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**GEOHERMAL ELASTOMERIC MATERIALS
(GEM) PROGRAM**

Final Report, October 1, 1976—June 30, 1979

By

**A. R. Hirasuna
G. D. Bilyeu
D. L. Davis**

**R. A. Sedwick
C. A. Stephens
G. R. Veal**

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MASTER

**L'Garde, Inc.
Newport Beach, California**

**U. S. DEPARTMENT OF ENERGY
Geothermal Energy**

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GEOTHERMAL ELASTOMERIC MATERIALS (GEM) PROGRAM

FINAL REPORT

FOR PERIOD 1 OCTOBER 1976 - 30 JUNE 1979

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A. R. Hirasuna
G. D. Bilyeu
D. L. Davis
R. A. Sedwick
C. A. Stephens
G. R. Veal

L'GARDE, INC.
1555 PLACENTIA AVENUE
NEWPORT BEACH, CALIFORNIA 92663

PREPARED FOR
UNITED STATES DEPARTMENT OF ENERGY
DIVISION OF GEOTHERMAL ENERGY
CONTRACT DE-AC03-77ET28309 (Formerly EG-77-C-03-1308)

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FORWARD

The technical information reported herein has been developed by L'Garde, Inc., Newport Beach, California, under the Geothermal Elastomeric Materials (GEM) Program, DOE contract DE-AC03-77ET28309 (formerly EG-77-C-03-1308).

The work is sponsored by the Division of Geothermal Energy. The Program Manager is Dr. Robert Reeber. Technical coordination assistance is provided by Dr. Patrick Cassidy and Mr. Anthony Adduci.

The effort is directed for L'Garde by Mr. Alan Hirasuna. The development of this report and the technology advancement achieved under the GEM Program are also attributable to the following personnel: Messrs. Gayle Bilyeu and Gordon Veal (Mechanical Design), Mr. Clifford Stephens (Rubber Chemistry), Mr. Douglas Hender (Heat Transfer Analysis), Drs. Mitchell Thomas and Norman Sjogren and Mr. Richard Wallstrom (Test Procedures), and Messrs. Don Davis, Richard Sedwick, and James Trailer (Fabrication and Evaluation Testing). Invaluable support in preparing this report was provided by Mmes. Pat Wall, Judy Winslow, Diane Friese, and Sylvania Cole.

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STATEMENT OF OBJECTIVES

The following are objectives which were accomplished under the GEM Program:

1. Define geothermal elastomeric seal application where immediate improvements will provide most benefit to the community.
2. Perform elastomer development and evaluation to meet requirements of 1. above (casing packer seal element to survive 260°C (500°F) for 24 hours).
3. Design, fabricate, evaluate, and operate evaluation tests focusing on the pertinent requirements of 1. above.
4. Evaluate current commercially available elastomers which were developed for oil tool equipment under the geothermal conditions.
5. Perform conceptualization of improvements for a packer system for geothermal applications.
6. Engender technology transfer to the extent possible within the scope of the contract.

ABSTRACT

This Final Report is a comprehensive description of the work performed by L'Garde, Inc., on the Geothermal Elastomeric Materials (GEM) Program under U. S. Department of Energy, Division of Geothermal Energy Contract DE-AC03-77ET28309 (formerly EG-77-C-03-1308). The first 12 month's progress was reported in DOE Report SAN/1308-1 which is included as Appendix A.

The primary program objective, to develop a geothermal packer elastomer to withstand 260°C (500°F) geothermal brine with 300 ppm H₂S, 1,000 ppm CO₂, 25,000 ppm NaCl in aqueous solution for 24 hours, was successfully accomplished. In fact the requirement for one elastomer was exceeded, compounds from four elastomeric polymer systems were successfully developed to meet the GEM requirements providing good flexibility for various situations.

Several secondary spin-offs also resulted. The compounds were developed for the casing packer seal application and it was demonstrated that these compounds are directly applicable to the static O-ring and other elastomer applications in similarly unusually severe environments. There is also indication based on drill bit seal tests that the basic compounds will be adaptable to high-temperature dynamic seal applications.

Another secondary spin-off is a different conceptual approach to the thermal casing packer problem. This approach concentrates on minimizing the stresses subjected on the sealing element. Since it is fundamentally different, it has a good chance of advancing thermal packer capability in a revolutionary manner as opposed to an evolutionary manner.

And finally, art was invented which addresses the same thermal packer capability problem that is fundamentally different from the other work. A patent application submitted by DOE is in progress for the "Cure-In-Place" process. The process results in reduced seal element stresses in the packed-off configuraion.

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1.0 INTRODUCTION AND SUMMARY

This Final Report is a comprehensive reporting of the technology developed by L'Garde, Inc., over the last 32 months under the Geothermal Elastomeric Materials (GEM) Program, United States Department of Energy Contract Number DE-AC03-77ET28309 (formerly EG-77-C-03-1308). The fundamental objective of the program is to develop elastomer compounds for the unusually severe downhole geothermal seal application.

1.1 PROGRAM ACCOMPLISHMENTS

The primary objective and several secondary objectives of the Program were successfully met. Though meeting the fundamental objective, to develop a casing packer seal elastomer compound which will operate in a 260°C (500°F) geothermal environment, was highly challenging and carried with it a definite probability of failure, L'Garde was fortunate to be able to conclude the program with very positive results. Packer seals which perform well in the oil field up to temperatures of about 150°C (302°F) run into reliability problems at higher temperatures especially when they get as high as 260°C. Though the stresses induced into the elastomeric element are substantially the same as at the lower temperatures, the loss in elastomer strength at 260°C is substantial and it cannot sustain the stress levels. Other common problems include hardening of the seal at higher temperatures and associated failure. The geothermal elastomeric packer seal problem at 260°C is significant and even the less demanding static O-ring seal is still a problem. Figure 1 rather lucidly illustrates the starting point of the geothermal packer seal development. These post mortem test specimens were run at 260°C in the synthetic brine. At these unusually severe conditions the seals did one of three things; extruded severely (B3), could not withstand the pack-off and cracked without sealing (220-3), or extruded and broke catastrophically (D3 and E3). For about the first 2/3 of the contract, it was doubtful that elastomer improvements alone would provide reasonable performance at the test conditions at 260°C.

Upon conclusion of the development, compounds based on four (one was required) separate elastomer systems molded into full-scale packer seals

FIGURE 1 -- SIM TEST POST MORTEM SPECIMENS, TYPICAL EARLY RESULTS

Company B EPDM -- This and L'Garde EPDM remained elastomeric and survived full 24 hours. Only difference L'Garde EPDM extruded 2.5 in. vs company B's 4.0 in.

L'Garde Peroxide-Cured Fluoroelastomer -- Failed because of inability to elongate sufficiently during seating.

Company D Epichlorohydrin -- Lost all structural strength and became soft and crumbly before seating.

Company E Non-Peroxide-Cured Fluoroelastomer -- Failed by breaking in the high stress region. Survived 3.75H with slow leak, then failed.

successfully sealed in laboratory simulated packer tests for the prescribed duty cycle - 260°C, in synthetic geothermal brine, differential pressure of 3,100 to 4,100 psi, and for at least 46 hours. The four systems were based on the following base polymers: Ethylene Propylene Diene Terpolymer (EPDM, Nordel*), Fluoroelastomer (FKM, Viton*), EPDM/FKM Blend (Nordel*/Viton*), and Propylene - TFE (AFLAS*). All four elastomer systems successfully met the Program objectives and show definite improvement over elastomer compounds which are commercially available. Measurable improvement of the hydrothermochemical stability was achieved in the synthetic geothermal brine which includes an aqueous solution of H₂S, CO₂, and NaCl at the following levels: 300 ppm, 1,000 ppm, and 25,000 ppm respectively. For these conditions, the Nordel compound is the most hydrothermochemically stable showing no effect after 22 hours. These results represent an effort which included formulating and testing 129 compounds and running 96 seal Simulation Tests.

Figure 2 shows post mortem test specimen of one of the better, earlier, Nordel Compounds, seal 217-II-1. This element sealed successfully at 260°C for the required 22 hours, but did suffer a significant level of extrusion. In contrast, one of the latest compounds is shown, post mortem seal 275-1 which is a Nordel/Viton Blend. Only a minor amount of permanent deformation resulted; the seal had an excellent appearance when removed from the test. This element sealed successfully under the same conditions as 217-II-1 except even a higher differential pressure, 3,600 vs 3,100 psi.

Compound 267 packer seals were molded from the Nordel EPDM compound for some packer company tests. The molded seals were provided to them and they tested the seals at 302°C (575°F) and 3,000 psi differential pressure in their laboratory packer simulation tester. The elements sealed successfully for five days and their comment was, "after the test they bounced off the floor just like before the test." They are currently planning to test these elements downhole.

A good quantitative demonstration of the accomplishments is seen through examination of the O-ring SIM Test data and comparing to commercially available compounds. These data are discussed in detail in paragraph 3.1.1, but are summarized here. A test was fabricated to enable static simulation testing of

*Trade names.

FIGURE 2 -- COMPARISON OF POST MORTEM SIM TEST RESULTS -
EARLY VS. FINAL COMPOUND

Early Nordel Compound

Final Nordel/Viton Blend Component

Close-up of Minor
Permanent Deformation

O-rings. The O-rings were tested at 260°C in the synthetic geothermal brine starting at 4,100 psi differential pressure. The test was set for 22 hours and if a compound failed before 22 hours the differential pressure was decreased by 1,000 psi and the test rerun. The reduction in differential pressure progressed to 2,100 psi where the testing stopped if the material failed.

Because this is an unusually severe environment, the GEM compounds have a distinct advantage in that they were developed specifically for this condition. Table I summarizes the final runs made for each of the compounds. The GEM Viton and Nordel compounds performed better than their commercial counterparts. The GEM 255 Viton held at 4,100 psi while the commercial counterparts both broke at 2,100 psi. The GEM 267 Nordel looked excellent after the 4,100 psi run and is capable of higher differential pressures while its counterparts showed incipient failure. There were no commercially comparable counterparts to the Nordel/Viton Blend or the AFLAS, both ran the full 22 hours at the full differential pressure. The Blend looked as good as the 267 Nordel and is also capable of higher differential pressures and the AFLAS suffered minor extrusion. There was no GEM counterpart to the DuPont Kalrez, however, it is of keen interest because it is one of the more chemically stable polymers. It is very expensive, but its expense is justifiable in some situations because of the longer life it renders. For the GEM synthetic geothermal brine environment the 3074 Kalrez did not fair as well as the four GEM compounds in the O-ring test, and in the first 12-month period coupon ageing tests were made on 3073 Kalrez which indicate that it is not as hydrothermochemically stable as the latest GEM compounds (the earlier Kalrez values are in Appendix A, pages 5 and 24). Specific compounding for the geothermal brine environment may result in similar improvements as was accomplished with the GEM elastomers.

Another good quantitative demonstration of the accomplishments is seen through a comparison of compound characteristics for early compounds against commensurate ones at the completion of the program. Table II illustrates the improvements as indicated by the percent of each of the four critical characteristics retained after ageing in brine for 22 hours. Table III lists the virgin and chemically aged values which are represented by the percentage numbers.

TABLE I -- SUMMARY OF O-RING SIM TEST DATA DEMONSTRATING
GEM ACCOMPLISHMENTS

Compound	Designation	ΔP , psi	Time, h	Comment
255-IV-2S-B	L'Garde GEM Viton	3100	22.0	Nibbled Slightly
V-709-90-3	Parker Fluoroelastomer	2100	10.5	Broke
V-747-75-2	Parker Fluoroelastomer	2100	5.25	Broke
267-II-1S-D	L'Garde GEM Norde1	4100	22.0	Excellent Condition
E-692-75-1	Parker EPDM	4100	22.0	Nibbled, 1½-2"
266-II-1S-C	L'Garde GEM Norde1/Viton Blend	4100	22.0	Excellent Condition
291-II-1-C	L'Garde GEM AFLAS	4100	22.0	Minor Extrusion 1" Nibbled 2x~0.5"
3074-3	DuPont Kalrez	2100	22.0	Nibbled 2"

TABLE II -- PROGRESS OF HYDROTHERMOCHEMICAL STABILITY
OF GEOTHERMAL ELASTOMERS

Elastomer	Ult. Tensile @ RT		Ult. Elong. @ RT		Shore A Hard @ 260°C		Extrusion Resist. @ 260°C	
	Early	Present	Early	Present	Early	Present	Early	Present
EPDM Early-E263 Present-267	75%	97%	--	105%	85%	100%	57%	103%
Viton Early-115 Present-255	14%	72%	46%	101%	73%	100%	32%	55%
EPDM/Viton Early-235 Present-266	80%	96%	63%	84%	110%	101%	128%	96%
AFLAS Early-268 Present-291	77%	93%	112%	118%	90%	100%	84%	87%

TABLE III -- GEOTHERMAL ELASTOMERS PROGRESS

Elastomer	Ult. Tensile @ RT. psi		Ult. Elong. @ RT %		Shore A Hard @ 260°C		Extrusion Resist @ 260°C, psia	
	V	CA	V	CA	V	CA	V	CA
EPDM Early-E263 Present-267	1363 1610	1020 1554	>840 141	>840 148	61 92	52 92	9.6 17.1	5.5 17.6
Viton Early-115 Present-255	1699 2195	244 1591	162 224	74 226	80 79	58 79	11.2 11.4	3.6 6.3
EPDM/Viton Early-235 Present-266	1882 1596	1506 1531	681 193	431 163	67 88	74 89	8.3 18	10.6 17.3
AFLAS Early-268 Present-291	1673 2335	1289 2162	394 134	442 158	69 95	63 95	6.7 17.4	5.6 15.2

Note that there is significant improvement reflected by the latest compounds. The 267 Nordel is virtually unchanged by the 22 hour ageing in the synthetic brine with respect to all four characterization parameters. Vast improvement was finally accomplished with the 255 Viton. There is room for improvement on the Extrusion Resistance especially, as is reflected by the Packer Seal Simulation Tests, however, the extrusion resistance is adequate to meet the requirements. The 266 Nordel/Viton is very stable with some minor degradation of the ultimate elongation. The 291 AFLAS shows some minor hydrothermochemical stability in the ultimate elongation. In general, all of the latest formulations showed very good stability considering the unusual severity of environment.

In addition to meeting the primary objective with four elastomer systems instead of the one required, a unique design approach was developed for a geothermal packer system which shows promise, and an innovative "Cure-In-Place" process was invented for which DOE has a current patent application. The identified packer design approach concentrates on minimizing the stresses to which the sealing element is subjected, hence, the name the "Min-Stress Packer Concept." Sufficient interest was generated such that DOE is funding development of an implementation of the concept. The "Cure-In-Place" process is a seal molding process

whereby the packer seal can be packed-off without inducing significant stresses in the seal, thus maximum reserve remains for resisting the differential pressure. It was shown that the concept provides good advantage for thermal packer applications and furthermore, will allow extremely extrusion resistant compounds, which otherwise could not be used, to be employed.

1.2 PREVIOUSLY REPORTED WORK

The first 12 of this 32-month effort was previously comprehensively reported in December 1977 under DOE report number SAN/1308-1. For completeness this report is herein included as Appendix A.

Much of the first 12-month's effort was spent designing, fabricating, and fine tuning the evaluation tests that were employed. Because of the unusually severe environmental requirement, the elastomers are required to operate at their upper limits. When there is comfortable margin between requirements and the elastomer capability, simple characteristics such as tensile strength, elongation, modulus, compression set, etc., are sufficient to identify the correct material for the job. However, in this instance where the capability of the elastomers is being used to its ceiling limits, it becomes especially important to assess the interactions between the various environmental factors when evaluating the operational sufficiency of the elastomers. This leads to tests which become a better and better simulation of the operational conditions and for GEM a good simulation test is essential. Therefore, special tests simultaneously simulating the temperature, chemistry, pressure, differential pressure, mechanical forces, etc. were designed and fabricated providing evaluation tests which correlate well with the actual requirements.

The special tests developed include an instrument to measure extrusion resistance of elastomer coupons, an autoclave and brine recipe for environmental ageing elastomer coupons, and a packer simulation test which submits a full-scale packer seal to downhole environments in the laboratory. The tests all worked out quite well providing a large quantity of extremely pertinent information in an expeditious manner. The resulting information provided good insight as to the thermal packer Achilles Heels.

A significant amount of compound development was also accomplished during the previous period. Unfortunately much of that early compounding did not result in any positive results and consequently is obsoleted by the later work. The interesting and successful elastomer development was accomplished during the later portion of the program reported herein for the first time.

The Min-Stress Packer Conceptual Approach developed during the first 12 months and the report in Appendix A includes a detailed explanation of the approach and concerns along with a sample implementation of the concept. The work identifies the critical failure modes for thermal packers and provides a means of raising the capability through addressing the failure modes.

1.3 FINAL REPORTING PERIOD

Work accomplished during the period from the end of the first 12-month's effort concluding with the end of this contract is comprehensively reported in the body of this report. The work culminated in the successful development of the Nordel, Nordel/Viton Blend, Viton, and AFLAS elastomer systems for the 260°C geothermal environment. The work was centered around the geothermal casing packer seal application with the thought that this will kill "two birds with one stone". The casing packer application submits the elastomeric element to unusually severe mechanical stresses and one of the sealing surfaces is unmachined casing. The thinking, which was substantiated, was that successful packer element elastomers should also work directly as static O-ring seals since the conditions are less severe with closer clearances and all machined surfaces.

Good substantiation of the progress made with the elastomer compounds development was accomplished through additional testing beyond the standard Screening Tests and packer seal Simulation Tests. O-ring Simulation Tests, higher temperature tests, and extended time tests were carried out by L'Garde to further explore and substantiate the capabilities of the elastomers developed. Independent testing of the L'Garde GEM compounds by other companies was also accomplished. Two packer companies ran their own laboratory Simulation Tests, Terra Tek tested the static seal packer compounds in their dynamic drill bit seal simulation test, and Sandia Laboratories submitted tensile coupons to a blow-out preventor environment.

All testing indicated that the L'Garde GEM elastomer compounds exceeded the capability of the other elastomers under evaluation except the drill bit seal test. Though the GEM blend compound performed well, as might be expected, the drill bit seal tests indicated that definite improvement is indicated through refining the compounds to include dynamic seal characteristics, primarily lubricity. Nevertheless, the Nordel/Viton compound performed well and sealed for more than 45 hours.

The above efforts involving other companies, and other applications served a second objective. These efforts provide good exposure of the technology to the community thus accomplishing a key DOE goal for these energy projects, technology transfer. The industrial community first-hand experience with the elastomers provides a much more lasting impression than reading about them in a technical report. If these experiences are successful the industrial participants will be self motivated to integrate the elastomer compounds into their product lines.

As with the Min-Stress Packer Conceptual Approach reported in Appendix A, another idea was pursued to solving the thermal packer problem that was also a different approach in a basic way. Rather than a direct attack on the failure symptom, i.e. developing or discovering a better material which will not extrude and break under the unusually severe geothermal packer environment, a means was found of alleviating the severity of the environment.

The concept invented to accomplish reducing the environmental severity is the "Cure-In-Place" concept. Realizing that a good deal of stress is created in the seal element from pack-off alone, the "Cure-In-Place" concept virtually eliminates this component of stress by packing-off the seal when it is still plastic prior to its being cured or vulcanized. The technique has the further advantage of enabling very high modulus elastomer compounds to be used which provides much improved extrusion resistance and which would otherwise crack and break during the pack-off operation if applied in the classical manner.

The "Cure-In-Process" concept is currently under domestic patent application by the DOE.

2.0 PROBLEM AND APPROACH DEFINITION

Section 2.0 describes the process whereby the specific objectives for the GEM Program performed by L'Garde, Inc., were defined. This effort was carried out at the beginning of the Program.

2.1 FORMULATION OF SPECIFIC OBJECTIVES

Seal materials are most commonly made from elastomers because they are the most practical seal material. They are economical, relatively very inexpensive except for a minority made from exotic polymers and are reuseable except for very severe environments. They are very reliable and forgiving with respect to installation and manufacturing tolerances of the mating parts to be sealed. Because of the forgiving nature of elastomeric seals, they can be successfully installed by unskilled mechanics and they can be installed in field environments. On the other hand metal seals are extremely sensitive to contamination and handling. L'Garde's experience with gold plated metal K-seals on the Simulation Test, reported in Section 4.0 of Appendix A, indelibly imprinted an appreciation for elastomeric seals. Extreme care is required for the metal seals to clean the sealing surfaces and to apply the correct and evenly distribute the preload. Furthermore, each of the three seal applications required development of special procedures for each unique set of circumstances to assure that the seal is delicately installed without abrasion or bumping. Elastomers have the added advantage of flowing and conforming to irregularities while providing elastomeric resistance to continued flow after seating. On the other hand plastic seals continue to flow after seating and do not achieve the stable equilibrium which is possible with elastomers and must be constantly recinched to maintain the sealing force.

In view of the multitude of benefits provided by elastomeric materials in seal applications, the GEM Program objective fulfills an important need. Development of elastomers to meet geothermal environments will extend their benefits into that regime.

The initial task defined specific program objectives within the overall goal to develop improved elastomers for high temperature geothermal seals. Visits were arranged with geothermal energy producers and well owners, well

tool and drilling equipment manufacturers, and Government laboratories performing related research and development. The purpose was to become familiar with problems being encountered through briefings such that L'Garde's program could be defined to best fill the needs of the geothermal community, i.e. applied R&D as opposed to pure R&D. More specifically, L'Garde's purpose was to identify that seal application which would benefit the geothermal community most if it were improved first.

The conclusion after digesting voluminous and often obscure and elusive data was that the community is in need of a formation packer. Formation packers are needed for interval testing during exploration to define the full potential of the reservoir, for drill stem testing to determine optimum well depth during the drilling operations; and for stimulation both hydraulic fracturing and fluid treatment. This conclusion was confirmed by Messrs. J. McNitt and J. Barnea's office at the UN and Dr. J. Rowley's office at LASL. However, though high-temperature formation packers are needed, development of elastomers for this application was judged too ambitious a goal for the first effort. Therefore, it was recommended and approved to first develop improved elastomers for casing packer elements.

2.2 DOWNHOLE WELL CONDITIONS

High-temperature downhole seals tend to fail from extrusion and/or hardening. The more interesting geothermal wells have temperatures of 260°C (500°F) and higher and it is not unusual to have compositions of the fluid which are unusually reactive to elastomeric compounds.

260°C causes most rubber compounds to harden by thermal breaking of double bonds and forming new crosslinks to form a three dimensional matrix with less and less ability to yield and recover when deformed. This action proceeds quite rapidly in air (oxygen). In water or steam at high temperatures the hot water acts as an active swelling and softening agent, sufficient to break crosslinkages causing most cured elastomers to devulcanize or revert and to become soft and weak. The geothermal well fluid often contains sulfur in the form of hydrogen sulfide. At high temperatures sulfur rapidly breaks double bonds and forms crosslinks until the rubber becomes hard and brittle. The

fluid also can contain considerable concentrations of metallic salts completely ionized. The effects of such salts on elastomeric compounds is not known.

2.3 EARLY CONSIDERATIONS OF ELASTOMERS

The development and evaluation of elastomers for this first period was confined to commercially available elastomers, reinforcing fillers and curing systems. The most common and lowest cost elastomers are the butadiene copolymers. These elastomers are copolymers of butadiene and styrene or butadiene and acrylonitrile (the latter is used in nearly all oil well seals because of its resistance to degradation by crude oil). These polymers have unsaturated backbone structure - $C = C - C - C = C$ - etc., the double bond being used to get fast curing with sulfur. Unfortunately only a few of the double bonds are used to form the sulfur crosslinkages; consequently sulfur in the geothermal fluid continues to break those remaining double bonds to form more sulfur crosslinks until the seal compound becomes very hard and weak, crumbling or cracking during use.

A logical step would be to consider elastomers free of excess double bonds in the backbone. There are a considerable number of these as discussed below.

Butyl rubber is a copolymer of isobutylene and small amounts of isoprene to give an elastomer with most of the backbone as single bonds. It has a long history of use for the curing bags where it is exposed to water at 177°C (350°F); however, it softens severely at 260°C and is slowly devulcanized by the hot water.

Epichlorohydrin polymers (chlorinated epoxy propane) have the required saturated backbone. The high concentration of pendent chlorine groups makes it very resistant to solvents and fuels. There was no information about resistance to high-temperature brine. A commercial formulation was selected for evaluation although softening at 260°C and extrusion failure was expected.

The polyacrylics (copolymers of ethyl acrylate and chlorovinyl ethyl ether or butyl acrylate and acrylonitrile) have the desired saturated backbone and are highly resistant to heat oxidation; however, neither are resistant to water or steam at high temperature.

The chloroprene elastomers have good oxidation resistance, but poor water resistance.

Ethylene propylene diene terpolymers are similar to the butyl rubbers in properties. They have the desired saturated backbone with a few double bonds to facilitate curing. They are widely used in tire curing bags where resistances to water at 350°F is required. It was selected for limited evaluation.

Silicone elastomers have the best high-temperature oxidation resistance and maintain their physical properties better at 260°C than any of the elastomers. The backbone is -Si-O-Si-O- which is thermally stable. No applicable information about resistance to sulfur or water or high temperatures was found. However, small amounts of oil cause severe degradation. Fluorosilicone elastomers are similar to the silicones except they have been fluorinated to give the compounds some resistance to oils. According to Dow Corning, applicability of silicone rubber to the GEM environment is uncertain, therefore, simple Screening Tests to determine the hydrolytic and sulfur resistance are recommended.

The fluoroelastomers (Vitons, Fluorels) are fluorinated hydrocarbons with completely saturated -C-C- backbone to give the best resistance to heat, oxidation and attack by sulfur. Peroxide cured Vitons were selected for compounding, evaluation of cure systems and reinforcing fillers principally because there was a considerable amount of data reported in the literature indicating good prospects in steam and fluids environments and, the Air Force Materials Laboratory has been experiencing success with them at 260°C for high performance aircraft hydraulic cylinder applications.

As a result of this task, it was determined that the elastomer development would be designed around the casing packer seal element operating at 260°C. Furthermore, it was determined that the polymers to be developed for this application was the then newly introduced peroxide cured family of Viton fluoroelastomers. After significant development, little success was experienced with the peroxide cured Vitons. Hence, other alternates were investigated in the interest of developing some improvements over what was then being used, primarily Nitriles (Buna N). Table IV shows all the basic polymer types which were

TABLE IV -- ELASTOMERIC POLYMERS COMPOUNDED UNDER GEM PROGRAM

Common Chemical Designation	Trade Name	Manufacturer	Comment
Fluoroelastomer (FKM)	Viton "E" type "G" type	DuPont	Bisphenol cured Peroxide/Triazine cures
	Fluorel 2170's 2181	3M	Bisphenol cured
Ethylene Propylene Diene (EPDM)	Nordel	DuPont	Peroxide cured
Propylene-TFE	AFLAS	Asahi Glass	Peroxide/Triazine cured
Perfluoroelastomer	Kalrez	DuPont	Finished parts only
Dimethylsilicone (VMQ)	Silastic	Dow Corning	
Fluorosilicone (FVMQ)	Silastic	Dow Corning	Resistant to hydrocarbons

finally investigated under the GEM Program. Within each polymer type several specific polymers may have been investigated. For example, there were 9 fluoroelastomer polymers investigated - Viton GH, Viton GLT, VT-R-4590, Viton E-60C, Fluorel 2174, Fluorel 2175, Fluorel 2178, Fluorel 2179, and Fluorel 2181.

2.4 SYNTHETIC GEOTHERMAL BRINE

A synthetic geothermal brine was developed to provide the simulated down-hole chemistry in the laboratory. This brine became the standard testing environment for all simulated environment packer seal and O-ring SIM Tests and autoclave chemical ageing.

Based on reports and discussions with Dr. J. Apps at the Lawrence Berkeley Laboratory, a specification was developed for a synthetic geothermal fluid. The approach was to avoid simply compiling all the maximums for each constituent that has been measured as this may result in unrealistically severe chemistry, rather to apply judgement and generate a specification which covers the majority of potential geothermal wells. For example total dissolved solids can run as high as a few hundred thousand ppm in the Salton Sea Area, however, the great majority of known potential wells are included at levels below 25,000 ppm.

The constituency specification used for the current SIM tests is as follows:

H_2S	300 ppm
$NaCl$	25,000
CO_2	1,000
H_2O	balance

The recipe developed by L'Garde for the synthetic geothermal brine takes into consideration factors such as practicality for a laboratory operation, supply, storage, and especially safety. Valuable suggestions were made by D. Shannon of Battelle Pacific Northwest and A. Troiano of Case Western Reserve University. The H_2S and CO_2 are formed from $Na_2S \cdot 9H_2O$ and $NaHCO_3$ respectively. The test uses a finite amount of H_2S thus limiting the potential exposure to personnel. If all of the H_2S were to escape into the room including the excess leftovers, the resulting concentration would be about 1 ppm as compared to OSHA's maximum allowable of 10 ppm. This approach is preferred over one where bottled H_2S is used and potential for lethal concentrations of H_2S exist. The recipe for the synthetic fluid is as follows:

$H_2S \cdot 9H_2O$	5.29 gms.
$NaHCO_3$	4.77 gms.
$NaCl$	56.64 gms.
H_2O distilled	1430.00 gms.
$HCl(0.1N)$	1.0 liter

3.0 MISCELLANEOUS TESTING

The bulk of the evaluation testing performed on the GEM Program was associated with the standard evaluation and development cycle of Screening Tests and SIM Tests at 260°C in the synthetic geothermal brine which are reported in Section 4.0. This evaluation and development cycle was specifically designed and developed for this program for the development of geothermal casing packer seal elastomers. In addition to this central theme, several peripheral supporting investigations were carried out by L'Garde and independently by other organizations and are so categorized below. These efforts verified the success of the elastomer development under the GEM Program.

3.1 IN-HOUSE PERIPHERAL TESTING

Significant valuable evaluation testing was performed outside the realm of the standard Screening and SIM Tests. These tests explored additional capability of the developed GEM elastomer compounds and their performance relative to commercially available high-performance compounds.

3.1.1. O-Ring SIM Testing

In that Kalrez is known to be applicable to unusually severe environmental requirements, there was interest to evaluate it for the GEM geothermal environment. However, because it is a very expensive elastomer, and it was questionable if a part as large and thick as the packer seal for the SIM Test could be molded from it, a more appropriate means than the packer seal SIM Test was needed for exotic elastomers. These requirements and barriers resulted in a modification to the packer seal SIM Test such that a standard O-ring could be the test specimen.

The packer seal SIM Test was modified to accept 2-329 O-rings (about 2 inch diameter and .25 inch cross-sectional diameter) as test specimens.

A. O-Ring Modification to SIM Test.

The statement-of-work required modification of the packer seal SIM Test to accept and test O-rings at temperature, under differential pressure, and in the synthetic geothermal environment. The bottom fixture of the SIM Test

which supports the packer seal was replaced by a 2.375 inch inside diameter cylinder which serves as the outside diameter sealing surface for a 2-329 O-ring. The high pressure supply from the brine pump feeds into the test fixture through a port at the center of the bottom. A plug with a standard 2-329 industrial static O-ring seal groove with no back-ups fits into the cylinder after the O-ring is installed. After insertion the O-ring fixture is held in place in the cylinder against the differential pressure by the ram which normally seats the packer seal. This presents a severe environment to the O-ring in that the static seal groove with no back-up is designed for a maximum of 1,500 psi while the O-ring SIM Test is usually started at 4,100 psi and 260°C. Figure 3 shows the fixture which fits inside the packer seal SIM Test vessel and modifies it for O-ring testing.

