chemistry of this resource was discussed in table 4.2-1.

One REDA pump, Type 8M675, operated for 1,359 hours at 733.3 feet until its power cable shorted because of mechanical damage. It was in the well for 8100 hours prior to failure and was started up 19 times. The failure was attributed to a poor cable splice [Stiger 1980; Scott 1982].

At the East Mesa 5MW pilot plant, an 80 hp REDA pump delivered 333°F, 2,000 ppm TDS brine for five months, 20 days. Brine produced by this pump contained around 1100 ppm carbon dioxide species, about half of which is free carbon dioxide. The brine also contained around 500 ppm chloride and had a pH of 5.5-6.5. Failure was due to a burned lead in the motor; it was determined that this failure was due to multiple restart attempts in a short time period, not to the geothermal environment. However, several other similar pumps have subsequently failed after less than three months because of electrical problems, especially brine infiltration into the motors through the seals and cable connections, and failure of the cablehead -- where the power cable passes through the wellhead assembly.

Another REDA pump of essentially the same construction, but with proprietary improvements, produced 350°-360°F brine for 7900 hours. This represents the longest successful run for a submersible pump in high-temperature geothermal service. In this pump, the motor was in an oil-filled housing pressurized from the surface, therefore the seal section was simplified. The cable was from Lawrence Cable [Werner 1982; Scott 1982].

Centrilift centrifugal submersible pumps were tested at the Raft River installation in 1979-1980 [Vandevier 1982; Stiger 1980]. These pumps were constructed of Ni-resist Type 1 Casting, Monel K-500 Shafting, 4140 barstock pieces, and mild steel motor and seal sections. There were no corrosion problems, but the 275-300°F temperature caused problems, especially with the electrical lead to the motor and the seal of the motor section. One pump ran 114 hours at 2,021 feet; another survived more than 815 hours at 1,042 feet.

An improved version of the above pump was tested at East Mesa, California. Details of the test are not available. One pump did run at 325°F for 30-40 days; another ran at 375°F for a short time [Vandevier 1982].

Anderson and Worthington Downhole Turbo Pump

The downhole turbopump is a close-coupled, hydraulic-turbine driven, single stage pump being developed by J.H. Anderson, Inc., and Worthington Pump Corporation. According to the developer's literature [Concoran 1981], the pump body is packed-off against the production casing. Geothermal fluid enters the pump section and is directed up the well casing to the surface. At the surface, a portion of the produced brine is tapped off, further pressurized by a surface pump, and directed down the pump support tube to the turbine inlet. The downflowing pressurized brine passes through the turbine, driving the pump, and is discharged into the brine leaving the pump section.

The pressure differential across the pump impeller gives rise to a downward axial thrust of the rotor. On the other hand, the pressure drop across the power turbine stages produces an upward thrust. The resultant upward thrust is partially compensated for by a balance piston. What remains is absorbed by the hydrodynamic thrust bearing. Filtered and cooled brine from the discharge of the surface pump is used to lubricate all bearings. Appropriate bushing type seals maintain the pump impeller. Lubricating water is supplied through a small separate feed line.

The casing, housing and boltings of the pump are of nodular iron and carbon steel. The pump impeller, turbine rotor, shafting, nozzles and impeller eye and shaft seals are of 17-4 PH. Static seals are of Viton. Bolting and fittings are of carbon steel.

A 1,400 gpm prototype has been tested at room temperature over a flow range of 750 gpm and at speeds of up to 12,000 rpm. The overall pump efficiency was 60 to 70 percent during a two-day run. Additional factory testing at temperatures to 350°F and field evaluations are underway.

If successful, this pump design will combine the best features of the lineshaft and electric submersible pumps. The electric motor will be above ground, eliminating the thermal and geometric problems of the submersible electric motor. However, there will be no lineshaft with its associated problems.

Weir Downhole Turbo Pump

Weir Pumps Ltd., of Glasgow, Scotland, has developed a close-coupled, hydraulically-driven downhole pump for oil or brine production at temperatures up to 390°F [Sheil, 1982]. Hydraulic power is supplied by topside equipment such as positive displacement or centrifugal pumps driven by electric motors, lightweight gas turbines, or diesel engines. A 320 hp unit has reportedly completed a test run of 2500 operating hours and 450 start-stops with no significant wear, performance loss, or performance problems. The unit was set at 2000 feet in a 170°F geothermal resource. Flow rate was varied from about 210 gpm to 2100 gpm.

The manufacturer estimates a run life of over one year in high-temperature geothermal resources up to 390°F with few, if any, refinements. If the unit can meet this expectation it could be considered a viable alternative to the lineshaft and submersible pumps. Its simplicity could be an asset.

