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INFORMAL REPORT

SHAPE MEMORY ALLOY SEALS
FOR
GEOTHERMAL APPLICATIONS.
FINAL REPORT

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for

Brookhaven National Laboratory

under Contracts 509927-S and 546251-S

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.

Under Contract No. DE-AC02-76CH00016 with the
U.S. Department of Energy

Rockwell International
Energy Systems Group

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**SHAPE MEMORY ALLOY SEALS
FOR
GEOTHERMAL APPLICATIONS
FINAL REPORT**

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ABSTRACT

The Energy Systems Group of Rockwell International, under contract to Brookhaven National Laboratory, is developing a novel temperature-actuated seal for geothermal applications. This program uses the shape memory property of nickel-titanium (Nitinol) alloys to achieve an improved seal in geothermal downhole pumps. This document reports the technical progress made during the contract periods of April 1980 through March 1981, under Contract 509927-S, and June 1981 through May 1982, under Contract 546251-S.

Nitinol flange face seals and pump shaft seals have been designed, fabricated, and tested. It has been demonstrated that the shape memory effect of Nitinol alloys can be utilized to activate and maintain a leaktight seal in geothermal environments.

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I. SUMMARY

Rockwell International's Energy Systems Group, under contract to Brookhaven National Laboratory, has completed a 2-year program to develop a novel temperature-actuated seal concept for geothermal applications. This seal concept uses the unique properties of a shape memory alloy (Nitinol) to perform the sealing function. A total of 13 Nitinol seals were fabricated under this program. Of these, four face seals were designed, fabricated, and tested during the first year by Raychem Corporation of Menlo Park, California. During the second year, nine seals, including both face and shaft types, were designed and fabricated by Energy Systems Group. Face-type seals, 2-1/4-in. diameter and 6-in. diameter, were tested by L'Garde, Inc., of Newport Beach, California, and Sperry-Vickers of Jackson, Mississippi, respectively. Shaft seals, 1-1/4-in. diameter, were tested by Kobe Pump of Huntington Park, California. These seal demonstration tests have shown that shape memory alloy seals can be actuated by temperature to develop a leaktight seal at pressures exceeding 4000 psi at 260°C (500°F). Supporting material tests have shown that the Nitinol alloys have a high resistance to corrosion in geothermal brine environments.

II. INTRODUCTION

The Energy Systems Group (ESG) of Rockwell International, under contract to Brookhaven National Laboratory (BNL), has completed a 2-year program to develop a novel temperature-actuated seal concept for geothermal applications. The Department of Energy (DOE) has been concerned for some time with the fact that the state of the art in seal technology constitutes a significant limitation in the exploitation of geothermal energy. Current seal materials are polymeric or elastomeric; while these have been improved by DOE-funded research, they still fall short of having a long enough life in the service environments at certain temperatures.

ESG's seal concept uses the unique properties of a "memory alloy" that will be fabricated in the cross-sectional shape and dimensions required to perform the desired sealing function. The memory alloy part can be cold formed, stretched, or otherwise shaped as desired to facilitate assembly of the units to be joined. When heated through a critical temperature range, the memory alloy is triggered to return to its original shape. As the part returns to its original shape, it contacts the surfaces of the retaining cavity in the seal assembly, and a high-equilibrium stress between the gasket and the sealing surfaces is developed to form a permanent, leaktight seal.

In ESG's seal concept, shown in Table 1, the contact stresses required to maintain metal-to-metal contact are provided by the memory alloy, not by applied pressure. Thus, if any deformation of the housing or flanges occurs during service, the unique characteristic of the memory alloy to seek its original shape will maintain internal stresses that are independent of the applied loads or changes in spacing between the flanges. Conventional metallic, static seals must have an externally applied contact load to maintain the contact stress required for sealing. Leakage paths that can occur in conventional metal seals are expected to be self-healing in the proposed seal designs. Table 2 lists some of the potential advantages of shape memory alloys for seal applications.

Table 1
Shape Memory Alloys

HOW THEY WORK:

THERMOMECHANICAL WORK TO "FIX" MEMORY PROPERTIES

FORM OR MACHINE TO SHAPE THAT IT WILL BE CALLED UPON TO REMEMBER LATER

CLAMP, HEAT TO IMPART THE MEMORY, AND QUENCH TO MARTENSITE PHASE

STRAIN/DEFORM TO ANY DESIRED INTERMEDIATE SHAPE

INSERT IN SEAL GLAND AND HEAT ABOVE THE CRITICAL TRANSFORMATION TEMPERATURE. PART WILL REMEMBER ITS ORIGINAL MEMORY SHAPE AND ATTEMPT TO RETURN TO IT, THEREBY EXERTING CONSIDERABLE FORCE ON SEALING SURFACES

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Table 2
Advantages of Shape Memory Alloys

- Nitinol seals are actuated by temperature, not by an externally applied load, and will be particularly applicable where remote sealing would be advantageous.
- Nitinol alloys have a low modulus of elasticity which allows deformation at low-stress levels, increasing conformability at mating surfaces.
- Nitinol alloys have good mechanical strength properties at geothermal temperatures.
- Nitinol alloys have good resistance to corrosion in geothermal environments.
- Nitinol alloys are metallurgically stable in geothermal environments and, unlike elastomeric materials, are not susceptible to hydrolytic instability or other degradation during service.
- Nitinol seals can be coated with soft metals or a nonmetallic material, if necessary, to seal components with nonuniform geometry or rough sealing surfaces.
- Nitinol seals can be coated with a nonmetallic material for applications with low electrical conductivity, dielectric, or other special properties.
- Nitinol seals can be coated by chrome plating or hardfacing for applications requiring wear resistance.

"Nitinol" is the generic name for a family of alloys composed of approximately 55% nickel and 45% titanium and is the preeminent engineering alloy exhibiting the shape memory effect. Nitinol was developed by the Naval Ordnance Laboratory (NOL), hence the acronym Ni Ti NOL. In this report, the acronym Nitinol will be used throughout to denote Ni-Ti shape memory alloys. When appropriate, specific trade names will be used and so noted.

The metallurgy, properties, and applications of Nitinol are detailed in Reference 1. For information, Table 3 summarizes some of the more pertinent physical properties. Thermal expansion is not included since it is so interwoven with the shape memory effect; for comparative purposes, a value of $10.4 \times 10^{-6}/^{\circ}\text{C}$ may be used. Mechanical properties are sensitive to prior processing, heat treatment, and composition, as well as the transformations. In general, the room-temperature tensile strength of Nitinol is 758 to 965 MPa (110,000 to 140,000 psi) with yield strengths of 207 to 552 MPa (30,000 to 80,000 psi). Reference 2, a source manual for information on Nitinol, is available from the U.S. Navy's Nitinol Technology Center.

Table 3
Physical Properties of Nitinol

Melting point	1275 ⁰ C (2327 ⁰ F)
Density	6.5 g/cm ³
RT electrical resistivity	70 $\mu\Omega\cdot\text{cm}$
RT elastic modulus	12 x 10 ⁻⁶ psi
Poisson's ratio	0.3
Hardness	R _c 30-40
Oxidation resistance	Excellent, below 500 ⁰ C (932 ⁰ F)
Hydrogen absorption	Will absorb at high pressures below 500 ⁰ C (932 ⁰ F)

In commercial applications of Nitinol, Raychem Corporation markets two self-actuated fastener devices that use the shape memory effect. One is a semipermanent make-break connecting device intended for electrical applications, marketed under the trade name CRYOCON. The other is a permanent tube and pipe coupling with the trade name CRYOFIT, used in high-pressure piping systems. They are being used commercially in aircraft, submarines, surface ships, rolling mills, and process plants for joining water, oil, and gas piping lines. Other known applications of shape memory alloys include a deployment mechanism for antennas and solar cell panels, a temperature monitoring device, a fan clutch, a de-icing switch, a diverter valve, a hot water valve, a ventilator control, a window opener, and orthodontic wires. In the field of

research and development, the shape memory properties of Nitinol are being exploited in the development of heat engines that will operate from low-grade waste heat energy.⁽³⁾

BNL Contract 509927-S funded the following tasks for the period of April 1, 1980, through April 30, 1981:

- Task 1 — Survey of Nitinol suppliers, geothermal pump manufacturers, and geothermal test facilities
- Task 2 — Characterization of Nitinol material properties
- Task 3 — Design studies for pump seals
- Task 4 — Demonstration tests of Nitinol seals.

All planned activities under Tasks 1, 2, and 3 were completed, and a seal for the Task 4 demonstration test was fabricated under this contract.

Contract 546251-S covered the continuation of the program during the period June 1981 through May 1982. Tasks 2 and 4 were continued, and three new tasks were authorized as follows:

- Task 5 — Pump seal design and fabrication
- Task 6 — Pump seal field tests
- Task 7 — Seal technology development.

This document is a final report covering technical progress during the 2-year program. A 12-month progress report covering the first year of the program was previously issued.* For completeness and continuity, the salient results are repeated in this final report.

III. TECHNICAL PROGRESS

A. Task 1 — Survey

A survey of Nitinol sources, geothermal pump manufacturers, and geothermal test facilities was conducted during April-June 1980. The conclusions and recommendations at that time were:

- Pump manufacturers expressed a need for improved seals to withstand geothermal environments and temperatures.
- The most expedient source of fabricated Nitinol seals would be by means of a subcontract with Raychem Corporation, an established manufacturer of shape memory alloy couplings and connectors.
- The most expedient method of demonstrating the applicability of a Nitinol seal in a geothermal pump would be to test seals in the geothermal turbine pump test loop being constructed by Sperry-Vickers at its Jackson, Mississippi, facility or in the DOE-owned geothermal Simulated Test Apparatus operated by L'Garde, Inc., in its facility at Newport Beach, California.
- Downhole pump seal field tests could be conducted by any of the pump manufacturers if the demonstration tests were successful.
- Nitinol corrosion tests could be conducted in the Department of Energy's East Mesa Geothermal Component Test Facility (GCTF) and in a Magnolia, Arkansas, geothermal well under the direction of personnel from TRW's Reda Pump Division of Bartlesville, Oklahoma.

*Warren H. Friske and Harry Schwartzbart, "Shape Memory Alloy Seals for Geothermal Applications — Twelve-Month Progress Report, April 1980-March 1981," ESG-81-16, May 30, 1981

• The primary goal of the program should be the design, fabrication, and testing of static, flange-type seals with diameters ranging from 3.5 to 23 cm (1-3/8 to 9 in.). Future development should include potential applications in rotary shaft seals.

1. Nitinol Suppliers. Raychem Corporation is a manufacturer of commercial hydraulic coupling and electronic connectors made from shape memory alloys and has developed a high level of expertise in Nitinol technology. They would not provide Nitinol mill products, but were willing to cooperate in the development of a Nitinol seal as a final product.