B. Discussion of O-Ring SIM Test Procedure.

The O-ring SIM Test turned out to be an excellent test for comparative evaluation of seal elastomers. For exotic elastomers such as Kalrez, making large packer seals is prohibitively expensive without even considering the possibility that it may not be possible to make a Kalrez packer seal test specimen because of the inherent molding difficulties associated with the polymer.

A number of O-ring SIM Tests were run all at 260°C, in synthetic geothermal brine, and at progressively lower pressures from 4,100 psi down to 2,100 psi until the seal successfully seals for 22 hours. If the seal material failed at the 4,100 psi starting point on each subsequent run the differential pressure was decreased 1,000 psi each time with a final try at 2,100 psi. No variations such as run time and temperature were made, however, additional variations in the run matrix such as these are easily accommodated.

C. Discussion Of O-Ring SIM Test Results.

The current favored L'Garde GEM packer seal compounds were run in the O-ring SIM Test and compared against commercially available counterparts. The commercial compounds selected were likely geothermal candidates which were identified by Dr. Charles Arnold of Sandia Laboratories in Albuquerque plus 3074 Kalrez, a Calidria filled compound provided by DuPont. To maintain full perspective it must be remembered that the L'Garde GEM compounds have the distinct advantage of being developed specifically for this unusually severe 260° geothermal brine environment.

FIGURE 3 -- O-RING SIM TEST FIXTURE

Overview of Fixture with Packer Seal Ram

Close-Up of O-Ring Fixture Prior to Insertion Into Cylinder

In general all four L'Garde GEM compounds; 255 Viton, 267 Nordel, 266 Nordel/Viton Blend, and 291 AFLAS; faired well. The 255 Viton and 267 Nordel faired better than Parker counterparts in the 260°C synthetic geothermal brine environment. All four faired better than the 3074 Kalrez compound. For this unusually severe environment, the 267 EPDM and the 266 EPDM/Viton Blend compounds looked and performed excellently.

Table V presents data associated with the 14 O-ring SIM Tests performed. Figure 4 shows the post mortem photographs of the fluoroelastomer compounds. The 255 Viton successfully sealed for the 22 hours at 3,100 psi differential pressure. Post mortem examination showed extremely minor damage. Very slight extrusion existed and was only apparent after very close inspection from a glancing profile view. Both the Parker V-709-90 and V-747-75 fluoroelastomer compounds broke after 10.5 and 5.25 hours respectively at the minimum test pressure of about 2,100 psi.

TABLE V -- O-RING SIM TEST IN SYNTHETIC GEOTHERMAL BRINE @ 260°C

Compound	Designation	ΔP , psi	Time, hr.	Comment
255-IV-1S-B	L'Garde Viton	4100	6.25	Broke
255-IV-2S-B	L'Garde Viton	3100	22.0	Nibbled Slightly
V-709-90-1	Parker Fluoroelastomer	4100	4.0	Broke
V-709-90-2	Parker Fluoroelastomer	3100	9.0	Broke
V-709-90-3	Parker Fluoroelastomer	2100	10.5	Broke
V-747-75-1	Parker Fluoroelastomer	4100	.15	Broke
V-747-75-2	Parker Fluoroelastomer	2100	5.25	Broke
267-II-1S-D	L'Garde Nordel	4100	22.0	Excellent Condition
E-692-75-1	Parker EPDM	4100	22.0	Nibbled, 1½-2"
266-II-1S-C	L'Garde Nordel/Viton	4100	22.0	Excellent Condition
291-II-1-C	L'Garde AFLAS	4100	22.0	Minor extrusion 1" Nibbled 2x 0.5"
3074-1	DuPont Kalrez	4100	.75	Broke
3074-2	DuPont Kalrez	3100	3.75	Broke
3074-3	DuPont Kalrez	2100	22.0	Nibbled 2"

FIGURE 4 -- FLUOROELASTOMER POST MORTEM O-RING SPECIMENS

GEM Viton
 $\Delta P = 4100$ psi

GEM Viton
 $\Delta P = 3100$ psi

Parker Fluoroelastomer
 $\Delta P = 4100$ psi

Parker Fluoroelastomer
 $\Delta P = 3100$ psi

Parker Fluoroelastomer
 $\Delta P = 2100$ psi

Parker Fluoroelastomer
 $\Delta P = 4100$ psi

Parker Fluoroelastomer
 $\Delta P = 2100$ psi

The L'Garde GEM 267 EPDM shown in Figure 5 successfully sealed for 22-hour run at the maximum differential pressure of 4,100 psi and was in excellent condition for this unusually severe environment when removed from the test fixture. Some permanent set was evident as indicated by the squaring of the O-ring on the low pressure side of the seal. The Parker E-692-75 EPDM also sealed the 22 hours at 4,100 psi, however, breakage was apparent over a 1½ to 2 inch section of the O-ring. Local extrusion and breakage was occurring which indicated incipient failure. Total failure would probably occur at this point with continued testing.

The L'Garde GEM 266 EPDM/Viton blend shown in Figure 5 also successfully sealed for the 22-hour run at the maximum differential pressure of 4,100 psi. It survived the test in excellent shape and looked the same as the 267 EPDM. No comparisons of commercial counterparts were available for the blend.

The L'Garde GEM 291 AFLAS shown in Figure 6 successfully sealed for the 22 hours at 4,270 psi differential pressure. There was minor extrusion over about a one-inch section with ½-inch sections on either side where rubber was nibbled away indicating incipient failure. No comparisons of commercial counterparts were available for the AFLAS.

A final commercial elastomer was tested, DuPont's 3074 Calidria filled Kalrez shown in Figure 6. It was necessary to reduce the differential pressure down to 2,100 psi before it successfully sealed for the entire 22-hour run. Post mortem observations indicated that incipient failure was occurring, nibbling was apparent over about a 2-inch section. It is not clear from the investigation to date whether the Kalrez failure mode at 260°C results from loss of mechanical properties purely due to thermoplastic type relaxation and/or whether there is hydrothermochemical damage to the polymer. Earlier chem ageing of tensile specimens reported in Appendix A and subsequent characterization measurements suggest some damage to the polymer is occurring.

FIGURE 5 -- EPDM AND BLEND POST MORTEM O-RING SPECIMENS

GEM Norde1 (EPDM)
 $\Delta P = 4100$ psi

Parker EPDM
 $\Delta P = 4100$ psi

GEM Norde1/Viton Blend
 $\Delta P = 4100$ psi

FIGURE 6 -- AFLAS AND KALREZ POST MORTEM O-RING SPECIMENS

GEM AFLAS
 $\Delta P = 4100$ psi

DuPont Kalrez
 $\Delta P = 4100$ psi

DuPont Kalrez
 $\Delta P = 3100$ psi

DuPont Kalrez
 $\Delta P = 2100$ psi

3.1.2 Extended Time Packer Seal SIM Tests

The baseline development packer seal SIM Testing was at 260°C and for 22 hours. Extending the investigation matrix in another dimension, i.e., longer duty cycles, is obviously of interest. Each of the favored compounds for each of the four elastomer systems - Viton, Nordel, Viton/Nordel Blend, and AFLAS, was tested in the packer seal SIM test for more than 22 hours. No changes were necessary to the fixture, the tests were simply continued for the desired extended time.

Table VI summarizes the extended runs and Figure 7 shows all the post mortem seals. All seals sealed successfully for the extended times of 46 and 94 hours. The nominal time planned was 46 hours; however, it was convenient to extend the 255 Viton and the 267 Nordel to 94 hours so they were arbitrarily run longer. The differential pressure was set at the maximum 260°C value established under the standard 22-hour runs. In all cases, there is some apparent evidence of the increased run time more for some than others. There is not sufficient data to determine if the seals had reached or were going to reach stable equilibrium after these extended run times.

TABLE VI -- SUMMARY OF EXTENDED TIME PACKER SEAL SIM TESTS
T = 260°C, 50 MIL DIAMETRAL GAP

Compound	Trade Name	Run Time, Hrs.	Diff. Press., psi	Comments Relative to 22 hr. Run
255-IX-2	Viton	94	4030	Extrusion on both ends, some breakage at chamfer.
267-II-8	Nordel	94	4240	Slight more extrusion
266-II-3	Nordel/Viton	46	4220	Slightly more extrusion at both ends.
275-II-1	Nordel/Viton	46	3310	Very slightly more permanent deterioration.
291-II-2	AFLAS	46	3530	Very slightly more extrusion.

FIGURE 7 -- POST MORTEM SIM TEST SEALS FOR EXTENDED RUNS

GEM VITON
 $\Delta P = 4080$ psi, 94 hrs.

GEM Nordel
 $\Delta P = 4240$ psi, 94 hrs.

GEM Nordel/Viton Blend
 $\Delta P = 4220$ psi, 46 hrs.

GEM Nordel/Viton Blend
 $\Delta P = 3310$ psi, 46 hrs.

GEM AFLAS
 $\Delta P = 3530$ psi, 46 hrs.

The 255-IX-2, Viton, was extruded at both ends of the seal where the elastomer bridged the gaps. After 22 hours there was only very minor extrusion at the low pressure end. The Nordel 267-II-8 seal looked very similar to its 22-hour run counterpart with only slightly more extrusion. The appearance was quite good. The 266-II-3 blend showed minor extrusion at the low pressure end of the seal and slightly increased over the 22 hour-run, about 3/16 vs. 1/16 inch. There was also incipient extrusion at the high pressure end of the seal where none existed previously. The most marked difference is the appearance. The Vitons typically show rust and a green deposit when they are removed from the SIM Test. This apparently results from the formation of hydrofluoric acid and subsequent attack of the Inconel vessel. After 22 hours the 266-1 blend seal was black and had no evidence of acid formation and attack on the metal parts from its Viton constituent. On the other hand, the 275-II-1 blend seal looked substantially like its 22-hour counterpart except for two points. The amount of permanent deformation was slightly more, almost unperceptably so. In addition, the increased test time resulted in a dulling of the appearance and some rust marks on the ID as is typical of the Viton seals. The 291-II-2 AFLAS seal looked very close to its 22-hour counterpart. There was very slightly more extrusion but the overall appearance was the same and quite good.

Considering all the seals run for extended times beyond the test standard of 22 hours and remembering the individual differences, i.e., the Viton and the Nordel were run for 94 hours vs. 46; all the favored seal materials from each elastomer system performed satisfactorily for their respective times. All seals appeared as if they will successfully seal beyond the extended run time except for some question regarding the 255 Viton. It appeared to be approaching a marginal state; however, if a stable equilibrium state was reached, its state after 94 hours was sufficient to provide a continuing seal.

3.1.3 315°C (600°F) Chem Ageing Tests

After success is achieved at one level, the next predictable event in the evolutionary sequence is determining how much higher it can go. With four elastomer systems successfully sealing at 260°C the predictable question arose and autoclave runs and Screening Tests on virgin and aged materials were made

to the extent that they could be fit into the remaining schedule. All factors except for temperature remained the same as the previous standard Screening Tests reported in Section 3.0 of the 12 Months Report. The elevated temperature chosen for these tests was 315°C (600°F) and the ageing was carried out for 22 hours in synthetic geothermal brine. Prior to the tests being run, there was no basis for any expectations except that 260°C was already getting pretty high for elastomers which have usual service temperatures quoted in the 177-204°C (350°-400°F) range and 315°C was reaching into the stratosphere.

To maintain perspective also remember that the formulations were developed for 260°C and they are not optimized for that temperature, rather, compound development was stopped once development was sufficient. Table VII shows the four compounds which were aged at 315°C and their resulting characteristics as compared to the virgin characteristics. The formulations and cures are shown in Table VIII. At the time this autoclave batch was run there was question as the effect of drying the Austin Black. This question was addressed but since the 255 compound was destroyed in ageing no new information regarding that question was developed.

TABLE VII -- SUMMARY OF 315°C (600°F) SCREENING TEST DATA

Compound	Comment	Extrusion psia		Shore A		Elong. %		Tensile psi		Swell %		Weight Gain %
		V	CA	V	CA	V	CA	V	CA	Width	Thick.	
255-B	4590, dried Austin Black	16.6	D	80	D	201	D	2392	D	D	D	D
255-VI	4590, not dried Austin Black	17.1	D	80	D	185	D	2216	D	D	D	D
266	1660/4590	17.9	17.9	87	97	195	23	1403	978	1.8	5.4	-13.4
267	1660 - 20 phr Polybutadiene	17.9	10.2	91	77	116	210	1257	817	.6	1.2	3.2
280	AFLAS, Luperco/Diak 3/5	13.6	4.0	82	47	211	301	2349	730	1.8	14.2	6.7

D = Destroyed

The degradation of the Viton 4590 compounds at 315°C is apparent. The 255 compound became so brittle the specimens were destroyed during the ageing. Measurable effect of the Viton constituent can be noted in the 266 blend compound where the elongation went from 19 to 23%. The 267 Nordel and the 280 AFLAS compounds came through with respectable retention of properties considering the 315°C (600°F) temperature. Based on the test results, Nordel and AFLAS both maintained measurable characteristics and are candidates for the 315°C environment.

TABLE VIII -- 315°C (600°F) FORMULATIONS AND CURES

Component	255-B	255-VI	280	Component	266	267
VT-R-4590 (DuPont)	100	100		Norde1 1660 (DuPont)	50	100
VT-X-5362 (DuPont)				VT-R-4590 (DuPont)	50	
AFLAS 100 (Asahi Glass)			100	Hypalon 20 (DuPont)	2.5	5
Austin Black (Cities Service)	10 Dried	10	10 Dried	Austin Black (Cities Service)	7.5	
Statex 160 (N110) (Cities Service)			50 Dried	Statex 160 (N110) (Cities Service)	52.5	75
Statex M568 (N-568) (Cities Service)	25 Dried	25		Maglite K (C.P. Hall)	2.5	
Maglite K (C.P. Hall)	3	3	3	Diak #7 (DuPont)	3	
Diak #7 (DuPont)	1.5	1.5	5	Luperco 130 XL (Ram Chemicals)	1.5	
Luperco 130 XL (Ram Chemical)	1.5	1.5	3	Cyanox 2246 (American Cyanamid Co.)	.25	.5
Polybutadiene #6081 (Polysciences, Inc.)				Thermoguard S (M&T Chemicals, Inc.)	2.5	5
Kel F Resin 800 (3M)				Polybutadiene #6081 (Polysciences, Inc.)	20	20
				Di-Cup R (Harwick Chemical Corp.)		3.5
Sheet Press Cure °F/Min Postcure Preheat 350°F N ₂ Purged	350/15 350-1h 400-1h 450-1h 500-17h	No Preheat* 350-1h 400-1h 450-1h 500-1h 550-1h 600-2h	350/20 350-1h 400-1h 450-1h 500-1h 550-1h 600-2h		350/60 400-1h 450-1h 500-1h 550-5h	350/60 400-1h 450-1h 500-1h 550-5h **
*Repostcured, higher temp						
**Repostcured, same as *						

3.2. OUTSIDE TESTING OF GEM COMPOUNDS

Considering the size of the contract, a fair amount of outside independent testing of the L'Garde GEM elastomers was accomplished. Rubber specimens made from the current favored packer seal compounds were provided to four different companies for testing in their applications. The ultimate purpose for supporting outside independent testing is to encourage transfer of the technology developed to the American industrial community. The secondary purpose is to obtain independent data points and benchmark data for the packer formulations developed by L'Garde. No additional compounding for the specific nonpacker applications was performed, whatsoever. The nonpacker applications include drill bit seals, and BOPs. Outside packer tests were also performed by two companies. Parts were molded by L'Garde for two packer applications and for the Terra Tek Drilling Bit Seal Test. Molded sheets were provided to Sandia for test compounds for the BOP environment.

3.2.1 Packer Company Tests

Both Packer Company G and Dresser/Guiberson tested L'Garde GEM compounds in their packer simulation test facilities. At this point in time, Company G is planning to test the 267 Nordel compound in the field in the near future. Test data generated to date are reported below.

A. Packer Company G Packer Tests.

Arrangements were made between Company G and L'Garde whereby L'Garde molded and provided compound 267 Nordel seals to Company G configuration specifications. The general dimensions of the packer seals are shown in Figure 8 which is sized for a 7-inch, 23-lb/ft casing. A photograph of an untested seal is shown in Figure 9. As can be seen the part is fairly large for a molded rubber part and has a rather thick cross section of about 1 inch.

Because of the thickness of the part and the stiffness of the compound, problems were encountered when the seals were compression molded. The problem which is common for thick parts was the existence of no knit planes within the interstices of the molded part. However, when brought reasonably

FIGURE 8 -- NOMINAL DIMENSIONS OF COMPANY G PACKER SEAL

FIGURE 9 -- PHOTOGRAPH OF UNUSED COMPANY G PACKER SEAL

under control though some level of defects remained they did not interfere with the performance of the seal.

For the 267 compound and the high-temperature application, L'Garde post cures and mechanically checks the seals. Both of these steps tend to uncover defects which normally would not be discovered. During post cure, gasses are generated and expanded in the interstices of the seal, breaking and expanding no knit or weak planes within the seal. The mechanical quality testing of its seal involves compressing the seal 300 mils in height with no restraining ID for the OD of the seal to seat against. The objective of this quality test is to reveal no knit planes by forcing them to surface through deforming seals. Under normal production circumstances with commercial companies Nordel seals would be compression molded, and visually inspected, thus many of the defects would go undetected.

Once the molding problems were reasonably in hand seals were provided to Company G. They tested five sets of two seals in their laboratory packer simulation test and at this writing plan to test a test packer dressed with the L'Garde GEM 267 compound in the field.

The laboratory simulation tests were carried out in steam, with a 3,000 psi differential pressure, and at various temperatures as shown by Table IX. At 302⁰C (575⁰F) the set of two elements sealed successfully for 5 days when the test was stopped for logistical reasons. The post mortem seal remained elastomeric, looked and felt good, and had the same Shore A hardness as before the exposure. There was permanent deformation and no knit planes separated, both are apparent in the cross section of both the seals after they were sectioned. For this severe environment and remembering that the compound was developed for 260⁰C and not even optimized, the success at 302⁰C is even more remarkable. The sectioned seals tested at 302⁰C are shown in Figure 10. Note that the C-1 seal has fewer molding defects as can be seen by the voids on the cross section and breaks on the outside surface.

Two subsequent sets of two seals were tested at 316⁰C (600⁰F) and they both sealed successfully for 6 and 8 days. Their testing was also terminated for logistical reasons. In both cases the rubber showed signs of reversion,

TABLE IX -- 267 NORDEL COMPOUND COMPANY G SEAL TESTS @ 3,000 PSI

Seals		Temperature, °C (°F)	Duration, Day	Comment
-VII-C-1	-VII-D-1	302 (575)	5	good seal, shut down, good condition
-XIII-3	-XIV-2	316 (600)	6	good seal, shut down, reversion but main- tained form
-XV-1	-XV-2	316 (600)	8	good seal, shut down, about same appearance as 6 days
-VIII-3	-X-2	329 (625)	2 3/4	good seal, packed, reversion/ extrusion

however, the seals tended to maintain their form, though somewhat plastic. Both seals are reported to look similar so the 6 and 8 day variation may indicate that a level of stable equilibrium was achieved.

One subsequent set of seals was tested at 329°C (625°F) and it suffered reversion to the point that the seals extruded through imperfections in the back-up and failed after 2-3/4 days. One of the post mortem seals shown in Figure 10 was permanently disfigured when it was removed from the tool. It is quite plastic because of the degradative reversion and was difficult to remove. These results were more typical of commercial compounds tested earlier at 288°C (550°F), in fact, no form remained with them. Company G also plans to run the 267 compound in a packer provided to a production company for an enhanced oil recovery steam injection application. The company has a "Huff and Puff" project and their objective is to heat the reservoir sufficiently to reduce the viscosity of the oil so it will flow and be pumpable. They inject steam into the well for about two weeks, remove the injection apparatus and then pump until the reservoir needs reheating. There is concern using an EPDM seal in an oil well because of degradation it may suffer from exposure to oil. However, the 267 Nordel compound is more resistant to hydrocarbon degradation

FIGURE 10 -- POST MORTEM SEALS FROM COMPANY G PACKER TESTS

302°C (575°F)
GEM Seal 267-VII-C-1

302°C (575°F)
GEM Seal 267-VII-D-1

329°C (625°F)
GEM Seal 267-VIII-3 or -X-2

than most EPDM compounds. Prior packers used in this "Huff and Puff" application are thought to have nitrile elements and are reported to have a problem with leakage, hence, it is reasonable to try the 267 compound.

B. Dresser/Guiberson Packer Tests.

Packer seals molded from 267 Nordel, 266 Nordel/Viton Blend, and 255 Viton compounds were provided to Guiberson for laboratory testing. The general dimensions of these seals are the same as those for the L'Garde SIM Test and are shown in Figure 6 of Appendix A. This packer seal which fits on a packer for a 4½ inch, 9.5-lb/ft casing. This seal configuration is reasonable for compression molding and no significant problems are encountered molding this seal from any of the compounds under examination.

The Guiberson laboratory simulation test utilizes a tri-element packer. Once they bring the system to temperature they then cyclicly pressurize alternating ends of the seal for 5-minute periods until failure occurs. The number of cycles the seal elements survive at a given differential pressure is their primary performance figure of merit. Relative to the L'Garde SIM test they are running a large clearance gap on their back-up, the seal must bridge a 200 mil gap on the diameter. They intend to cover a broad temperature range from 149°C (300°F) to 260°C (500°F). They also plan to introduce means into their procedure to allow time for hydrothermochemical degradation of the elastomers.

At this point in time they have tested the L'Garde GEM 267 Nordel and 275 Nordel/Viton Blend compounds at 177°C (350°F). Their conditions differ from the GEM conditions in two important and related aspects; the temperature, 177°C vs 260°C, and the clearance gap, 200 mils vs 50 mils on the diameter. In L'Garde's development at 260°C it was judged necessary to narrow the clearance gap to 50 mils. In talking with packer companies it was determined that 50 mils would be conservative relative to general design practices for thermal packers. Most thermal packers have a back-up system which is expanded out to meet the casing and provide near perfect back-up to the elastomer and on this basis a 50 mil diametral gap is conservative or larger than should actually

be encountered. The higher temperature L'Garde is contending with leads to very hard compounds which may be less than optimum at lower temperatures.

At 177°C and with the 200 mil gap the 267 Nordel compound survived for two complete cycles at 6,000 psi. This performance is in the same ballpark as Guiberson's highest performance nitrile compound which represents excellent performance for an EPDM. They have not tested the L'Garde GEM compounds at lower differential pressure at this date.

Guiberson also tested L'Garde's 275 Nordel/Viton blend at the same conditions; 177°C, 6,000 psi, and 200 mil gap. The results were similar to those of the 267 Nordel even though the compound is substantially different, eg. ultimate elongations are 141% for 267 and 71% for 275.

They have not tested the L'Garde GEM compounds at differential pressures less severe than 6,000 psi at this date. Based on these sparse data L'Garde tentatively concludes that 6,000 psi and a 200 mil gap is too severe a mechanical stress for the currently considered elastomers without benefit of some reinforcement at the gap or a reduction in gap size.

Guiberson plans to broaden their test matrix to include higher temperatures and additional soak time to allow time for hydrothermochemical degradation on the seal element. L'Garde expects that the benefits of the GEM compounds will emerge under these more severe conditions.

3.2.2 Terra Tek Drill Bit Seal Tests

Terra Tek designed, built, and is operating a drill bit seal simulation test. They have tested several commercially available elastomers as well as some experimental compounds by commercial companies. They have the ability to test two types of drill bit seals, an oval seal patented by Reed and a standard 2-329 O-ring. It is not clear at this writing if one seal configuration provides a more severe environment than the other. The results to date do not clearly point one way or the other.

L'Garde provided Terra Tek with five GEM compounds as 2-329 O-rings. The compounds were all developed for the packer application which is a static seal

which requires significant deformability for pack-off. The dynamic drill bit application has different requirements and additional development of the compounds for lubricity and abrasion resistance will be beneficial. Furthermore, reinforcing fibrous fillers are also probably usable to advantage for the drill bit seal because very little deformation is required for installation or operation and there is a definite need for reinforcement to resist the "slip-stick" phenomena. The five compounds provided are the 255 Viton, 266 Nordel/Viton Blend, 267 Nordel, and 290 and 291 AFLAS.

Due to Terra Tek's funding limitations at this writing, it was clear that they would not be able to test all compounds provided. L'Garde recommended that they test the 266 Nordel/Viton Blend first. At this time, they were able to test two seals made from the 266 Blend and 2 seals each from 290 and 291 AFLAS compounds.

The results from the limited testing by Terra Tek is quite interesting and indicates promise for application of the basic GEM packer compounds to the drill bit seal application with some refining compounding. Terra Tek ran the 266 blend compound O-rings in the drill bit tester at 200°C (392°F) with sand and cuttings present. The seal performed for 45 hours prior to failing which is good performance. The interesting aspect was apparent when the seal was removed, one-third of the cross section was worn away at the time the seal failed and the test was stopped. Thinking that this was an anomaly, Terra Tek repeated another identical test and the results were virtually the same when they stopped the test after 47 hours. These tests indicate basic viability of the packer compounds for the drill bit seal application. Based on the very limited data it appears that the 266 seals are gradually being worn away and will directly benefit from refining compounding development to provide characteristics for dynamic seals, primarily lubricity.

Terra Tek was additionally able to test all the AFLAS O-rings provided them which were made from the 290 and 291 compounds. A general problem was experienced with the AFLAS O-rings; i.e., insufficient knitting of the rubber took place across the parting line and the seal parted circumferentially at this point. This reflects the molding problem which was experienced with the AFLAS

and it is apparent that the mold release which finally worked also contaminated the rubber causing weak planes.

In general, the AFLAS compounds sealed on the order of 10-20 hours and after this amount of time there did not seem to be any adverse wear or abrasion problems. One of the 290-2 compounds did not break at the mold part line but did break through the cross section near the location of a thermocouple placed on the seal. This seal failed after 10.5 hours and its failure is apparently correlated with the thermocouple installation.

To summarize, the hydrothermochemical stability of the GEM packer elastomer compounds is valuable to the geothermal drill bit application. L'Garde GEM packer elastomers were tested in Terra Tek's drill bit seal tester, and the 266 Nordel/Viton Blend survived for 45 to 47 hours. The seals were quite worn but did not appear to suffer any hydrothermochemical degradation. Refining compound development considering the dynamic seal requirement for lubricity is definitely in order. Based on good reports of Kalrez with fibrous fillers, investigation of the same filler systems are in order using the GEM compounds as a base. The AFLAS seal tests were inconclusive because of the problem with a weak plane at the mold parting line. Molding problems need to be further solved before reasonable AFLAS O-rings can be made for further testing.

3.2.3 Sandia BOP Environment Testing

Sandia Laboratories/Albuquerque undertook a study in behalf of a manufacturer of blow-out preventors (BOP). The objective of the study was to determine the thermal stability and steam resistance of various elastomers and to select rubbers for use as ram seals in a BOP. Sandia evaluated seven elastomer compounds by comparing virgin physical characteristics against environmentally aged characteristics. The ageing was performed on tensile specimens placed in 260°C steam for 100 hours plus 14 hours heat-up and some period for cool-down. Five tensile measurements each of both the virgin and aged materials were made at room temperature.

L'Garde provided Sandia with cured elastomer sheets made from four elastomers for this testing; 255 Viton, 267 Nordel, 266 Nordel/Viton Blend, and

the 291 AFLAS. As with the other outside tests, the formulations provided were those developed under the GEM Program for the geothermal packer seal application. No provisions were made for the specific conditions of the tests and the GEM compounds developed for geothermal brine at 260°C were directly supplied. Sandia compared the four L'Garde GEM compounds against one each of peroxide and bisphenol cured Vitons and a compound provided them by the BOP company (914-80). The 914-80 compound is believed to be bisphenol cured fluoroelastomer. The results of the measurements are presented in Table X.

TABLE X -- SANDIA MEASUREMENTS, 260°C (500°F) STEAM FOR 100 HRS. PLUS

Elastomer	Tensile Strength, psi			Elongation %		
	Virgin	Aged	% Retained	Virgin	Aged	% Retained
255 L'Garde Viton 4590	2312	1376	60	121	135	112
267 L'Garde Nordel	1395	1261	90	71	60	85
266 L'Garde Blend	1596	1410	88	111	71	64
291 L'Garde AFLAS	2321	1799	78	170	87	51
Sandia Viton GH	1301	364	28	172	45	26
Sandia Viton E-60-C	864	D	--	145	D	--
914-80	882	D	--	148	D	--

D = Destroyed

Based on these evaluation tests, Sandia recommended that the L'Garde GEM 267 Nordel compound be considered for the BOP application; more generally it can be seen that the four GEM compounds faired better as a group than the other three corroborating the L'Garde results. The Sandia Viton GH compound maintained measurable characteristics while the E-60-C and the 914-80 compounds became so brittle that the specimens could not be measured.

4.0 GEOTHERMAL PACKER SEAL COMPOUND DEVELOPMENT

This section contains the details regarding the GEM packer seal compound development which occurred since the previous 12-month's report. As the Program evolved, it included development of different elastomer systems - Viton, Nordel, Nordel/Viton Blend, and AFLAS. At least one compound from each of the four systems successfully met the GEM requirements as tested in the packer Simulation Test. For convenience the report is organized with a subsection assigned to each of the four elastomer systems.

Any references to synthetic geothermal brine imply a standard brine developed by L'Garde and used in the Simulation Tests and autoclave ageing. The constituency is as follows:

H ₂ O	300 ppm
CO ₂	1,000
NaCl	25,000
H ₂ O	Balance
pH (ending)	5-7

4.1 FLUOROELASTOMERS

As originally planned, the geothermal packer seal compound development program was to center around the peroxide cured fluoroelastomers or Viton "G type" polymers only. At the time the program was initiated, the Air Force had experienced significant success with the fluoroelastomers for high performance aircraft hydraulic seal applications which are exposed to similar unusually severe environments. They experience the same high temperature regime as this requirement but are dynamic seals and exposed to hydraulic fluid (Ref.10). Because of success experienced by the Air Force at the similarly severe high temperature environment, in addition to the improved steam and fluids resistance reported by DuPont with the peroxide cured Vitons (Refs.5 and 6); the "G type" Vitons provided a logical and promising starting point for development of elastomer compounds for the high temperature geothermal packer seal application.

However, the development of the Viton compounds did not occur as quickly as anticipated. The synthetic geothermal environment with the 260°C aqueous

solution of H_2S , CO_2 , and $NaCl$ proved to be quite severe, embrittling the compounds after 22 hours, such that specimens could not be bent 180° without breaking and with corresponding ultimate elongations in the negligible to 80% range. Definite compounding progress was made with the most current compounds, especially with respect to hydrothermochemical stability where improvement was most needed. Compound 255 retains a good percentage of the virgin values of the critical characteristics after chem ageing in synthetic geothermal brine at $260^\circ C$. The oxide acid acceptor, Austin Black, and cure system all proved critical. A total of 68 formulations were evaluated.