Class 20 cast iron appears to be the generally accepted material for the bowl and impeller in lineshaft pumps. This material has worked well in low-temperature geothermal brine. Nickel-aluminum bronze and carbon steel have also been used successfully, although there can be significant corrosion of the carbon steel [Nichols and Malgieri 1978].

Lineshaft bearings have normally been made of Alloy 838 leaded red bronze or graphite-impregnated Teflon. The Teflon appears to lose strength at temperatures above 320°F. Leaded red bronze bearings are usable up to 330°F with Type 416 shaft and filtered fresh water lubrication if the calcium concentration is kept low enough to prevent scaling of the bearings. Failsafe softener operation is required. Corrosion by hydrogen sulfide may also pose a longer term problem for the leaded red bronze bearings.

Table 9.3-1 summarizes standard materials used in lineshaft and submersible pumps. Elastomeric materials resistant to brine and oil at temperatures of 500°F are discussed in Section 6. Some of these materials may be useful for seal and insulation components.

Lineshaft Pump Bearing/Shaft Combinations

Solar Turbines International is conducting tests to select materials for bearings/shafts combinations for geothermal downhole lineshaft pumps. These tests are run on test rigs at simulated downhole conditions of temperature and pressure, with clean water simulating operation of enclosed, water-lubricated bearings.

Temperature and pressure were initially kept at 365°F and 190 psig, but were reduced to 200°F and 8 psig after problems with the shaft packing material in the bearing housing. Because these changes affected the viscosity of the lubricating brine, the load was changed to maintain the initial minimum film thickness and position and the maximum film pressure as constants. It

TABLE 9.3-1. STANDARD MATERIALS USED IN LINESHAFT
AND SUBMERSIBLE PUMPING SYSTEMS

Pump Component	Lineshaft Pumps Peerless ¹	Submersible Pumps	
		Centrilift	Reda
Motor Insulation	NA ²	Epoxy ³	Varnish ³
Bowls/Diffusers	Cast Iron	Ni-Resist	Ni-Resist
Impellers	Cast Iron	Ni-Resist	Ni-Resist
Pump Shaft	316 Stainless Steel	K Monel	K Monel
Pump Bowl Bearings	Bronze	Bronze	Bronze
Production Tubine	Carbon Steel	Carbon Steel	Carbon Steel
Lubrication Column	Carbon Steel	NA	NA
Lineshaft	1040 Steel	NA	NA
Lineshaft Bearings	SAE 67 Bronze Graphite-impregnated Teflon	NA	NA
Cable Insulation	NA	CL-81 ⁵	Redared ⁴

¹Recent East Mesa experience using enclosed oil-lubricated lineshaft

²NA = not applicable

³Specific formulations not disclosed

⁴Reda designation: insulation material not reported

⁵A proprietary EPDM (ethylene propylene terpolymor)

Source: Personal communications with individual manufacturers.

was assumed that with these constants, bearing wear should be similar to that at the initial conditions [Solar 1981]. This assumption may be correct if corrosion and solids precipitation are not a problem.

Characteristics of the bearing materials being tested are presented in Table 9.3-2a. Some of the more promising materials are also the more expensive, but the cost may be compensated for by a longer operating life.

One shaft material, 416 stainless steel with a hardness of HRC 19-22, was used in all shaft tests. Two coatings, plasma-sprayed Tribaloy 700 and a nickel-chromium-boron-silicon alloy, were applied to the shaft to assess their performances and to assess the influence of journal surface hardness on bearing and shaft wear. Shaft characteristics are shown in Table 9.3-2b.

Table 9.3-3 compares the wear results of the standard SAE660 bronze bearing/416SS shaft combination with the top two performers in this study. These two alternatives show an 8- to 12-fold improvement in overall wear resistance when lubricated with filtered water. They were rapidly worn when abrasive particulates were added to the lubricant, illustrating the need for excellent lubricating water quality control in geothermal pumping operations. Because the test conditions did not simulate the thermochemical stress of downwell operation the results should be applied with caution. In addition to the hard bearing materials, two L'Garde elastomers were tested as compliant bearings. Both were equally good at 200°F, but failed rapidly at 365°F [Hosang 1982].

The shaft packing in the bearing housing leaked excessively and unpredictably during the early part of the test at initial temperature and pressure. Because of this problem, several types of packing material were tested. Results of these tests are shown in Table 9.3-4.