The U.S. Navy's Nitinol Technology Center is a producer of Nitinol ingots and some mill products. The center's primary charter is to emphasize Nitinol technology; therefore, it preferred to be a "supplier of last resort."

Unitek Corporation maintains an inventory of rod and wire products for their commercial orthodontic devices. While Unitek did provide some material from their inventory for the material characterization studies of Task 2, they were considered to be a user of Nitinol, not a supplier.

Titanium Metals Corporation of America can provide Nitinol in ingot form or in semi-finished bar stock. However, their minimum lot size is 50 lb; this is far more material than is required for the program.

Carpenter Technology is considering Nitinol as a potential business field. Their activities have been limited to research and development testing with no production experience to date. They were considered to be a potential source of Nitinol but not for the current program.

Nitinol rod and wire products are now being produced using powder metallurgy techniques by Special Metals Corp. This process offers potential improvements in alloy homogeneity and fabricability.

Raychem was selected to design, fabricate, and test small seals under Task 3. Although this effort was successful, Raychem declined to fabricate the seals required for the demonstration tests of Task 4. Material for the demonstration test seal was subsequently procured from the Nitinol Technology Center.

2. Pump Manufacturers. The survey of pump manufacturers indicated that Sperry-Vickers could contribute most to the seal design phase of the program. Their turbine-type pump gains efficiency with increased geothermal fluid temperatures; since Nitinol seals, unlike elastomers, are not temperature-limited, Sperry-Vickers recognized a real advantage in using a Nitinol seal in current pump designs. This was reflected in their willingness to participate in the Task 4 seal demonstration tests as well as in the design phase.

TRW-Reda and Centrilift were more concerned with current-generation geothermal systems where temperatures do not exceed 176 to 204°C (350 to 400°F). For this service, elastomeric seals, although short-lived, are used. It was concluded that, while they were eager to participate, their contributions to the current program would be limited. Their greatest contribution would come during follow-on phases of the program when field testing of the pumps utilizing Nitinol seals becomes a reality.

Two Los Angeles-area manufacturers, Peerless Pump and Pacific Pump, expressed interest in the Nitinol seal concept but could not participate in the current program. A third local pump manufacturer, Kobe, Inc., was contacted during the second year of the program. Kobe needs an improved static shaft seal for submersible pumps. Nitinol shaft-type seals were provided to Kobe for demonstration tests under Task 4.

Worthington Pump Corp. and J. Hilbert Anderson, Inc., are jointly developing a turbo-pump for geothermal service. Their immediate applications are for low-temperature tests; therefore, Nitinol seals are not required at this time.

Both Sperry-Vickers and TRW-Reda subsequently participated in seal design discussions with ESG and Raychem under Task 3.

Several seal manufacturers were also contacted. There is a potential application for seals utilizing the Nitinol concept as the static seal member of the rotating shaft seals.

3. Test Facilities. This survey indicated that Sperry-Vickers offered the best capability for conducting the planned demonstration test of a Nitinol seal (Task 4). They have an in-house test facility for development testing of pumps and pump components, and a Nitinol seal could be used as a direct replacement of an elastomeric O-ring.

L'Garde has a suitable test facility for testing seals. However, it is limited to small, 5-cm (2-in.) diameter seals. Seals were subsequently tested by L'Garde under Task 4.

TRW-Reda, Centrilit, Worthington, and Barber-Nichols could not contribute to the demonstration tests; however, they could provide the vehicles for full-scale pump tests in follow-on phases of the program.

During the second year of the program, it was determined that Kobe had a seal test facility capable of testing to 232°C (450°F). Seals were subsequently tested by Kobe under Task 4.

4. Materials Test Facilities. As a part of Task 2, Materials Characterization, it was planned to conduct corrosion tests to assess the corrosion behavior of Nitinol alloys in a geothermal environment. The identification of potential materials test facilities was a part of this survey. Two test facilities were selected: (1) the DOE-owned East Mesa Geothermal Component Test Facility (GCTF) near Holtville, California, and (2) the Magnolia, Arkansas, test facility operated by Dow Chemical. These facilities offer two extremes in corrosion potential: The East Mesa geothermal fluid is considered to be relatively benign, while the Magnolia fluid is reported to be one of the most corrosive. Arrangements were made with DOE and Westec Services to initiate testing at the GCTF. Arrangements for testing in the Magnolia facility were made through TRW's Reda Pump Division.

During the second year of the program, arrangements were made for static autoclave corrosion tests by L'Garde, Inc. These tests had the advantage of using a synthetic brine composition with a controlled hydrogen sulfide content.

B. Task 2 - Materials Characterization

1. Corrosion Tests - East Mesa GCTF. The first corrosion test was conducted in the East Mesa GCTF during December 1980-January 1981. Nitinol-type materials then available for testing included: (1) sheet specimens of Raychem's proprietary alloy "Tinel A," an alloy with a subzero transformation temperature; (2) rod specimens of conventional Nitinol, an alloy with an elevated transformation temperature 66°C (150°F), provided by Unitek; (3) U-bend stress-corrosion specimens from Raychem's Tinel A; and (4) commercial "Tinel Cryofit" couplings provided by Raychem. For reference, test specimens of carbon steel, Type 304 stainless steel, Viton rubber, and neoprene rubber were included.

The test manifold was a 91-cm (36-in.) long section of 20-cm (8-in.) diameter, Schedule 40, seamless carbon steel pipe per ASTM A53. The manifold was flanged at each end and fitted with inlet and outlet piping. A photograph of the manifold as installed on the FCTF test pad is shown in Figure 1a. Insertion of the specimen test fixture in the manifold is shown in Figure 1b. The test fixture with specimens attached is shown in Figure 2. The fixture was constructed of Type 304 stainless steel. The sheet coupons were attached with carbon steel bolts and nuts, with the specimens insulated by Teflon spacers to prevent galvanic attack. The rod-type specimens from Unitek's Nitinol alloy were drilled and attached with Chromel wire without any Teflon spacers. The two Cryofit couplings were wired to the fixture's support rods.

a. Corrosion Test Manifold

b. Insertion of Corrosion Test Fixture

Figure 1. Corrosion Test Assembly at East Mesa Geothermal Component Test Facility

The test was exposed to geothermal brine for a total of 42 days, with 25 days at hot-flow conditions. The brine was from East Mesa Well 8-1, with a composition as given in Table 4. The brine temperature was 149 to 154°C (300 to 310°F) and its pressure, 0.69 to 0.72 MPa (100 to 105 psi). The test manifold was orificed to give a flow rate of 0.63 l/s (10 gal/min).

A total of 12 Tinel A coupons were tested, three coupons at each of four locations. Of these 12 coupons, 10 had corrosion rates in the range of 0.04 to 0.94 mg/dm²·day (0.01 to 0.21 mils/year), one showed a slight weight gain of 0.17 mg/dm²·day (0.04 mils/year), and one had a higher corrosion rate of 0.47 mg/dm²·day (1.05 mils/year). The latter coupons were inspected with a binocular microscope; there was no visual justification for the abnormal corrosion rates. For the 10 accepted data points, the average corrosion rate was 0.05 mg/dm²·day (0.10 mils/year). These data are in good agreement with

Figure 2. Test Fixture and Specimens for East Mesa Corrosion Test

Table 4
Liquid Brine Chemical Analysis
East Mesa Geothermal Wellhead 8-1
Unflushed, 1978
(concentration in ppm)

Sample	Aug 3	Aug 24	Sep 19	1976 ^a	1974 ^b
Fe	0.03	0.50		0.10	1.1
Mn				0.05	
Sr	1.6	1.7	2.4	2.1	1.6
Mg	<0.05	0.13		0.05	1.6
SiO ₂	246	235	244	389	263
B	1.6	2.0		1.6	3.3
Ca	1.4	12.6	12.0	8.5	41
Na	539	615	557	610	723
K	36	42	36	70	42
Li	1.1	1.5		1.1	2.0
Cl	705	820	695	500	555
HCO ₃	445	455	470	420	670
SO ₄	150	120		175	225
TDS	1756	1940	1790	1600	2463
pH	6.20	6.00	6.98	6.27	7.68
Cond	2850	3250	2660	3200	
S				1.0	
F				1.6	
NO ₃ ⁻				0.34	

^a From Geothermal Research Investigations, April 1977, p. 37. This value, like the one of 1974, is included here for comparison.

^b From Geothermal Research Investigations, November 1974, p. 33.

corrosion rates reported by TRW-Reda for coupons of the same alloy exposed to H₂S-saturated brine from Magnolia, Arkansas, for 68 days. In comparison, six Type 304 stainless steel coupons had corrosion rates in the range of 48 to 61 mg/dm²·day (8.6 to 10.9 mils/year), two orders of magnitude higher. The results are summarized in Table 5. Six reference carbon steel coupons were severely scaled, showing 10 to 30% increases in thickness.

Some Tinel A coupons showed minor crevice corrosion and pitting associated with the Teflon spacers used to prevent galvanic attack. However, there was no evidence of crevice corrosion or pitting on either of two commercial Cryofit couplings, which have built-in crevices, or on the two U-bend specimens, all from the same Tinel A alloy. Also, there was no visual evidence of pitting corrosion of the as-fabricated rod specimens of the conventional Nitinol alloy. The observed crevice corrosion was in the form of an intermittent white corrosion layer between the Teflon spacer and the specimen. After the corrosion product was removed by brushing, the depth of corrosion was determined to be superficial. In general, the pits were too small to be readily visible to the unaided eye and were initially detected under low-power (7x to 30x) binocular examination. The largest pit was found to be about 0.05 cm (20 mils) in diameter and 0.05 cm (20 mils) deep. Further testing will be required to determine if crevice corrosion and/or pitting will be a real problem in geothermal service.

Both Tinel A U-bend stress corrosion specimens failed, while the reference Type 304 stainless steel specimens remained intact. (These U-bend specimens were stressed beyond their yield strength.) The results indicate that Nitinol-type alloys are susceptible to stress corrosion cracking in geothermal fluids at very high stress levels. Further testing is required to establish the threshold stress levels below which stress corrosion cracking will not occur. This corrosion mode may not be a factor in a pump seal since the applied stresses will be compression rather than tension.

Two commercial elastomeric materials, neoprene and Viton, were included in the test. Two standard O-rings, 1.27-cm (0.5-in.) ID, were assembled between Teflon spacers. The nuts were tightened just enough to retain the O-rings in position, not enough to cause any deformation. Figure 3 shows the O-rings after the test, along with one as-received O-ring for reference. The neoprene, in particular, was severely swollen and distorted. The Viton O-ring suffered less distortion but actually shrank in diameter. Both types of O-rings had a 14% permanent set. These specimens illustrate the limited life of elastomeric materials in this geothermal brine.