It is expected that further progress may be possible. The development of fluoroelastomers was stopped once a compound was developed which sealed successfully in the SIM Test for 22 hours.

4.1.1 Current Favored Fluoroelastomer Compound

Compound number 255 is the current recommendation for fluoroelastomer casing packer seal element elastomer based on the compound development accomplished to date. Potential for further improvement is considered to be excellent. The following is the formulation and cure cycle. Note VT-R-4590 is a Viton polymer in the development phase. When commercialized, DuPont then gives the polymer a Viton designation.

A. Fluoroelastomer Formulation 255.

VT-R-4590 (DuPont)	100 phr
Austin Black (Slab Fork Coal)	10
Statex M-568 (N-568, FEF) (Cities Service)	25
Maglite K (C. P. Hall)	3
Diak #7 (triallylisocyanurate) (DuPont)	1.5
Luperco 130XL (Ram Chemicals)	1.5

Press Cure: $350^\circ F/30$ min.

Post Cure: N_2 Atmosphere

$300^\circ F$ preheat

$50^\circ F/hr.$ Step-up to $500^\circ F$ started at insertion.

$500^\circ F$ for 17.5 hours

B. Capability Threshold Runs.

A matrix of Simulation Test runs were made as a function of temperature and differential pressure to provide capability threshold data as a function of temperature for the 255 Viton compound. The matrix is shown in Table XI.

TABLE XI -- CAPABILITY THRESHOLD MATRIX FOR VITON COMPOUND 255

<div>Temp. ΔP</div>	260°C (500°F)	204°C (400°F)	140°C (300°F)
Maximum ΔP	255-II-2 512°F 3600 psi Broke @ 20h 14'	255-III-2 383°F 3600 psi Very Minor Extrusion 22h	255-III-3 292°F 3100 psi No Extrusion 22h
Reduced ΔP	255-III-1 503°F 3100 psi Moderate Extrusion 22h		

Figure 11 shows the four post mortem seals, three of which sealed for the full 22 hours. The 255-II-2 seal at 500°F and 3,600 psi failed after 20 hours. The 255-III-1 seal at 3,100 psi and 260°C survived the full 22-hour run time. It extruded moderately with local damage only, no damage occurred on the inside of the seal through the thickness as was the experience with earlier compounds. The seal at 204°C (400°F) barely extruded at the maximum stress region. No damage was experienced by the seal tested at 149°C (300°F).

All of the above SIM Tests were run with 50 mil diametral gap back-up rings and in the standard SIM Test synthetic geothermal fluid. To obtain the maximum differential pressure, the pressure was increased in 1,000 psi steps until the seal unseated and then the pressure was backed off to a stable packed-off level. Apparently the unseating is being caused by a radial component of

FIGURE 11 -- CAPABILITY THRESHOLD MATRIX POST MORTEM SEALS
GEM VITON 255 FLUOROELASTOMER

260°C (500°F)
 $\Delta P = 3600$ psi

260°C (500°F)
 $\Delta P = 3400$ psi

149°C (300°F)
 $\Delta P = 3100$ psi

204°C (400°F)
 $\Delta P = 3600$ psi

force created by the pressure which overcomes the seating force created through "squashing" the seal. At 260°C, this tended to occur at about 4,500-5,000 psi on high-pressure side or a differential pressure of about 3,600-4,100 psi with a squashing force of about 22,000 lbs. The temperature affects the unseating pressure level through the corollary stiffening of the seal as the temperature is reduced. For a constant squashing force at lower temperatures, the stiffer seal will not sustain as high a differential pressure without unseating.

The temperatures shown are measured at the outside of the vessel radially from the center of the seal specimen and inside the band heater. This temperature is about 10°F over the seal temperature at 500°F and equal to the seal temperature at 300°F. The pressures shown in the maximum row are the differential pressures to which the system was backed-off after the seal unseated at a higher pressure. The time shown is the elapsed time the seal ran at pressure and temperature. It starts after the fixture is raised to test temperature, which takes about 2 hours, and then pressurized and ends when the seal fails or after 22 hours.

The threshold testing indicates that the L'Garde Viton compound 255 can withstand about 3,100 psi differential pressure at 260°C with backup providing a maximum 50 mil diametral gap. At about 204°C (400°F), the seal capability exceeds the run value of 3,600 psi differential pressure. The full capability threshold could not be measured because of the test fixture limitation.

4.1.2 Discussion of Compound Development

A major accomplishment was achieved in developing hydrothermochemically stable fluoroelastomers which meet the GEM geothermal packer requirements. The unusually severe geothermal environment includes H₂S, CO₂, NaCl, and H₂O at 260°C. Typically exposure of the fluoroelastomer to this environment causes it to harden and become very brittle. It was typical of tensile dogbones made from early compounds to be broken when they were carefully straightened for mounting in the tensile tester.

A. Progress Accomplished.

Significant progress was made. Fluoroelastomer compounds which have good hydrothermochemical stability were finally developed. Table XII compares typical early results against the current most favored compound.

TABLE XII -- COMPARISON OF EARLY VS FINAL RESULTS FOR FLUOROELASTOMERS

Formulation	Ult. Tensile @ RT, psi		Ult. Elong. @ RT, %		Shore A Hard. @ 260°C		Extrusion Resist. @ 260°C, psia	
	V	CA	V	CA	V	CA	V	CA
Early 115 (CA/V)	1699	244 (14%)	162	74 (46%)	80	58 (73%)	11.2	3.6 (32%)
Present 255 (CA/V)	2195	1591 (72%)	224	226 (100%)	79	79 (100%)	11.4	6.3 (55%)

As mentioned earlier compound 255 does not represent an optimized compound rather one which was sufficient to meet the GEM requirements; it is expected that additional progress is still possible, but not within the scope of the present contract.

Critical characteristics are compared for early compound 115 against 255 for both the virgin condition (V) and the chem aged (CA) condition after 22 hours exposure to the synthetic geothermal brine at 260°C and saturation pressure. The percentages in parentheses show the percent value retained after ageing. Note that for 255 all values are good in the absolute sense and also all have much improved stability through chem ageing then the early compound 115.

The SIM Test results approach the operational "proof-of-the-pudding" since it is a good simulation of actual downhole conditions experienced by the packer elastomer. Unfortunately, the current results are somewhat clouded and the data do not clearly support the conclusions which are apparent from the fundamental characteristics shown in Table XII. Additional time could not be allocated to the Vitons to generate the data needed for full clarification.

SIM Tests of early fluoroelastomer compounds typically resulted in breakage of the seal when it was seated or as the differential pressure was established. Figures 13 and 14 of the previous 12-months report (Appendix A) show photographs of all the early fluoroelastomer seals tested during the first 12 months. During the subsequent Viton development, it was judged that the 175 mil diametral gap between the back-up ring and the vessel was too severe a test at 260°C since all the Viton compounds, though improved as compared to earlier ones, were experiencing breakage that was still too severe to differentiate compound improvements. Consequently, starting with Viton Compound 255, all subsequent SIM testing uses back-up rings with a 50 mil diametral gap.

Another item clouding the issue pertains to breakage of the back-up rings. The top back-up ring broke during the runs of Seal 248-III-2 and 249-3 on its second run. The chamfered lip developed cracks which allowed the chamfer to flare more and tending to close the gap between the back-up ring and the vessel. Consequently, those runs are uncertain because the flared ring provides more complete back-up to the seal.

Compound 255 was selected to conclude this fluoroelastomer study and for final performance threshold testing reported in paragraph 4.1.1B above because it showed good overall hydrothermochemical stability in the environment and sealed successfully in the packer SIM Test for 22 hours.

B. Compound Trade Offs.

This paragraph presents the detailed data generated in support of the fluoroelastomer development.

1) Detailed Screening and SIM Test Data.

Table XIII presents a summary of the fluoroelastomer Screening Test and evaluation data generated during this contract period. The compounds numbered 227 through 255 are formulations compounded by L'Garde using DuPont's VT-R-4590, a peroxide cured "Viton", as the base polymer. The Fluorel A, B, and C formulations were provided by 3M and use their Fluorel 2100 series bisphenol cured Fluorels. LGV-1 and 2 are formulations compounded by Jet Propulsion Laboratory using DuPont's Viton GH, a peroxide cured Viton. The formulations and cures for the L'Garde compounds are presented in Table XIV.

TABLE XIII -- SUMMARY OF FLUOROELASTOMER SCREENING TEST DATA

Compound	Comment	Extrusion psia		Shore A		Elong. %		Tensile psi		Swell %		Wt. Gain &
		V	CA	V	CA	V	CA	V	CA	Width	Thick.	
227-1/2	4590, 5 phr Maglite K	11.7	6.0	79	80	201	154	1995	1232	1.2	-0.5	1.3
228-1/2	4590, 10 phr Maglite K	14.0	8.9	82	85	172	101	2021	1050	1.2	1.0	1.0
229-1/2	4590, 20 phr Maglite K	15.2	14.0	84	96	150	37	2249	1065	2.2	1.0	0.3
230-1/2	4590, 30 phr Maglite K	14.0	>17.9	86	98	130	22	2351	1007	2.7	4.0	0.4
231-1/2	4590, 20 phr Maglite K, 20 phr Austin	11.5	12.7	78	94	229	45	2243	909	2.6	1.6	0.4
236-2	4590, 5 phr Maglite K 35 phr Austin, 16h @ 500°F	9.1	6.3	79	78	219	185	2084	1261	1.1	1.7	1.3
237-2	4590, 3 phr Maglite K	11.0	5.1	79	76	234	214	1990	1272	1.2	1.3	1.5
238-III-1	4590, 1 phr Maglite K, lot 101, 50°F/h, 100°F/h	8.0	4.9	76	71	237	247	1933	1231	1.2	1.7	1.7
238-V-1	4590, 1 phr Maglite K, lot 104, 50°F/h, 100°F/h					279		1691				
238-VI	4590, 1 phr Maglite K, lot 104, 50°F/h	9.4	3.9	78	74	231	242	1554	1056	1.1	1.9	1.4
243-1	4590, 0 phr Maglite K	8.7	4.4	74	62	245	297	1863	1048	1.0	4.0	3.2
244-1	4590, 5 phr Maglite K, 35 phr Austin, 17.5h @ 500°F	8.7	5.8	78	77	220	192	2230	1366	0.8	1.7	1.3
245-1	4590, 3 phr MgO microfibers,	7.8	3.6	72	67	215	249	1854	1097	1.2	3.3	2.6
247-1	4590, 5 phr Maglite K, 10 phr Austin	6.7	6.3	70	66	405	337	2336	1128	1.6	1.9	1.6

TABLE XIII -- SUMMARY OF FLUOROELASTOMER SCREENING TEST DATA (Continued)

Compound	Comment	Extrusion psia		Shore A		Elong. %		Tensile psi		Swell %		Wt. Gain %
		V	CA	V	CA	V	CA	V	CA	Width	Thick.	
248-III	4590, 10 phr Austin, 55 phr Statex M568	>18	13.5	91	92	67	56	1651	1317	1.5	1.9	1.3
249-I/II	4590, 10 phr Austin, 25 phr Statex M568	14.0	8.2	81	85	204	169	2385	1487	1.8	2.5	2.2
255	4590, 10 phr Austin, 25 phr Statex M568, 1.5 Diak #7	11.4	6.3	79	79	224	226	2195	1591	1.9	2.8	2.4
*Fluorel A	2181	8.7	4.3	72	76	465	69	1756	613	-0.3	-5.9	-9.3
*Fluorel B	2174/2175, 90/10, 3M	13.9	15.7	86	96	207	29	2335	1153	0.9	1.2	-3.3
*Fluorel C	2175/2179, 20/80, 3M	15.8	6.1	85	85	620	56	2253	924	-0.2	-2.3	-6.0
LGV-1	Viton GH, JPL	9.1	4.0	73	58	389	405	1956	716	-0.1	-0.7	-1.1
LGV-2	Viton GH, JPL	8.9	3.1	75	58	275	267	1812	369	2.1	3.0	-0.5

*Not developed for this specific environment

TABLE XIV -- FLUOROELASTOMER FORMULATIONS

Compound No. Component	227	228	229	230	231	236	237	238	243	244	245	247	248	249	255
VT-R-4590 (DuPont) Lot	100 101	100 101	100 101	100 101	100 101	100 101	100 101/104/ 1009	100 101/104	100 101	100 101	100 101	100 101	100 104	100 104	100 104
Austin Black (Slab Fork Coal Co.)	40	40	40	40	20	35	35	35	35	35	35	10	10	10	10
Statex M-568 (Cities Service)													55	25	25
MgO Microfibers (Versar, Inc.)											3				
Maglite K (C. P. Hall)	5	10	20	30	20	5	3	1		5		5	2	3	3
Diak #7 (Pink) (DuPont)										3					
Diak #7 (DuPont)	3	3	3	3	3	3	3	3	3		3	3	3	3	1.5
Luperco 130XL (Ram Chemicals)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Seal Press Cure, °F/Min.	350/15*	350/15*	350/15*	350/15*	350/15*	350/30	350/30	350/30	350/15*	350/15*	350/15*	350/15*	350/30	350/30	350/30
Seal Post Cure Preheat, °F	300	300	300	300	300	300	300	300	300	300	300	300	350	350	350
Step rise, $T_{start}/\frac{°F}{h}$	350/50* 400/100	350/50* 400/100	350/50* 400/100	350/50* 400/100	350/50* 400/100	350/50 400/100	350/50 400/100	350/50 400/100	350/50* 400/100	350/50* 400/100	350/50* 400/100	350/50* 400/100	350/50	350/50	350/50
Max. Temp, °F/h 1 Atmosphere	500/16 N ₂	500/16 N ₂	500/16 N ₂	500/16 N ₂	500/16 N ₂	500/16 N ₂	500/17.5 N ₂	500/17.5 N ₂	500/17.5 N ₂	500/17.5 N ₂	500/17.5 N ₂	500/17.5 N ₂	500/17.5 N ₂	500/17.5 N ₂	500/17.5 N ₂

*ASTM sheets only.

It was apparent from the testing that the chem ageing of the test specimens in the autoclave was a much more severe ageing environment than the operational application. "Dogbones" which are cut from 75-100 mil sheets have a very large surface area exposed to the brine when compared to the volume of rubber involved. In the real application the parts are thick and only a small portion of the surface area is exposed to the brine. The balance of the surface is sealed against metal mandrels, casing, back-up, etc.

Table XV presents the Packer Simulation Test data. The more promising compounds from the Screening Tests were advanced to SIM test evaluation. Figure 12 shows the balance of the post mortem SIM Test seals which are not shown in Section 3.1.2 (Extended Time Packer Seal SIM Tests) in Figure 6 above.

The general development procedure used entailed developing the compounds to acceptable levels of hydrothermochemical stability in the synthetic geothermal brine at 260°C, as measured in the Screening Tests. Once accomplished, the formulation development emphasis was shifted toward developing extrusion resistance as measured by the Extrusion Resistometer and the SIM Test. The mechanical properties were developed to accomplish successful seating of the seal without breaking or cracking while still resisting extrusion between the back-up rings and the vessel ID.

2) Acid Acceptor.

As regards hydrothermochemical stability of the fluoroelastomers in the synthetic geothermal brine, the acid acceptor was identified to be an important compounding constituent. Sublimed litharge is recommended by DuPont to maximize resistance to swell and hydrolysis of the crosslinks of the Viton compounds.

Experiments hereunder with both Viton GH and VT-R-4500 resulted in brittle compounds after chem ageing in the geothermal brine when higher levels of acid acceptors are used. Parametric measurements were made with level of the acid acceptor, Maglite K (MgO). Figures 13, 14, 15, and 16 show the sensitivity of the characteristics; ultimate tensile strength, ultimate elongation, Shore A hardness, and extrusion resistance. All characteristics except tensile strength are particularly sensitive to the level of Maglite K. The dashed line represents

TABLE XV -- FLUOROELASTOMER SIM TEST RUNS

Run	Formulation	Duration Hrs.	ΔP psi	T set °F	Diametral Gap Mils	Comment
36	237-III-2	-0-	760	500	175	Broke through thickness
37	249-1	-0-	1898	500	175	Broke through thickness
38	249-3	-0-	2942	500	25	Unseated, shut down
39	248-III-2	22	2100	500	175	Back-up ring broke
40	255-2	-0-	1997	500	175	Inside of seal OK
41	249-3	22	3070	500	50	2nd run, ring broke
42	255-1	-0-	2885	500	25 (top)	Unseated
43	255-II-1	-0-	2393	500	50	Unseated
44	255-II-2	21	3520	500	50	Broke through thickness
45	255-III-1	22	3115	500	50	Moderate extrusion
46	255-III-2	22	3545	400	50	Minor extrusion
47	255-III-3	22	3153	300	50	No extrusion
73	255-VI-1	22	3770	500	50	Major extrusion, new sodium sulfide
91	255-IX-1	1	4030	500	50	Broke outside edge, pressure too high
92	255-IX-2	94	3240	500	50	Major extrusion

data measured on virgin material and the solid line data on material chem aged in the synthetic geothermal brine for 22 hours. Where the two curves are close to one another or coincident indicate levels of good hydrothermo-chemical stability. As can be seen, better stability occurs at levels below 5 phr but some level of instability still exists as is indicated by the tensile strength. The major problem experienced with the Vitons was embrittlement resulting from exposure to the brine environment. This being the case, the elongation was most influential in deciding the optimum acid acceptor level.

FIGURE 12 -- BALANCE OF POST MORTEM
SIM TEST SEALS RUN @ 260°C (500°)
GEM VITON FLUOROELASTOMETERS

$\Delta P = 760$ psi, 0 hrs.

$\Delta P = 2,100$ psi, 22 hrs.

$\Delta P = 1,898$ psi, 0 hrs.

$\Delta P = 2,942$, 0 hrs.

FIGURE 12 -- BALANCE OF POST MORTEM
SIM TEST SEALS RUN @ 260°C (500°F)
GEM VITON FLUOROELASTOMERS (Continued)

$\Delta P = 2,885 \text{ psi}, 0 \text{ hrs.}$

$\Delta P = 1,997 \text{ psi}, 0 \text{ hrs.}$

$\Delta P = 2,393 \text{ psi}, 0 \text{ hrs.}$

$\Delta P = 3,770 \text{ psi}, 22 \text{ hrs.}$

$\Delta P = 4,030 \text{ psi}, 1 \text{ hrs.}$

FIGURE 13 -- EFFECT OF ACID ACCEPTOR ON ULTIMATE TENSILE STRENGTH
VT-R-4590, FORM. 227-230, 237, 238

FIGURE 14 -- EFFECT OF ACID ACCEPTOR ON ULTIMATE ELONGATION
VT-R-4590, FORM. 227-230, 237, 238

FIGURE 15 -- EFFECT OF ACID ACCEPTOR ON SHORE A HARDNESS
VT-R-4590, FORM 227-230, 237, 238

FIGURE 16 -- EFFECT OF ACID ACCEPTOR ON EXTRUSION
RESISTANCE VT-R-4590, FORM 227-230,
237, 238

Number one priority was to achieve sufficient stability to prevent catastrophic embrittlement. Number two priority was to achieve high extrusion resistance resulting from better material not more brittle material.

Based on these data and after consideration of all the inter-relating factors, a level of 3 phr was selected for the GEM Viton compounds. This level is not considered to be the final chapter, however, this level was maintained throughout the program because compounds sufficient to pass the SIM Test were formulated using this quantity.

3) Austin Black.

L'Garde's experience with Austin Black supports results measured by the Air Force Materials Laboratory and DuPont. During the first 12 months period, data was generated that clearly indicate that formulations with Austin Black have superior stability in the synthetic geothermal brine. It's use resulted in compounds which maintained values of ultimate elongation of 75% or greater of virgin values after ageing in brine, far superior to other results at that time. It was previously thought that the Austin Black provided reinforcing capability equal to MT black because varying ratios of each from 20/80 to 60/40 for a consistent combined total of 50 phr resulted in virtually no change in characteristics. Since that time the function relegated to the Austin Black is that of a hydrothermochemical stabilizer because of doubts as to its contribution to reinforcement. The question remains as it was not fully clarified.

4) Bisphenol Cured Fluoroelastomers.

As previously mentioned the fluoroelastomer work concentrated on the peroxide cured Vitons because they were believed to fit the environment better than the other fluoroelastomer systems. After a significant amount of evaluation testing and development with very few encouraging results, other polymers were considered including bisphenol cured fluoroelastomers. A Viton E-60-C and three Fluorel compounds (2181, 2174/2175, 2175/2179) were screened. After chem ageing in the synthetic geothermal brine these compounds became very brittle much as the earlier peroxide cured Vitons. At this time it is unclear if the bisphenol, and for that matter the amine cured fluoroelastomers, can be

developed to perform up to or better than the peroxide cured fluoroelastomers in the GEM geothermal environment. Similar improvements might be possible with the Austin Black and cure system adjustments.

5) Miscellaneous Compounding Aspects.

The peroxide cured Viton development was terminated when progress was sufficient to successfully seal in the SIM Test for 22 hours. Significant progress was required to achieve this state where the seals were flexible enough to pack-off without cracking, and stable enough and high enough modulus to maintain the seal for 22 hours. There are two compounding aspects which indicate potential for further improvement, the cure system and the filler system.

A high crosslink density is obviously more desirable for better hydrothermochemical stability, however, that must be traded-off with the need for significant deformation without breakage. In addition and closely related is the filler systems. Some experimentation with the filler system was initiated once relatively stable compounds were achieved. FEF black was used to improve the plastic flow characteristic of the compound in its "green" or uncured state and to improve its tensile strength. Further exploration beyond the scope initiated is warranted.

Further confusion is caused by lot variations of the Viton, VT-R-4590. Because it is still in the development phase, fairly significant changes can occur from lot to lot. For example, compound 238 was made from both lot 101 and 104 and resulting ultimate tensile strengths were 1933 and 1691 psi respectively. This difference is of the same magnitude of the improvements we are striving towards.

In any event, many questions remain with the fluoroelastomers and warrant further investigation since they hold up relatively well in a high-temperature aerobic (oxygen) environment. Applications such as BOP elastomeric seals located at the wellhead may be more appropriately made from fluoroelastomers because they are more stable than the EPDM's in an aerobic atmosphere.

4.2 ETHYLENE-PROPYLENE DIENE MONOMER (EPDM)

The development of elastomer compounds for the high-temperature geothermal packer seal was originally intended to be based on peroxide cured fluoroelastomers (Viton "G type" polymers). The goal of the program was to develop a seal that would survive for 22 hours in a 260°C aqueous solution of H₂S, CO₂ and NaCl. The seal is required to span a .050-inch diametral gap with a 3,100 to 4,100 psi differential across it.

As development of the Viton continued, it became more doubtful that packer seals could be made from it which successfully met the GEM requirements. As a result the development of compounds using other basic materials was begun. One such polymer is ethylene-propylene diene monomer (EPDM), a total of 21 compounds were evaluated. This subsection documents the "EPDM" development effort.

4.2.1 Current Favored EPDM Compound

Compound number 267 is the current recommendation for EPDM casing packer seal element elastomer based on the compound development accomplished to date.

A. EPDM Formulation 267.

Component

Norde1 1660 (DuPont)	100 phr
Hypalon 20 (DuPont)	5
Statex 160 (N110, SAF) (Cities Service)	75
Cyanox 2246 (American Cyanamid)	0.5
Di-Cup R (Harwick Chemical Corp.)	3.5
Thermoguard S (M & T Chemicals, Inc.)	5
Polybutadiene #6081 (Polysciences, Inc.)	20

Press Cure: 350°F/60 minutes

Post Cure: N₂ atmosphere

350°F preheat

50°F/hr. Step-up to 550°F. Started at insertion.

550°F for 5 hours

B. Capability Threshold Runs.

Several Simulation Test runs were made as a function of temperature and differential pressure to provide capability threshold data as a function of temperature for the 267 Nordel compound. The test matrix is shown in Table XVI.

TABLE XVI -- CAPABILITY THRESHOLD MATRIX FOR NORDEL COMPOUND 267

Seal No.	ΔP , psi	Temp. °C (°F)	Comments
267-1	4190	260 (500)	22 hrs. Very Minor Extrusion
267-2	3870	204 (400)	22 hrs. No Extrusion
267-3	3240	149 (300)	22 hrs. No Extrusion

Figure 17 shows the three post mortem seals all of which seal for 22 hours at their maximum differential pressures. The seals all look excellent and the 260°C 267-1 seal appears worse than it actually is because of the shredded nature of the extruded rubber. The extrusion resistance of the 267 Nordel EPDM compound is considered to be excellent.

All of the above SIM Tests were run with 50 mil diametral gap back-up rings and in the standard SIM Test synthetic geothermal fluid. For the maximum Δp cases, the pressure was increased in 1,000 psi steps until the seal unseated. Apparently, the unseating is being caused by a radial component of force created by the pressure which overcomes the seating force created through "squashing" the seal. At 260°C, this tended to occur at about 4,500-5,000 psi on the high pressure side or a differential pressure of about 3,600-4,100 psi with a squashing force of about 22,000 lbs.

The temperatures shown are measured at the outside of the vessel radially from the center of the seal specimen and inside the band heater. This temperature is about 10°F over the seal temperature at 500°F and equal to the seal temperature at 300°F. The pressures shown are the differential pressures

FIGURE 17 -- CAPABILITY THRESHOLD MATRIX POST MORTEM SEALS GEM NORDEL 267 EPDM

260°C (500°F)
 $\Delta P = 4,190$ psi

204°C (400°F)
 $\Delta P = 3,870$ psi

149 (300°F)
 $\Delta P = 3,240$ psi

to which the system was backed-off after the seal unseated at a higher pressure. The time shown is the elapsed time the seal ran at pressure and temperature. It starts after the fixture is raised to test temperature and pressure which can take about 2 hours and ends when the seal fails or after 22 hours.

The threshold testing indicates that the L'Garde GEM EPDM compound 267 can withstand about 4,200 psi differential pressure at 260°C (500°F) with backup providing a maximum 50 mil diametral gap. As explained previously with the fluoroelastomers, the seals unseat at lower differential pressures at lower temperatures.

4.2.2 Discussion of Compound Development

The EPDM compound development was initiated as a backup to the peroxide cured fluoroelastomer development when it became doubtful that compounds would be developed which met the unusually severe GEM environment. L'Garde has high-temperature experience with EPDM on Air Force applications and knew that in a nonaerobic environment EPDM is a good candidate. Other than the omnipresent question of hydrothermochemical stability extrusion resistance was also a real question with the EPDM's.

A. Progress Accomplished.

Significant progress was made with excellent geothermal packer compounds resulting. Final EPDM compounds have good extrusion resistance plus very good hydrothermochemical stability. Table XVII compares test results of the current recommended EPDM compound with an early formulation to contrast and show the extent of the development.

Critical characteristics are compared for compound 267 against E263 for both the virgin condition (V) and the chem aged (CA) condition after 22 hours exposure to the synthetic geothermal brine at 260°C. The percentages in parentheses show the percent value retained after ageing. Note that for 267 all values are good in the absolute sense and also have perfect stability through chem ageing, an unexpected bonus. The E263 compound is beyond the capability of the tensile tester, hence the >840%. This perfect stability

TABLE XVII -- COMPARISON OF EARLY VS FINAL RESULTS FOR EPDM'S

Compound	Ult. Tensile @ RT, psi		Ult. Elongation @ RT, %		Shore A Hard. @ 260°C		Extrusion Resist. @ 260°C, psia	
	V	CA	V	CA	V	CA	V	CA
Early E263 (CA/V)	1363	1020 (75%)	>840	>840 (N/A)	61	52 (85%)	9.6	5.5 (57%)
Present 267 (CA/V)	1610	1554 (97%)	141	138 (98%)	92	92 (100%)	17.1	17.6 (103%)

implies that the 267 Nordel EPDM has additional capacity for higher temperature and/or longer duty cycles, especially when considering the over exposure the tensile coupons experience as compared to operational packer seals.

The results of the SIM Test, which is a good simulation of actual downhole conditions experienced by the packer elastomer, support the Table XVII data and indicate that compound 267 can indeed provide an excellent seal at 260°C and 4,200 psi differential pressure for at least 22 hours.

B. Compound Trade-Offs.

This paragraph presents the detailed data generated in support of the EPDM development.

1) Detailed Screening and SIM Test Data.

Table XVIII presents all the Screening Test and evaluation data generated during this contract period. The compounds all use DuPont Nordel EPDM polymers. The polymers investigated were Nordel 1070, Nordel 1635, and Nordel 1660. The formulations and cures for the compounds are presented in Table XIX.

It was apparent from the testing that the chem ageing of the test specimens in the autoclave was a much more severe ageing environment than the operational application. "Dogbones" which are cut from 75-100 mil sheets have a very large surface area exposed to the brine when compared to the volume of rubber involved. In the real application the parts are thick and only a

TABLE XVIII -- SUMMARY OF EPDM SCREENING TEST DATA

Compound	Comment	Extrusion psia		Shore A		Elong. %		Tensile psi		Swell %		Wt. Gain %
		V	CA	V	CA	V	CA	V	CA	Width	Thick.	
223	Norde1 1070, No Hypalon	9.5	7.8	53	47	>840	>840	1138	1263	.5	-1.7	2.8
224	1070, 65 phr Statex 160	10.2	8.5	63	58	>840	>840	1535	1525	1.1	-1.0	4.6
225	1070, 70 phr Statex 160	11.1	8.5	65	65	>840	>840	1689	1612	-1.2	.5	4.7
226	1070, 75 phr Statex 160	12.1	9.3	68	65	>840	>840	1770	1676	1.0	-0-	5.0
246	1635	14.1	14.4	82	79	509	529	1612	1458	.79	.61	4.24
250	1635, 20 phr Polybutadiene	16.4	~18	88	89	167	171	1464	1491	.26	-.19	1.92
253	1070, 80 phr Statex 160	10.0	9.3	74	70	614	655	1156	1071	.69	1.14	4.42
254	1070, 85 phr Statex 160	10.2	10.4	76	72	567	585	1034	917	.49	.93	4.51
256	1660	15.0	14.5	81	80	540	560	1940	1953	.79	.67	3.52
257	1635, Haven 551	17.2	14.7	89	83	258	436	1688	1837	.06	.19	2.22
258	1635, 50 phr Statex 160	14.3	11.9	84	84	237	240	1719	1677	.16	.43	2.02
259	1635, 10 phr Polybutadiene	17.1	~18	89	86	235	237	1525	1507	.46	-.007	2.83
262	1660, 10 phr Polybutadiene	>18	>17.6	87	88	237	243	1587	1578	.46	.53	2.23
263	1660, 5 phr Polybutadiene	16.9	16.0	86	86	302	314	1561	1656	.26	.16	2.77
264	1660, 10 phr Hypalon	14.6	13.8	85	85	380	388	1572	1565	.59	.15	3.55
265	1660, 20 phr Hypalon	17.2	15.3	88	87	242	263	1099	1118	1.16	.91	4.03
267	1660, 20 phr Polybutadiene	17.9	17.7	92	92	141	138	1610	1554	.46	.41	2.29

TABLE XIX -- EPDM FORMULATIONS

Compound No. Component	223	224	225	226	246	250	253	254	256	257	258	259	262	263	264	265	267
Nordel 1070 (DuPont)	100	100	100	100			100	100									
Nordel 1635 (DuPont)					100	100				100	100	100					
Nordel 1660 (DuPont)									100				100	100	100	100	100
Hypalon 20 (DuPont)		5	5	5	5	5	5	5	5	5	5	5	5	5	10	20	5
Statex 160 (N110) (Cities Service)	65	65	70	75	75	75	80	85	75	75	50	75	75	75	75	75	75
Cyanox 2246 (American Cyanamid Co.)	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5	5
DI-Cup R (Harwick Chemical Corp.)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Thermoguard S (M&T Chemicals Inc.)		5	5	5	5	5	5	5	5	5	5	5	5	5	10	20	5
Polybutadiene #6081 (Polysciences Inc.)						20					20	10	10	5			20
Haven 551 (C. P. Hall)									10								
Sheet Press Cure °F/Min.	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60	350/60
Seal Press Cure °F/Min.						350/90			350/90	350/90			350/90		350/90		350/90
Post Cure Preheat Temp.	200	200	200	200	200	350	350	350	200	200	350	350	200	200	350	350	350
Nitrogen Purged	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	200-1h 250-1h 300-1h 350-1h 400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h

small portion of the surface area is exposed to the brine. The balance of the surface is sealed against metal mandrels, casing, back-up, etc.