TABLE 9.3-2a. BEARING/SHAFT STUDY: BEARING MATERIALS

	SAE 660 Bronze	TiB ₂	Alumina (A-47)	TC-30	Si ₃ N ₄ (SN-501)	WC (55-A)
Source	Peerless Pumps	Solar	Kyocera	Kyocera	Kyocera	GE (Carbology Mining Products)
Composition	83Cu-75n-7Pb-32n	TiB ₂ coating on Ti6Al4V	99% pure Al ₂ O ₃	Ti carbide Ti nitride Cermet W-Mo- Ni-Co binder	Sintered Si ₃ N ₄	WC 13Co-binder
Hardness	RH _A 21.5	RH _A 86 Knoops 3300	Vickers 1650 RH _A 87*	Vickers 1650 RH _A 87*	RH _A 87*	RH _A 88.2
Surface Finish	15-25 μm*	20 μm*	5-8 μm*	1.5 μm*	16 μm*	1-2 μm
Linear Coeff. of Thermal Exp.	18 x 10 ⁻⁶ in/in °C	9.7 x 10 ⁻⁶ in/in °C (Ti)	6.8 x 10 ⁻⁶ in/in °C	7.6 x 10 ⁻⁶ in/in °C	3.5 x 10 ⁻⁶ in/in °C	6.0 x 10 ⁻⁶ in/in °C
Appearance (color)	Bronze	Light gray	Dense white	Dense metallic	Dense, dark gray	Dark gray
Cost	\$20/ea	N/A	N/A	500 pc \$215 ea 1000 pc \$200 ea 2000 pc \$190 ea	500 pc \$140 ea 1000 pc \$130 ea 2000 pc \$120 ea	\$92.30 ea
Other Comments	Baseline Material Bulk density 8.0	Solid coating process - sprayed then fired in an inert atm for 4 hr 215°F 0.5 mils thick	95.7% theo- retical den- sity Bulk density 3.82*	EDM machinable. Mirror surface finish is a natural result of manufacturing process. Bulk Density 6.0	Bulk density 3.3	Bulk density 14.2

*Measured values
N/A = Not available
Source: Solar 1981

TABLE 9.3-2b. BEARING/SHAFT STUDY: SHAFT MATERIALS

	416SS	Tribaloy T-700 Coating on 416SS	Ni-Cr-B-Si Coating on 416 SS
Source	Castle Metals San Diego, CA	Flame Spray, Inc. San Diego, CA	Solar
Composition	Nominal 0.15 C (max) 1.25 Mn (max) 1.00 Si (max) 12-14 Cr 0.15 S (min) Fe (balance)	Ni - 50% Mo - 32% Si - 3% Cr - 15%	Ni - 86% Cr - 9.5% Si - 2.5% B - 1.5% Al - 0.5%
Hardness	R _c 19-22* (15N - 70.5)	Vickers - 470* (R _c - 47)	Vickers 440 with particles up to Vickers 920* (R _c 44.5 to 67.5) Sonadur - RC68*
Surface Finish	16 μin. or better	16 μin. or better	16 μin. or better
Spray Parameters	Not applicable	- Flame sprayed 8-10 mils thick - Porosity: <8% - Plasma arc voltage: 70V - Plasma arc current: 500A - Argon hydrogen plasma gas - Argon carrier gas - Air cooling - Target nozzle distance: 4.5 in. nom - Target velocity: 60-120 sfm - Bond coat: nickel base	- Flame sprayed 8-10 mils thick - Porosity: 5% - Plasma arc voltage: 50V - Plasma arc current: 400A - Argon hydrogen plasma gas - Argon carrier gas - Air cooling - Substrate Temp: 250°F - Target nozzle distance: 4 in. nom - Target velocity: 50 sfm - Base coat: 89.5 Ni - 5.5 Al - 5 Mo

*Measured values
Source: Solar 1981

TABLE 9.3-3. BEARING/SHAFT STUDY: RESULTS
(STANDARD COMBINATION AND TWO BEST PERFORMERS)

<u>Materials</u> <u>Bearing</u> <u>Shaft</u>	<u>Run</u> <u>Duration</u> (hrs)	<u>Test Results</u>	
		<u>Wear</u> (mils)	<u>Wear Rate</u> (mpy)
<u>Water Lubricant</u>			
SAE660	650	9	121
416SS	650	14	189
WC 55-A	750	1	12
Ni-Cr-Si-boride ^a	750	1	12
TC-30	650	0.2	2.7
T-700 ^a	650	2.5	34
<u>Water Lubricant plus Abrasive Grit</u>			
WC 55-A	61	0.2	29
Ni-Cr-Si-boride	61	6	862
TC-30	61	0.8	115
T-700	61	20.5	2944

^a hard facing on 416SS shaft

Notes: 1) See Tables 9.2a and b for details about these materials.

2) Test conditions designed to simulate the physiomechanical stresses due to operation at 190 psig and 365°F, but did not simulate the thermochemical stresses of actual geothermal operation.