2. Corrosion Tests - TRW-Reda Pump Division. Arrangements were made with TRW-Reda Pump Division to conduct corrosion tests on two Nitinol-type alloys: (1) sheet specimens of Raychem's proprietary Tinel A and (2) rod-type specimens of the conventional Nitinol alloy procured from Unitek Corporation, the same materials tested at East Mesa GCTF. These tests were conducted during September-November 1980.

Specimens of each alloy were exposed for 68 days to (1) a simulated geothermal fluid in a laboratory corrosion rate test and (2) a geothermal brine at the Magnolia, Arkansas, test facility. The test temperature was 98°C (209°F). The composition of the test fluids was considered to be proprietary information; however, the brine was reported to be "very aggressive with a high level of hydrogen sulfide" (i.e., 25 to 30% of gases is H₂S). On this

Table 5
Test Results for East Mesa Geothermal Corrosion Test

		Weight (grams)		ΔW	Area (in. ²)	Corrosion Rate (MPY) ^a
		Pre-	Post-			
1	Tinel A	4.5832	4.5804	-0.0028	3.2453	0.08
2		4.7950	4.7947	-0.0003	3.2379	0.013
3		4.8623	4.8632	+0.0009	3.3342	-0.04
4		3.5800	3.5555	-0.0245	3.2104	1.05
5		4.7352	4.7312	-0.0040	3.2538	0.17
6		3.1176	3.1175	-0.0001	3.1855	0.004
7		3.5353	3.5317	-0.0036	3.1601	0.16
8		3.4692	3.4666	-0.0026	3.1753	0.11
9		4.4359	4.4310	-0.0049	3.2301	0.21
10		3.0380	3.5348	-0.0032	3.1749	0.14
11		4.2069	4.2046	-0.0023	3.1924	0.10
12		3.2888	3.2884	-0.0004	3.1808	0.02
13	304 SS	3.1771	2.8736	-0.3035	3.7779	8.94
14		3.1768	2.8795	-0.2973	3.7661	8.78
15		3.1382	2.8480	-0.2902	3.7703	8.56
16	304 SS	3.0883	2.7318	-0.3565	3.7684	10.52
17		3.0546	2.6608	-0.3938	3.7663	11.63
18		3.1740	2.8050	-0.3690	3.7682	10.89

^aMPY - mils per year, calculated from formula

$$MPY = \frac{534 W}{DAT}$$

where:

W = ΔW in mg

D = density in g/cm³

A = area in in.²

T = time in hours (25 days or 600 h, at hot-flow conditions)

Figure 3. Elastomeric O-Rings after 42-Day Exposure to East Mesa Geothermal Brine

basis, the calculated H_2S level in the brine was ~ 2200 ppm by weight. The laboratory test fluid was similar in composition to the geothermal brine except that there was no hydrogen sulfide. The corrosion rates in both tests were determined to be 0.5 to 0.6 $mg/dm^2 \cdot day$ (0.08 to 0.11 mils/year), and there was no visual corrosion or pitting. The corrosion rate data were in good agreement with the East Mesa test results. The presence of hydrogen sulfide did not have any apparent effect on the corrosion resistance, but further testing is required to confirm this in higher temperature brines.

3. Corrosion Test — L'Garde. A Nitinol corrosion test was conducted during September and October 1981 by L'Garde, Inc., of Newport Beach, California, in a synthetic brine with a controlled H_2S level of 300 ppm, at $260^\circ C$. The test medium was more aggressive than for the corrosion tests conducted last year, i.e., the East Mesa geothermal brine is relatively benign with a temperature range of 149 to $154^\circ C$ (300 to $310^\circ F$), and although the Magnolia, Arkansas, test was in a H_2S -saturated fluid, the temperature was very low, about $98^\circ C$ ($209^\circ F$).

The Nitinol material used in this test was procured from the U.S. Navy's Nitinol Technology Center as plates, 20 by 19 by 0.8 cm (8 by $7\frac{1}{2}$ by $\frac{5}{16}$ in.). For these corrosion tests, a portion of one plate was hot-rolled at $600^\circ C$ ($1112^\circ F$) to an intermediate strip 1.42 mm (0.056 in.) thick and a final strip thickness of 0.71 mm (0.028 in.).

The test matrix consisted of (1) ten Nitinol corrosion rate coupons from 0.71 -mm (0.028 -in.) strip, (2) three Type 304 stainless steel corrosion rate coupons from 0.76 -mm (0.030 -in.) stock, for reference, (3) three Nitinol bent beam stress corrosion coupons stressed at 50, 75, and 90% of yield strength,

(4) three Nitinol U-bend corrosion coupons stressed at >100% of yield strength, (5) one Type 304 stainless steel U-bend stress corrosion coupon stressed to 100% of yield strength, and (6) four Nitinol crevice corrosion couples. The specimens are shown in Figure 4.

Figure 4. Specimens for L'Garde Autoclave Corrosion Test in a Simulated Geothermal Brine Containing 300 ppm H_2S at $260^{\circ}C$ ($500^{\circ}F$)

The test was scheduled to run 30 days, with an interim inspection after 15 days. When the autoclave was opened for the interim inspection, it was found that there was no brine, presumably because of an undetected leak. Five corrosion rate coupons and one crevice corrosion couple were removed for interim evaluation. The autoclave was then refilled with brine, and testing of the remaining specimens was continued.

The results of the L'Garde test are summarized in Table 6. The ten Nitinol corrosion rate coupons showed weight gains ranging from 1.21 to 3.09 $mg/dm^2 \cdot day$; the three reference Type 304 stainless steel coupons showed weight losses ranging from 2.36 to 2.60 $mg/dm^2 \cdot day$. There were no cracks detected in the six Nitinol and one stainless steel stress corrosion specimens. One of the Nitinol crevice corrosion couples showed a band of shallow pitting indicating incipient crevice corrosion. Pitting was observed in various degrees on all Nitinol specimens, more so on those exposed for 32 days. Thirty pits were counted on one surface of one specimen. The largest pit detected on the Nitinol specimens, measured with a toolmaker's microscope, was about 3.8-mm (0.05-in.) diameter and 0.25 mm (0.01 in.) deep. Pitting was much more widespread on the stainless steel specimens, with the dimensions of the pits about the same as for the Nitinol pits.

Table 6
Results of L'Garde Corrosion Test

Specimen number	ΔW (g)	Area (in. ²)	Corrosion rate ^a (mg/dm ² ·day)	Remarks
NiTi 1	+0.0116	2.36	+2.38	12 pits ^b
NiTi 2	+0.0063	2.36	+1.29	8 pits
NiTi 3	+0.0092	2.36	+1.89	30 pits
NiTi 4	+0.0059	2.36	+1.21	23 pits
NiTi 5	+0.0111	2.36	+2.28	13 pits
NiTi 6	+0.0068	2.36	+2.63	4 pits
NiTi 7	+0.0080	2.36	+3.09	3 pits
NiTi 8	+0.0065	2.36	+2.51	5 pits
NiTi 9	+0.0047	2.36	+1.82	4 pits
NiTi 10	+0.0036	2.36	+1.39	14 pits
SS 1	-0.0168	3.13	-2.60	Many pits
SS 2	-0.0161	3.31	-2.36	Many pits
SS 3	-0.0166	3.34	-2.40	Many pits

Stress Corrosion Specimens

NiTi 1	50% yield strength.	No cracks.	Some pits.
NiTi 2	75% yield strength.	No cracks.	Some pits.
NiTi 3	90% yield strength.	No cracks.	Some pits.
NiTi 4-6	>100% yield strength.	No cracks.	Some pits.
SS 1	>100% yield strength.	No cracks.	Severely pitted.

Crevice Corrosion Couples (4). One couple showed band of shallow pits at crevice.

^aTest duration: 17 days for Specimens 6-10, 32 days for all others

^bPits observed at 7x magnification.

Test fluid: synthetic brine with 300 ppm H₂S

Test temperature: 260°C

4. Corrosion Test 2 — East Mesa. A second corrosion test was conducted in geothermal brine at the East Mesa Geothermal Component Test Facility (GCTF) in January 1982. The test array, including materials, was identical to that of the L'Garde test (Figure 4). The specimens were mounted on the test fixture and inserted in a test manifold supplied with brine from Well 6-2. The fluid temperature was 174°C (345°F) and the pressure, 350 psi. Based on 1978 analyses, the liquid brine has a total dissolved solids (TDS) content of 4220 ppm at a pH of 6. The H_2S content was not reported, but is presumed to be very low. This test was conducted to compare the corrosion behavior of the Nitinol being used for seals in the demonstration tests (Task 4) and field test (Task 6) with that of the Tinel (Raychem's proprietary alloy) tested under the first year's program.

The specimens were removed after 30 days and returned to ESG for evaluation. It was observed at that time that all of the specimens were coated with oil. In discussions with GCTF personnel, we determined that there had been an oil leak in the downhole pump. It was observed that pump oil in the geothermal brine being pumped to the surface entered the test manifold and coated the specimens. In view of this uncontrolled test environment, the specimens were ultrasonically cleaned in solvent to remove the oil and returned to GCTF for retesting. The test manifold was flushed and then reinstalled in Well 8-1, the artesian well used in the first year's test. This retest was conducted for 33 days; the fluid temperature was 160°C (320°F).

The test specimens were removed from the test manifold and returned to ESG for evaluation. As before, a film of oil was observed on all specimens; it was assumed that residual oil in the manifold was not removed during preparation for the retest. Because of the oil, the validity of this corrosion test is suspect. However, the corrosion rates were determined, as summarized in Table 7, and specimens were inspected for pitting, stress corrosion cracking, and crevice corrosion. The Nitinol corrosion rates ranged from a weight loss of $0.86\text{ mg/dm}^2\text{-day}$ to a weight gain of $0.26\text{ mg/dm}^2\text{-day}$ for the reference Type 304 SS. There was no indication of stress corrosion cracking or crevice corrosion and very little pitting.