The general development procedure used entailed developing the compound to acceptable levels of hydrothermochemical stability in the synthetic geothermal brine at 260°C, as measured in the Screening Tests. Once accomplished, the formulation development shifted to performance evaluation in the SIM Tests and the EPDM mechanical properties were then developed to improve the extrusion resistance. Table XX presents the SIM Test data. Figure 18 shows the balance of the post mortem SIM Test seals which are not shown in Section 3.1.2 (Extended Time Packer Seal SIM Tests) or Figure 17 above.

TABLE XX -- EPDM SIM TEST RUNS

Run	Formulation	Duration Hrs.	P, psi	T set °F	Diametral Gap Mils	Comment
48	256-3	22	3390	500	50	Minor Extrusion
49	257-2	22	4100	500	50	Moderate Extrusion
51	250-1	22	4190	500	50	Moderate Extrusion
52	262-1	22	4120	500	50	Moderate Extrusion
53	217-II-1	22	3060	500	50	Major Extrusion
54	264-1	22	4150	500	50	Moderate Extrusion
55	256-II-1	22	3530	500	50	Moderate Extrusion
56	256-II-3	22	4090*	500	50	Major Extrusion
57	267-1	22	4190	500	50	Moderate Extrusion
59	267-2	22	3870	400	50	Minor Extrusion
60	267-3	22	3240	300	50	No Extrusion
88	267-II-8	94	4240	500	50	Moderate Extrusion

*Pressure went up to 4900 during the night and then was relieved back to 4090 the next morning.

FIGURE 18 -- BALANCE OF POST MORTEM SIM TEST SEALS RUN AT 260°C

$\Delta P = 3,390$ psi, 22 hrs.

$\Delta P = 4,100$ psi, 22 hrs.

$\Delta P = 4,190$ psi, 22 hrs.

$\Delta P = 4,120$ psi, 22 hrs.

FIGURE 18 -- BALANCE OF POST MORTEM SIM TEST SEALS RUN AT 260°C (Continued)

$\Delta P = 3,060$ psi, 22 hrs.

$\Delta P = 4,150$ psi, 22 hrs.

$\Delta P = 3,530$ psi, 22 hrs.

$\Delta P = 4,090$ psi, 22 hrs.

2) Chlorosulfonated Polyethylene/Antimony Trioxide Stabilization Systems.

The Thermal Stabilization System consisting of Hypalon 20 and Thermoguard S were added to provide temperature stability. Comparing compounds 223 and 224 show questionable improvement in stability but improvement in the extrusion resistance. After the compounding effort was shifted from Nordel 1070 to Nordel 1635 and finally to Nordel 1660, an effort was made to determine if the 5 phr of Hypalon 20 and 5 phr of Thermoguard S were the optimum quantities. Sensitivity to this constituent pair was examined on compounds 256, 264 and 265. As can be seen from the Screening Test data for these compounds, increasing the amount of Hypalon and Thermoguard S results in a monotonic increase in modulus at break, and a commensurate decrease in ultimate tensile and ultimate elongation. The extrusion resistance is essentially unaffected and the hardness is slightly increased. Hydrothermochemical stability is only slightly degraded. As a result of these tests it was concluded that there is questionable benefit to increasing their levels so they were maintained at 5 phr of Hypalon 20 and 5 phr of Thermoguard S.

3) Nordel EPDM Polymers.

The EPDM polymers used in the compounding studies were Nordels manufactured by DuPont. Three different Nordel polymers were evaluated; 1070, 1635, and 1660.

A comparison of compounds 226, 246, and 256 shows that the 1600 series Nordels have better stability to the extrusion resistance measurements than does the 1070. The higher molecular weight 1660 polymer does not register much difference with its 1635 relative except for a 20% higher ultimate tensile strength. Tensile strength is deemed to be an important characteristic related to seal failure from breakage, hence, Nordel 1660 was selected as the favored polymer.

4) Miscellaneous Compounding Aspects

Statex 160 (N110, SAF) is added as reinforcement to improve the extrusion resistance and tensile strength. Several compound compositions were evaluated in order to determine the impact of variations in the quantity of Statex 160

from 65 to 85 phr. The corresponding compounds are 224, 225, 226, 253, and 254. Essentially no improvement in extrusion resistance was noted at least not to the levels required for good packer seal performance. However, based on this sensitivity study, 75 phr of Statex 110 appeared optimum on the basis of tensile strength.

Varying the quantity of Polybutadiene does not seem to have much affect on the hydrothermochemical stability of either the Nordel 1635 or 1660. Examining the Nordel 1635 compounds 250, 258, and 259, it was apparent that the 10 to 20 phr levels provided good improvement in extrusion resistance. It was not entirely clear which might be more optimum but following the criteria that higher modulus was better, the 20 phr level was selected for subsequent compounding.

Haven 551, trimethylol propane trimethacrylate, was added to the compound to increase the cross link density in an effort to increase the extrusion resistance. Improvements in the virgin compounds resulted, however, the improvements were not hydrothermochemically stable. Therefore, there was no further consideration of Haven 551.

4.3 EPDM/FLUOROELASTOMER BLEND

The development of elastomer compounds for the high-temperature geothermal packer seal was originally intended to be based on peroxide cured fluoroelastomers (Viton "G type" polymers). The goal of the program was to develop a seal that would survive for 22 hours in a 260°C aqueous solution of H₂S, CO₂, and NaCl. The seal is required to span a .050-inch diametral gap with a 3,100-4,100 psi differential pressure across it.

As development of the Viton progressed, it became more and more of a concern that the Vitons could not be developed to meet the GEM requirements. As a result, the development of other elastomer systems was initiated. One of the alternate systems is a blend of the fluoroelastomers and EPDM. A total of seven compounds were evaluated. This subsection documents the results of the "blend" development effort.

4.3.1 Current Favored "Blend" Compound

Compound number 275 is the current recommendation for a Viton/EPDM casing packer seal element based on the development work accomplished for this program.

A. EPDM/Fluoroelastomer Formulation 275.

Norde1 1660 (DuPont)	50 phr
VT-R-4590 (DuPont)	50
Hypalon 20 (DuPont)	2.5
Austin Black (Slab Fork Coal)	7.5
Statex 160 (N110 SAF) (Cities Service)	52.5
Maglite K (C. P. Hall)	2.5
Diak #7 (trialyl isocyanurate) (DuPont)	3
Luperco 130XL (Ram Chemicals)	1.5
Cyanox 2246 (American Cyanamid)	.25
Thermoguard S (M&T Chemicals, Inc.)	2.5
Polybutadiene 6081 (Polysciences, Inc.)	20
Press Cure:	350°F/60 min.
Post Cure:	N ₂ Atmosphere
	350°F preheat
	50°F/hr. step-up to 550°F started at insertion.
	550°F for 5 hrs.

B. Capability Threshold Runs.

Several Simulation Test runs were made as a function of temperature and differential pressure. The test matrix is shown in Table XXI. Figure 19 shows the three post mortem seals. The Blend seal number 275-1 was easily the best performer of all the elastomer candidates for the concluding SIM Tests at 260°C. The seal looked very good when it was removed from the test and the only apparent change was a very minor degree of permanent deformation suffered at the low pressure back-up gap. Seals 275-2 and 275-3 show very little evidence that they were even tested.

TABLE XXI -- CAPABILITY THRESHOLD DATA FOR
NORDEL/VITON BLEND COMPOUND 275

Seal No.	Δp (psi)	Temp. °C (°F)	Comments
275-1	3760	260 (500)	22 hrs. No Extrusion
275-2	2800	204 (400)	22 hrs. No Extrusion
275-3	2270	149 (300)	22 hrs. No Extrusion

All of the above SIM tests were run with 50 mil diametral gap back-up rings and in the GEM standard SIM Test synthetic geothermal fluid. To obtain the maximum Δp for each run, the pressure was increased in 1,000 psi steps until the seal unseated. Apparently, the unseating is being caused by a radial component of force created by the pressure which overcomes the seating force created through "squashing" the seal. This tended to occur at about 4,500-5,000 psi on the high pressure side or a differential pressure of about 3,600-4,100 psi with a squashing force of about 22,000 lbs. Because the 275 compound is very stiff, at the lower temperatures it unseated below the 3,600-4,100 psi differential pressure range. This is expected for the stiffer materials when the squashing force is held constant. The temperature effect on the unseating pressure of the seals is especially prevalent with the Blend 275 compound. Note that at 149°C only 2,270 psi could be sustained across the seal.

The temperatures shown are measured at the outside of the vessel radially from the center of the seal specimen and inside the band heater. This temperature is about 10°F over the seal temperature at 500°F and equal to the seal temperature at 300°F. The pressures shown are the differential pressures to which the system was backed-off after the seal unseated at a higher pressure. The time shown is the elapsed time the seal ran at pressure and temperature. It starts after the fixture is raised to test temperature and pressure which can take about 2 hours and ends when the seal fails or after 22 hours.

FIGURE 19 -- CAPABILITY THRESHOLD MATRIX POST MORTEM SEALS
GEM NORDEL/VITON 275 BLEND

260°C (500°F)
 $\Delta P = 3760$ psi

204°C (400°F)
 $\Delta P = 2800$ psi

149°C (300°F)
 $\Delta P = 2270$ psi

The threshold testing indicates that L'Garde EPDM/fluoroelastomer compound 275 can withstand about 3,800 psi differential pressure at 260°C with back-up providing a maximum 50 mil diametral gap.

4.3.2 Discussion of Compound Development

The basis for the development of this compound was to increase the extrusion resistance of the EPDM compounds while maintaining the hydrothermochemical stability of the EPDM to the extent possible.

A. Progress Accomplished.

Significant progress was made. EPDM/Viton Blend compounds which have good extrusion resistance plus good hydrothermochemical stability were developed. Table XXII compares test results of the earlier Blend compounds with the present recommended Nordel/Viton Blend compounds. Compound 275 provides maximum extrusion resistance for packer seals and compound 266 is less extrusion resistant but is more hydrothermochemically stable.

TABLE XXII -- COMPARISON OF EARLY VS. FINAL RESULTS FOR NORDEL/VITON COMPOUNDS

Formulation	Ult. Tensile @ RT psi		Ult. Elong. @ RT %		Shore A Hard @ 260°C		Extrusion Resist. @ 260°C, psia	
	V	CA	V	CA	V	CA	V	CA
Early 235 (CA/V)	1882	1506 (80%)	681	431 (63%)	67	74 (110%)	8.3	10.6 (128%)
Present 266 (CA/V)	1596	1531 (96%)	193	163 (84%)	88	89 (101%)	18.0	17.3 (96%)
Present 275 (CA/V)	1738	1602 (92%)	71	43 (60%)	98	96 (98%)	17.9	17.7 (99%)

Critical characteristics are compared for the early 235 compound against present 266 and 275 compounds for both the virgin condition (V) and the chemically aged (CA) condition after 22 hours exposure to the synthetic geothermal-brine at 260°C. The percentages in parentheses show the percent value of each characteristic retained after ageing. Note that for the present 266 and 275 compounds all values are good in the absolute sense and also have excellent stability through chem ageing except for elongation. The elongation hydrothermochemical stability is very good for 266 and fair for the 275 blend. The SIM Test results, which is a good simulation of actual downhole conditions experienced by the packer elastomer, verify the quality of the 266 and 275 Blend compounds. Both compounds performed very well in the packer seal SIM Tests.

B. Compound Trade-Offs.

This subsection presents the detailed data generated in support of the Nordel/Viton blend development.

1) Detailed Screening and SIM Test Data.

Table XXIII presents all the Screening Test and evaluation data generated during this contract period. The compounds numbered 235 through 275 are formulations compounded by L'Garde using DuPont's VT-R-4590, a peroxide cured "Viton" as one blend polymer component and DuPont's Nordel 1070 or Nordel 1660 as the other. The formulations and cures for the compounds are presented in Table XXIV.

It was apparent from the testing that the chem ageing of the test specimens in the autoclave was a much more severe ageing environment than the operational application. "Dogbones" which are cut from 75-100 mil sheets have a very large surface area exposed to the brine when compared to the volume of rubber involved. In the real application the parts are thick and only a small portion of the surface area is exposed to the brine. The balance of the surface is sealed against metal mandrels, casing, back-up, etc.

TABLE XXIII -- SUMMARY OF EPDM/FLUOROELASTOMER BLEND SCREENING TEST DATA

Compound	Comment	Extrusion, psia		Shore A		Elong., %		Tensile, psi		Swell, %		Wt. Gain %
		V	CA	V	CA	V	CA	V	CA	Width	Thick.	
235	Norde1 1070/VT-R-4590	9.3	10.6	67	74	681	431	1882	1506	.7	-0-	1.9
241	1070/4590 Blend	8.7	10.2	70	68	552	479	1397	1371	.4	1.0	2.4
242	Same as 241 with Hypalon	10.6	12.2	78	75	449	441	1550	1434	.6	1.1	2.9
260	1070/4590 More Hypalon	13.3	13.3	85	81	390	409	1468	1510	1.2	.8	4.2
261	1070/4590 More 4590	16.6	15.2	85	85	244	225	1366	1334	1.0	.5	3.7
266	1660/4590	18	17.3	88	89	193	163	1596	1531	1.0	1.2	2.6
275	1660/4590 + Polybutadiene	17.9	17.7	98	96	71	43	1738	1602	.8	.4	2.6

TABLE XXIV -- NORDEL/VITON BLEND FORMULATIONS

Component	235	241	242	260	261	266	275
Norcel 1070 (DuPont)	75	75	75	75	50		
Norcel 1660 (DuPont)						50	50
VT-R-4590 (DuPont)	25	25	25	25	50	50	50
Hypalon 20 (DuPont)			3.75	7.5	2.5	2.5	2.5
Austin Black (Cities Service)	10	10	10	4.9	7.5	7.5	7.5
Statex 160 (N110) (Cities Service)	50	50	50	55.1	52.5	52.5	52.5
Maglite K (C.P. Hall)	4	1.25	1.25	1.25	2.5	2.5	2.5
Diak #7 (DuPont)	3	3	3	3	3	3	3
Luperco 130 XL (Ram Chemicals)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Cyanox 2246 (American Cyanamid Co.)	.125	.125	.125	.37	.25	.25	.25
Thermoguard S (M&T Chemicals, Inc.)			3.75	7.5	2.5	2.5	2.5
Polybutadiene #6081 (Polysciences, Inc.)							20
Sheet Press Cure °F/Min	350/60	350/60	350/60	350/60	350/60	350/60	350/60
Seal Press Cure °F/Min						350/90	350/90
Post Cure 350°F, preheat Nitrogen purged	200-1h 250-1h 300-1h 350-1h 400-1h 450- $\frac{1}{2}$ h 500- $\frac{1}{2}$ h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h	400-1h 450-1h 500-1h 550-5h

Based on the Screening Test results shown in Table XXIII two compounds were selected for SIM Tests. These compounds, 266 and 275, were subjected to SIM Tests at various temperatures and pressures. The results of these SIM Tests are shown in Table XXV. Both compounds performed very well, the 275 compound is virtually completely extrusion resistant but has an ultimate elongation of 71%. Compound 266 is not quite extrusion resistant and has an ultimate elongation of 163% which may be needed under certain applications. The selection of compound 275 as the current recommended compound was almost arbitrary but was based primarily on post test examination of the test articles. These test seals are shown in Figures 19 and 20.

TABLE XXV -- NORDEL/VITON BLEND SIM TEST RUNS

Run	Formulation	Duration Hrs.	ΔP , psi	T Set °F	Diametral Gap Mils	Comments
61	266-1	22	4230	500	50	Moderate extrusion
63	275-1	22	3760	500	50	Minor extrusion
64	275-2	22	2800	400	50	No extrusion
65	275-3	22	2270	300	50	No extrusion
75	266-II-3	46	4220	500	50	Heavy moderate extrusion
89	275-II-1	46	3310	500	50	Minor extrusion

The development procedure used for the Blends was quite abbreviated because it drew on earlier developments for both the EPDM and the Viton. It was only necessary to compound seven formulations to achieve striking success with blend compounds.

FIGURE 20 -- BALANCE OF POST MORTEM SIM TEST SEALS RUN
@ 260°C (500°F) GEM NORDEL/VITON BLEND

$\Delta P = 4230$ psi, 22 hrs.

2) Acid Acceptor.

During development of the fluoroelastomer compound described in 4.1 above, a parametric study was made regarding the effects of the level of the acid acceptor Maglite K (MgO). The results indicated that all properties with the exception of tensile strength are very sensitive to the level of Maglite K. A level of 3 phr was eventually selected for the fluoroelastomer compounds which were under development during the same period the blend compounding effort reported here was progressing. The first compound (compound 235) of the blend contained 4 phr of Maglite K. Based on the fluoroelastomer work the level was adjusted and a level of 1.25 phr was found to be close to optimum as noted in the improvements of compound 241 over 235. The quantity of Maglite K was correspondingly doubled when the amount of fluoroelastomer was doubled when going from compound 260 to 261.

3) Chlorosulfonated Polyethelene/Antimony Trioxide Stabilization System.

The thermal stabilization system consisting of Hypalon 20 and Thermoguard S was added to provide temperature stability for the EPDM. These constituents are an extension of the EPDM development reported in 4.2 above. The stabilization system provided additional advantages for the blend compounds in the tensile strength and especially in the extrusion resistance. Shore A hardness showed moderate gain and in general resulting in a higher modulus elastomer. While the absolute value of the percent elongation was decreased, the overall stability of this parameter was significantly improved. Hydrothermochemical stability of the remainder of the parameters were essentially unaffected by the addition of the stabilizers. While the proportion of stabilizing components was not truly optimized for the compound, 2.5 phr of Hypalon 20 and 2.5 phr of Thermoguard S were the levels used to advantage for this study.

4) Austin Black.

Austin Black was originally included in the compound to provide both reinforcement and stability in the geothermal brine. Development work on the fluoroelastomer compounds reported in 4.1 above indicated that it was a good hydrothermochemical stabilizer for the Vitons but provided questionable reinforcement. As a result, the amount of Austin Black was reduced and the amount of Statex (N110, SAF) increased an equal amount.

5) Nordel/VT-R-4590 Ratio.

VT-R-4590 was originally added to the Nordel to enhance its extrusion resistance. The early compounds that included 75% Nordel were not able to provide levels of extrusion resistance which were needed, greater than about 13 psia. In view of this, the ratio of Nordel/VT-R-4590 was increased from 75/25 to 50/50 at compound 261. This change resulted in a significant increase in extrusion resistance to 16.6 psia with only a minor decrease in the percent elongation and extrusion resistance stability. In consonance with the EPDM development which was occurring in parallel, Nordel 1660 was factored into the Blend work because of the positive improvements experienced with the EPDM's. Changing to Nordel 1660 from Nordel 1070 at compound 266 resulted in a material

that showed significant improvement in extrusion resistance with values bordering on the capability of the chart recorder. The results of SIM Tests shown in Table XXV confirm that the improved extrusion resistance as measured with the Extrusion Resistometer correlates well with the actual performance of the packer seal.

4.4 PROPYLENE - TFE, AFLAS

The development of elastomer compounds for the high-temperature geothermal packer seal was originally intended to be based on peroxide cured fluor-elastomers (Viton "G type" polymers). The goals of the program were to develop a seal that would survive for 22 hours in a 260⁰ aqueous solution of H₂S, CO₂ and NaCl. The seal is required to span a .050-inch diametral gap with a 3,100-4,100 psi pressure differential across it.

As development of the Viton progressed, it became more and more of a concern that the Vitons could not be developed to meet the GEM requirements. As a result the development of compounds using other polymers was begun. JPL on a related elastomers effort identified and did some preliminary compounding experimentation with AFLAS. AFLAS is a propylene-TFE compound manufactured by Asahi Glass Co. of Japan. L'Garde continued development of AFLAS beyond the initial JPL effort. AFLAS was integrated into the L'Garde GEM Program along with the Viton, EPDM and Blend development. A total of 20 compounds were evaluated. This subsection documents the results of the L'Garde "AFLAS" development effort.

4.4.1 Propylene - TFE Current Favored (AFLAS) Compound

Compound number 291 is the current recommendation for an AFLAS casing packer seal element based on the development work accomplished for this program. The following is the formulation and cure cycle.

A. AFLAS Formulation 291.

AFLAS 100 (Asahi Glass Co.)	100 phr
Statex 160 (N110, SAF) (Cities Service)	50
Maglite K (C. P. Hall)	3
Luperco 130XL (Ram Chemicals)	5
Diak #7 (Triallyl isocyanurate) (DuPont)	5
Polybutadiene #6081 (Polysciences Inc.)	5

Press Cure: 350°F, 20 minutes

Post Cure: N₂ Atmosphere
 350°F for 4.5 hr.
 400°F for 0.5 hr.
 450°F for 0.5 hr.
 500°F for 2.5 hr.

B. Capability Threshold Runs.

Several Simulation Test runs were made as a function of temperature and differential pressure. The matrix is shown in Table XXVI. Figure 21 shows the four post mortem seals three of which sealed for the full 22 hours. The 291-2 seal at 204°C (400°F) and 3,683 psi unseated at 15.5 hours during the night. The seal was in good condition when it was removed. The differential pressure was reduced to 3,237 psi and seal 291-3 was run to the 22 hour maximum at 204°C. All seals looked good with 291-1 and 291-3 suffering only minor local damage.

TABLE XXVI -- CAPABILITY THRESHOLD DATA FOR AFLAS COMPOUND 291

Seal No.	Δp , psi	Temp., °C (°F)	Comments
291-1	4237	260 (500)	22 hrs. Minor Moderate Extrusion
291-2	3683	204 (400)	15.5 hrs. Unseated, Very Minor Extrusion
291-3	3237	204 (400)	22 hrs. Very Minor Extrusion
291-II-1	2132	149 (300)	22 hrs. No Extrusion

FIGURE 21 -- CAPABILITY THRESHOLD MATRIX POST MORTEM SEALS
GEM AFLAS 291 PROPYLENE - TFE

260°C (500°F)
 $\Delta P = 4,237$ psi

204°C (400°F)
 $\Delta P = 3,683$ psi

204°C (400°F)
 $\Delta P = 3,237$ psi

149°C (300°F)
 $\Delta P = 2,132$ psi

All of the above SIM Tests were run with 50 mil diametral gap back-up rings, and in the standard SIM Test synthetic geothermal fluid. For the maximum differential pressure cases, the pressure was increased in 1,000 psi steps until the seal unseated. Apparently, the unseating is being caused by a radial component of force created by the pressure which overcomes the seating force created through "squashing" the seat. At 260°C this tended to occur at about 4,500-5,200 psi on the high pressure side or a differential pressure of about 3,600-4,300 psi with a squashing force of about 22,000 lbs. The temperature effect on the unseating pressure of the seals is especially prevalent with the AFLAS 291 compound. Note that at 149°C only 2,132 psi differential pressure could be sustained across the seal.

The temperatures shown are measured at the outside of the vessel radially from the center of the seal specimen and inside the band heater. This temperature is about 10°F over the seal temperature at 500°F and equal to the seal temperature at 300°F. The pressures shown are the differential pressures to which the system was backed-off after the seal unseated at a higher pressure. The time shown is the elapsed time the seal ran at pressure and temperature. It starts after the fixture is raised to test temperature and pressure which can take 2 hours and ends when the seal fails or after 22 hours.

The threshold testing indicates that L'Garde's AFLAS compound 291 can withstand about 4,200 psi differential pressure at 260°C (500°F) with back-up providing a 50 mil diametral gap. The differential pressure capability falls off to 2,100 psi at 149°C (300°F) for the 20,000 lb., seating force. Further compounding and/or higher seating force should increase the differential pressure capability.

4.4.2 Discussion of Compound Development

The AFLAS compound development was explored because relative little was known about its capabilities which appeared, at minimum, interesting based on Screening Test measurements on the JPL compounds. Development of the AFLAS for the geothermal environment fulfills a requirement of the Statement of Work.

A. Progress Accomplished.

Significant progress was made. AFLAS compounds which have good extrusion resistance plus reasonable hydrothermochemical stability were developed. Table XXVII compares test results of the current recommended AFLAS compound with one from earlier in the development cycle. Compound 291 does not represent an optimized compound, rather one which was sufficient to meet the GEM requirements; it is expected that additional progress is still possible, but not within the scope of this contract.

TABLE XXVII -- COMPARISON OF EARLY AFLAS COMPOUND VS.
FINAL RESULTS FOR AFLAS COMPOUNDS

Compound	Ult. Tensile @ RT, psi		Ult. Elong. @ RT, %		Shore A Hard. @ 260°C		Extrusion Resist. @ 260°C, psia	
	V	CA	V	CA	V	CA	V	CA
Early 268 (CA/V)	1782	1348 (76%)	363	416 (115%)	71	61 (86%)	7.5	5.7 (76%)
Present 291 (CA/V)	2335	2162 (93%)	134	158 (118%)	95	95 (100%)	17.4	15.2 (87%)

Critical Characteristics are compared for compound 291 against 268 for both the virgin condition (V) and the chem aged (CA) condition after 22 hours exposure to the synthetic geothermal brine at 260°C (500°F). The percentages in parentheses show the percent value retained after ageing. Note that for 291 the tensile strength and the extrusion resistance are especially good as well as the overall hydrothermochemical stability.

The results of the packer seal "SIM" Test, which is a good simulation of actual downhole conditions experienced by the packer elastomer, support the Table XXVII data and indicate that compound 291 can seal at 260°C (500°F) and 4,200 psi pressure for at least 22 hours.

B. Compound Trade-Off's.

This subsection presents the detailed data generated in support of the AFLAS development.

1) Detailed Screening and SIM Test Data.

Table XXVIII presents a summary of the Screening Test and Evaluation data generated during this contract period. The compounds numbered 268 through 291 are formulations compounded by L'Garde using primarily AFLAS 100 and some AFLAS 150 polymers by Asahi Glass Co. LGA-1 and LGA-2 are formulations compounded by Jet Propulsion Laboratory using AFLAS 150. The formulations and cures for the L'Garde compounds are presented in Table XXIX.

From the beginning of the AFLAS development, its primary problem was extrusion resistance with hydrothermochemical stability being secondary. Much of the compound development was aimed at raising the extrusion resistance to the mid to high teen level while maintaining good sealing characteristics and ageing stability. As can be seen from the Screening Test data the critical improvements are related to the cure system and the use of polybutadiene.

As compound development progressed the more extrusion resistant formulations were advanced from Screening Tests to packer seal SIM Tests. Table XXX is a summary of the AFLAS SIM Tests. Figure 22 shows the balance of the SIM Test seals which is not shown in Section 3.1.2 (Extended Time Packer Seal SIM Tests) and Figure 21 above.

The progression of seals shown in Figure 22 illustrate the trade-off which exists between extrusion resistance and the ability to pack-off the seal without breakage. The modulus must be low enough to allow significant compression of the height of seal and radial expansion for pack-off without breaking, while being high enough to enable bridging of gaps without excessive extrusion. The 274-3 seal is an example of breakage and the LGA-1-1 is an example of insufficient extrusion resistance. The LGA-1-1 was a compound formulated and provided by JPL, and represents some of the first AFLAS work done on the overall DOE elastomers development program.