Source: Hosang 1982

TABLE 9.3-4. PACKING MATERIALS USED IN BEARING TEST MACHINE

Material ^a	Designation	Rating ^b	Comments
Grafoil ribbon (tight wrap)	G6396	Good	Performs excellently at lower temperatures
Grafoil ribbon (loose wrap)	G6396	Poor	Completely inadequate at high pressure (not tested at low pressure)
Graphite filament yarn	1625GF	Fair	Good in conjunction with Grafoil
Teflon braided yarn	C-1040	Poor	Leaked uncontrollably even at low pressure
TFF molded packing sets	CVH Size 1678		If adjusted correctly, per- forms excellently at lower temperatures (not yet tested at high temperatures)
Jacketed "super- seal" plastic packing	Superseal 6J	Fair-Poor	Hardened after exposure to brine

^aAll packing material supplied by John Crane

^bExcellent - Very little leakage, little or no adjustment necessary
 Good - Little leakage, occasional adjustment necessary
 Fair - Controllable leakage if adjusted frequently
 Poor - Virtually uncontrollable leakage

Source: Solar 1981

Nitinol Shape Memory Alloy Seals

Rockwell International [Friske and Schwartzbart 1982] has tested the nickel-titanium alloy Nitinol for possible use as a pump seal. This alloy has a mechanical memory: when heated to temperatures above its transition temperature it "remembers" its initial shape and attempts to return to it. The force exerted as the alloy changes shape can be used to initiate and/or maintain the seal.

Some of the more pertinent characteristics of Nitinol are given in Table 9.3-5. Though thermal expansion is connected with the shape memory effect, a value of $5.36 \times 10^{-6}/^{\circ}\text{F}$ may be used for comparative purposes. Mechanical properties are sensitive to prior processing, heat treatment and composition. In general, the room temperature tensile strength is 110 to 140 ksi and yield strength 30 to 80 ksi.

A corrosion test at the East Mesa (California) Geothermal Component Test Facility showed corrosion rates to be 0.01 to 0.21 mils/year. During the test the alloy was exposed for 25 days to hot-flow conditions of 300° to 310°F, 100 to 105 psi and 10 gal/min. flow. Total exposure time was 42 days. By comparison, the corrosion rates of Type 304 stainless steel coupons were two orders of magnitude higher than that of the Nitinol; neoprene and Viton elastomeric o-rings were severely degraded. However, the Nitinol specimens did indicate susceptibility to crevice corrosion, pitting, and stress corrosion cracking.

TABLE 9.3-5. PHYSICAL PROPERTIES OF NITINOL

Physical Property	Value
Melting point	2327°F
Density	6.5 gm/cu. cm
RT electrical resistivity	70 ohm-cm
RT elastic modulus	12×10^{-6} psi
Poisson's ratio	0.3
Hardness	HRC 30-40
Oxidation resistance	Excellent, below 932°F
Hydrogen absorption	Will absorb at high pressures below 932°F

Source: Friske and Schwartzbart 1982

A second corrosion test, conducted by TRW-REDA personnel at the Magnolia, Arkansas, test facility, showed corrosion rates of 0.08 to 0.11 mils/year with no visible corrosion. In these tests the alloy was exposed for 68 days at 209°F to a hydrogen sulfide-saturated geothermal brine and to a laboratory test fluid of similar composition except that it contained no hydrogen sulfide. Also, a 20-day test in carbon dioxide-saturated water in a Texas oil well showed no visible corrosion.

The application of a soft coating on the Nitinol for sealing rough surfaces and hard coatings for wear resistance was studied. Copper and nickel were successfully electroplated, but the plating of chromium from a conventional chrome bath was unsuccessful. Tests with nitrogen gas indicated that a seal design with a flattoothed cross section is superior to a circular design.

Nitinol flange face seals and pump shaft seals have been designed, fabricated and tested. Such seals can generate sealing forces of 30,000 psi. Demonstration tests have shown that the shape memory effect can generate and

maintain a leak-tight seal in the geothermal environment--synthetic geothermal brine at 500°F and 1500 psid--for more than ten days. One toothed-design seal was pressurized to 4200 psid in 600°F water without leaking. Seals have been tested in bench fixtures at Sperry-Vickers, L'Garde, and Kobe. All tests yielded successful results after initial adjustments. Leaking after cool-down was noted in a number of cases [Friske and Schwartzbart 1982].

Because they have not been used in any geothermal pump, the impact of this new technology is difficult to quantify. Available data suggests that these seals will be a significant improvement both in terms of ceiling temperature and consistency of performance as compared to elastomeric counterparts. Further testing will be required to verify the usefulness of these seals in geothermal applications.

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