5. Elevated-Temperature Tensile Tests. Elevated-temperature tensile tests were conducted at 260°C (500°F) and 371°C (700°F). The material tested was Raychem's proprietary alloy Tinel A in strip form. Nine strip samples were provided by Raychem; eight were $2.54 \times 20 \times 0.063\text{ cm}$ ($1 \times 8 \times 0.025\text{ in.}$) and one was $2.54 \times 20 \times 0.089\text{ cm}$ ($1 \times 8 \times 0.035\text{ in.}$). One standard 5-cm (2-in.) gauge-length test specimen was machined from each strip. The remainder of the strip was retained for supporting tests, e.g., hardness, composition, metallography. The tensile tests were made with a Riehle 1,200- to 12,000-lb capacity testing machine equipped with a load-strain recorder. Specimens were gripped top and bottom with flat, tapered wedges. Specimens were heated with a three-zone, resistance-heated clamshell furnace. Temperature control was maintained with thermocouples attached to the top, middle, and bottom of the reduced section of the test specimen. (Note: The thermocouples were wired to the specimen, since spot welding to this alloy was not successful.) Temperatures were maintained with $\pm 5.5^{\circ}\text{C}$ ($\pm 10^{\circ}\text{F}$) of the specified temperature for 1/2 h prior to testing.

Table 7
Results of East Mesa GCTF Corrosion Test

Specimen number	ΔW (g)	Area (in. ²)	Corrosion rate (mg/dm ² ·day)
NiTi 11	+0.0167	2.36	+0.26
NiTi 12	+0.0116	2.36	+0.18
NiTi 13	-0.0026	2.36	-0.04
NiTi 14	-0.0552	2.36	-0.86
NiTi 15	+0.0154	2.36	+0.24
NiTi 16	+0.0141	2.36	+0.22
NiTi 17	+0.0077	2.36	+0.12
NiTi 18	+0.0090	2.36	+0.14
NiTi 19	+0.0039	2.36	+0.06
NiTi 20	+0.0077	2.36	+0.12
SS 4	-0.0074	3.13	-0.11
SS 5	-0.0102	3.13	-0.16
SS 6	-0.0093	3.13	-0.14

Testing of these Tinel A specimens required some modifications to conventional techniques. In the first two tests, it was found that the tapered wedge grips did not effectively grip the Nitinol ($\sim 32 R_C$ hardness) and slippage resulted. For subsequent specimens, nickel "doublers" were welded to the grip sections to provide a softer metal surface that would allow the tapered wedges to grip the specimen; this proved to be successful. Also, for the first two specimens tested, failure occurred at the upper knife edge of the extensometer grip; for subsequent tests, a copper shim was assembled over the knife edge to prevent "biting" into the specimen.

The resultant temperature properties are summarized in Table 8 and shown graphically in Figure 5. The data indicate that, in the 260 to 371°C (500 to 700°F) range, tensile strength will exceed 689 MPa (100 ksi), and 0.2% yield strength will exceed 345 MPa (50 ksi). The alloy has low ductility, in the range of 3.5 to 18% elongation, and brittle fracture characteristics were indicative of notch sensitivity. The latter is believed to contribute to the larger than expected spread in test data. The modulus of elasticity was in the range of 43 to 50 GPa (6.3 to 7.3 x 10⁶ psi), compared to 200 GPa (30 x 10⁶ psi) for steels.

The hardness of the Tinel A specimens was in the range of 48 to 55 Rockwell-N30 in the as-received condition. This is comparable to 26 to 35 on the Rockwell-C scale. Hardness values of each strip were reproducible within

Table 8
Tinel A Tensile Properties

	Test Temperature			
	RT	500°F	600°F	700°F
No. Samples	1	2	3	2
UTS (ksi)				
Average	96.7	119.9	118.4	110.6
Maximum		123.7	131.4	113.3
Minimum		116.1	98.7	107.8
PL (ksi)				
Average	45.9	41.1	45.5	53.5
Maximum		34.4	55.8	64.0
Minimum		47.7	34.3	58.7
0.2% YS (ksi)				
Average	73.5	63.3	73.7	79.5
Maximum		73.3	112.5	85.3
Minimum		53.2	62.7	73.7
E (10⁶ psi)				
Average	5.6	6.8	6.4	6.7
Maximum		7.3	6.5	6.8
Minimum		6.3	6.3	6.6
Elongation (%)				
Average	>2.8	6.3	12.3	6.2
Maximum		9.0	18.1	5.1
Minimum		3.5	6.8	7.3

Figure 5. Tensile Properties of Raychem's Tinel A

± 2 Rockwell numbers. After testing, the hardness increased slightly. Since the hardness of one room-temperature specimen also increased, this change in hardness is attributed to work hardening rather than to exposure to elevated temperature.

6. Metallography. Metallographic techniques were developed to resolve the microstructures of the Tinel A and conventional Ni-Ti Nitinol alloys. After considerable experimentation, the preferred etchant was found to be 12 vol % HNO_3 - 6 vol % HF - 8 vol % H_2O . Etching time is a critical variable requiring the expertise of an experienced metallographer; the specimen must be removed from the etchant at the precise instant that a greyish film develops on the surface. Using this technique, the grain structure of Tinel A strip was resolved (Figure 6a). At a higher magnification, the oriented structure of the complex Ti precipitates is resolved (Figure 6b).

a. Grain Structure

b. Precipitate Structure

Figure 6. Typical Microstructures of Raychem Corporation's Tinel A Alloy,
25-mil Sheet

In contrast, the microstructure of the conventional Nitinol rod provided by Unitek shows a random distribution of small spherical precipitates (Figure 7). These precipitates are typical of Nitinol alloy microstructures. They do not affect the shape memory alloy properties, per se; however, they can change the Ni:Ti composition, and this secondary effect can change the transformation temperature, if not considered in the nominal alloy charge.

The Nitinol material used in this current program was procured from the U.S. Navy's Nitinol Technology Center as plates 20 by 19 by 0.8 cm (8 by 7-1/2 by 5/16 in.). Chemical analysis showed that the composition was 55.0% Ni (gravimetric) and 45.9% Ti (atomic absorption). The as-received plate stock was used for the demonstration and pump test seals of Tasks 4 and 6, respectively.

A portion of one plate was hot-rolled at 600°C (1112°F) to an intermediate strip 1.42 mm (0.056 in.) thick and to a final strip thickness of 0.71 mm (0.028 in.) for test samples. Microstructure of the Nitinol in the three thicknesses is shown in Figures 8, 9, and 10.

A section of the hot-rolled strip was formed into a U-bend shape to determine the transition temperature of this particular material. When it

Figure 7. Microstructure of Nitinol Alloy
Provided by Unitek Corporation,
0.200-in.-diameter Rod

a. 100X

b. 500X

Figure 8. Microstructures of Nitinol Plate, 0.8 cm (5/16 in.) Thick

a. 100X

b. 500X

Figure 9. Microstructures of 1.42-mm (0.056-in.) Nitinol Strip

a. 100X

b. 500X

Figure 10. Microstructures of 0.71-mm (0.028-in.) Nitinol Strip

was immersed in hot water, there was no recovery up to the boiling temperature. The material was then heated in an oven; recovery began at 104°C (220°F). This was higher than the 65°C (150°F) typical of this composition.

7. Coatings. Feasibility studies were completed for applying soft coatings (for sealing rough surfaces) and hard coatings (for wear resistances) on Nitinol. After considerable experimentation, it was found that an immersion copperplate could be formed in a solution containing HF and copper ions introduced by the addition of a small amount of copper fluoborate. The immersion-plated strip was then electroplated in a fluoborate bath. The resultant copperplated specimen was subjected to rigorous bend tests; the coating had excellent adherence and ductility characteristics. Photomicrographs of a copperplated Tinel A specimen (Figure 11) revealed that a bond, free of porosity and impurities, was attained. A few tests were made to define the best conditions for applying the immersion copperplate. Better results were obtained with a high (30 wt %) HF concentration and a low (2%) concentration of copper fluoborate than when the reverse concentrations were used. About 0.5 to 1 min at ambient temperature appears adequate to obtain an acceptable immersion coating.

In nickel plating experimentation, a Tinel A specimen was pre-treated with an immersion copperplate, as described above for copper plating, and then electroplated with nickel. The resultant nickel plating (Figure 12) was less adherent than the electroplated copper but much more adherent than nickel coating previously applied without the prior immersion copperplate.

The above work was carried out with Tinel A specimens previously plated and stripped. For this reason, it is probable that some modifications may be required for electroplating on new specimens. The work does indicate that both copper plating and nickel plating of Nitinol alloys are feasible. Attempts to chrome plate Nitinol specimens by established procedures have not been successful. The application of a wear-resistant surface, as in hard chrome electroplate, will require additional research and experimentation to establish feasibility.

It is recognized that numerous other coating techniques are available; however, none of these was investigated under the current program. The necessity for further work in this area will be dictated by the performance and leaktight integrity of uncoated seals.

C. Task 3 — Design Studies

1. Objective. The seal design studies were initiated as a coordinated effort between ESG, Raychem, and two geothermal pump manufacturers (TRW-Reda and Sperry-Vickers). As a result of this effort, a purchase order was placed with Raychem Corporation to conduct a design/test program in which small 5-cm (2-in.) seals for flanged joints were designed, fabricated, and tested. The key objectives of this effort were (1) selection of an appropriate Ni-Ti shape memory alloy, (2) selection of one or more appropriate seal designs, and (3) fabrication and testing of the sample.

2. Design Concept. Figure 13 shows the general concept chosen for evaluation. A binary alloy (nominally 55% nickel and 45% titanium) with a transformation temperature from martensite to austenite above ambient was chosen. The unrestrained transformation temperature is nominally 71°C (160°F).

a. 100X

b. 500X

Figure 11. Photomicrographs of Copperplated Tinel A

a. 100X

b. 500X

Figure 12. Photomicrographs of Nickel-Plated Tin1 A

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Figure 13. Design Concept
for Shape Memory Seals

CIRCULAR CROSS-SECTION DESIGN

TOOTHED CROSS-SECTION DESIGN

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Figure 14. Prototype Design Details

Because the transformation temperature rises under stress, the actual value for an installed seal is unknown, although higher than the nominal. One of the designs evaluated was of a circular cross section (Figure 13). The martensitic ring is installed at room temperature into the sealing groove (Figure 13a). The flange bolts are tightened and the soft martensitic ring is flattened (Figure 13b). When heated during use, the material changes to the austenite and tries to "recover" to the circular geometry. In doing this, it exerts substantial force on the interface as shown in the exaggerated Figure 13c. The yield strength of the Tinel is typically 414 MPa (60,000 psi). The ring/flange "system" will come to an equilibrium where the forces exerted by the Tinel ring are balanced by the transformation temperature; the equilibrium point will shift depending on the pressure, temperature, etc., of the assembly. It is possible that one or more of the parts may exceed its yield strength and be permanently deformed if the design equilibrium favors one part over another.

3. Design Details. Figure 14 shows dimensional details of the two experimental seals. They were nominally based on a Parker Number 2-329 O-ring size. They were manually machined and annealed after the machining process. The seal of circular cross section was tested in a flange with a standard O-ring groove. The toothed seal was tested in flanges with flat surfaces.