TABLE XXVIII -- SUMMARY OF PROPYLENE-TFE (AFLAS) SCREENING TEST DATA

Compound	Comment	Extrusion Resist. @ 260°C, psia		Shore A @ 260°C		Ult. Elong. @ RT, %		Ult. Tensile @ RT, psi		Swell %		Wt. Gain %
		V	CA	V	CA	V	CA	V	CA	Width	Thick.	
268	AFLAS 100, Short Post Cure	6.7	5.6	69	63	394	442	1673	1289	.93	3.85	3.07
	AFLAS 100, Long Post Cure	7.5	5.7	71	61	363	416	1782	1348	1.26	4.37	3.15
269	AFLAS 100, No Austin	7.0	~6.0	64	54	487	552	1804	1519	1.26	2.68	3.28
270	AFLAS 100, More Statex 160	7.7	6.0	80	72	272	303	2105	1702	.86	1.98	3.20
271	AFLAS 100, Sublimed Litharge	6.6	5.5	72	63	433	413	1743	1303	.56	2.42	2.18
272	AFLAS 100, Adjust cure system	5.1	5.2	69	67	421	466	1453	1251	.73	2.07	3.02
273	AFLAS 150	8.3	3.8	75	69	293	274	1525	1094	.76	1.07	2.97
274	AFLAS 100 - Polybutadiene	13.4	14.8	96	97	169	90	2100	2171	.83	.65	2.78
279	AFLAS 100, Luperco/Diak .5/5	5.9	6.5	68	66	366	376	1689	1457	.46	2.08	3.35
280	AFLAS 100, Luperco/Diak 3/5	12.5	13.1	81	77	295	301	2583	2283	.29	.96	2.93
281	AFLAS 100, Luperco/Diak 1/3	6.9	6.7	69	65	350	345	1874	1649	.23	2.77	3.44
282	AFLAS 100, Luperco/Diak 1/7	7.1	7.5	73	70	356	327	1672	1653	.13	1.95	3.03
283	AFLAS 100 - 1.5 MgO	7.5	7.4	70	60	339	402	2035	1664	.19	1.53	2.93
284	AFLAS 100 - 20 phr Statex M568, 20 phr Statex 160	6.9	7.0	62	55	553	573	1839	1667	.39	3.05	2.64
285	AFLAS 100 - 20 phr Statex M568, 30 phr Statex 160	7.2	7.2	61	61	433	426	1852	1679	.36	1.73	3.21
286	AFLAS 100 - 20 phr Statex M568, 40 phr Statex 160	7.3	7.3	70	59	291	379	1836	1621	.83	3.23	3.55
287	AFLAS 100 - Polybutadiene	17.8	15.0	96	94	83	71	2865	2629	.59	2.38	2.68
288	AFLAS 100 - Luperco/Diak 4/5	13.1	11.9	85	83	210	260	2693	2423	.60	1.41	2.46
289	AFLAS 100 - 10 phr Polybutadiene 4/5	16.5	14.8	95	97	137	115	2651	2212	.66	1.07	2.89
290	AFLAS 100 - 5/5	12.6	11.0	86	84	219	288	>3035	2556	.13	1.50	2.77
291	AFLAS 100 - 5 phr Polybutadiene 5/5	17.4	15.2	95	95	134	158	2335	2162	.56	1.70	2.50
LGA-1	JPL AFLAS 150	7.8	6.1	63	59	519	630	2774	2002	.40	.53	.28
LGA-2	JPL AFLAS 150	5.5	3.1	57	46	580	>840	1798	1275	.86	3.01	1.70

C

Compound No. Component	268	269	270	271	272	273	274	279	280	281	282	283	284	285	286	287	288	289	290	291
AFLAS 100 (Asahi Glass)	100	100	100	100	100		100	100	100	100	100	100	100	100		100	100	100	100	100
AFLAS 150 (Asahi Glass)						100														
Statex 160 (N110) (Cities Service)	50	50	65	50	50	50	50	50 DRY	50 DRY	50 DRY	50 DRY	50 DRY	20 DRY	30 DRY	40 DRY	50 DRY	50 DRY	50 DRY	50 DRY	50 DRY
Maglite K (C. P. Hall)	3	3	3		3	3	3	3	3	3	3	1.5	3	3	3	3	3	3	3	3
Lupercol 130XL (Ram Chemicals)	2	2	2	2	1	2	2	.5	3	1	1	2	1	1	1	3	4	4	5	5
Diak #7 (DuPont) (Received)	2 4/21/78	2 4/21/78	2 4/21/78	2 4/21/78	5 4/21/78	2 4/21/78	2 4/21/78	5 4/21/78	5 4/21/78	3 4/21/78	7 4/21/78	2 4/21/78	5 4/21/78	5 4/21/78	5 4/21/78	5 4/21/78	5 4/21/78	5 12/7/78	5 12/7/78	5 12/7/78
Austin Black (Cities Service)	10		10	10	10	10	10	10	10	10	10 DRY	10 DRY				10 DRY	10 DRY	10 DRY	10 DRY	10 DRY
Polybutadiene #6081 (Polysciences Inc.)							20	20	20	20						20				
Sublimed Litharge (E. T. Horn)				15																
Statex M-568 (M568) (Cities Service)													20 DRY	20 DRY	20 DRY					
Sheet Press Cure ^{OF} /Min	200/15										320/30	320/30	320/30	320/30	320/30	350/20	350/20	350/20	350/20	350/20
Seal Press Cure ^{OF} /Min	320/30	320/30	320/30 250/30 350/120	320/30	320/30	320/30	320/30 320/60 320-4½h	320/30	320/30 250/30 350/60	320/30							250/30 350/60	250/30 350/60	250/30 350/60	250/30 350/60
Post Cure N ₂ Atmos. Preheat 350 ^{OF}	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2½h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-1h 400-1h 450-1h 500-2h	350-4½h 400-½h 450-½h 500-2½h	350-4½h 400-½h 450-½h 500-2½h	350-4½h 400-½h 450-½h 500-2½h	350-4½h 400-½h 450-½h 500-2½h	350-4½h 400-½h 450-½h 500-2½h

TABLE XXX -- PROPYLENE-TFE (AFLAS) SIM TEST DATA

Run	Formulation	Duration Hrs.	ΔP psi	T set °F	Diametral Gap Mils	Comments
72	274-3	-0-	3615	500	50	Broke through thickness
74	280-1	22	3727	500	50	Major extrusion, one side partially collapsed
76	288-1	22	3593	500	50	Moderate extrusion
77	287-1	22	4154	500	50	Moderate extrusion
78	290-1	22	4231	500	50	Moderate extrusion
79	289-1	15	4222	500	50	Moderate extrusion, broke ≈1" outside edge
81	291-1	22	4237	500	50	Moderate extrusion
83	291-2	15.5	3683	400	50	Minor extrusion, unseated during nite
84	291-3	22	3237	400	50	Minor extrusion
85	291-II-1	22	2132	300	50	No extrusion
90	291-II-2	46	3532	500	50	Moderate extrusion
50	LGA-1-1	-0-	4100	500	50	Broke through thickness. Major extrusion.

2) Cure System.

The AFLAS compounding for the geothermal packer seal application was sensitive to the cure system components Luperco 130XL (a solid diperoxide formulation containing 45% by weight of 2,5 - Dimethyl -2,5-di (t-butylperoxy) hexyne-3) and Coagent Diak #7 a reactive poly functional triazine (triallyl isocyanurate). The proportions of these two constituents was examined from 0.5 to 5 phr Luperco and from 2 to 7 phr Diak #7. Significant improvement of the extrusion resistance emerged for Luperco 130XL levels of 3 to 5 and a Diak #7 level of 5 phr.

FIGURE 22 -- BALANCE OF POST MORTEM SIM TEST SEALS
RUN @ 260°C (500°F) GEM AFLAS

$\Delta P = 3,615$ psi, 0 hrs.

$\Delta P = 3,727$ psi, 22 hrs.

$\Delta P = 3,593$ psi, 22 hrs.

$\Delta P = 4,154$ psi, 22 hrs.

FIGURE 22 -- BALANCE OF POST MORTEM SIM TEST SEALS
RUN @ 260°C (500°F) GEM AFLAS (continued)

$\Delta P = 4,231$ psi, 22 hrs.

$\Delta P = 4,222$ psi, 15 hrs.

$\Delta P = 4,100$ psi, 0 hrs.

The tentative conclusion was based on the limited data points and potential for further improvement exists with an extension of the study. The cure system constituency was definitely out of the optimum regime at the beginning of the AFLAS studies and the commensurate insufficient crosslink density was reflected in poor seal characteristics.

However, independent of the future possibility for further improvement, the present 291 compound performs well and meets the GEM packer seal requirements. AFLAS is a viable high-temperature geothermal seal elastomer.

3) Miscellaneous Compounding Aspects.

Austin Black was carried into the AFLAS compounding from the fluoroelastomer work. In that the Austin Black, which is a natural product of bituminous coal fines, provides a stabilizing effect to the Vitons, and the mechanism is currently unknown; it was reasonable to include it into the AFLAS compounding. It was determined that it did not provide any significant contribution to the AFLAS compounding and is not included in the current best 291 compound.

For nearly all the AFLAS compounding, the Statex 160 (N110, SAF) black was held at a constant 50 phr. Early during the development 65 phr was considered but another associated problem prevented this from providing additional tensile strength. Molding and milling difficulties were encountered with the AFLAS which prevented levels of SAF black above 50 phr. An experiment was tried with compounds 284, 285, and 286 where a constant 20 phr of Statex M-568 (N568, FEF) black was used and complemented with 20, 30, and 40 phr of SAF. This technique resulted in virtually constant characteristics even though the level of SAF changes by a factor of two.

AFLAS is different from vinylidene fluoride type fluoroelastomers because it does not have acidic vulcanization products, therefore, there is no requirement for a metal oxide acid acceptor. Magnesium oxide is used, however, to provide heat resistance. Maglite K was nominally used at a 3 phr level and a molar equivalent level of sublimed Litharge was used in compound 271. Virtually no change resulted.

Polybutadiene 6081 was used to increase the extrusion resistance and it had a direct effect. Levels equal to that used in the EPDM systems resulted in seals that were too brittle and broke. The current favored 291 AFLAS compound has 5 phr of Polybutadiene 6081.

Primarily AFLAS 100 was used for the GEM Program. AFLAS 150 is an improved, more processible polymer with better compression set while maintaining the same tensile strength with less ultimate elongation. A small amount of AFLAS 150 was obtained from JPL and compounded into formulation 273 for comparison with AFLAS 100. Compound 273 suffered a reduction in extrusion resistance after brine ageing down to 46% of the virgin value. On this basis all further AFLAS development was carried out using AFLAS 100.

4.5 MISCELLANEOUS ELASTOMERIC POLYMERS

In addition to the above polymer systems investigated, assessments of a dimethylsilicone, a fluorosilicone, and a 3M compound of unknown formulation were made. Silicone elastomers were of interest because they have the best high-temperature oxidation resistance and maintain their physical properties better at 260°C than any of the elastomers. The backbone is -Si-O-Si-O- which is thermally stable, however, no applicable information about resistance to sulfur or water or high temperatures was found. However, small amounts of oil cause severe degradation. Fluorosilicone elastomers are similar to the silicones except they have been fluorinated to give the compounds some resistance to oils. According to Dow Corning, applicability of silicone rubber to the GEM environment is uncertain, therefore, simple Screening Tests to determine the hydrolytic and sulfur resistance were made.

Table XXXI shows the results of the Screening Tests. The dimethyl and fluorosilicone test compounds were completely destroyed during the standard autoclave ageing in the synthetic geothermal brine at 260°C. The compounds were broken into small pieces by the time they were removed from the autoclave.

TABLE XXXI -- SUMMARY OF MISCELLANEOUS SCREENING TEST DATA

Compound	Comment	Extrusion psia		Shore A		Elong. %		Tensile psi		Swell %		Wt. Gain %
		V	CA	V	CA	V	CA	V	CA	Width	Thick.	
LS-70	Fluorosilicone	6.7	D	69	D	320	D	936	D	D	D	D
TR-70	Dimethylsilicone	9.8	D	75	D	572	D	990	D	D	D	D
48746-35	3M, Formulation unknown	9.8	-0-	71	28	552	68	3113	49	4.0	38.0	-3.0

D = Destroyed

3M provided a compound with which they had no experience in the GEM type environment, however, there was the possibility that it may have performed under the unusually severe conditions. Hence, it was tested with the possibility in mind. Though it was not destroyed, it reverted and became soft, showing no promise.

5.0 CURE-IN-PLACE CONCEPT

The current day elastomeric casing packer system places conflicting requirements on the seal element and the conditions become unusually severe at geothermal temperatures. First the seal needs to be pliable or of low enough modulus to be significantly deformed without cracking from the as molded run-in configuration to the packed-off configuration. Once packed-off, it is then best for the seal to be stiff and of high modulus to enable the material to bridge gaps without excessive extrusion. Hence, a critical balance must be struck between the conflicting requirements to develop a material that is low enough modulus to deform without cracking yet high enough modulus to successfully bridge the required gaps. Striking this balance becomes increasingly difficult if not impossible as the temperature increases to geothermal levels on the order of 260°C.

5.1 BASIC CONCEPT

The Cure-In-Place Concept provides a potential solution for the above dichotomy. It provides a material which is low modulus during deformation and high modulus when performing as a seal. The basic concept is simple, an uncured but fully molded seal is installed on the packer. The packer is lowered into the operating position, the seal is deformed to its packed-off configuration, the seal is heated or allowed to heat up, and cured for the specified time period, the seal is then firmly packed-off, and then operated in the normal manner.

Feasibility of the Cure-In-Place Concept was evaluated during the current contract period. Several runs were made on the SIM test to perfect the curing of the seal and a subsequent six performance test runs were made where differential pressure was applied across the seal. Feasibility of the Cure-In-Place Concept was proven and the DOE is currently applying for a domestic patent on the art.

5.2 DISCUSSION OF FEASIBILITY EVALUATION TESTS

A stepwise process was performed to incrementally develop and evaluate the feasibility of the Cure-In-Place Concept. The three steps are molding the seal, curing of the seal, and performance testing and compound development. The standard SIM Test seal specimen described in Section 4.0 of Appendix A was used for this development. Table XXXII summarizes the Viton formulations used for these cure-in-place tests and Table XXXIII summarizes the runs on the SIM tester starting with the cure-in-place only runs. Much of the effort was spent learning how to produce good seals using the cure-in-place process.

Peroxide curing agent seals, which were molded but uncured or partially cured to various extents, were evaluated as to their applicability for the Cure-In-Place Concept. Seals were cured from 2 minutes to the full 30 minutes in the cure press with no further curing, i.e. no post cure as with the standard cure cycle. Problems were encountered with the seals that were press cured for a short time in that at temperature their strength was low and they deformed as they were removed from the mold. The problem was academic, however, because with the peroxide cured Viton compounds (VT-R-4590) the green strength of the uncured rubber is more than sufficient for the preoperational requirements of the packer. A technique was perfected which produces excellent molded but uncured seals.

The technique starts with a heated mold to reduce the viscosity of the rubber to achieve good flow and then it is allowed to cool prior to removing the seal. The mold is preheated to 93°C (200°F), sufficiently low such that insignificant crosslinking occurs, the rubber is inserted into the mold, the mold is closed with 50 tons of force, the heater power turned off, and the force is maintained for 3.5 hours. The seal is removed when cool and with no attendant deformation problems when the mold is pried open.

Given good quality molded seals the next developmental process addressed was that of curing the seal. The molded seal is assembled into the Simulation Test. Water is loaded into the test fixture and the seal is compressed 120 mils. The heater is then set at a temperature of 260°C (500°F)

TABLE XXXII -- CURE-IN-PLACE FORMULATIONS

Formulation Component	227	238		248	
VT-R-4590 (DuPont)	100	100		100	
Austin Black (Cities Service)	40	35		10	
Maglite K (C.P. Hall)	5	1		2	
Diak #7 (DuPont)	3	3		3	
Luperco 130 XL (Ram Chemicals)	1.5	1.5		1.5	
Statex-M568 (Cities Service)				55	
Cure °F/Time	350° mold to 50 ton release	SEALS thru-10 125° mold Power off. Leave in press overnite.	SEALS -11 on 150° mold	SEALS -2 3½ hrs.	SEALS -3
Post Cure in SIM Tester in	H ₂ O	H ₂ O #8 in nitrogen	H ₂ O	H ₂ O	Brine

TABLE XXXIII -- CURE-IN-PLACE TEST RUNS

Run	Formulation	Mold °F/Min.	Post Cure	Test	Squash Post Cure/SIM	Comment
23	227-6	350/0	H ₂ O	No	.25	Cracked, extruded and tough
24	238-3	125 off overnite	H ₂ O	No	.20	Rough and extruded; softer compound
25	238-4	125 off overnite	H ₂ O	No	.15	2-1/8" holes; cracked top and bottom
26	238-5	125 off overnite	H ₂ O	No	.12	4-3/32" holes
27	238-6	125 off overnite	H ₂ O	No	.11	4 holes, squash then add H ₂ O under pressure
28	238-8	125 off overnite	Nitrogen	No	.12	4 holes, no H ₂ O Nitrogen purged; 1 .6" vertical crack
29	238-9	125 off overnite	H ₂ O	No	.12	RTV-106, seal looks good
30	238-11	150 off overnite	H ₂ O	Yes	.12/.10	RTV-106, seal unseated between 3500-4000#
31	238-V-12	150 off overnite	H ₂ O	Yes	.12/0	RTV-106, broke (shattered) after 1 min. @ 4500# (trying for 5000#)
32	238-V-13	150 off overnite	H ₂ O	Yes	.12/.20	RTV-106, 3400# failed
33	238-V-14	150 off overnite	H ₂ O	Yes	.12/.122	RTV-106, 2000#, failed after 7 mins.
34	248-2	150 off 3½ hrs.	H ₂ O	Yes	.12/.05	RTV-106, 4800#, 22 hrs. -- start @ 4000#, crept to 4800# (over 2 hrs.)
35	248-3	150 off 3½ hrs.	Brine	Yes	.12/.15	RTV-106, 4200#, 22 hrs. -- start @ 4000#, crept to 4200#

and for the formulations tested the seals were cured for 24 hours (this is variable with each formulation and a conservatively long time was used here). Inspection of the first attempt revealed that extremely rough sealing surfaces were being produced on the inside of the seal. Figure 23 shows the surface roughness which resulted from the first tries at curing a seal in place. After much investigation it was determined that the roughness was caused by liquid being entrapped behind the seal, and as it heated and expanded, it impressed the roughness into the rubber. An attempt to allow escape of the fluid through holes drilled through the thickness of the seal was made with no success. This resulted with water being trapped in the hole and severe vertical cracking of the seal occurred in the vicinity of the holes as the water thermally expanded. The problem was finally solved by sealing the ends of the seal element with silicone rubber, RTV 106. Figure 24 shows the smooth ID surface which results when the seal ends are sealed with RTV 106.

Once the molding and curing problems were solved performance testing was initiated by running the Simulation Test with a differential pressure and monitoring leakages. Five runs were made with formulation 238 with various compression displacements after curing ranging from 0-200 mils. The differential pressures were increased incrementally until failure of the seal which occurred from 2,000 to 4,500 psi for this formulation. Because the seals were not withstanding the maximum differential pressures a highly loaded compound, 248, was tried with success. Figure 24 shows a cross section of a cure-in-place seal made from compound 248. As expected, a minor amount of extrusion took place as the seal was deformed into its operational configuration. Minor cracks which are apparent no knit lines are attributed to low molding pressure exerted on the rubber with the large 150 mil diametral gap at the back-up ring. The no knit lines did not interfere with the successful performance of the seal, however, it would be desirable to eliminate them if possible. Systems with reduced gaps should apply higher pressure on the rubber during cure and reduce and/or eliminate the imperfections.

Most importantly, however, is the fact that the cured seal did not extrude once the elastomer was cured. This 248 compound was the first and only seal tested to have successfully sealed maximum differential pressure of

FIGURE 23 -- FIRST ATTEMPT CURE-IN-PLACE SEAL

FIGURE 23 -- SUCCESSFUL CURE-IN-PLACE SEAL

4,000 psi at 260°C for a full 22 hours with a large 150 mil diametral gap at the back-up. The formulation for compound 248 is as follows:

<u>Component</u>	<u>phr</u>
VT-R-4590 (DuPont)	100
Austin Black (Slab Fork Coal)	10
Statex M-568(N-568)	55
Maglite K (C. P. Hall)	2
Diak #7 (DuPont)	3
Luperco 130XL (Ram Chemicals)	1.5

5.3 CONCLUSION

The Cure-In-Place Concept was proven to provide the advantage for thermal packer applications through 1) minimization of seal stress through virtual elimination of the stress component due to compression pack-off and 2) enabling very high modulus extrusion resistant compounds to be employed which would crack when used with as standard packer. The concept is interesting but more than just an academic brainteaser. With the geothermal application a means is required to keep the seal cool until it is deformed to the packed-off configuration and ready for curing. Systems that employ cryogenics, for example, are a possible practical system solution.

A natural application for the Cure-In-Place Concept is in the oil field. Similar thermal packer problems exist on enhanced oil recovery projects where steam is injected into the reservoir to heat the oil. For this application a packer could be lowered into the cold well, the packer preset and then steam flowed to provide the temperature cause the elastomer to cure-in-place. Once cured the packer is permanently set and the installation is ready for operation.

As envisioned, the Cure-In-Place Concept provides a means to increase the temperature capability of current day compression casing packers. System concepts are feasible which either prevent the heat from raising the temperature of the seal element until the proper time for curing or heat the seal for curing at the proper time. System studies are needed to determine the ultimate practicality and applicability of the concept.

REFERENCES

1. Arnold, C. Jr., "Evaluation of Elastomers for Blow-Out Preventors," Memo to Distribution, 19 April 1979, Sandia Laboratories, Albuquerque, NM 87115.
2. Hirasuna, A. R., et al., "Geothermal Elastomeric Materials, Twelve-Months Progress Report, October 1, 1976 - September 30, 1977," DOE Report Number SAN/1308-1, December 1977, L'Garde, Inc., Newport Beach, CA 92663.
3. Hirasuna, A.R., "Cure-In-Place Concept," IR 174, 10 August 78, L'Garde, Inc., Newport Beach, CA 92663.
4. Hirasuna, A. R., "Development of Fluoroelastomer Compounds," IR 183, 15 June 79, L'Garde, Inc., Newport Beach, CA 92663.
5. Kojima, G., Kojima, H., Tabata, Y., "A New Fluoroelastomer Derived From Tetrafluorethylene and Propylene," Joint Meeting of the Rubber Division, American Chemical Society and The International Rubber Conference, 1976, San Francisco, CA, 5-8 October 1976.
6. MacLachlan, J. D. and Hallenbeck, A., "A New Fluoroelastomer for Improved Fluids Resistance," 110th Meeting of the Rubber Division, American Chemical Society, San Francisco, CA, 5-8 October 1976.
7. Pelosi, L. F. and Hackett, E. T., "Improved Steam Resistance for Fluoroelastomers," 110th Meeting of the Rubber Division, American Chemical Society, San Francisco, CA, 5-8 October 1976.
8. Sedwick, R. A., "Procedure for Preparation of EPDM/Fluoroelastomer Blend Compound GEM 266," Drawing Number 10668, 11 June 79, L'Garde, Inc., Newport Beach, CA 92663.
9. Sedwick, R. A., "Procedure for Preparation of EPDM/Fluoroelastomer Blend Compound GEM 275," Drawing Number 10699, 11 June 79, L'Garde, Inc., Newport Beach, CA 92663.
10. Sedwick, R. A., "Procedure for Preparation of Propylene-TFE Compound GEM 291," Drawing Number 10670, 11 June 79, L'Garde, Inc., Newport Beach, CA 92663.
11. Sieron, J. K., Private conversation, various dates, Air Force Materials Laboratory, Wright-Patterson AFB.
12. Veal, G. R., "GEM EPDM/Fluoroelastomer Compound Development," IR 184, 14 June 79, L'Garde, Inc., Newport Beach, CA 92663.
13. Veal, G. R., "GEM AFLAS Compound Development," IR 185, 19 June 79, L'Garde, Inc., Newport Beach, CA 92663.

14. Veal, G. R., "GEM EPDM Compound Development," IR 186, 21 June 79, L'Garde, Inc., Newport Beach, CA 92663.
15. Wallstrom, R. J., "Procedure for Preparation of Fluoroelastomer Compound, GEM 255," Drawing Number 10590, 8 November 78, L'Garde, Inc., Newport Beach, CA 92663.
16. Wallstrom, R. J., "Procedure for Preparation of EPDM Compound GEM 267," Drawing Number 10589, 8 November 78, L'Garde, Inc., Newport Beach, CA 92663.
17. Winzenried, R., "O-Rings Made From Packer Seal Formulations for Drill Bit Seal Testing," Letter to Hirasuna, 15 June 1979, Terra Tek, Salt Lake City, UT 84108.

APPENDICES

SAN/1308-1

GEOHERMAL ELASTOMERIC MATERIALS

**Twelve-Months Progress Report,
October 1, 1976—September 30, 1977**

By

A. R. Hirasuna

G. D. Bilyeu

D. L. Davis

C. A. Stephens

G. R. Veal

December 1977

Date Published

Work Performed Under Contract EG-77-C-03-1308

**L'Garde, Incorporated
Newport Beach, California**

U. S. DEPARTMENT OF ENERGY
Geothermal Energy

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GEOTHERMAL ELASTOMERIC MATERIALS

TWELVE-MONTHS PROGRESS REPORT
FOR PERIOD 1 OCTOBER 1976 - 30 SEPTEMBER 1977

Published December 1977

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A. R. Hirasuna
G. D. Bilyeu
D. L. Davis
C. A. Stephens
G. R. Veal

L'GARDE, INC.
1555 PLACENTIA AVENUE
NEWPORT BEACH, CALIFORNIA 92663

PREPARED FOR THE
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
DIVISION OF GEOTHERMAL ENERGY
UNDER CONTRACT EG-77-03-1308

FORWARD

The technical information reported herein has been developed by L'Garde, Inc., Newport Beach, California, under the Geothermal Elastomeric Materials (GEM) Program, ERDA Contract EG-77-03-1308.

The work is sponsored by the Utilization Technology Branch, Division of Geothermal Energy. Branch Chief is Mr. John Walker and the Program Manager is Dr. Robert Reeber. Technical coordination assistance is provided by Dr. Patrick Cassidy and Mr. Tom Chester.

The effort is directed for L'Garde by Mr. Alan Hirasuna. The development of this report and the technology advancement achieved under the GEM Program are also attributable to the following personnel: Mssrs. Gayle Bilyeu and Gordon Veal (Mechanical Design), Mr. Clifford Stephens (Rubber Chemistry), Mr. Douglas Hender (Heat Transfer Analysis), Drs. Mitchell Thomas and Norman Sjogren (Test Procedures), and Mssrs. Don Davis, Richard Sedwick, and James Trailer (Fabrication and Evaluation Testing).

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STATEMENT OF OBJECTIVES

The following are objectives to be accomplished under the GEM Program:

1. Define geothermal elastomeric seal application where immediate improvements will provide most benefit to the community.
2. Perform elastomer development and evaluation to meet requirements of 1) (casing packer seal element to survive 260°C (500°F) for 24 hours).
3. Design, fabricate, evaluate, and operate evaluation tests focusing on the pertinent requirements of 1).
4. Evaluate current commercially available elastomers which were developed for oil tool equipment under the geothermal conditions.
5. Perform conceptualization of improvements for a packer system for geothermal applications.

ABSTRACT

This 12-month Progress Report is a comprehensive description of work performed by L'Garde, Inc., on the GEM Program under ERDA Contract EG-77-C-03-1308. The objective of the first phase of the ERDA Elastomers Program is to develop elastomers for packer seal element applications which will survive downhole geothermal well chemistry at 260°C (500°F) for 24 hours.

To achieve this development, a three level elastomer testing and evaluation program was established. The first level Screening Tests, is a broad screening of potential candidates and with the end objective to filter out the more promising candidates for more expensive subsequent testing. The battery of tests include standard ASTM tests and a special test developed by L'Garde to test extrusion resistance using specimens all made from sheet stock. The second level or Simulation Tests provide a laboratory equivalent of downhole conditions using synthetic geothermal fluid. Full scale packer seals are tested under simulated operational conditions by a test fixture developed by L'Garde. The third level or In-Situ Tests which are currently in the planning, provide for testing the most favored materials in-situ in the geothermal well. A test module was designed by L'Garde which provides for testing of the specimen without interfacing with the well casing. A test module freely hanging on a wireline has much lower probability of causing a problem, such as becoming lodged in the well, as compared to an operational casing packer. This maximizes the number of wells (hence geothermal environments) where access can be gained and In-Situ Testing performed.

During this period commercially available polymers were investigated. Most of the work centered around formulating peroxide cured Vitons and some on EPDMs, butyls, and resin cured Vitons. Of the formulations tested to date the EPDMs appear most promising and the peroxide cured Vitons next most promising. However, data is too sparse to make any firm conclusions at this time.

Minor tasks were performed evaluating current commercially available elastomers used in oil tools and conceptualization of casing packer for the geothermal application.

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1.0 INTRODUCTION AND SUMMARY

This 12-month Progress Report is a comprehensive reporting of the technology developed by L'Garde, Inc., under the Geothermal Elastomeric Materials (GEM) Program, Contract Number EG-77-03-1308. The fundamental objective of the program is to develop elastomers for the downhole geothermal seal application. Figure 1 shows the overall flowchart of the Program. The crosshatched box indicates where future candidates will enter the evaluation system.

Seal materials are most commonly made from elastomers because they are the most practical seal material. They are economical, relatively very inexpensive except for a minority made from exotic polymers and are reuseable except for very severe environments. They are very reliable and forgiving with respect to installation and manufacturing tolerances of the mating parts to be sealed. Because of the forgiving nature of elastomeric seals, they can be successfully installed by unskilled mechanics and they can be installed in field environments. On the other hand metal seals are extremely sensitive to contamination and handling. L'Garde's experience with gold plated metal K-seals on the Simulation Test, reported in Section 4.0, indelibly imprinted an appreciation for elastomeric seals. Extreme care is required for the metal seals to clean the sealing surfaces and to apply the correct and evenly distribute the preload. Furthermore, each of the three seal applications required development of special procedures for each unique set of circumstances to assure that the seal is delicately installed without abrasion or bumping. Elastomers have the added advantage of flowing and conforming to irregularities while providing elastomeric resistance to continued flow after seating. On the other hand plastic seals continue to flow after seating and do not achieve the stable equilibrium which is possible with elastomers and must be constantly recinched to maintain the sealing force.

In view of the multitude of benefits provided by elastomeric materials in seal applications, the GEM Program objective fulfills an important need. Development of elastomers to meet geothermal environments will extend their benefits into that regime.

During this contract period the formation or open-hole packer was identified as the device that is currently critical to the development of geothermal energy and where improvements will yield good return. In that the formation packer in geothermal environments represents an extremely difficult engineering problem, this first elastomer development effort has been focused on a less ambitious goal, the casing packer seal application. Rubber development for the casing packer element "kills two birds with one stone", as those materials which work successfully for the packer seal will most probably work well for O-ring seals. The O-ring application is less severe because both surfaces are machined, the clearances are small and the required deformation of the O-ring is small compared to a casing packer seal element.

FIGURE 1 -- PROGRAM FLOWCHART

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The geothermal environment imposes extraordinary requirements on the casing packer seal element. The geothermal temperature and chemistry both substantially reduce the elastomeric seals ability to withstand the significant internal stresses which are generated in the rubber as the seal is compressed endwise to cause it to expand circumferentially and seat against its OD and ID. Because of the severe and complex nature of the materials and structural requirements of the seal, special tests have been designed and developed.

A three-step graduated testing and evaluation of material candidates is used. The first step, "Screening Tests", is a battery of tests performed on specimens made from sheet stock. The tests include standard ASTM tests and a special test developed by L'Garde, the Extrusion Resistometer or Punch Test. It tests the extrusion resistance of the candidate materials, a key property for geothermal packer seals. The purpose of the Screening Tests is to quickly and efficiently filter out the less qualified materials candidates to maximize coverage of potential materials and minimize the amount of more expensive subsequent testing and evaluation.

The second step, "Simulation Tests", is a laboratory equivalent of downhole operational conditions. Under the Screening Tests chemically aged flat samples are run through the battery of tests after they have been chemically aged in the autoclave. In contrast, the Simulation Test uses a full-scale, 4-inch packer seal as the test specimen and simultaneously submits it to the operational chemistry, temperature, pressure, differential pressure, and the seating forces for the required duration of the test. Based on comments from oil tool personnel regarding the post mortem specimens, the fixture is providing a good simulation of the actual packer.

The third step, as currently planned, is to test the most promising candidates from the SIM Test downhole in a geothermal well. At operational depths the specimen will be exposed to the unaltered fluid and no questions exist as to whether the specimen exposure is representative. Any possibilities of fluid modifications which may occur because of temperature or pressure changes or dilution or contamination of the fluid from other strata are eliminated. A testing module was designed which operates much as the laboratory SIM test fixture except down in the geothermal well. The design of the module is such that it is not necessary for interface with the well casing. This enables preservation of the post mortem test data and minimization of the potential for becoming lodged in the well. Minimization of the risk to the well will result in wider access to test wells and, hence, a wider variety of test chemistries. In addition, the module uses a wire-line hoist as opposed to the more complex and expensive tubing string.