4. Test Results - Pressure Testing in Water. Figure 15 shows the setup for pressure testing in water. The heat sink was added after the first test. The accumulators were added after the second test. The bolts were torqued to 70 ft·lb in each test. Water tests were made at temperatures to 315°C (600°F) and pressures as high as 41.2 MPa (6000 psi). Gas pressure tests were made with compressed nitrogen at room temperature only with pressures to 6.9 MPa (1000 psi). The detailed procedure for each of the four tests is as follows:

a. Seal 1, Circular Cross Section

1. The part was assembled and pressurized to 20.6 MPa (3000 psi) with water. No gas leak-testing was done on this part.

2. The pressure dropped to 10.3 MPa (1500 psi) in about 1 h. No leaks were detected. The valve was turned around and the part repressurized to 20.6 MPa (3000 psi).

3. The pressure dropped to 16.7 MPa (2425 psi) in about 2 h.

4. The pressure was reduced to 1 MPa (150 psi) and the temperature increased to 315°C (600°F).

5. The pressure fluctuated between 19.3 MPa (2800 psi) and 24.8 MPa (3600 psi) at the hot temperature for 2-1/2 h.

6. The test was terminated when the pressure gauge became very hot and was believed dangerously close to bursting.

7. On cooling down, the flange bolts were loose.

b. Seal 2, Circular Cross Section.

1. The part was assembled and nitrogen gas-tested up to 3.45 MPa (500 psi), where a bubble leak was detected at one of the flange bolts.

2. The pressure was released, the flange bolts retightened to 70 ft·lb, and the assembly pressurized with nitrogen to 5.5 MPa (800 psi), where it again leaked at a flange bolt. The pressure was released and the bolts checked for tightness. No discrepancy was detected.

3. The assembly was proof-pressurized to 20.6 MPa (3000 psi) of water and held for 1/2 h without evidence of a leak.

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Figure 15. Test Equipment Setup

4. A heat sink was added between the oven and the gauge to prevent the gauge from overheating. The pressure was reduced to 0.7 MPa (100 psi).
 5. The assembly was heated to nominally 315°C (600°F) and held for about 2 h. The pressure fluctuated between 20.6 MPa (3000 psi) and 24.8 MPa (3600 psi) during this time. Evidence of a leak was detected, and the assembly required additional pressurizing. The leak was at the coupling disconnect outside the oven.

6. The part was allowed to cool overnight. No pressure was detected in the morning.

7. On disassembly, signs of a leak were detected. The flat flange was also indented where the seal was made. The flange bolts were also loose.

c. Seal 3, Toothed Cross Section.

1. The part was assembled and nitrogen gas-tested to 6.9 MPa (1000 psi) for 5 min without evidence of a leak.

2. The part was proof-pressured to 20.6 MPa (3000 psi) at room temperature and held for 15 min without evidence of a leak.

3. An accumulator was added to the setup to help control the pressure during the temperature test.

4. The assembly was heated, but control of the temperature/pressure combination was unsatisfactory. The heat was turned off and the assembly allowed to cool overnight.

5. Morning inspection revealed that the bolts were loose to about 25 to 30 ft·lb.

6. The assembly was retorqued to 70 ft·lb and proof-pressurized to 20.6 MPa (3000 psi) at room temperature without leak detection.

7. The assembly was heated and reached a pressure of 42.1 MPa (6100 psi) at a temperature of about 182°C (360°F) in 1/2 h. The heat was turned off, and the assembly allowed to cool.

8. Another examination revealed that the bolts required retightening from their value of 30 to 35 ft·lb. The assembly was again proof-pressure tested to 20.6 MPa (3000 psi) with no detectable leaks.

9. Another attempt was made with results similar to Steps 7 and 8 above.

10. A second accumulator was added.

11. The assembly was heated to 315°C (600°F) and held a pressure of 29 MPa (4200 psi) for about 3 h. The oven was turned off and the assembly allowed to cool overnight.

12. On the following morning, the indicated pressure at room temperature was zero. The assembly was pressurized to 20.6 MPa (3000 psi) without leaks being detected.

d. Seal 4, Toothed Cross Section.

1. The seal was assembled in the usual way and nitrogen gas-tested to 6.9 MPa (1000 psi) for 5 min without detection of a leak.

2. The assembly was pressurized with water to 20.6 MPa (3000 psi) at room temperature for 1/2 h without any sign of a leak. Pressure was reduced to 0.7 MPa (100 psi).

3. The assembly was heated to 315°C (600°F) at a pressure of 22.6 MPa (3275 psi) from a temperature of 25°C (77°F) at a pressure of about 0.7 MPa (100 psi) in 1 h. The oven was turned off and the assembly allowed to cool overnight.

4. Inspection in the morning revealed a pressure of about 0.35 MPa (50 psi).

5. The part was proof-pressure tested to 20.6 MPa (3000 psi) with no detectable leaks.

5. Test Conclusions. This task demonstrated that it is feasible and practical to fabricate flange-type static seals from Nitinol alloys. Figure 16 shows the two seal designs, circular cross section and tooth cross section, after testing. Seals of each design were leaktight in room-temperature tests using nitrogen gas at pressures to 6.9 MPa (1000 psi) and water to 20.6 MPa (3000 psi). The circular-cross-section seals showed evidence of slight leakage (i.e., pressure fluctuation, pressure drop) when tested in 315°C (600°F) water at pressures to about 20.6 MPa (3000 psi); however, one seal of the toothed-cross-section design was pressurized to 29 MPa (4200 psi) and a second to 22.6 MPa (3275 psi) in 315°C (600°F) water without leakage.

In these tests, both the seals and the flanges underwent some permanent deformation in the process of heating the restrained seals from the martensite to the austenite phases. The temperature cycling loosened the flanges but did not appear to affect the seal integrity after retightening. These tests indicated that the toothed design is superior to the circular cross section.

a. Test Seal 1, Circular Section

b. Test Seal 3, Toothed Cross Section

Figure 16. Two Seals Designed, Fabricated, and Tested by Raychem Corporation

However, some of the evidence of leakage in the circular-cross-section seals may be attributable to the test equipment itself; improvements were made prior to testing the toothed design. Optimization of the seal designs is required for correct operation. This includes sizing and deformation to optimize sealing forces generated by the shape memory alloy, establishment of maximum flange bolt torques to prevent permanent deformation or overstressing where seal forces are generated, and assessment of configuration and tolerances for optimum leak tightness.

D. Task 4 - Demonstration Tests

In this task, it was planned that Raychem would fabricate a 15-cm (6-in.) seal and that Sperry-Vickers would conduct a demonstration test in their geothermal pump test loop. Raychem advised that they could not participate in this task because all available manpower had been assigned to current in-house projects that had top priority. This meant that a new source of Nitinol was required. The U.S. Navy's Nitinol Technology Center agreed to provide Nitinol stock for the demonstration seals, and three plates, 20 by 19 by 0.8 cm (8 by 7-1/2 by 5/16 in.), were procured in March 1981 for \$2,550, approximately \$190/lb. Machining the Nitinol stock to the required seal configuration was to be done in ESG's shop. A trial 5-in.-diameter seal similar to Raychem's flat, toothed design was machined to develop machining practices prior to embarking on the fabrication of the demonstration seals.

1. Seal Demonstration Tests at Sperry-Vickers.

a. Seal Design and Fabrication. A 15.2-cm (6-in.) diameter face seal, designated ESG-2, was machined from the 0.79-mm (5/16-in.) Nitinol plate stock. The seal was also a modification of the tooth design developed by Raychem and was designed for direct substitution for a standard size 2-258 elastomeric O-ring in Sperry-Vickers' turbine pump assembly. A sketch of the seal design is shown in Figure 17.

The seal's memory shape was fixed by heating to 500°C (932°F) for 1/2 h and air cooling. It was plastically deformed by pressing it between hardened steel platens, using a Riehle Universal Test Machine. The thickness of the seal was reduced from 3.08 mm (0.1212 in.) to the intermediate shape thickness of 2.95 mm (0.1162 in.), a reduction of 8.3% in the sealing lands.

b. Demonstration Test 1. The seal was delivered to Sperry-Vickers' Aerospace-Marine-Defense Division, Jackson, Mississippi, in January 1982. It was initially intended that the seal would be installed directly in the Sperry-Vickers turbine pump that was to be tested in their geothermal pump test loop. This plan was changed since there was no practical way to monitor the seal for leakage. Instead, a seal test fixture was fabricated for installation in a bypass line in the test loop. This test fixture was instrumented to measure the pressure differential across the seal; any change in ΔP would be directly related to leak rates.

The seal was initially assembled with a torque of 50 in.-lb on the flange bolts and determined to be leaktight when pressurized with air. However, for the demonstration test, the bolts were untorqued until there was a definite leak. If the leak stopped after the temperature was raised above the transformation temperature of the Nitinol ($>104^\circ\text{C}$), this would prove the seal concept. When the cold loop water was valved into the test fixture, there was an

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Figure 17. Face Seal Design for Sperry-Vickers
Demonstration Tests

excessive water leak that did not seal as the loop water's temperature increased to about 132°C (270°F). The seal assembly was then removed and disassembled. Inspection revealed that the Nitinol seal had fully recovered. This indicated that there had been too large a gap between the flanges and that the seal was not restrained, thus there were no sealing forces. The Nitinol seal was reformed (about 1 mil in thickness) using the flange bolts to apply the load and reassembled with about 10 in. lb torque. This torque permitted only a small leak. The hot (149°C/300°F) loop water was then valved into the test fixture, and this time the leak stopped.

After cooling, the seal developed a leak, presumably because of the small amount of deformation (1-mil reduction in thickness, 1.6%). The seal was returned to ESG.

c. Demonstration Test 2. ESG-2 was heat-treated again at 500°C (932°F) and then resized to an intermediate-shape thickness of 2.93 mm (0.1153 in.), a deformation of 7.2%. Sperry-Vickers reinstalled the seal in the test fixture and valved in water at 113°C (235°F); the seal leaked. Based on transformation temperature tests conducted on this material, it was postulated that the actual seal temperature was too low. This was confirmed when inspection after disassembly indicated that there was no change in the thickness of the seal; thus, the transformation temperature had not been attained. Sperry-Vickers planned to conduct a retest of the seal at a higher temperature. However, their geothermal pump test program was terminated before this retest could be completed.

2. Seal Demonstration Tests at L'Garde.

a. Seal Design and Fabrication. Two 5.2-cm (2-in.) diameter face seals were machined from the 0.8-cm (5/16-in.) Nitinol plate stock procured from the Nitinol Technology Center. The seal design was a modification of the tooth design developed by Raychem under Task 3. The seal was designed for direct substitution for a standard size 2-329 elastomeric O-ring. A sketch of the seal design is shown in Figure 18.

Both seals were machined in ESG's machine shop. The first seal, designated ESG-3, was fabricated in November 1981 and used in the first three tests at L'Garde. The second seal, designated ESG-9, was fabricated in March 1982 and used in the final endurance and shutdown tests.

Each seal was heated to 500°C (932°F) for 1/2 h and air cooled to fix its memory shape. It was then plastically deformed by pressing it between two hardened steel platens using a Riehle Universal Test Machine. The first seal (ESG-3) was pressed at a load of 60,000 lb; the thickness was reduced from 5.56 cm (0.2190 in.) to its intermediate-shape thickness of 5.42 mm (0.2132 in.). Assuming that all deformation occurred in the 0.030-in. sealing lands, this amounts to a plastic strain of about 9.6%, i.e., $[(0.2190 - 0.2132)/0.060] \times 100 = 9.6\%$. This was higher than the target reduction of 8%, the amount of deformation that gives the Nitinol maximum recovery stresses. The second seal (ESG-9) was reduced from 5.79 mm (0.2280 in.) to 5.68 mm (0.2237 in.), a reduction of 7.1% in the sealing lands.

The seals were delivered to L'Garde, Inc., Newport Beach, California, for testing under Purchase Order N275-175ZKX. Seal ESG-3 was tested during the period of January 28 to February 11, 1982. ESG-9 was tested during the period of March 12 to March 22, 1982.

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Figure 18. Face Seal Design for L'Garde Demonstration Tests

b. Test Setup. The test equipment was originally designed, built, and used to test up to four elastomer O-rings simultaneously under a differential pressure up to 5000 psi and at a temperature up to 315°C (600°F). Its development was funded by the U.S. Department of Energy.

The pressure control and instrumentation are shown schematically in Figure 19. N₂ Tank 2 is the source for the front-face pressure. Nitrogen pressure in the pump drive cylinder results in an 11.7 pressure amplification in the displacement hydraulic fluid. Each of the four piston accumulators contains 115 cm³ of the test fluid and serves one of the seals being tested. Should one of the seals in the test chamber fail, the piston accumulator bottoms out, forcing its contents past the failed O-ring into the back pressure accumulator. The back-face fluid is held at a constant pressure by N₂ Tank 1.

The test chamber is heated by eight strip heaters on the outside of an Inconel outer cylinder. Temperature feedback for control is provided by a single thermocouple. A controller automatically adjusts the voltage to the heaters so that heating constantly takes place.

Instrumentation consists of eight pressure gauges, six thermocouples in the test section, and four accumulator position locators. The thermocouples and pressure gauges are read and recorded manually. The piston positions are recorded on a strip chart so that leak rate and/or time of catastrophic failure is easily determined. A photograph of the setup is shown in Figure 20.

A face seal test fixture was designed and built for the Nitinol seal. This hardware is made of 316 stainless steel and mates with the Inconel test chamber. In the bottom, there is a 3.96-mm (0.156-in.) diameter hole for a thermocouple. The thermocouple, when installed, is less than 2.54 mm (0.1 in.) from the face seal. The test fixture and the Nitinol seal are shown in Figure 21.

c. Proof of Principle Test. The objective of this test was to demonstrate that activation of the Nitinol seal produced sealing. Nitinol seal ESG-3 was installed in the test fixture. Twelve 18-8 stainless steel 3/8-in.-diameter bolts were torqued finger tight. After the installation in the test fixture, tap water was added to the test setup. Prior to heating, the leak rate was measured. A pressure of 200 psi was applied, and the leak rate over a 2-min period was calculated at 27 cm³/min from the oscillograph trace (Figure 22). (The water volume is linear over 24 mm on the traces in this section; therefore, each millimeter represents 4.8 cm³ of water.) This procedure was tried again at 400 psi, but all the water was expended at about the time 400 psi was reached (Figure 23). The leak rate near the end of this test (0.45- to 0.49-min region) was about 800 cm³/min.

The test seal was then heated to approximately 149°C (300°F). Pressure was applied for a few minutes, and the leak rate was recorded. The pressure was increased in steps as shown in Figure 24. There was no leakage observed at pressures of 800 psi or below. At 1000 psi, a 1-cm³/min leak rate was observed. The pressure was reduced to 400 psi to determine if leakage stopped; it did. This indicated that activation of the seal by heat produced a seal, i.e., prior to seal activation, the leak rate was at least 800 cm³/min.

After pressure was increased to approximately 1000 psi again, leakage resumed. The pressure was then increased to 1500 psi. At about the time 1500 psi was reached, there was sudden loss of water. During cooldown, 800-psi pressure was applied, and a leak rate of 1 cm³/min occurred (Figure 25).

Figure 19. O-Ring Test Schematic

Figure 20. O-Ring Test Facility

Figure 21. Nitinol Seal and Test Fixture

Figure 22. Preheating Leakage — Constant Pressure

Figure 23. Preheating Leakage — Increasing Pressure

Figure 24. Leakage at Temperature

Figure 25. Leakage During Cooldown

Figure 26. Leakage at Room Temperature (after heating)

When the system was at room temperature, pressure was once more applied in steps. As shown in Figure 26, leakage started before the 1000-psi level seen in Figure 24, but the leakage rate was well below that observed prior to seal activation.

Condition	Temperature	Leak rate (cm ³ /min)	
		200 psi	400 psi
Preactivation	20°C (68°F)	27	800
Postactivation	149°C (300°F)	0	0
Postactivation	20°C (68°F)	1/2	2-1/2 - 15-1/2

The test fixture was disassembled. It was noted that the seal did mark the stainless steel surfaces. The sealing areas were barely feelable with the fingernail but were not measurable. The seal thicknesses measured at 90° intervals were 0.21475, 0.2147, 0.2141, and 0.2150 in. The pretest thicknesses were 0.2130, 0.2114, 0.2118, and 0.2120 in., respectively. The posttest inner diameter ranged from 1.996 to 1.997 in., while the posttest outer diameter was 2.541 in. The pretest inner and outer diameter dimensions had been 1.995 and 2.543 in., respectively.

It was concluded that activation of the Nitinol seal did result in a sealing capability.

d. Requirements Test. The objectives of the second test of ESG-3 were to demonstrate (1) again that activation of the Nitinol seal produced sealing and (2) that the seal would operate at a temperature of 260°C (500°F) and a 1500-psi differential pressure. Prior to this test, the seal had been returned to ESG where it was heat-treated again at 500°C (932°F) and compressed to a 0.124-mm (0.0049-in.) thickness. This was 8.2% plastic deformation in the sealing lands.

The major difference between this test and that of Section III.D.2.c is that the twelve 3/8-in.-diameter bolts were each torqued to 25 in.-lb rather than finger tight. This applied a calculated load on the seal of approximately 5000 lb. The seal area was 0.47 in.; therefore, the prestress in the seal near the sealing surface was around 10-1/2 ksi. As before, tap water was used as the test fluid.

Prior to heating, the leak rate was measured as a function of pressure as seen in Figure 27. In comparing these results with those of the prior test, it is evident that the higher torque on the bolts reduced the preactivation leak rate.

Pressure was removed, and the system was heated to approximately 149°C (300°F). Pressure was then applied in steps to 1500 psi and held constant while temperature was increased to 260°C (500°F). No leakage was evident throughout this procedure. The requirements having been met, pressure was increased in steps above 1500 psi while the temperature was held at 260°C (500°F). There was no leakage until 4250 psi of pressure was applied, and all

Figure 27. Preheating Leakage (67°F)

Figure 28. Leakage at Temperature

Figure 29. Leakage at Room Temperature

the water flowed past the seal in seconds. The accumulator was then refilled, and the pressure was again increased in steps while at 260°C (500°F). This time there was no leakage until 3700 psi was applied — at which pressure the water again flowed past the seal in seconds. Table 9 provides the temperature and pressure history for the above procedure. Figure 28 shows the oscillograph trace when the seal failed.

The system was allowed to cool overnight without pressure on the seal. Pressure was then applied in steps. As seen in Figure 29, leakage started well before the 3700- to 4100-psi region of the hot test (Figure 28). The postactivation leak rate is greater than the preactivation leak rate. The data show that the seal must be kept at temperature in order to maintain its high-pressure sealing capability.

The test fixture was disassembled. The sealing area on the stainless steel surfaces was more visible than on the prior test (Section III.D.2.c), but the grooves (if any) were not feelable.

The ring thicknesses (in inches) were measured at 90° intervals: (1) outer ring — 0.2120, 0.2130, 0.2126, and 0.2121 in.; (2) inner ring — 0.2120, 0.2126, 0.2126, and 0.2120 in.

The high spot on the outer ring at Position 2 had been noted prior to test. Pretest measurements ranged from 0.2114 to 0.2130 in. The outer diameter ranged from 2.541 to 2.544 in. after the test. Prior to test, the outside diameter was measured at 2.545 in. The inner diameter ranged from 1.993 to 1.998 in. after the test, compared to a pretest measurement of 1.998 in.

e. Endurance Test 1. The objective of this test was to operate the seal for approximately 10 days in brine at 260°C (500°F) with a 1500-psi differential pressure. Prior to this test, the seal had been returned to ESG where it was heat-treated again and the sealing lands deformed 6.9%.

The twelve 3/8-in.-diameter bolts were each torqued to 25 in.·lb, the same as for the prior test (Section III.D.2.d). Brine was backfilled into the system. The brine (manufactured by L'Garde) has the following nominal composition and pH:

- a. H₂S: 300 ppm
- b. NaCl: 25,000 ppm
- c. CO₂: 1,000 ppm
- d. H₂O: balance
- e. pH: 5.

Prior to heating, the leak rate was measured as shown in Figure 30. A constant leak rate did not occur; the average leakage was 10 cm³/min at a differential pressure of ~150 psi. In the prior test (Figure 29), such a leakage was not observed until a 800-psi pressure was reached. The seal or its installation appeared to have been better in the prior test.

The assembly was heated to 260°C (500°F). Temperature and pressure histories for the test are provided in Table 10. The goal was to operate at 2400 psi front-face pressure and 900 psi back-face pressure. In this manner, there would be brine on both sides of the seal, resulting in a conservative and perhaps a more realistic test. Initially, front-face pressure increased because of the expansion of the heating brine.