The elastomer formulation effort was concentrated on the peroxide cured Viton family during this contract period as candidates to improve geothermal packer seals. Because the peroxide cured Viton results were not overwhelmingly promising some effort was also spent investigating EPDM, butyl, and resin cured Vitons. The SIM tests revealed that an important contributor to the failure of the packer seal is the substantial internal stresses which are generated within the seal as it is seated. A critical balance is required to be struck between modulus, ultimate elongation, and ultimate tensile strength of the material to

allow it to be deformed while seating yet to be stiff and strong enough to bridge gaps. Striking this balance becomes increasingly difficult if not impossible as the temperature increases.

The following is prefaced with the fact that insufficient data exists to make firm conclusions and any conclusions are preliminary and tentative. At this point it appears that EPDM holds the most promise of the elastomers developed and tested thus far. Viton also holds promise, but is more extensively degraded by the synthetic geothermal fluid. Both are recommended for further development. Table I shows the typical effect of chemically ageing EPDM, Viton, and Kalrez in synthetic geothermal fluid for 24 hours at 260°C. The data reflects work reported in Section 3.2. The testing and evaluation has also resulted in a unique concept of "curing the seal in place" to preclude the stressing of the seal as it is seated. Future effort is recommended to test the feasibility and practicality of this concept.

A minor task under the GEM Program was evaluation of the current commercially available elastomers in the SIM Test to provide a reference for the ERDA developed elastomers. Five materials were received from five different companies. The elastomers included two Nitriles, one EPDM, one Epichlorohydrin, and one Viton.

Separate from the elastomer development, another minor task was performed. L'Garde developed a conceptual design of a casing packer improved to provide better potential in the geothermal environment. The design serves as a model providing guidance for development of current elastomers which may have potential, and new polymers synthesized under the sister efforts being performed by Jet Propulsion Laboratory and Hughes Aircraft Company. An adapter for the SIM Test is planned which will test O-ring specimens, rather than packer seal specimens. This will offer a practical alternative for the very expensive elastomers.

TABLE I -- EFFECT OF CHEMICAL AGEING IN SYNTHETIC GEOTHERMAL FLUID

ELASTOMER	APPEARANCE	ULTIMATE TENSILE @ RT	ULTIMATE ELONGATION @ RT	EXTRUSION RESISTANCE @ 260C	SHORE A @ 260C
EPDM (E263)	FAIR	75%*	N/A	57%	85%
Viton (201)	POOR	48%	73%	77%	80%
Kalrez (3073)**	GOOD	53%	230%	94%	84%

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* Exceeds capability of tester, 840% elongation, maximum tensile stress recorded.

** No development of Kalrez for this specific application was performed; cured test sheets were obtained directly from du Pont to get "a data point".

2.0 PROBLEM AND APPROACH DEFINITION

Section 2.0 describes the process whereby the specific objectives for the GEM Program performed by L'Garde, Inc., were defined.

2.1 FORMULATION OF SPECIFIC OBJECTIVES

The initial task defined specific program objectives within the overall goal to develop improved elastomers for high temperature geothermal seals. Visits were arranged with geothermal energy producers and well owners, well tool and drilling equipment manufacturers, and Government laboratories performing related research and development. The purpose was to become familiar with problems being encountered through briefings such that L'Garde's program could be defined to best fill the needs of the geothermal community, i.e. applied R&D as opposed to pure R&D. More specifically, L'Garde's purpose was to identify that seal application which would benefit the geothermal community most if it were improved first.

The conclusion after digesting voluminous and often obscure and elusive data was that the community is in need of a formation packer. For example, formation packers are needed to evaluate specific strata in a well for identification of low quality cool zones or highly corrosive zones. This conclusion was confirmed by Mr. J. Barnea's office at the UN and Mr. J. Rowley's office at LASL. Copies of communications with them are included in Appendix A and B. However, though high temperature formation packers are needed, development of elastomers for this application was judged too ambitious a goal for the first effort. Therefore, it was recommended and approved to first develop improved elastomers for casing packer elements.

2.2 DOWNHOLE WELL CONDITIONS

High temperature downhole seals tend to fail from extrusion and hardening. The more interesting geothermal wells have temperatures of 260°C (500°F) and higher and it is not unusual to have compositions of the fluid which are unusually reactive to elastomeric compounds.

260°C causes most rubber compounds to harden by thermal breaking of double bonds and forming new crosslinks to form a three dimensional matrix with less and less ability to yield and recover when deformed. This action proceeds quite rapidly in air (oxygen). In water or steam at high temperatures the hot water acts as an active swelling and softening agent, sufficient to break crosslinkages causing most cured elastomers to devulcanize or revert and to become soft and weak. The geothermal well fluid often contains sulfur in the form of hydrogen sulfide. At high temperatures sulfur rapidly breaks double bonds and forms crosslinks until the rubber becomes hard and brittle.

The fluid also can contain considerable concentrations of metallic salts completely ionized. The effects of such salts on elastomeric compounds is not known.

2.3 EARLY CONSIDERATIONS OF ELASTOMERS

The development and evaluation of elastomers for this first period was confined to commercially available elastomers, reinforcing fillers and curing systems. The most common and lowest cost elastomers are the butadiene copolymers. These elastomers are copolymers of butadiene and styrene or butadiene and acrylonitrile (the latter is used in nearly all oil well seals because of its resistance to degradation by crude oil). These polymers have unsaturated backbone structure - $C = C - C - C = C$ - etc., the double bond being used to get fast curing with sulfur. Unfortunately only a few of the double bonds are used to form the sulfur crosslinkages; consequently sulfur in the geothermal fluid continues to break those remaining double bonds to form more sulfur crosslinks until the seal compound becomes very hard and weak, crumbling or cracking during use.

A logical step would be to consider elastomers free of excess double bonds in the backbone. There are a considerable number of these as discussed below.

Butyl rubber is a copolymer of isobutylene and small amounts of isoprene to give an elastomer with most of the backbone as single bonds. It has a long history of use for the curing bags where it is exposed to water at 177°C (350°F); however, it softens severely at 260°C and is slowly devulcanized by the hot water.

Epichlorohydrin polymers (chlorinated epoxy propane) have the required saturated backbone. The high concentration of pendent chlorine groups makes it very resistant to solvents and fuels. There was no information about resistance to high temperature brine. A commercial formulation was selected for evaluation although softening at 260°C and extrusion failure was expected.

The polyacrylics (copolymers of ethyl acrylate and chlorovinyl ethyl ether or butyl acrylate and acrylonitrile) have the desired saturated backbone and are highly resistant to heat oxidation; however, neither are resistant to water or steam at high temperature.

The chloroprene elastomers have good oxidation resistance, but poor water resistance.

Ethylene propylene diene terpolymers are similar to the butyl rubbers in properties. They have the desired saturated backbone with a few double bonds to facilitate curing. They are widely used in tire curing bags where resistances to water at 350°F is required. It was selected for limited evaluation.

Silicone elastomers have the best high temperature oxidation resistance and maintain their physical properties better at 260°C than any of the elastomers.

The backbone is -Si-O-Si-O- which is thermally stable. No applicable information about resistance to sulfur or water or high temperatures was found. However, small amounts of oil cause severe degradation. Fluoro-silicone elastomers are similar to the silicones except they have been fluorinated to give the compounds some resistance to oils. According to Dow Corning, applicability of silicone rubber to the GEM environment is uncertain, therefore, simple Screening Tests to determine the hydrolytic and sulfur resistance are recommended.

The fluoroelastomers (Vitons, Fluorels) are fluorinated hydrocarbons with completely saturated -C-C- backbone to give the best resistance to heat, oxidation and attack by sulfur. Peroxide cured Vitons were selected for compounding, evaluation of cure systems and reinforcing fillers principally because there was a considerable amount of data reported in the literature indicating good prospects in steam and fluids environments and, the Air Force Materials Laboratory has been experiencing success with them at 260°C for high performance aircraft hydraulic cylinder applications.

As a result of this task, it was determined that the elastomer development would be designed around the casing packer seal element operating at 260°C. Furthermore, it was determined that the base elastomer to be developed for this application was the then newly introduced peroxide cured family of Viton fluoroelastomers.

3.0 SCREENING TESTS

The Screening Tests are the first level evaluation of potential elastomer candidates for the geothermal seal application. A battery of simple tests using specimens cut from sheet stock are used for evaluation. The Screening Tests are designed to cover a lot of ground at the expense of preciseness of the simulation of all the operational conditions and thereby provide a bulk filter thus quickly eliminating the poorer performers prior to going into the more expensive subsequent testing.

Prior to initiation of the SIM Tests reported in Section 4.0 an abbreviated set of Screening Tests were run to generate data for refinement of the formulations as well as to investigate candidates other than peroxide cured Vitons which were previously being investigated exclusively. This work is reported in Section 3.2.

3.1 SCREENING TESTS

Thirty-five Viton formulations have been mixed and screened. The Screening Tests include the L'Garde Extrusion Resistometer or Punch, compression set, Shore A hardness, ultimate tensile strength, and ultimate elongation tests. The tests were performed on virgin material, material chem aged in synthetic geothermal fluid, and material aged in the ambient room, as a control for the chem aged material.

Based on the results of the Screening Tests, the following fillers were selected for continued development in the Simulation testing portion of the Program: 30 phr Austin Black, 30 phr HTS graphite, 5 phr Kevlar 29, and 20 phr Asbestine 3X. Other indicated improvements are use of VT-R-4590 as the base elastomer, increased level of Litharge, possible decreased amount of Diak #7, and post cure at 500°F and limit oxygen in the post cure environment.

3.1.1 Screening Test Approach

The basic development testing approach taken by L'Garde regarding programs such as GEM where high performance elastomers are involved, is to test critical performance parameters throughout the various phases of testing along with standard ASTM tests. Generally, only standard ASTM tests are used such as tensile and elongation at break, modulus at 100% Shore A hardness, tear strength, compression set, etc. For high performance applications where ultimate capability of the elastomer is required, the standard tests provide a good relative "feel" as to the progress or lack of progress being made from formulation to formulation, however, invariably the standard test results are usually not well correlated with performance in the application. Hence, to evaluate true development progress special tests are preferred.

For the 260°C (500°F) packer seal application, it was established that the most probable critical failure mode is extrusion of the seal past its back-up, i.e. for rubber which remains elastomeric. For the nitriles which harden at 260°C, and become very nonelastomeric, extrusion is not the primary problem. Hardening can provide somewhat of a temporary advantage by preventing further extrusion, however, because the rubber has lost all its resilience it can no longer withstand jarring disturbances. For materials of interest which provide the elastomeric qualities throughout the performance period a special Punch Test was designed and fabricated to test extrusion resistance at 260°C. Each of the Screening Tests is described and discussed in detail below.

The Screening Tests are designed around specimens made from sheet stock using the standard ASTM sheet mold and 1/2 inch sheet. Extrusion Resistometer, swell test, tensile/elongation dogbone specimens are cut from standard ASTM test sheets which are 6 inch x .6 inch x approximately 80 mils. The compression set and Shore A hardness specimens are cut from 3.5 inch x 3.5 inch x approximately 500 mil sheet. The specimen dimensions are shown in Table II. The use of specimens cut from sheet stock enable the tests to be relatively inexpensive, allowing screening of a maximum number of candidates. Figure 2 shows the specimens set up for an autoclave run.

All materials are tested in two states while every tenth formulation is tested in three states. The tests are run for all formulations in the virgin state within a few days of completion of post cure, and in the chemical aged state after 24 hours of ageing in a synthetic geothermal fluid at 260°C. The constituency of the geothermal fluid is as follows:

H ₂ S	300 ppm
CO ₂	1000
NaCl	25,000
H ₂ O	Balance
pH (ending)	5 - 7

On every tenth formulation, tests are performed on material which has resided in the ambient room for the same amount of time after post cure as the chem aged specimens when they are tested. This is a control to separate out the positive or negative effects that have occurred because of the elapsed time as opposed to the chemical ageing.

3.1.2 Formulation Matrix

The screening is structured around a filler study based on the following nominal formulation:

Viton GH	100 phr
MT Black, N908	50-X
Filler Candidate	X
Sublimed Litharge	3
Diak #7	4
Luperco 130 XL	1.5

TABLE II -- SCREENING TEST SPECIMEN CONFIGURATIONS

Test	Sheet Thickness Mils	Specimen Dimensions Inches
Punch	80	0.75 dia.
Ultimate tensile	80	1.31 L x .25W x .08T test section
Ultimate elongation	80	same as tensile
Swell	80	2L x 1W x .08T
Compression set	500	OD x ID x .50T cut in half
Shore A hardness	500	remains after compression set extracted

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FIGURE 2 -- SPECIMENS PREPARED FOR AUTOCLAVE
CHEMICAL AGEING

75 mil Dogbone and Rectangular Specimens, and 500 mil Compression Set and Hardness Specimens

75 mil Dogbone and Rectangular Specimens

Viton GH was used for most formulations because it is stocked on the west coast. The 50 phr level of filler is based on evaluation of formulations with 30, 40, and 50 phr of MT black evaluated on the Extrusion Resistometer. The data showed a monotonic improvement with 50 phr performing the best so all the screening tests were performed at the 50 phr level. It was expected that the optimum filler level is beyond the 50 phr level and a point that was investigated during the Simulation Test period. Litharge is used as the acid acceptor because it is reported to produce better properties in the water/steam environment than the other metal oxides and hydroxides.

The filler candidates investigated are shown in Table III.

In addition to the filler options, the sensitivity to base elastomer was investigated. Both VT-R-4590 and Viton GLT were considered in addition to Viton GH. Sensitivity to the amounts of Litharge and Diak #7 were also investigated.

The nominal cure is a press cure at 177°C (350°F) for 10 minutes. Post cure was 24 hours at 233°C (450°F) in an air oven. Other post cures were a 260°C (500°F) and a 288°C (550°F) post cure for 14 hours with the rubber sealed in aluminum foil to limit oxygen exposure. Various temperature schedules were also investigated in bringing the temperature up to the post cure level.

3.1.3 Test Fixtures and Measurements

All measurements taken during the Screening Tests are discussed. Except for the L'Garde Extrusion Resistometer all measurements are standard ASTM tests and for those only points unique to the GEM measurements are discussed. A summary of the measurements taken for each formulation are shown in Table IV.

A. L'Garde Extrusion Resistometer

The Extrusion Resistometer was designed to provide a measure of the elastomers extrusion resistance. Conceptually it is similar to a paper hole punch with the punching resistance depending on the resilience, hardness, and shear strength of the test material. Figure 3 shows a cross section of the test fixture. The 3/4 inch disk specimen is pinched between the bottom cup which holds the band heater and the neck support which houses the punch. The upper piston/cylinder is thermally isolated from the lower test section and provides the punching force when gas pressure is applied to the piston.

The overall test setup is shown in Figure 4. After assembly, the entire fixture is surrounded with insulation and placed into the vacuum chamber shown. The test section is brought up to the 260°C test temperature and held at constant temperature for 14 minutes before testing. The nitrogen supply for the force cylinder is maintained at a constant supply pressure of 50 psig and supplied through a fixed orifice. This assures that consistent repeatable pressure (force) build up transient results for each run. The pressure is recorded and the maximum magnitude taken as the figure of merit for extrusion resistance.

TABLE III -- FILLER CANDIDATES

Product	Description	Producer
Austin Black	Bituminous Coal Fines	Slab Fork Coal Company
Fibrene C-400	Acicular Platy Talc	Cyprus Industrial Minerals Co.
Carbon Wool 3A, 4A	Amorphous Carbon Fibers	Barnebey Cheney
HTS Graphite, 1 mm	Intermediate Modulus Graphite Fibers, PAN precursor	Hercules, Inc.
Kevlar 29, Chopped ¼ in.	Filaments coated with Resourcinal Formaldehyde Latex System	du Pont
MgO Microfibers, 6-8 microns	Material being developed for Air Force	Versar, Inc.
Cotton Flock, S/60	Natural	Microfibre, Inc.
Nylon Flock, S/16	Natural	Microfibre, Inc.
Asbestine 3X	Fibrous Acicular Magnesium Silicate	C. P. Hall

TABLE IV -- SPECIMEN MATRIX FOR EACH SCREENING TEST FORMULATION

TEST	(1) SHEET	VIRGIN	CHEM AGED (CHEM EFFECTS TEST)	AMBIENT AGED	TOTAL
Punch Test	1	1	1	,1	2,1
3/4" Disk	2 3	1	1	,1	2,1
Swell (D471)	1		1		1
1" x 2" x .080"	2		1		1
	3		1		1
Dog Bones	1	1	1	,1	2,1
Die C	2	1	1	,1	2,1
	3	1	1	,1	2,1
Compr. Set	$\frac{1}{2}$ "	3	3	,3	6,3
Hardness	$\frac{1}{2}$ "	1	1	1	2,1

(1) For each formulation made 3-80 mil sheets, 1-500 mil sheet.

FIGURE 13-- EXTRUSION RESISTOMETER

PUNCH TEST FIXTURE

FIGURE 4 -- L'GARDE EXTRUSION RESISTOMETER SETUP

Prior to initiating the testing program for the GEM materials, an evaluation of the Extrusion Resistometer was made. Three Viton formulations with 30, 40, and 50 phr of filler were tested. Eight specimens cut from 4 different cured sheets of each formulation for a total of 24 tests were run. The specimens were run in random order.

The results of the evaluation indicate that the test is quite repeatable and differentiates well between the formulations. The coefficient of variation (standard deviation divided by the mean value) is 5.19% or in other words greater than 65% of an infinite number of measurements will fall within $\pm 5.19\%$ of the mean value. A good test will have a coefficient of variation of about 10% or less. Also from these data, two redundant measurements of each formulation will provide a 95% confidence that their means falls within about $\pm 10\%$ of the true mean. Regression analysis indicated no correlation between the results and the thickness of the sheets from which the specimens were cut. A two step failure occurs when the specimen is punched. First, the rubber is bulged into the punching hole and the outer laminates are popped off through a tensile failure. Then the punch shears out the remaining portion of the plug. It is not clear whether the maximum punch force occurs during the tensile failure or the shearing phase. In any event, because of the complex nature of the failure the resistive force is not correlated with specimen thickness. In fact, the values of the ultimate shear stress which normalizes out the thickness were calculated and they resulted in a worse coefficient of variation, 8.95%, than when the thickness was ignored.

The figure of merit value used is the number of divisions taken directly from the chart recorder. Twenty-five (25) divisions corresponds to a 29.2 lb. force exerted on the rubber by the 3/16" diameter punch.

B. Volume Swell

Swell on specimens which were chem aged were measured in accordance with ASTM D471. 1 x 2 x .080 inch specimens were used.

C. Ultimate Tensile Strength and Elongation

Dogbones were cut from .080 inch sheets with Die C and measurements made in accordance with ASTM D412. Measurements of rubber in all three states were made; virgin, chem aged, ambient aged. Elongation was calculated based on jaw travel. Tests were made indicating insignificant slippage of the specimen at the jaws was occurring.

D. Compression Set

Measurements were made in accordance with ASTM D1414 and D395 Method B except the chem aged specimens are not removed from the fixture for cooling. The specimens are the shape of a washer cut in half with a 1.13 inch OD x 0.39 inch ID x 0.5 inch thick. The specimens were nominally compressed 25% and measured in all three states. For the chem aged specimens, the fixture was placed into the autoclave and for the virgin and ambient aged specimens they were set in the ambient room for 24 hours.

The compression set tests of chem aged material have since been rejected as not meaningful. Because of practical constraints the autoclave and specimens must be cooled before the autoclave can be opened and the specimens removed from the fixture. Hence, the specimens cannot be cooled in an unrestricted state, i.e. removed from the fixture, as per the ASTM specification.

E. Hot Hardness

Shore A Durometer measurements were made in accordance with ASTM D2240. The specimens used were the remains of the 3.5 inch x 3.5 inch x 0.5 inch block after three 1.13 inch plugs were removed for compression set. All specimens were prepared by preheating to 260°C on a preheated 0.5 inch aluminum plate. The 260°C plate and rubber are placed in the durometer fixture on an insulated surface; two measurements are taken, the specimen is flipped, two more measurements are taken, the specimen is flipped again, and then one last measurement. Hardness measurements were also made on all three states; virgin, chem aged, and ambient aged.

F. Autoclave

A mild steel autoclave, shown in Figure 5, was made from 600 lb. pipe fittings for use in chem ageing the material. It was thought that because of the near neutral pH of the synthetic geothermal fluid that the reaction between the H₂S and iron would be acceptably slow. However, after the first run it was apparent that the H₂S was fully reacting with the iron as there was no hint of H₂S odor. Qualitative analysis confirmed this. In the interest of schedule, it was agreed with ERDA to go ahead, as is, with the Screening Tests but to make sure that this does not happen in the subsequent Simulation Tests. Thus the formulations which graduate to the Simulation Tests will see the H₂S environment during the entire test cycle.

The autoclave has eight electric band heaters supplying about 9200 watts to assist heat-up of the vessel which is placed in a 260°C oven. About 3 hours are spent bringing the vessel up to 260°C and about 1.5 hours to bring it down to about 66°C. The heating is maintained for 22 hours from the time the vessel achieves 205°C.

3.1.4 Discussion of Results

Table V is a summary of the averaged measurements taken during the Screening tests. The Extrusion Resistometer data is considered to be the most pertinent with the other measurements providing reinforcing supplementary information. Shown in the left hand column are the variables investigated. All except for the last five were filler studies at differing levels. The bottom five include sensitivity to the base elastomers, levels of the acid acceptor Litharge, level of the coagent Diak #7, and a control which is the same as the Fibrene C400 in the previous filler study. This same 30 phr Fibrene C400 formulation was the nominal one which was perturbed with the VT-R-4590, Viton GLT, 15 phr Litharge, and 2 phr Diak #7. In addition, the post cure on the bottom five was 288°C for 14 hours and rubber was tightly sealed in aluminum foil with pleats to allow for any gas expansion. The aluminum foil was used to minimize the oxygen in contact with the rubber.

FIGURE 5 -- SCREENING TEST AUTOCLAVE

TABLE V -- AVERAGED SCREENING TEST RESULTS

Filler/Variable	phr	Clave Run	Comment	Punch, Divisions			Shore A Hardness			Elong. @ Brk, %			Tensile @ Blk, psi			Comp. Set,			VOL Swell % CA
				V	CA	AA	V	CA	AA	V	CA	AA	V	CA	AA	V	CA	AA	
Austin Black	10	1	Leak	30.8	24.7		75.4	71.2		209	173		1739	802		15	90		- .9
	20	↓	"	28.3	25.3		77.6	68.0		189	152		1570	799		16	91		3.1
	30	↓	"	30.0	28.5		77.6	69.6		202	148		1703	854		14	93		4.7
Fibrene C400	10	↓	Leak	27.8	23.2		77.4	71.6		270	81		1866	399		15	103		7.5
	20	2	Very Brittle, CA	26.8	19.8		76.4	71.0		285	---		1829	---		14	120		- .9
	30	↓	" " "	29.3	22.5		76.8	77.8		265	---		1693	---		14	127		- .7
Carbon Wool, 3A 4A	10	↓		27.5	19.8	35.0	78.8	48.6	78.2	188	41	190	1742	201	1734	13	104	3	4.9
	20	↓		25.5	19.3		77.6	48.2		169	25		1827	164		10	100		2.1
	30	6	Disk Rupture	27.3	15.8		77.8	56.6		151	72		1930	363		12	---		13.3
	10	6	" "	27.3	15.0		78.0	59.2		192	86		1542	243		16	---		10.9
HTS Graphite	10	7	Disk Rupture	30.5	14.5		80.0	57.8		162	74		1699	244		15	---		8.9
	20	7	" "	29.5	15.5		81.2	55.4		114	89		1925	391		13	---		9.0
	30	4	" "	33.0	14.0		81.6	56.3		129	99		2377	464		15	99		2.9
Kevlar 29	3	↓		30.5	13.0		83.0	66.4		199	92		1936	409		27	119		- .3
	5	↓		33.0	18.0		85.8	74.6		129	64		1971	493		28	127		-1.2
	7	↓		33.5	17.0		86.8	76.6		82	41		2201	604		27	134		1.1
MgO Microfibers	10	↓		26.8	15.3	24.0	75.8	54.6	73.8	267	139	235	1581	290	1605	21	100	3.4	- .4
	20	↓		25.3	15.5		74.0	53.4		277	126		1441	326		20	104		-1.1
	35.3	6		22.3	13.0		72.2	56.8		305	91		1354	381		22	110		1.2
Cotton Flock	10	↓	Very Brittle, CA	27.2	27.7		82.4	92.6		115	20		1370	602		27	127		-5.3
	20	↓	" " "	27.8	37.3		83.4	---		74	13		1675	576		29	139		-12.0
Nylon Flock	10	↓		31.0	15.0		79.6	68.4		207	67		1781	413		20	107		-1.7
	20	7		28.0	17.8		80.2	69.2		167	81		1600	568		21	127		0
Asbestine 3X	10	↓		34.0	13.5		77.4	66.2		269	147		1827	478		18	100		-1.4
	20	↓		33.0	16.1		75.8	77.6		224	104		1599	458		16	119		-1.9
	30	↓		26.0	15.3		75.4	85.0		265	77		1855	531		26	129		.7
VT-R-4590	N/A	5	550°F Post Cure	24.3	19.5	22.0	75.2	75.0	74.4	181	85	164	2013	566	1934	3	123	8	1.2
Viton GLT	N/A	↓	" " "	20.5	13.8		70.4	55.8		361	187		2032	433		10	125		-5.9
Litharge	15	↓	" " "	24.8	26.0		79.6	84.2		185	46		1708	627		16	129		- .2
Diak #7	2	↓	" " "	22.3	15.3		70.4	70.6		297	158		1434	452		11	115		-2.2
Fibrene C400	30	↓	" " "	22.5	16.3		74.4	78.2		270	99		1577	413		10	135		-3.7

Anomalies occurred on two autoclave runs. We experienced a gasket leak on the Austin Black/Fibrene C400 run as noted. When the autoclave was opened at the end of the run there was only about 2 inches of liquid left in the bottom. On the Carbon Wool/HTS Graphite run, the burst disk ruptured during the heat-up cycle. The compression set specimens disintegrated so measurements could not be made. The balance of the specimens were subsequently chem aged, hence, have seen two heat-ups and one rapid depressurization.

In general, the synthetic geothermal fluid does significantly affect the rubber. The Austin Black formulations were least affected, however, its data is clouded by the fact that there was a gasket leak and the fluid level was down to about 2 inches when the vessel was opened. Looking at the virgin Extrusion Resistometer data for the Austin Black shows that the values are virtually independent of level of Austin Black, implying that its properties as a filler are equal to that of MT black. The chem aged results indicate improvements with increasing amounts of Austin Black. This result is consistent with the experience of du Pont and the Air Force.

The Fibrene C400 and the cotton flock specimens became unacceptably brittle after chem ageing. It was difficult, if possible, to straighten the dogbones sufficiently to mount them in the tester jaws without breaking them. The carbon wool and HTS Graphite specimens which survived the rapid decrease in pressure when the burst disk ruptured have a lumpy blistered surface. This also correlates with the higher values of swell for these specimens. A question has arisen regarding the manner in which the specimens are prepared for chem ageing. They are all cut from the sheet stock exposing fiber ends and then chem aged, thus promoting wicking of the fluid. The operational situation involves molded parts whereby all surfaces would tend to be sealed by the elastomer. This uncertainty will not enter into the subsequent Simulation Tests as the specimen will be a molded part.

The last five sets of measurements provided a wealth of information. As a set they were post cured differently, 14 hours at 288°C and sealed in aluminum rather than 24 hours at 233°C in air. The Fibrene C400 formulation is the same as the previous 30 phr formulation and was used for control purposes.

Comparing the control cases, it is apparent the 288°C temperature and/or the aluminum wrap was a definite benefit. A 99% elongation at break resulted as compared to a specimen that was too brittle to handle. The Punch Test results are down by about 25% which indicates a trade-off exists between sacrificing extrusion resistance for elastomeric properties.

Then comparing the other 4 cases to the control case several other important points became apparent. The VT-R-4590 is clearly a better base elastomer for the GEM application than is Viton GLT or GH. The Punch Test results, virgin and chem aged, are better while the other properties are maintained in an acceptable range. Additional Litharge, 14 phr vs 3, shows good Punch Test results especially for the chem aged state. However, the elongation at break is low indicating a trade-off to determine the optimum level. The lower level of Diak #7, 2 phr vs 4, resulted in improved elongation at break.

3.2 ABBREVIATED SCREENING TESTS

Abbreviated Screening Tests were run prior to starting into the Simulation Tests to determine optimum filler and litharge levels, optimum post cure conditions, and to evaluate Kalrez, EPDM, butyl, and resin cured Viton elastomers. The Kalrez was originally requested as a commercially available material for the evaluation described in Section 4.5.1, SIM testing. However, because of the expense of the material and the uncertainty as to whether the thick packer type seal could be made from Kalrez, it was not practical to consider evaluating it along with other currently commercially available elastomers at this time. In lieu of the above, Kalrez sheet samples were obtained from du Pont and chemically aged in these abbreviated tests to obtain "some" data. Subsequent to the Screening Tests reported in Section 3.1, the Viton development was not showing any overwhelmingly positive results, so EPDM's, butyl and the resin cured Viton compounds from the Air Force Materials Laboratory were also included in these tests to provide possible backups to the peroxide cured Vitons.

Table VI shows the test data which include Extrusion Resistometer Measurements, Shore A hardness, elongation at break, tensile strength at break, swell measurements, and weight measurements for virgin and chemically aged conditions. Three die C dogbones and two 1" x 2" specimens cut from Standard ASTM sheets were chem aged. The hardness and swell measurements were taken on the rectangular ends of the dogbones and the weight measurement on the entire dogbone. The Extrusion test specimens were cut from the rectangles. Table VII gives the formulations for the inhouse compounds.

In terms of physical appearance after the chem ageing the Kalrez, compounds 3073 and 3074 looked the best. They had smooth surfaces and by outward appearance were not significantly degraded by the chem ageing. The EPDM compounds were next best, E261 through E263. They showed some crazing which was apparent when the dogbones were stretched. The butyl B264, severely reverted and was very sticky and soft. The resin cured Viton, V265, became quite brittle and lost its properties. The L'Garde Vitons showed signs of ageing and the crazing was apparent in the relaxed position.

The EPDM's show good potential for the packer seal application. All three formulations had greater than 840% elongation before and after chem ageing. The Extrusion test, hardness, and tensile strength at maximum elongation fell off as a result of chem ageing and E262 which has Tetrone A blistered on the surface. E263 was selected for further development in the SIM test phase because it was least sensitive to chem ageing showing a relatively small reduction.