Table 9
Requirements Test, Temperature and Pressure History

Time after start of heating (min)	Temperature (°F)	Pressure ^a (psi)
0	67	50
12	231	50
18	277	50
26	293	100
32	300	100
43	299	300
48	297	550
53	301	700
56	302	800-850
62	300	900-950
66	301	1000
69	301	1100
72	300	1200
75	300	1300
78	301	1400-1450
81	300	1500
90	360	1500
105	458	1500
122	500	1500
128	505	1750
130	508	2000
132	506	2350
135	502	2500
137	501	2750
139	502	3000
141	502	3250
143	502	3500
145	502	3750
147	502	4100
153	502	4250 FAILURE
154		0
159	496	1700
161	497	2000+
162	497	3050
165	497	3200
169	499	3700 FAILURE

^aPressure was changed to value given at time indicated and held constant until next time interval.

Figure 30. Preheating Leakage

Figure 31. Second Leak at Temperature

Table 10
Endurance Test Temperature and Pressure History

Time after start of heating (min)	Temperature (°F)	Pressure ^a (psi)	
		Front-face	Back-face
12	289	50	0
18	334	90	0
23	379	150	0
26	399	170	0
46	457	350	0
49	471	400	0
56	482	480	400
59	486	500	405
63	497	550	408
66	500	1500	408
68	500	1575	900
74	494	2300	910
Brine surged past seal			
79	496	1500 ^b	0
84	498	1300 ^b	0
85	499	1100 ^b	850
89	503	1150 ^b	860
101	530	850	0
110	547	950	0
113	557	1020	0
121	565	1275	0
124	567	1280	0
125	568	1300	0
127	569	1400	0
130	571	1500	0
143	570	1520	0
165	566	1500	0
174	565	1525	0
392	Brine surged past seal		
1104	542	150	0

^aDuring heating, pressure increased gradually due to brine expansion. At relatively constant temperatures, pressures were increased at time indicated and held approximately constant until the next time period.

^bBrine was seeping past the seal during the 79- to 100-min test period (see Figure 18).

When the differential pressure reached 1400 psi (2300 psi front face and 910 psi back face), the 115 cm³ of water flowed past the seal in seconds. The accumulator was refilled. A 1500-psi front-face pressure with zero back-face pressure was applied. While there was only a minor leak this time (see Figure 31), it was still a leak and too great for an endurance test. The differential pressure was reduced as low as 250 psi without achieving a seal. The temperature was then increased to about 299°C (570°F) in the hope of developing a seal. This worked, as shown in Table 10. A 1500-psi front-face pressure (with no back-face pressure) was held.

A back-face pressure should not make it more difficult to seal as long as the differential pressure remains constant. The testing would imply otherwise, i.e., a 2300-psi front-face and a 910-psi back-face pressure produced a massive failure. A few minutes later, however, a 1500-psi front-face pressure and no back-face pressure produced only a slight leak. The reason for this is unknown. It was decided to run the test without a back-face pressure.

After 262 min (4-1/2 h), the brine surged past the seal, as determined from the oscillograph trace. Note that the temperature dropped during the night from 296 to 283°C (565 to 542°F). The temperature at the time of failure is unknown. This reduced temperature may have relaxed the seal enough to allow the brine past.

The heat was turned off. A few hours later, the leak rate at 49 to 52°C (120 to 125°F) was measured (shown in Figure 32). The seal held pressure at 440 psi and started leaking at 525 psi.

After the seal was removed, thicknesses were measured and compared to ones taken prior to test (Table 11). These were then compared to similar data from the successful second test as seen in Table 12. The data show that the seal thickness varied by more than 0.005 in. before and after the unsuccessful test but by less than 0.001 in. before the successful test. This waviness is postulated as the cause of premature failure. It would appear to be a credit to the concept, however, that it did as well as it did, i.e., holding 1500-psi brine for nearly 4 h after installing the seal with only 25 in.·lb torque on each bolt.

The outer diameter before installation was 2.544 to 2.548 in.; after testing, it was 2.544 to 2.546 in. The inner diameter was 1.996 to 1.998 in. after installation and 1.996 to 1.998 in. after testing.

f. Endurance Test 2. The objective of this test was to repeat the endurance test for 10 days in brine at 260°C (500°F) with a 1500-psi differential pressure using a new seal of identical design, designated ESG-9.

The twelve 3/8-in.-diameter bolts were each torqued to 50 in.·lb. This applies a calculated load on the seal of approximately 10,000 lb. The seal area was 0.47 in.²; therefore, the prestress in the seal near the sealing surfaces was about 21,000 psi (prior to heating).

Brine was backfilled into the system. Prior to heating, the differential pressure across the seal was increased in steps until 1500 psi was achieved. There was no leakage. The differential pressure was then reduced to zero but with 900-psi pressure on both sides of the seal. This pressure keeps the brine in solution during heating and testing.

The seal temperature was increased to 260°C (500°F), at which time the front-face pressure was increased to 2400 psi, producing a differential pressure of 1500 psi. Again there was no leakage, nor was there any during the

Figure 32. Post-Heating Leakage

Table 11
Measured Thicknesses (in.)

Position	V	1	2	3
Outer ring				
Before test	0.2124	0.2100	0.2074	0.2114
After test	0.2137	0.2107	0.2084	0.2116
Inner ring				
Before test	0.2122	0.2099	0.2072	0.2114
After test	0.2134	0.2107	0.2086	0.2117

Table 12
Seal Thickness Comparisons

	Test 2	Test 3
Average thickness (in.)		
Before test	0.2121 ^a	0.2102
After test	0.2124	0.2111
Thickness variation (in.)		
Before test	0.0006 ^a	0.0052
After test	0.0010	0.0053
Thickness growth (in.)		
Minimum	N/A	0.0002
Maximum	N/A	0.0014
Average	0.0003	0.0009

^aBased upon four measurements rather than eight.

full 10 days (240 h) of the test. The average temperature during the test was 259°C (498.5°F). Generally, the temperature was within 2°F of this; however, the temperature extremes were 255°C (491°F) and 263°C (506°F).

The pressure-producing equipment has high-pressure seals that do have friction. Therefore, the pressure varied considerably during the test. The average pressure was 1598 psi, while actual pressure varied from 1400 psi to 1950 psi. The 10-day endurance test was completed successfully.

g. Shutdown Test. At the conclusion of the successful Endurance Test 2, additional tests were conducted to further evaluate the performance of the seal (ESG-9). These tests included pressurization at temperature until leakage occurred and monitoring leakage, if any, as the seal cooled to ambient temperature. The pressure was increased in steps with the seal temperature still at 260°C (500°F). At a differential pressure of 1800 psi, there was no leakage. A leak rate of 2-1/2 cm³/min occurred at 2200 to 2250 psi. Pressure was increased to 2500 psi, and the brine surged past the seal in seconds. Figure 33 shows the trace for this portion of the test.

The accumulator was then refilled with brine, and the differential pressure was set at 1500 psi (2400 psi front face and 900 psi back face). Because of the prior leak, the seal had cooled to 254°C (490°F). The seal held the pressure.

The heat was turned off and the test section cooled with the differential pressure maintained at 1500 psi. When the seal temperature reached 85°C (185°F) (79 min after the heat was turned off), a 13-1/2 cm³/min leak rate started. One minute later the brine surged past the seal (see Figure 34).

The system was disassembled. To the eye, the Nitinol seal and its stainless steel interfaces were in good condition. No corrosion was evident except that surfaces were blackened by the brine. The seal has two rings of contact with the steel on both sides of the seal. Between these rings, the seal and steel were shiny since these areas were not exposed to new brine. Subsequent macroscopic examination revealed some pitting on the sealing surfaces.

It was not clear if the seal indented the steel. Feeling the interface by fingernail gave the impression that there was some indentation, but it could have been the etching of the steel by the brine.

Thickness measurements of the ring were taken 90° apart before and after the 10-day test:

Position	Thickness (in.)			
	1	2	3	4
Outer ring				
Before test	0.2231	0.2247	0.2240	0.2232
After test	0.2228	0.2231	0.2230	0.2225
Inner ring				
Before test	0.2235	0.2250	0.2243	0.2235
After test	0.2225	0.2230	0.2230	0.2225

PRESSURE (psi)

LEAK RATE (cm³/min)

Figure 33. Effect of Increasing Pressures (500°F)

TEMPERATURE (°F)

LEAK RATE (cm³/min)

Figure 34. Effect of Decreasing Temperature (1500 psi)

From the above, it is seen that the thickness decreased as much as 0.002 in. Thickness variation was 0.002 in. prior to the test but only 0.001 in. after the test. The outer and inner average diameters after the test were 2.547 and 2.026 in. (The seal apparently expanded to rest against the gland's outer diameter.)

h. Summary of L'Garde Demonstration Tests. The objective of the first test (Section III.D.2.c) was to demonstrate that activation of the Nitinol seal produced sealing. The seal was installed with bolts, each torqued finger tight. The seal leaked rapidly at only 200 psi prior to heating. After heating to 149°C (300°F), the seal did not leak at 800 psi and only slightly at 1000 psi. The objective of the first test was met.

The primary objective of the second test (Section III.D.2.d) was to demonstrate that the seal would function at 260°C (500°F) and a 1500-psi differential pressure. Each bolt holding the seal was torqued to 25 in. lb. Prior to heating, there was no leakage below 400 psi. After heating, the seal held at 4000 psi and leaked at 4250 psi. The objectives of the second test were met.

The objective of the third test (Section III.D.2.e) was to demonstrate that the seal would operate for about 10 days in brine at 260°C (500°F) with a 1500-psi differential pressure. The installation torque level was 25 in. lb as in the second test. Prior to heating, the seal leaked at about 10 cm³/min at only 150 psi (compared to 800 psi for such a leak rate on the prior test). At 260°C (500°F) and 1500 psi, there was leakage. The temperature was increased to about 299°C (570°F), and the seal held the 1500 psi. Less than 4-1/2 h later, the brine flowed past the seal. It is believed that the seal did not perform in the third test because its pretest (and posttest) thickness varied by more than 0.005 in. In the previous (successful) test, the seal's pretest thickness varied by less than 0.001 in.

The objective of the fourth test (Section III.D.2.f) was to repeat the 10-day endurance test in 260°C (500°F), 1500-psi brine. This test was successful in that the seal remained leaktight under the scheduled test conditions.

The objective of the final shutdown tests (Section III.D.2.g) was to evaluate the performance limits of the seal subjected to the endurance test of Section III.D.2.f. The seal remained leaktight at 260°C (500°F) until pressurized to 2200 to 2500 psi. It retained leak-tightness at 1500 psi, but began to leak when cooled to 85°C (185°F).

The results of these tests are summarized in Table 13.

3. Demonstration Test at Kobe.

a. Seal Design and Fabrication. A 31.75-mm (1-1/4-in.) Nitinol shaft seal was designed and fabricated for testing by Kobe, Inc., of Huntington Park, California. The seals were machined from 7.94-mm (5/16-in.) plate stock. The seal was designed for assembly in a conventional 2-218 O-ring gland. The fabrication procedure consisted of machining to predetermined undersize dimensions, heat-treating it to affix its memory shape, and then sizing it for assembly on a 31.75-mm (1-1/4-in.) shaft. A sketch of the as-machined seal design is given in Figure 35.

The as-machined seal was heat-treated at 500°C (932°F) for 1/2 h and rapidly cooled in air. The seal was then deformed in two dimensions. The thickness was reduced from 4.70 mm (0.185 in.) to 4.47 mm (0.176 in.), a reduction of 1.8%, by pressing between platens in the Riehle Universal Testing

Table 13
Summary of L'Garde Tests

Test	Objective	Result
1. Proof of principle	Demonstrate that activation of the seal produces sealing.	Successful
2. Requirements	Demonstrate that the seal would function at 500°F and 1500-psi differential pressure.	Successful
3. Endurance	Demonstrate that the seal would operate 10 days in brine at 500°F and a 1500-psi differential pressure.	Unsuccessful; but this seal thickness varied by over 0.005 in. and did not seal.
4. Endurance	Same as 3.	Successful
5. Shutdown	Assess performance limits.	Seal remained leaktight to 2200 to 2500 psi. Seal retained leak-tightness at 1500 psi. Seal leaked when cooled to 85°C (185°F).

Machine. The inside diameter was expanded from 29.74 mm (1.171 in.) to 38.89 mm (1.531 in.) using an expansion tool. When heated above the transformation temperature, the Nitinol member will strive to (1) increase in width to its shape memory dimension, thus exerting sealing forces against the mating surfaces of the gland, and (2) decrease in diameter to its shape memory dimension, thus exerting sealing forces against the mating surfaces of the shaft.

Three such seals, designated ESG-4, ESG-5, and ESG-6, were fabricated and delivered to Kobe during the period January to July 1982. Two of the seals were subjected to Kobe's conventional seal endurance test in oil. The oil temperature was 232°C (450°F). One seal was exposed for 2 weeks and the second for 4 weeks. The seals were pressure tested after cooling to room temperature, and Kobe reported that both leaked. Since no pressure tests had been made at elevated temperatures (i.e., above the transformation temperature of the Nitinol), Kobe agreed to conduct another endurance test in 232°C (450°F) oil with intermittent pressure-testing for leak tightness at about 121°C (250°F). Kobe reported that the seal was leaktight at temperatures above 135°C (275°F) but did leak at 121°C (250°F).

This problem of leakage is believed to be related to the onset of transformation and resultant relaxation of sealing forces during cooling. This condition can be overcome by using a Nitinol composition that has a lower transformation temperature.

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Figure 35. Shaft Seal Design for Kobe Demonstration and Pump Tests

E. Tasks 5 and 6 — Pump Seal Tests

These tasks covered the design, fabrication, and testing of Nitinol seals on a commercial geothermal pump in either a field pump test facility or in a downhole pump operation. The 31.75-mm (1-1/4-in.) diameter shaft seals being tested by Kobe under Task 4 (see Section III.D.3) were initially designed and fabricated for testing on Kobe's centrifugal-type submersible pump. One of the seals is presently scheduled for such a pump test in DOE's trailer-mounted geothermal pump test rig now in service at Kobe's Oklahoma City plant. Scheduling of this pump test is dependent on the results of seal demonstration tests being continued by Kobe.

F. Task 7 — Nitinol Technology Development

The objectives of this task were to maintain technical liaison with Nitinol suppliers and pump manufacturers and to evaluate more cost-effective seal fabrication techniques. Contacts made under this effort, and their interests in Nitinol, are summarized. For completeness, this tabulation includes the contacts made during the initial survey, as reported under Task 1.

1. Nitinol Sources.

a. Special Metals Corp.
New Hartford, New York	Produces Nitinol rod and wire products by powder metallurgy process. Tubular products for seal fabrication are feasible. A potential source for Nitinol seal stock.
b. Raychem Corp.
Menlo Park, California	A commercial supplier of shape memory alloy devices; not interested in supplying Nitinol mill products for other uses.
c. Nitinol Technology Center
U.S. Navy NSWC
Silver Spring, Maryland	Not a commercial source of Nitinol. Could provide stock for development purposes but only as "a supplier of last resort."
d. Titanium Metals Corp.
Henderson, Nevada	Can provide large ingots. 50-lb minimum only.
e. Carpenter Technology
Reading, Pennsylvania	Developing ingot casting and fabrication processes. No commercial products produced to date.
f. Nitinol Devices
Escondido, California	Produces wire for shape memory devices.

2. Geothermal Pump Manufacturers.

a. Kobe, Inc.
Huntington Park, California	Immediate applications for shaft seals in commercial submersible pumps.
b. Peerless Pump
Montebello, California	Interested for future applications in centrifugal pumps.
c. Pacific Pump
Huntington Park, California	Interested for future applications in centrifugal pumps.
d. TRW-Reda
Bartlesville, Oklahoma	Interested for future applications in centrifugal pumps.
e. Centrilift, Inc.
Claremore, Oklahoma	Interested for future applications in centrifugal pumps.
f. Sperry-Vickers
Jackson, Mississippi	Immediate application in turbine pumps. However, Sperry-Vickers' pump program has been terminated. Turbine pump development is continuing at Sperry Research.

g.	Worthington Pump,
H. Hilbert Anderson, Inc.
York, Pennsylvania	Interested in future applications in turbine pumps when low-temperature tests are completed.
3. <u>Miscellaneous.</u>		
a.	Rocketdyne Division,
Rockwell International
Canoga Park, California	Electron beam welding of Nitinol rod for seal fabrication at lower cost.
b.	Nitinol Technology Center
U.S. Navy NSWC
Silver Spring, Maryland	Review of Nitinol properties as applicable to geothermal seals.
c.	Radian Corp.
Austin, Texas	Properties of Nitinol as a material of construction for geothermal applications.
d.	Plasma Physics Lab
Princeton, New Jersey	Future applications for remote seals in Tokamak fusion reactors.
e.	Shape Memory Motors
Berkeley, California	Energy conversion in heat engines.

IV. DISCUSSION

Materials characterization studies conducted during the first year of the program covered corrosion resistance, tensile properties, plating, and metallography of Nitinol-55 (55% Ni - 45% Ti) and Raychem Corporation's proprietary "Tinel" alloy. It was shown that Nitinol-type alloys had a high resistance to general corrosion in the geothermal fluids of East Mesa, California, and Magnolia, Arkansas. However, the tests indicated that these materials may be susceptible to pitting and stress corrosion cracking.

Further corrosion testing was conducted by L'Garde and the East Mesa GCTF to evaluate the corrosion resistance of the actual Nitinol material being used in the demonstration and pump seal tests. Tests conducted by L'Garde were in an aggressive synthetic brine containing 300 ppm H₂S at a temperature of 260°C (500°F). It should be recognized that the tests at both facilities were compromised. At L'Garde, the initial autoclave test leaked; thus the actual time in brine and the effects of concentrated dry salt represent uncertainties in the test results. In the East Mesa tests, the test fluid was contaminated with oil; this probably affected to some degree the true exposure to the geothermal fluid. The test results reported should, therefore, be accepted as qualitative rather than quantitative data in any analyses of corrosion behavior. Despite the anomalies in the tests, it was concluded that: (1) Nitinol alloys are highly resistant to general corrosion in geothermal brines; (2) contrary to the results of the first year's tests, there was no indication of susceptibility to stress corrosion cracking; (3) these Nitinol alloys are susceptible to pitting corrosion, albeit a minor effect in tests to date; and (4) Nitinol alloys are superior to stainless steels in geothermal environments.

In the seal demonstration tests, it was shown that the shape memory effect of Nitinol alloys can, in practice, be utilized to generate and maintain a leaktight seal in a geothermal environment. This was demonstrated for flange-type face seals in short-term pressure tests, in which sealing was

accomplished by heating the Nitinol seal above its transformation temperature range, and longer term endurance tests, in which the seal remained leaktight in 260°C (500°F) brine for a period of 10 days. It was reported that the seals tended to leak when subsequently cooled below the transformation temperature. In this respect, it should be recognized that all of these seal tests were made using a Nitinol alloy that had a relatively high transformation temperature range, starting at 105°C (220°F), and that only one design each was tested for flange face-type and shaft seals. It is believed that these apparent problems can be eliminated by selecting an alloy composition with a lower transformation temperature and by optimizing the seal designs.

The field pump tests have not been conducted as planned under the current effort. This delay is attributed to the schedule slippages in the demonstration tests, which were planned to precede the pump tests. Seals were designed and fabricated for both turbine and centrifugal types of downhole geothermal pumps. However, the turbine pump program has been terminated, thus cancelling the planned pump test for flange-type seals. The planned pump test for shaft seals in a centrifugal pump has been delayed pending the results of demonstration tests being continued by Kobe.

Technical liaison with the pump industry has indicated that the need for improved, high-temperature, long-life pump seals is real. Every pump manufacturer contacted during this program expressed interest in the shape memory alloy seal concept, requested to be kept informed on progress, and agreed to consider such a seal in his particular pump application if all demonstration tests proved successful. On the other hand, it is obvious that most of the manufacturers consider this to be a long-term rather than a near-future need. It is believed that this wait-and-see atmosphere is generated by current economic and political conditions rather than by technical considerations. Similarly, there are several newcomers in the Nitinol product field, but progress has been slow, reflecting the low demand in today's market. One of the new and promising innovations in this area is the production of Nitinol products by the powder metallurgy process. To date, the primary products have been bar and wire. However, tubular shapes, which have immediate applications in seal fabrication, have been produced. Powder metallurgy offers the advantages of improved material quality as well as probable fabrication cost reductions.

V. CONCLUSIONS AND RECOMMENDATIONS

Nitinol flange face seals and pump shaft seals have been designed, fabricated, and tested under this program.

Demonstration seal tests have shown that the shape memory effect of Nitinol alloys can be utilized to generate and maintain a leaktight seal in the geothermal environment.

Seal endurance tests have shown that shape memory alloy seals can maintain leak-tightness in a geothermal brine at 260°C (500°F) temperature and 1500-psi pressure for exposures exceeding 10 days.

Nitinol seals have been fabricated for full-size pump tests. It is recommended that the testing of these seals be conducted either in field test rigs or in downhole pumps.

All seal tests to date have been made using one alloy and first-effort seal designs. It is recommended that future efforts include Nitinol alloy compositions with lower transformation temperatures and seal design optimization studies.

Material tests continue to show that Nitinol alloys have excellent corrosion resistance in geothermal brine and are generally superior to stainless steels. It is recommended that corrosion testing be continued to further evaluate the potential for pitting corrosion.

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