The Viton formulations 201 to 203 were tested to determine an optimum nominal level of filler. The differences were not substantial in the 50-70 phr of Austin Black, however, later work with the SIM tests showed these levels to be too high. They resulted in cracking of the SIM test seal because the rubber was not sufficiently pliable to be seated. These tests did confirm the antioxidant effect of the Austin Black. As previously experienced in the earlier screening tests but uncertain because of autoclave gasket leaks, the Austin

TABLE VI-- ABBREVIATED SCREENING TEST RESULTS

Filler/Variable	phr	Comment	Extrusion psia, 260°C		Shore A, 260°C		Elong A Brk%		Tensile @ Brk psi		Swell %		Weight Change
			V	CA	V	CA	V	CA	V	CA	Width	Tkness	
3073 K/Calidria			8.8	8.3	92	77	100	230	4377	2337	1.9	4.8	3.4
3074 K/Kev.			8.5	6.2	91	74	49	208	3619	1831	3.5	11.1	8.6
E261		Blistered	7.2	5.5	66	43	>840	>840	>2167	>1080	-.7	0	-2.1
E262 w/Tet.A			12.1	5.2	65	41	>840	>840	>2758	>720	-.1	0	.5
E263 w/o Tet.A			9.6	5.5	61	52	>840	>840	>1363	>1020	-.6	0	-1.1
B264		Reverted	4.3	1.1	72	5	528	153	1414	45	2	5.3	7.3
V265		Hardened	6.9	2.5	77	70	340	19	1559	189	-.1	-4.5	12.9
201 4590/Austin	50	No Fibrous Fillers	7.8	6.0	89	71	165	121	1884	901	1.0	1.0	-.2
202 4590/Austin	60	No Fibrous Fillers	8.3	6.5	91	74	122	96	2000	866	.8	1.4	-.1
203 4590/Austin	70	No Fibrous Fillers	8.8	9.1	94	72	105	79	1912	946	1.0	3.8	-.05
205 GH/C400/Lith	10		7.9	7.0	84	79	199	38	1495	500	.8	2.1	-5.7
206 GH/C400/Lith	7		7.4	7.1	84	77	237	49	1631	456	.7	-1.7	-5.1
207 4590/C400/Lith		14H,N ₂ , 233C(450F)	8.9	5.7	88	68	205	122	1959	563	.6	1.7	-2.5
208 4590/C400/Lith		14H,N ₂ , 260C(500F)	9.6	6.8	86	70	206	116	1990	595	.3	1.8	-2.2
209 4590/C400/Lith		14H,N ₂ , 288C(550F)	9.1	7.5	87	72	186	118	2000	681	.9	.3	-2.2
211 4590/C400/Maglite	6	14H,N ₂ , 260C(500F)	9.7	10.2	88	76	163	86	2240	734	.9	5.9	1.0

TABLE VII -- ABBREVIATED SCREENING TEST FORMULATIONS

Component	201	202	203	205	206	207	208	209	211
VT-R-4590	100	100	100			100	100	100	100
Viton GH				100	100				
Austin Black	50	60	70						
MT Black				20	20	20	20	20	20
Fibrene C400				30	30	30	30	30	30
Maglite D									6
Litharge	3	3	3	10	7	3	3	3	3
Diak #7	4	4	4	4	4	4	4	4	4
Luperco 130XL	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Cure °F/Min.	350/10	350/10	350/10	350/10	350/10	350/10	350/10	350/10	350/10
Postcure °F/hrs.	450/24	450/24	450/24	550/14	550/14	450/14	500/14	550/14	500/14
Atmosphere	air	air	air	Al Foil	Al Foil	N ₂	N ₂	N ₂	N ₂

Black tends to decrease the loss in tensile strength from chem ageing from a factor of 3 to 4 down to a factor of 2. This effect has been observed by both du Pont and the Air Force and du Pont is currently trying to identify the beneficial constituent in the Austin Black. The constituency is not well defined because it is a natural product made of bituminous coal fines. The level of litharge was investigated and compared to earlier results as it appeared to help maintain the Extrusion test results through chem ageing. However, the loss in elongation was severe, down to the 7 phr level so the original 3 phr level was maintained. Compounds 207 through 209 are the same formulations but post cured from 450 to 550°F for 14 hours in a nitrogen atmosphere. A trend does exist as a function of the post cure temperature, but the differences were not deemed significant. Comparing 211 containing Maglite D and 208 containing litharge shows 211 to maintain its level on the Extrusion Test, however, the associated loss of elongation is considered a significant negative and therefore not viable alternative for increasing the extrusion resistance.

The figure-of-merit for the Extrusion Resistometer or Punch Test has been changed starting with this set of data. Previously the number of divisions on the recorder were taken as the figure-of-merit as regression analysis of the fixture evaluation data revealed this to be a more repeatable technique than to calculate and use shear strength. However, a problem evolved when a new pressure transducer was used. Having different calibrations, 10 units on the recorder implied different punch forces or piston pressures depending on which transducer was used. Consequently, the implied absolute pressure is now being used as the figure-of-merit which eliminates the problem of differing calibrations and transfer functions.

In summary, based on these abbreviated tests it appears that the Kalrez is relatively unaffected by the synthetic fluid. Compound 3073 with Calidria, a pure asbestos, appears more stable of the two with about a factor of 2 increase in elongation and decrease in tensile strength after chem ageing. The EPDM compounds maintained their elastomeric properties well through the chem ageing, however, some crazing was apparent when the dogbone was stretched. Compound E263 was selected for further development as it was least sensitive to the synthetic fluid. The Austin Black was confirmed to have a definite antioxidant effect rendering the Viton to be more stable in chem ageing. The other variables examined in these tests did not produce any significant interest or promise.

4.0 SIMULATION TESTS

The Simulation (SIM) Tests are designed to provide a good simulation of the casing packer seal operational environment in the laboratory. The SIM Test fixture applies all environments simultaneously, i.e. the fluid pressure, differential pressure, temperature, mechanical forces, and the chemistry to a full scale packer type seal. The fraction of the compounds which survive the SIM Test evaluation are presently planned to be tested in-situ in an actual geothermal well.

4.1 SIMULATION TEST FIXTURE DESCRIPTION

The SIM test fixture seats and tests a full scale packer type seal as shown in Figure 6. The seal is a solid rubber cylinder with 45° chamfers on each end and typical of elements which seat against a 4.0 inch ID casing. Figure 7 shows a piping and instrument diagram of the overall test system and Figure 8 is a photograph composite. The test chamber houses the seal specimen which is mounted over a center mandrel. Rings back-up either side of the seal and a ram driven by a hydraulic cylinder pushing on the top back-up ring deforms the seal such that it seats against the ID of the vessel and the center mandrel. The chamber is electrically heated and insulated to maintain the fixture at the desired test temperature. A true power proportioning controller is used as opposed to the more common on-off controller where the period of the on-off cycle is adjusted proportionally to the error. Thus under steady state conditions a constant current of about 4 amps or about 900 watts is provided to make up the heat loss. This provides a constant temperature environment for the seal. The fluid exiting the chamber goes through an ice bath heat exchanger and into a Monel accumulator. A 316SS piston cylinder positive displacement pump stores pressurized fluid at room temperature which enters the test chamber and replaces the fluid as it leaks by the seal and into the accumulator. The pump is driven by a nitrogen cylinder which applies a constant force to the pump. A linear potentiometer senses the position of the pump and its signal is recorded, thus total leakage and leak rate can be determined within 5-10 cc. The sequence of events for the test is as follows:

1. Assemble fixture and fill pump, test chamber, and bottom of accumulator with room temperature fluid.
2. Pressurize system to 875 psig to maintain all gasses in solution.
3. Heat test chamber up to temperature, about 1 hour.
4. Seat seal.
5. Pressurize pump up to desired differential pressure across the seal.

FIGURE 6 -- SIM TEST SPECIMEN CONFIGURATION

FIGURE 7 -- SIMULATION TEST APPARATUS
P & I DIAGRAM

Close-up of Control Panel & Test Section

General View of SIM Test

FIGURE 8 -- SIMULATION TEST

Close-up of Positive Displacement Fluid Pump

6. Allow test to run until pump is fully displaced or 22 hours has elapsed.
7. Cool system, about 2 hours.
8. Disassemble.

4.2 SIM TEST FIXTURE DESIGN

The SIM test fixture operates at 260°C (500°F) and up to 5000 psig with a geothermal synthetic fluid which includes aqueous solutions of H₂S and NaCl. The presence of the hydrogen and chloride ions are of particular concern for the design because of the vulnerability to stress corrosion cracking and hydrogen embrittlement. Safety considerations of these possible failure modes was a very important aspect of the design effort. The safety aspect is uncompromising in that uncertainties must be almost entirely eliminated before it becomes prudent to move ahead and accept the consequences.

The material used was a basic concern. Inconel 600 or 624, Hastalloy C, Titanium CP, and 316SS (lower temperature components) were considered; availability as well as price were important factors along with corrosion resistance. Industry experience at Niland indicated that Carpenter 20 and 316SS at geothermal temperatures will probably crack as indicated by the pitting. Titanium would have been preferred because of slightly better machineability, however, its ASME allowable design strength per the pressure vessel code is about 25 to 40% of Inconel 600. Consequently Inconel 600 was used for all the tension carrying components which experience the test temperature while 316SS was used for all other components except external flanges which were made from fire-box steel.

The seals were another design aspect which required extensive investigation. At 260°C and with the specified chemistry, there was no candidate which clearly met the requirements. For obvious reasons, in terms of general material type, metal seals were considered as opposed to elastomeric seals. C-seals, K-seals, and self-energizing O-ring seals were considered. The O-ring seals appear most economical, even though they were good for only one use, however, based on the experience of the various vendors at the time the decision was made it was very questionable that they would perform sufficiently (since then, we have located a knowledgeable and competent vendor and have successfully tried his Teflon coated O-ring seals). The C-seals were the next preference when the original decision was made, however, their delivery was unacceptable. We ultimately used the gold plated metal K-seals. The gold plate provides a malleable surface which conforms to irregularities on the sealing surface and it is inert. The K-seals are reuseable, but, begin to leak as the gold sealing surfaces become scratched.

Figure 9 is a schematic of the K-seal shown in a typical application. The sealing occurs at the surfaces on the tips of the two legs of the K which are sprung out to a height greater than the backbone of the K. When the mating

FIGURE 9 -- K-SEAL CONFIGURATION

Typical K-seal application showing the configuration and orientation of the seal and the sealing surface.

surfaces are tightened together, the legs are squeezed thus providing a sealing force. The pressure inside the vessel provides an additional self-energizing seal force. The circumferential sealing faces are 15 mils wide and the extent of contact of the 15 mils wide surface depends on the tolerance of the two mating parts and the seal itself. Microscopic inspection of one of the seals which was having leaking problems revealed that only 10-20% or 1-3 mils of the surface was contacting. It becomes obvious that the K-seals must be handled with extreme care and any minor foreign particles or irregularities on any of the sealing surfaces can result in leaks.

This first-hand experience with metal seals indelibly emphasizes the advantages of elastomeric seals, the fact that they are infinitely more forgiving than their metal or plastic seal counterparts. Under normal circumstances elastomeric seals can be significantly deformed without taking a permanent set. On the other hand, plastic or metal seals cannot be deformed nearly to the extent of rubber to achieve a "seated" position or configuration. Plastic will tend to flow and needs constant retightening to maintain its seal while rubber seals are in stable equilibrium. Both plastic and especially metal require very close tolerance mating parts, on the order of tens of microinches and they must be handled very delicately using special procedures and precautions.

The overall configuration of the SIM test tends to be of high aspect ratio or relatively long and skinny so sliding parts must be held to close clearances and tolerances to prevent cocking of the parts and subsequent binding and gauling. To achieve the required tolerances and finishes, all of the critical parts required grinding as the finishing machining process.

Especially critical to the SIM test are the clearances and configuration of the back-up rings surrounding the seal specimen. Figure 10 shows a schematic of the cylindrical seal with chamfered ends in the relaxed state and the seated state. The seal slides over a center mandrel and is backed up on either end with back-up rings; the ram behind the upper back-up ring slides relative to the center mandrel thereby shortening the seal and causing it to flow radially to seat against both its ID and OD. Substantial stress and elongations are generated especially on the top ram end, and this area is where failures tend to occur in the rubber. Figure 11 shows photographs of the center portion of the fixture with the seal and the ram installed over the mandrel. The overall photograph shows the assembly and the close-up shows the seal area with the ram backed off such that the seal and back-up ring chamfers and the center mandrel are visible.

The clearance and back-up ring geometry are critically correlated to the SIM test results. Testing was started with flat back-up rings, i.e. they were not chamfered to conform to the seal chamfer. With the flat configuration, tests were run with diametral clearances between the OD of the back-up rings and the ID of the vessel of 13, 25, and 175 mils. The clearances were tested using a commercial Nitrile compound run in the test at 300°F. Catalogs indicate that common diametral clearances for packers with fixed back-up systems is between 100 - 200 mils for a seal of the specimen size. This information along with no evidence of extrusion at 13 and 25 mils resulted in the jump to 175 mils. In addition the flat back-up rings were later replaced

FIGURE 10 -- SEAL DEFORMATION

FIGURE 11 -- SIM TEST INTERNAL FIXTURE

Internals of SIM Test with seal, back-up rings, and seating ram in place.

Close-up of seal and back-up rings with seating ram backed off.

by rings with chamfers to spread the load across more area on the ends of the seal. This is consistent with those packers which have clearances on the order of 175 mils.

Figure 9 shows the critical dimensions of the fixture. The center mandrel OD is 2.8728 inches, the back-up rings OD are 3.825 inches, and the vessel ID is 4.0 inches. With the chamfered back-up rings the ram displaces about 0.3 inches under a load of about 10,000 lbs. during the seal seating. The finish of the parts which interface with the seal element is 32 microinches.

4.3 SEAL SPECIMEN MOLD

A relatively simple two-part, mild-steel mold was designed and fabricated for molding the packer seal specimens. Figure 12A is a photograph of the mold. The rubber load is placed in the bottom of the mold, the upper half with the male guide pins is positioned, and the mold placed in the cure press. A 50 ton force is applied as quickly as possible, about 1 minute. Typical press cure cycle for Viton is 30 minutes at 350°F.

We had significant difficulty lining out the mold to produce acceptable parts. Most effective release which was being used on flat samples was a silicone release, Dow Corning Emulsion 34, as opposed to Kraxo 1711 recommended by du Pont. The same silicone release was used on the packer seal mold and knit problems occurred along a circumferential line on the inside of the seal at the base of the bottom chamfer. After much testing and inquiring, it was deduced that the problem must result from entrainment of the release. After unsuccessfully trying several types and application procedures of Frekote 33 which is a nonsilicone release that is reported to be excellent with Vitons by multiple reliable sources (see Figure 12B), the mold was Teflon coated. This solved the knitting problem and since applying Teflon we have had no problems molding resin and peroxide cured Vitons, EPDM, Nitrile, and Epichlorohydrin.

A Nitrile seal was made from a commercial company's compound (provided to L'Garde as uncured rubber) and submitted to the company for their quality control tests. They report that the resulting molded part was of excellent quality.

4.4 SYNTHETIC GEOTHERMAL FLUID

Based on reports and discussions with Dr. J. Apps at the Lawrence Berkeley Laboratory, a specification was developed for a synthetic geothermal fluid. The approach was to avoid simply compiling all the maximums for each constituent that has been measured as this may result in unrealistically severe chemistry, rather to apply judgement and generate a specification which covers the majority of potential geothermal wells. For example total dissolved solids can run as high as a few hundred thousand ppm in the Salton Sea Area, however, the great majority of known potential wells are included at levels below 25,000 ppm.

FIGURE 12A -- SIM TEST SPECIMEN MOLD

FIGURE 12B -- SPECIMEN THAT DID NOT RELEASE FROM MOLD

The constituency specification used for the current SIM tests is as follows:

H ₂ S	300 ppm
NaCl	25,000
CO ₂	1,000
H ₂ O	balance

The H₂S and CO₂ are formed from Na₂S·9H₂O and NaHCO₃ respectively. The test uses a finite amount of H₂S thus limiting the potential exposure to personnel. If all of the H₂S were to escape into the room including the excess leftovers, the resulting concentration would be about 1 ppm as compared to OSHA's maximum allowable of 10 ppm. This approach is preferred over one where bottled H₂S is used and potential for lethal concentrations of H₂S exist. The recipe for the synthetic fluid is as follows:

Na ₂ S·9H ₂ O	5.29 gms.
NaHCO ₃	4.77 gms.
NaCl	56.64 gms.
H ₂ O distilled	1430.00 gms.
HCl(0.1N)	1.0 liter

4.5 SIM TEST RESULTS TO DATE

The SIM testing for the reported contract period is divided into two categories: evaluation of currently available commercial materials and evaluation of compounds developed under this contract.

4.5.1 Commercial Materials Evaluation

The currently available commercial materials were obtained through a process which included inquiries with companies, and selecting and obtaining material samples from five. The questionnaire shown in Appendix C was sent to a mailing list obtained from the well tool composite catalog (Reference 15) containing all companies which appeared to deal in well equipment requiring high temperature elastomeric seals. Approximately 75 questionnaires were mailed out with 16 companies responding of which 9 were interested in participating in the evaluation.

One of the questions asked regarded anonymity, whether the companies were concerned if their names were associated with the test data. The respondents who offered to contribute rubber samples generally requested that their company names not be tied to the evaluation results so the tests were run on a coded basis. Five different compounds were requested including 2 Nitriles or Buna N's, 1 Ethylene Propylene Terpolymer (EPDM), 1 Fluoroelastomer (Viton), and 1 Epichlorohydrin. The following guidelines were used in selecting candidates:

1. The materials are elastomers as opposed to plastics to enable significant deformation of the seal for seating.
2. Representatives of all the high temperature base elastomers in use were desired.
3. Specific formulations that had been applied to larger seals such as packer elements or chevrons as opposed to "O" rings, were favored.
4. Formulations with high temperature experience were favored.
5. No more than one formulation from any one tool company or molded products supplier was requested.

The codes assigned are as follows:

Company A	Nitrile or Buna N
Company B	Ethylene Propylene Terpolymer (EPR or EPDM)
Company C	Nitrile or Buna N
Company D	Epochlorohydrin
Company E	Viton

4.5.2 In-House Materials

The in-house materials evaluated in the SIM tests were the most promising candidates graduated from the previously run Screening Tests. The compounds evaluated during the Screening test phase were all peroxide cured Vitons. Upon completion of the screening there was concern that the ultimate performance of the peroxide cured Vitons may not be sufficient so as a back-up one high temperature butyl compound, three high temperature EPDM compounds, and one resin cured Viton compound were run through abbreviated Screening Tests. These materials were chemically aged in the synthetic geothermal fluid and the butyl reverted extensively, the resin cured Viton became quite brittle while the EPDM's indicated promise. The EPDM's remained elastomeric and the formulation chosen for continued development in the SIM testing lost about 25% of its tensile strength.

4.5.3 Test Data

19 complete tests were run on the SIM test during this contract period. The first 9 of the 19 served to calibrate the fixture and to get a basic assessment of the nature of the test, i.e. how long the specimens would run before failure, failure mode, severity of the clearances and back-up ring configuration, whether the differential pressure should be cycled, etc? Table VIII is a summary of the runs. The alphanumeric specimens, e.g. A-3, correspond to the specimens made from the commercially available compounds. The A designates Company A and the 3 means that it was the third specimen made from that compound. The numeric specimens are in-house compounds and the suffix number means the same thing as with the alphanumeric specimens. Except as noted all tests were run near 260°C

TABLE VIII -- SIM TEST SUMMARY

Sequence No.	Specimen No.	Compound	Duration Hrs:Min	Inches Extrusion	Set Temp. °C	Diamet. Gap, Mils	Configuration
1	215-3	VT-R-4590, Austin 70 phr	5:52	Nil	260	13	Flat
2	215-2	VT-R-4590, Austin 70 phr	:07	Nil	260	13	Flat
3	A-3	Nitrile	24:	Nil	149	13	Flat
4	A-2	Nitrile	24:	Nil	149	25	Flat
5	A-6	Nitrile	11:	0.5	260	175	Flat
6	213-3	VT-R-4590, Asbestine 3X	:00	Nil	260	175	Flat
7	220-3	VT-R-4590, Austin 65 phr	:00	Nil	260	175	Flat
8	216-2	VT-R-4590, Kevlar	:00	Nil	260	175	Flat
9	105-II-1	Viton GH, Austin/MT	:05	Nil	260	175	Flat
10	216-1	VT-R-4590, Kevlar	:00	<0.1	260	175	Chamfered
11	A-5	Nitrile	24:	1.75	260	175	Chamfered
12	105-II-2	Viton GH, Austin/MT	:47	Nil	260	175	Chamfered
13	B-3	EPDM	24:	3.75	260	175	Chamfered
14	217-2	EPDM	24:	2.5	260	175	Chamfered
15	C-4	Nitrile	1:13	4.5	260	175	Chamfered
16	D-3	Epichlorohydrin	:00	N/A	260	175	Chamfered
17	E-3	Viton	3:44	No Meas.	260	175	Chamfered
18	222-3	VT-R-4590, Austin 40 phr	:03	0.75	260	175	Chamfered
19	221-2	VT-R-4590, Maglite K	:38	0.75	260	175	Chamfered

(500°F). Because of a calibration change the tests ran at about 245°C (470°F). To maintain consistency in the latter tests the setting was not changed, however, it will be adjusted in future testing. The formulations of all in-house compounds tested are shown on Table IX. They were cured for 30 minutes at 177°C (350°F) and post cured for 16 hours at 260°C (500°F).

Through Test No. 9 adjustments were being made on the fixture to key into the severity range appropriate for the 24 hour packer application. The No. 3 and No. 4 test specimens were made from Company A's Nitrile and tested at 149°C (300°F), its approximate upper limit, to determine the response of a commercially proven material to the SIM test fixture. The back-up ring diametral gap was enlarged to 175 mils as a result of these tests as the seals appeared nominal with the only apparent change being flattening of the chamfers. The 175 mil gap was based on commercial packer configurations without expandable back-up where seals of this size must span gaps of the order of 100 to 200 mils. Test No. 5 through No. 9 assess the effect of different compounds at 260°C. Because all the Viton seals failed upon pressurization there was concern that the flat back-up rings induced unduly high stresses on the seal so they were replaced with chamfered back-up rings.

It became apparent at this point that the only way the numerous uncertainties could be pinned down was to generate some facts in the form of data so tests No. 10 through No. 19 were run as a consistent set all under the same conditions, i.e. 260°C and chamfered back-up rings with 175 mil diametral gap.

Table X is a post mortem physical description of each of the specimens. Those that failed upon pressurization appeared to be too hard and failed in tension in a macroscopic sense, i.e. major cracks developed or chunking failures occurred. Those that survived for some period of time were more pliable but failed in tension on a more submacroscopic bases, i.e. small particles broke off at the high stress point and recombined to form an extrudent which helped to seal the gap annulus on the downstream side of the seal.

Figure 13 shows some typical post mortem specimens. The Company B EPDM is a more extreme case where the seal failed in a submacroscopic sense and the failed particles then recombined to form an extrudent. The intact portion of the seal and the extrudent were both quite pliable and resilient. The L'Garde EPDM compound looked basically the same except its extrudent was about 2.5 inches high vs the 4.0 inches shown. The Company A Nitriles were similar in appearance except the extrudent was smoother and very brittle. The L'Garde Viton maintained its integrity, however, it failed by cracking at the high stress points and at weak points created during the molding process. The Company D Epichlorohydrin lost all its structural integrity here, as well as in the Extrusion Resistometer test in vacuum, and in the hot hardness test in air. The Company E Viton survived with a slow leak for 3.75 hours. It may show improvement if it is made harder. The balance of the specimens tested during this period are shown in Figure 14.

Table XI shows the virgin properties of the materials which were SIM tested. The function of these measurements is quality control to assure that the rubber has been properly mixed and cured.

TABLE IX -- SIM TEST FORMULATIONS

Component	105	213	215	216	217	220	221	222
VT-R-4590 Viton GH Nordel 1070	100	100	100	100	100	100	100	100
Austin Black MT Black SAF Black Kevlar Asbestine 3X Maglite K Litharge Antioxidant 2246 Hypalon 20 Antimony Trioxide	10 40 3	45 20 3	70 3	60 5 3	65 65 0.5 5 5	65 3	35 30	40 3
Luperco 130XL Diak 7 Dicup R	1.5 4	1.5 3	1.5 3	1.5 3	3.5	1.5 3	1.5 3	1.5 3

TABLE X -- POST MORTEM OBSERVATIONS OF SIM TEST SPECIMENS

Specimen No.	Description
215-3	Chamfered ends yielded flat. Circumferential cracking on the inside of the seal approximately at the bottom edge of the chamfer. Light brown deposits at vapor escape flaws. Room temperature Shore A 80-85.
215-2	More severe chunking or breaking at the base of the chamfer along the parting line than -3. Also circumferentially cracked on the inside at the base of the chamfer. Room Temperature Shore A 95-100.
A-3	In excellent shape, no surface cracks. Some permanent deformation -- top chamfer nearly flat, bottom chamfer flattened somewhat. Circumferential dimples on the inside where we have been experiencing failure on other specimens but no break. Room Temperature Shore A 85-90.
A-2	Situation ditto as for A-3 in all respects.
A-6	Extrudent approximately 1/2 inch. Severe chunking catastrophic failure on about 30 degree section of seal. Both chamfers flattened and the failure on the 30 degree section is completely through the height of the seal. Room Temperature Shore A 85-90. Extruded pieces of rubber extremely brittle, breaks like hard plastic.
213-3	Breakage and about 1/4 inch of extrusion evident at the top chamfer on the outside. Bottom chamfer from the outside is in good shape. Some evidence of breakage at vapor escape flaws. Cracked circumferentially along the base of the chamfer along the inside of the seal. One area on the inside has a severe chunking failure. Room Temperature Shore A 90-95.
220-3	Looks to be in relatively good shape. Chamfers are intact except for one area of about 10 degrees on the top chamfer. There is a circumferential cracking on the inside along the base of the two chamfers and there is one "L" shaped crack coming vertically down the outside surface and then going circumferentially at the base of the bottom chamfer. The "L" shaped crack traverses through a vapor escape flaw that was previously marked before the test. Room Temperature Shore A about 95.
216-2	Appears very similar to 220-3 and in relatively good shape. Chunking failure at the top chamfer over a distance of about 20 degrees. Circumferential cracks on the inside at the base of the chamfers. Room Temperature Shore A hardness 95-100.
105-II-1	Rubber failed catastrophically in the high stress area along the top of the chamfer. Rubber broken into little 1/4 inch chunks. Bottom chamfer in good shape. Wide circumferential cracking around the bottom inside at the base of the chamfer. Room Temperature Shore A 85-90.

TABLE X (continued)

Specimen No.	Description
216-1	Extruded a minor amount, 1/8 of an inch or so. No cracking on the inside as experienced on the other specimens at the base of the chamfer. Cracking and some failure at the base of the chamfer on the outside, both ends. Three failure points on the inside of the seal around the mid-section appear to be weak points. Chamfers in good shape. Room Temperature Shore A 95-100.
A-5	Extruded about 1-3/4 inches. Extrudent very hard and brittle. Breaks like hard plastic. Minor cracking on the inside of the seal right at the dimple point where the stress apparently was very high but otherwise the inside surface is in pretty good shape. Some blistering on the inside. Outside failures point at the base of the bottom chamfer. One crack in the midsection on the outside surface. Hardness approximately 90-95 but very hard to measure because there are no good flat surfaces.
105-II-2	A lot better shape than 105-II-1. No cracking on the inside. No circumferential cracking at the base of the chamfers. There is about a 70 degree circumferential crack, however, in the midsection below the base of the top chamfer. Had a great deal of extrudent, little 1/4 inch chunks, look like the other 105. Failure looks to be primarily at the flowplane of the rubber coming out of the part-line. Both chamfers are in good shape and have reassumed the original chamfer angle. Room Temperature Shore A about 80-85.
B-3	Experienced most extrusion of any of the specimens at 3.75 inches. The intact part of the seal, however, is in very good shape and no evidence of cracking except for minor cracking at the very high stress points along the circumferential dimple on the inside of the seal. Extrudent is intact and sitting on the seal like a crown. Extrudent has a rough, irregular, corduroy look. Room Temperature Shore A about 80, but is very difficult to measure because of a very narrow, flat surface being available.
217-2	Very similar in appearance to B-3. Not as much extrusion, about 2½ inches. Also appears very good except very minor cracking at the high stress points along the circumferential dimple on the inside. Bottom chamfer in good shape. Top chamfer intact too, as was the top chamfer on B-3. Room Temperature Shore A, about 85 but difficult to measure because no good flat surfaces.
C-4	Almost completely gone. The bottom chamfer failed in a section about 30 degrees wide or so. Extrudent is still pliable and held together. Looks more like the EPDM extrusion as opposed to the Nitrile extrusion of earlier specimens; that is it has a rough corduroy look rather than being smoothed out through the extrusion process. Practically nothing left on this seal. Top chamfer is intact completely circumferentially but after this amount of extrusion its pretty well broken at the base. Hardness readings are difficult but are around 85 or so.

TABLE X (concluded)

Specimen No.	Description
D-3	Most catastrophic failure of all. It was evident the seal broke during seating. Post mortem it was a handful of rubber chunks. The consistency is like cheddar cheese breaking in a crumbly fashion. Visual evidence of a fibrous filler in the rubber.
E-3	The next most catastrophic failure. Top chamfer intact. Broke along the mold flowplanes. No evidence of internal circumferential cracking at the base of the bottom chamfer on the inside of the seal. Only about half an inch section of the cylindrical portion left intact; the rest of the seal has been extruded and broken into small crumbly pieces, except some minor amounts are matted together. Pieces still resilient. Room Temperature Shore A difficult to measure therefore uncertain, but about 75.
222-3	About .75 inches of extrusion. No circumferential cracking at the bases of the chamfers on the inside, however, there is a circumferential crack at the midpoint on this seal. Circumferential on the outside of the base at the bottom chamfer and also breakage at the base of the top chamfer where the rubber was extruding out. Chamfers look to be in good shape. Room Temperature Shore A 85 to 90.
221-2	No evidence of circumferential cracking on the inside of the base of the chamfers, however, there is circumferential cracking at the midpoint -- two sets; one that goes a little over 180 degrees, the other that goes about 80 degrees or so. Chamfers in good shape. Extrudent about 3/4 of an inch. Bottom chamfer on the outside shows some evidence of breakage -- not all the way around -- two sections, one about 90 degrees and the other about 45 degrees. Room Temperature Shore A about 95.

45

FIGURE 13 -- SIM TEST POST MORTEM SPECIMENS, TYPICAL RESULTS

Company B EPDM -- This and L'Garde EPDM remained elastomeric and survived full 24 hours. Only difference L'Garde EPDM extruded 2.5 in. vs Company B's 4.0 in.

L'Garde Viton -- Failed because of inability to elongate sufficiently during seating.

220-3

46

Company D Epichlorohydrin -- Lost all structural strength and became soft and crumbly before seating.

D 3

Company E Viton -- Failed by breaking in the high stress region. Survived 3.75H with slow leak, then failed.

E 3

FIGURE 14 -- BALANCE OF POST MORTEM SIM TEST SPECIMENS
SHOWN IN ORDER OF TESTING

215-3

215-2

A-3

A-2

A-6

213-3

216-2

105-II-1

FIGURE 14 -- BALANCE OF POST MORTEM SIM TEST SPECIMENS SHOWN
SHOWN IN ORDER OF TESTING (CONTINUED)

216-1

A-5

105-II-2

217-2

C-4

222-3

221-2

TABLE XI -- SUMMARY OF VIRGIN PROPERTIES
COMMERCIAL & L'GARDE CANDIDATE PROPERTIES

Specimen	Tensile @ RT psi	Elongation @ RT %	Hardness @ 500°F Shore A	Extrusion Resist psia
A	3476	302	82.2	>18
B	2424	653	65.6	13.5
C	2000	813	61.2	11.5
D	1524	812	----	3.6
E	1506	408	72.6	8.7
213	1758	127	79.2	13.3
216	2438	63	85.2	16.2
217	>1537	>840	62.8	8.9
220	1708	107	82.8	>18
221	2260	141	81.2	>18
222	1657	179	76.4	16.8

4.5.4 Conclusions

At this point it is obvious the data is much too sparse to make any firm conclusions regarding best elastomers. The casing packer type seal with solid rubber elements require extraordinary performance of the elastomer especially at higher temperatures. The process of seating the seal significantly deforms the rubber and induces high stresses at the base of the chamfers. AT 260°C the strength of the rubber was exceeded for all specimens tested resulting in macroscopic cracking and immediate failure of the seal or sub-macroscopic cracking and maintenance of the seal with the part that remains intact plus the extrudent in the gap annulus.

Although the Company A Nitrile and the Company B and L'Garde EPDM's held their seal for the full test cycle in spite of the breakage and extrusion of the rubber, this is not the condition one would consider satisfactory as a nominal design. However, if this is the only way the seals will work under the required conditions and the system maintains a seal for the required period of time, the bottom line objective is satisfied.

One aspect of the packer seal which is quite apparent is the complex combination of rubber characteristics required to fulfill the requirement. Figure 15 figuratively illustrates the point. The problem tends to revolve around the modulus and the ultimate tensile strength and elongation. In addition the fulcrum or balance point for these trade-offs shift depending on the degree of backup around the seal element. If minimum backup is provided a high modulus elastomer must be used to provide the stiffness to bridge the gap. At the same time, however, the rubber must be able to elongate sufficiently to allow the seal to seat without breaking. At 260°C this balance becomes more and more difficult to strike, if not impossible because of the significantly reduced ultimate tensile strength and elongation. On the other hand if maximum backup (virtually no gaps) is provided, a low modulus/high elongation compound is desirable such that it can be seated at a minimum stress level. The maximum back-up case is not so deeply wedged between conflicting requirements because it does not need the high modulus having no gaps to bridge and hence is more amenable to high temperature applications.

On the basis of the 19 SIM tests which have been run, it appears that the EPDM shows more promise than the Vitons. Future compounding to develop an EPDM which will not extrude as much and a Viton which will deform more before it cracks is planned. These indicated directions for future development are based on the results and observations of the SIM Test, a level of insight not possible on simpler tests. The SIM Test evaluates the conflicting requirements of extrusion resistance versus deformability of the elastomer.

The results of the SIM Test which demonstrate the extraordinary performance required of the casing seal elastomer has lead to identification of an idea to relieve the critical requirements. The excessive stresses which cause seal failure are induced when the seal is deformed and seated. If the material were plastically as opposed to elastomerically deformed when it is seated internal stresses would not be generated in the material. This led to the question of the possibility for increasing the potential of the

FIGURE 15 -- PACKER ELASTOMER TRADE-OFFS

elastomeric casing seals by partially seating but fully deforming them in an uncured or partially cured state, "curing them in place" and then fully seating the seals. Several practical questions arise as to timing, preventing the curing until the seal is seated, green strength of the elastomer, etc. However, one can conceive of ways to forestall curing, for example, adjusting cure temperature and rates through cure system design, cryogenic cooling systems to keep the part from heating up until after it is partially seated, etc. In addition, there are applications outside of the geothermal industry such as the oil industry steam floods which are very amenable to the "cure-in-place" concept. The steam injection packer can be partially set in the cold hole and steam then circulated down to the packer to heat up, maintain temperature, and cure the seal. Once the seal is cured the packer can be fully set and then placed into operation.

In that there is good potential to work out the practical problems if the "cure-in-place" concept proves practical from the standpoint of the elastomers, L'Garde is recommending investigation of the feasibility of the "cure-in-place" concept.

5.0 PACKER IMPROVEMENT CONCEPTUALIZATION

The Improvement Conceptualization Task reported, herein, represents a minor fraction of the overall GEM effort. Conceptualization of future systems plays an important role in applied materials development, because with the inherent lead time required for materials development the materials being developed now must be applicable to the systems in use several years hence. An additional potential benefit is derived, as this minor effort may result in some fresh ideas and concepts which will benefit the geothermal community.

The conceptualization was performed by personnel who have no oil tool experience which has its good and bad points. The bad are quite obvious they cannot be as efficient, and they are vulnerable to reinventing the wheel and repeating errors of the past. On the other hand, they do not have preconceived ideas and approaches to the design which are developed for efficiency's sake, hence possess a frame of mind which allows discovery of practical ways to accomplish objectives that may have been previously rejected as impractical.

The GEM Program includes the development of a conceptual design of an oil tool device improved for geothermal service. The device selected was an inflatable, resettable casing packer. Several companies, both users and suppliers, were contacted in order to identify problems and limitations of existing designs.

Three goals were established for the effort. These goals include:

- withstanding the geothermal environment;
- having improved retraction ratio over typical solid rubber seal element devices;
- having reset capability.

One limitation of the existing inflatable packers is the tendency of the elastomeric seal to extrude when exposed to the high temperature environments 260°C (500°F) of geothermal applications. In order to prevent the extrusion of the elastomer a design (Figure 16) was conceived that provides essentially a 100% mechanical backup of the elastomer sealing element by use of a metallic backup ring and also by providing a metallic fabric to span any gaps existing in the primary backup system. In addition a valving system concept (Figure 17) was developed to allow the packer to be repeatedly inflated and deflated so it could be reset without removal and refurbishment.

The concept shown meets all of the goals which were originally set. The design is conceptual and therefore its ultimate validity will only be proven after additional feasibility evaluation and ultimately development of the hardware. However, several aspects are worthy of attention and further interest, such as the valving subsystem, the seal backup subsystem, and the

FIGURE 16 -- INFLATABLE PACKER CONCEPT

QTY REQD	CODE IDENT	PART OR IDENTIFYING NO.	NOMENCLATURE OR DESCRIPTION
PARTS LIST			
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ARE: FRACTIONS DECIMALS ANGLES ± .005 ± .005 ± .005		CONTRACT NO.	
MATERIAL		APPROVALS	DATE
FINISH		CHECKED	
NEXT ASSY USED ON		DRAWN BY <i>W. L. L.</i> 4/1/73	
APPLICATION		DO NOT SCALE DRAWING	
		GARDE, INC. 100 PACIFIC BEACH SAN DIEGO, CALIF. 92108 INFLATABLE THERMAL CASING PACKER CONCEPT SIZE CODE IDENT NO. DRAWING NO. D 1F668 SK0052 SCALE 1/16" = 1" SHEET 1 OF 1	

FIGURE 17 -- VALVING SYSTEM CONCEPTUAL DESIGN

QTY REQD	CODE IDENT	PART NO	NOMENCLATURE / DESCRIPTION	SPECS, SIZE, SUPPLIER, ETC.	ITEM NO.
			PARTS LIST		
			ORIG. <i>11/10/68</i>	GARDE, INC.	1550 PLACENTIA AVENUE NEWPORT BEACH CALIFORNIA 92660
			MATERIAL	CHK	VALVE SYSTEM
				APPD	
				APPD	
NEXT ASSY	USED ON	FINISH/HEAT TREAT		SIZE	CODE IDENT NO
APPLICATION				1F668	SK-0053
				SCALE 1/1	RELEASE SHOT / OF /

inflatable "minimum stress" seal element. The inflatable "minimum stress" seal is a direct application of L'Garde's inflatable structure expertise as applied to Air Force projects.

5.1 STATEMENT OF WORK REQUIREMENT

Task 4.2.2 entitled "Device Design Improvements" states "the overall device design will be assessed with strong consideration of its current problems and inefficiencies -- design improvements will be generated favoring those which include incorporation of new concepts as opposed to relatively minor improvement of the existing device".

The output for this task will be a cross-sectional assembly drawing. The device selected (with ERDA concurrence) is an inflatable resettable casing packer.

To provide the background information needed to design a casing packer and to understand some of the major problems encountered with these devices when they are used in a geothermal environment, several commercial companies were visited or contacted. Among those were Union Oil Company, Baker Oil Tools, Lynes, Inc., and Dresser Industries / Guiberson Division. These companies were contacted primarily to determine the problems and limitations they were experiencing with elastomeric materials but as part of the discussions the limitations of the packers themselves were discussed. Union Oil is one of the major developers in the Geysers area and a major user of equipment for geothermal applications. The remainder of the companies are manufacturers of packers. The information obtained pointed out the following problems encountered with casing packers:

- The elastomers extrude at geothermal temperatures.
- The existing inflatable designs are good to about 400°F.
- Baker has a non inflatable elastomer design that is good to 675°F.
- None of the high temperature packers are resettable.

5.2 PACKER DESIGN

5.2.1 Environmental and Operational Requirements

- A. Temperature -- up to 500°F, based on the program goal to develop an elastomer with a temperature capability of 500°F.
- B. Pressure -- 5000 psi static pressure, based on conditions experienced on the LASL Hot Dry Rock Experiment. 5000 psi differential pressure, based on the specification for Lynes Production Inspection Packer #300-01 for a 5 5/8 inch O.D. packer in a 7.3 inch diameter hole (30% expansion).

- C. Expansion Ratio -- 23% based on the specification for a Lynes Production Injection Packer with 30% to 42% expansion ratio for a 5 3/4 inch O.D. tool and the Baker expansion ratios that range from 7% to 14%. Expansion ratio is the (casing I.D. -- tool run in diameter) $\div$ (tool run in diameter).
- D. Tool Bore Ratio -- 38% (packer thru hole $\div$ casing I.D.). The 38% was selected based on the specifications for Baker Retrievable Casing Packer which has a tool bore ratio ranging from 33% to 47%.
- E. Casing I.D. Tolerance -- $\pm .13$ inches. Allowable tolerances on the casing inside diameters ranges from $\pm .017$ to $\pm .135$ for casing sizes up to 8.84 inches inside diameter and as high as $\pm .284$ inches for inside diameters up to 12.715 inches. This data was taken from the specification guide for the Baker Model "G" Retrievable Packer.
- F. Elastomer Support -- Discussions with various members of the oil tool industry led to the conclusion that the elastomer when subjected to higher temperatures will probably extrude through gaps larger than 10 mils. Therefore, the maximum allowable gap is set at 10 mils.

5.2.2 Design Rational

An inflatable concept was selected in order to meet the requirement for a large expansion ratio. Inflatable packers are presently being produced by Lynes, Inc. A simplified cross section of the Lynes Packer is shown in Figure 18. A review of this design and pictures of failed units (note, the Lynes unit was one of the better performers for LASL at 200°C) used in the LASL Hot Dry Rock Experiment pointed out two apparent areas requiring improvement in the design when the device is used for high temperature geothermal applications.

1. The elastomeric seal material itself is required to carry all the loads imposed on it by the differential pressure across the packer; i.e., there is not metal structure to prevent the rubber from extruding.
2. The elastomeric seal material is stressed in tension by the inflation stretching and also in shear because the reinforcing convoluted metal substructure bends and stretches to provide the larger inflated diameter while the elastomer only stretches. See Figure 19.

As the operating temperature increases causing the elastomer strength to reduce, these internal stresses in the elastomer exceed its strength resulting in packer failure.

FIGURE 18 -- LYNES PACKER

FIGURE 19-- SCHEMATIC OF LINES INFLATABLE ELEMENT

In order to maximize the temperature at which an elastomer can be used in a packer it is necessary to minimize, and preferably eliminate, the stresses in the elastomer. This approach, regardless of the elastomer selected, provides a design that utilizes the elastomer's capabilities to their utmost. Therefore, in order to eliminate these stresses, two conditions must be incorporated in the design.

1. Complete backup of the seal with an expandable mechanical system that is capable of carrying all differential pressure loads and that eliminates all gaps or passages greater than 10 mils.
2. A bladder configuration that can be expanded by the inflatable with little or no stretching of the bladder and seal elastomer. That is, the bladder when inflated, will merely unfold to take the expanded diameter. Some stretching will be necessary to account for the normal tolerances on the casing inside diameter.

The major design problem in this task was to satisfy the first item. Several different ideas and concepts of expandable structural backup rings were evaluated, three examples are shown in Figures 20, 21, and 22. A variation of concept "C" (Figure 22) was eventually selected as the primary backup structure but with an inflatable actuator. This type of ring, although relatively gap free, still has gaps larger than 10 mils. In order to eliminate these gaps a metal fabric woven from Inconel wire was provided between the bladder elastomer and the backup ring. This was done to bridge the gaps and essentially eliminate all gaps larger than 10 mils.

FIGURE 20 -- BACK-UP RING CONCEPT 'A'

FIGURE 21 -- BACK-UP RING CONCEPT 'B'

FIGURE 22 -- BACK-UP RING CONCEPT 'C'

The second item is more easily satisfied by simply fabricating the main bladder and seal in a convoluted configuration (Figure 23). The end portions of the bladder where the thick seal material is not required is made as thin as possible since this area requires the most bending and folding to retract it. These relatively tight folds will overstress the elastomer if the material is thick and required to make tight bends.

An 8 inch I.D. casing size was arbitrarily selected as the packer size for which a conceptual design would be developed that demonstrates the various ideas and concepts generated under this task. This packer conceptual design is shown in Figure 16 and the valve system design required to set, deflate, and reset the packer is shown in Figure 17.

5.2.3 Design Description

A. Back-Up Ring

The back-up ring system consists of six ring segments mounted on individual leaf springs. The segments are supported top and bottom by flanges that are an integral part of the packer mandrel. The leaf springs provide the force to return the segments to their stowed position when the packer is deflated for resetting. The segments are moved into position against the casing wall by the actuating bladder which is inflated prior to inflating the main packer seal bladder. As the ring segments are moved radially outward by the actuator bladder, gaps begin to develop between the segments. These gaps are bridged by six separate links that are attached to the segments by means of pins that slide in slots in the links (see Figure 16 - Section "BB" and Detail 'D'); all small gaps that exist (between sliding parts or between the ring segments and the casing) are bridged by the metal fabric woven of 6 mil Inconel wire (see Figure 16, Detail 'D'). The back-up ring system is the same at both the top and bottom of the packer.

B. "Minimum Stress" Bladder and Seal

The main bladder consists of Kevlar 29 (160,000 psi ultimate at 500°F) reinforced elastomer that is capable of being inflated. The configuration of the end portions and method of attaching the bladder to the packer mandrel are shown in Detail 'D' of Figure 16. The end portions of the bladder are molded in the inflated shape and rely on the memory forces of the seal section to hold them in the deflated stowed position. The seal area consists of the basic Kevlar reinforced elastomer material overlayed with a thicker piece of the elastomer to provide sufficient resilience to develop the casing seal. The sealing section of the bladder is molded in a convoluted shape as shown in Figure 16, Section "CC". The expanded free diameter of the bladder is sized to just fit the minimum casing diameter, in this case 7.88 inch, if the casing was actually the maximum diameter, 8.13, then the bladder would be required to stretch a maximum of only 3%. The bladder is inflated only after the back-up rings have been deployed, therefore, there should never be any loads on the elastomer other than the pressure forces it is required to seal against.

FIGURE 23 -- PACKER CONCEPT

C. Valve System

The valve system shown in Figure 17 enables the packer to be resettable. The pressures selected to operate the system are somewhat arbitrary and depending on the applications can be adjusted to be considerably different. (NOTE: The inflation pressure of Lynes Packers is 2000 to 3000 psi). Inflating-deflating-reinflating sequence is described below:

1. Inflating Sequence -- Pump a 4000 psi ball down the drill string and pressurize to 430 psi to start the valve opening. The actuator bladder port is full open at 640 psi causing the back-up rings to set. Continued pressurizing fully opens the main bladder port at 850 psi and inflates the bladder. Pressurizing to 4000 psi shears the ball thru completing the setting procedure.

2. Deflating Sequence -- Pump a 930 psi ball down and pressurize to 850 psi. This pressure will cause both the actuator and main bladder ports to be uncovered and locked open. Continued pressurizing will shear the ball thru allowing the pressure to go to ambient.

3. Reinflating Sequence -- Pump a 4000 psi ball down and pressurize to 1300 psi. This pressure fully opens and unlocks the valve. Pressurizing to 3400 psi releases the ball detents and traps the pressure inside the bladders. Continued pressurizing shears the ball thru at 4000 psi. When reinflating both the actuator bladders and main bladder are pressurized simultaneously but since the actuator bladders have so much less volume they will be pressurized first assuring the setting of the back-up rings prior to inflation of the main bladder.

D. Detailed Calculations

Detailed calculations are shown in Appendix D.

5.3 CONCLUSIONS AND RECOMMENDATIONS

This study has resulted in a packer concept with three unique components, a) the elastomer back-up system, b) the "minimum stress" bladder configuration, and c) the valve system.

The first two items apply directly to the problem of employing an elastomer in a high temperature packer environment, the third item provides a means of mechanizing the first two. The shear ball valving system is an interesting approach and its potential warrants further detailed design/development effort. The back-up ring system concept and "minimum stress" bladder concept both provide potential solutions to the problem of elastomers failing at high temperature. The concepts developed in this study provide the potential for a packer design that develops the maximum capability of the elastomer regardless of the compound.

In view of the potential advantages of the packer concept developed during this study it is recommended that further study be instituted to further evaluate feasibility of the concept.

REFERENCES

1. Alexander, J. E. and Omura H., "Processing Peroxide-Curable Fluoroelastomers", Paper No. 12, October 1976, 110th Meeting of the Rubber Division, American Chemical Society, San Francisco, California.
2. Baker, L. E., et. al, "Well Logging Technology and Geothermal Applications: A Survey and Assessment with Recommendations", SAND-75-0275, May 1975, Sandia Laboratories, Albuquerque, New Mexico.
3. Blair, A. G., et. al., "LASL Hot Dry Rock Geothermal Project", LA-6525-PR, October 1976, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.
4. Boyer, H. E., Editor, Metals Handbook, Vol. 10, Failure and Prevention Analysis, 8th Edition, 1975, American Society for Metals, Metals Park, Ohio.
5. Ender, D. H., "Evaluation of Seal Materials for Deep Sour Gas Wells", Paper No. 102, April 1975, Corrosion/75, National Association of Corrosion Engineers, Toronto, Ontario.
6. Finlay, J. B., et. al., "Peroxide-Curable Fluoroelastomers", Paper No. 11, October 1976, 110th Meeting of the Rubber Division, American Chemical Society, San Francisco, California.
7. Hallenbeck, A. and MacLachlan, J. D., "A New Fluoroelastomer For Low Temperature Applications", Paper No. 15, October 1976, 110th Meeting of the Rubber Division, American Chemical Society, San Francisco, California.
8. Hirasuna, A. R., "Summary of Limited Industry Survey", Information Release No. 170, December 1976, L'Garde, Inc., Newport Beach, California.
9. Hirasuna, A. R., "Screening Test Report", Information Release No. 172, April 1977, L'Garde, Inc., Newport Beach, California.
10. MacLachlan, J. D. and Hallenbeck, A., "A New Fluoroelastomer for Improved Fluids Resistance", Paper No. 14, October 1976, 110th Meeting of the Rubber Division, American Chemical Society, San Francisco, California.
11. Pelosi, L. F., and Hackett, E. T., "Improved Steam Resistance For Fluoroelastomers", Paper No. 13, October 1976, 110th Meeting of the Rubber Division, American Chemical Society, San Francisco, California.
12. Sieron, J. K., "New Reinforcement and Stabilization Systems for Extreme Environment Elastomers", AFML-TR-66-376, April 1967, Air Force Materials Laboratory, Wright Patterson Air Force Base.

13. Stephens, C. A., "Regression Analysis with APL", TR 02.714, September 1976, IBM, San Jose, California.
14. Veal, G. R., "Inflatable Thermal Casing Packer Concept", Information Release No. 171, March 1977, L'Garde, Inc., Newport Beach, California.
15. "Composite Catalog of Oil Field Equipment and Services", 1976, World Oil, Gulf Publishing Co., Houston, Texas.
16. "Geothermal Brine Data File", 17 November 1976 Revision, Lawrence Berkeley Laboratory, University of California, Berkeley, California.
17. "Geothermal Environmental Materials", Technical Proposal LTP-052, March 1976, L'Garde, Inc., Newport Beach, California.
18. "Materials for Values for Resistance to Sulfide stress Cracking in Production and Pipeline Service", NACE Standard MR-01-75, March 1975, National Association of Corrosion Engineers, Houston, Texas.
19. "VIP, Viton . . . Innovating for Progress", du Pont, Wilmington, Delaware.

APPENDICES

APPENDIX A

UNITED NATIONS

NATIONS UNIES

POSTAL ADDRESS—ADRESSE POSTALE UNITED NATIONS, N. Y. 10017
CABLE ADDRESS—ADRESSE TELEGRAPHIQUE UNATIONS NEW YORK

2 December 1976

REFERENCE: EC 333/1

Dear Mr. Hirasuna,

Mr. Barnea has asked me to respond to your letter to him of 17 November 1976, requesting recommendations of devices in which the use of high temperature elastomers would advance the progress of geothermal energy development.

Certainly, we agree that down-hole formation packers would be at the top of our list. The lack of high temperature packers prevents us from making flow tests or drill-stem tests of specific productive zones below the first productive zone encountered by the drill. Consequently, we can only obtain flow test data from mixed zones, and our test data from deeper productive zones is restricted to cold water injection tests, which in many cases, do not give the data we need.

We rarely have need for casing packers as our completions are made either with slotted liners or open hole, rarely with perforated casing. If the industry ever reaches the stage of applying hydro fracturing techniques for well stimulation, casing packers would be required, but even in this case, the packers would not necessarily have to withstand high temperatures.

The development of packers for rotating drilling heads would be the second item on our list. We have found that aerated water is an ideal geothermal drilling fluid, but one of the disadvantages of the system is the need for frequent replacement of expensive drilling-head packers, which become brittle rather quickly due to the temperature of the return fluids. For the same reason, blow-out preventor rubbers also require more frequent replacement than normal, but not as frequent as the rotating packers.

Yours truly,

A handwritten signature in dark ink, appearing to read "J. R. McNitt".

J. R. McNitt
Technical Adviser
Energy Section

Energy and Mineral Development Branch
Centre for Natural Resources,
Energy and Transport

Mr. Alan R. Hirasuna
GEM Program Manager
Garde, Inc.
1555 Barentia Avenue
Newport Beach, California 92660

cc: Mr. Joseph Barnea, UNITAR

APPENDIX B

UNIVERSITY OF CALIFORNIA
LOS ALAMOS SCIENTIFIC LABORATORY
(CONTRACT W-7405-ENG-36)
P.O. BOX 1663
LOS ALAMOS, NEW MEXICO 87545

IN REPLY
REFER TO: G-DOT
MAIL STOP: 570

September 28, 1977

Mr. Alan R. Hirasuna
L'Garde, Inc.
1557 Placenta Avenue
Newport Beach, CA 92660

Dear Alan:

This is another "chapter" in the high temperature formation packer story. I have enclosed a brief description of our most recent experience with the Lynes, Inc. inflatable packer system. As you will note these units operated satisfactorily at 180°C. Indeed Lynes has indicated that they will attempt to develop a system for 200° - 300°C service. I still consider that to be a difficult and risky undertaking! As a result we will very likely initiate an evaluation of high temperature compression packer systems (see enclosed copy of letters to Halliburton Services and Guiberson Dresser). I wonder if you have made any "breakthroughs" on your project in the elastomer area? Do you have a report on your initial work completed yet?

Our next drilling and fracturing needs may be as much as a year to a year and a half away, so we have some time yet to develop a source for a suitable high temperature formation packer system.

For your information I have enclosed:

- (1) LASL Hot Dry Rock Geothermal Project High-Temperature Inflatable Packers, GT-2 Redrill
- (2) Physics Today January 1977 Vol. 30 No. 1
- (3) LASL Mini-Review 77-8
- (4) LA-6906-MS
- (5) LA-6889-MS
- (6) ERDA-DGE Programs in Logging Technology (1976-77)

The last item lists the FY 76-77 ERDA-DGE Logging R&D efforts and I am curious if you are aware of the last entry and if anything significant has resulted from the Hughes work?

We appreciate your continued interest in our HDR geothermal project and want to continue to urge L'Garde toward a successful development of a high temperature elastomer -- there is still a great need throughout the geothermal industry as well as for many of the ERDA R&D projects.

Very truly yours,

John C. Rowley

JR:kd

Encl: a/s

cc: A. Blair/R. Brownlee w/o encl.
G. Nunz w/o encl.
J. Hill w/o encl.
R. Pettitt w/o encl.
M & R (2)
File

APPENDIX C

1555 PLACENTIA AVENUE
NEWPORT BEACH, CALIFORNIA 92663
TELEPHONE (714) 546-4671 & (714) 645-4880

Gentlemen:

L'Garde, Inc. is contracted by the Energy Research and Development Administration (ERDA) Geothermal Division to develop high temperature elastomers or rubber materials for application to equipment for exploration, drilling, assessment, and production of geothermal resources. As a minor part of this effort L'Garde is tasked to evaluate five (5) currently available, commercial, high-temperature elastomers used for these applications as O-ring seals, packer seals, cable feed-through seals, etc. The purpose of this letter is to initiate the process whereby representative samples of the currently employed, commercially available elastomers can be obtained.

Evaluation of the elastomers will be accomplished using laboratory tests simulating geothermal well conditions. Temperatures may be as high as 260°C (500°F), pressures as high as 5000 psi, differential pressures across the seal as high as 5000 psi, for a duration on the order of 24 hours. A testing procedure, yet to be finalized, will be used whereby quantitative relative ranking of all samples will be accomplished. For example, all elastomers could be exposed to 260°C and the time to failure measured. The constituency of the synthetic geothermal fluid that the samples will be exposed to is as follows:

H ₂ O	balance
H ₂ S	300 ppm
NaCl	25,000 ppm
CO ₂	1,000 ppm
pH	5-7

In order to accomplish this task in as efficient, comprehensive, and fair manner as possible, we are herein initiating the process by distributing

the enclosed questionnaire to as broad a distribution as practical. Based on these responses we will be requesting samples to be submitted for testing. We will be testing five materials judged to represent the best available, and we will choose the samples to be tested in a manner which allows consideration of as many base elastomers as practical which have high temperature potential which is at least as good as Nitrile or Buna N.

Based on the responses to question 9 on the questionnaire, we will either label all or none of the data with the associated Company name. In no instance will we violate a Company's request to remain confidential. ERDA would prefer to use company names to provide maximum practical application of the data, so if a representative number of companies allow linking their Company name with the data we will chose our samples from that group. If the majority of the companies wish to remain confidential, we will publish data in a coded format and each company whose sample is tested will be informed as to their own and only their own identification code so they can identify their data. The data will include the following identification: 1) company name or code, 2) base elastomer (eg. Nitrile), and 3) application (eg. packer chevron seal). The data will be evaluation measurements taken by L'Garde.

If you are interested in pursuing the opportunity to have your material evaluated for geothermal application, please fill out the enclosed questionnaire. The questionnaires to be taken under consideration must be received by L'Garde by 4:30 PM, March 23, 1977.

Sincerely,

Alan R. Hirasuna
Geothermal Environmental Materials
Program Manager

ARH:pw
Enclosure

Questionnaire Regarding Your Best High Temperature Elastomer
for Geothermal Applications

Yes No

1. Do you wish to supply a sample of your highest temperature elastomer, on the order of 1 to 2 lbs. (all Kalrez to be tested will be obtained directly from du Pont)?

2. What is your base elastomer, eg. Nitrile or Buna N, Ethylene Propylene, Viton, etc.? The base elastomer will be used to identify the published test data.

3. For what applications has the elastomer been successfully used, eg. packer casing seal, packer formation seal, packer internal O-ring seal, etc.?

4. What is the time, temperature and environment that the seals in 3) operate satisfactorily?

Yes No

5. Are you willing to supply at no cost uncured stock with curing instructions should we have a specific mold to fabricate parts to fit our fixture? If NO, please explain.

6. Are you willing to supply at no cost cured parts made to our dimensional requirements? If NO, please explain.

7. How much lead time do you need to deliver the required material?

8. Do you have any suggestions that may improve this testing? If YES, please state.

9. Would you object to having your company name published, identifying the test data? Please state feelings.

10. Person to Contact _____

Company _____

Address _____

City/State/Zip _____

Phone No. () _____

11. Please send any brochures or information describing the elastomer and its performance which may assist us in choosing representative candidates. As you might imagine, it will be very difficult to choose between the various Nitrile formulations each with its own superior proprietary ingredient.

APPENDIX D

PACKER IMPROVEMENT CONCEPTUALIZATION DESIGN CALCULATIONS

A. Maximum Gap

The maximum gap in the back-up ring will exist between the ring and the casing. Since the ring will be made to fit the nominal case diameter when expanded a gap will exist when the casing diameter is either more or less than nominal. The maximum gap is calculated as follows:

$$\text{Maximum Gap} = d - D$$

$$d = r - a$$

$$\theta = \arcsin \frac{l}{r}$$

$$a = r \cos \theta$$

$$d = r(1 - \cos \theta)$$

$$D = R - A$$

$$A = R \cos \phi$$

$$D = R(1 - \cos \phi)$$

$$\phi = \arcsin \frac{l}{R}$$

$R = 4.02$ high side of segment tolerance.

$r = 3.94$ low side of casing tolerance.

l is determined from the stowed configuration of the back-up ring.

$$l = 3.25 \tan 30^\circ = 1.876$$

$$\theta = \arcsin \frac{1.876}{3.94} = 28.44^\circ$$

$$\theta = \arcsin \frac{1.876}{4.02} = 27.818^\circ$$

$$d = 3.94 (1 - \cos 28.44^\circ) = .4755$$

$$D = 4.02 (1 - \cos 27.818^\circ) = .4646$$

$$\text{Gap} = .4755 - .4676 = .0109$$

$$\text{Max Gap} = C = R - R_1$$

$r = 3.98$ low side of segment tolerance

$R = 4.06$ high side of casing tolerance

$$R_1 = \sqrt{(a+b)^2 + l^2}$$

$$b = R - r = 4.06 - 3.98 = .08$$

$$l = 1.876$$

$$a = \sqrt{r^2 - l^2} = \sqrt{3.98^2 - 1.876^2} = 3.510$$

$$R_1 = \sqrt{(3.510 + .08)^2 + 1.876^2} = 4.05$$

$$\text{Gap} = 4.06 - 4.05 = .01$$

B. Back-Up Ring Link

The small link between the bladder and ring segments that functions as a bridge over the gap between the expanded segments is required to resist the 5000 psi differential pressure across the packer without shearing out or undue deflection.

Link Width = $W = 1 \text{ in.}$

Link Material is Inconel 718.

$$\sigma_{\text{yield}} = 150,000 \text{ psi}$$

$$\sigma_{\text{UTS}} = 180,000 \text{ psi} \quad (\text{MIL-HNDBK-5, page 6-52})$$

Shear

$$\sigma_{\text{shear}} = \frac{p l w}{2 t w} = \frac{5000}{2(.25)} = 10,000 \text{ psi } -(OK)$$

Bending

$$\sigma_{\text{bending}} = \frac{M c}{I} = \frac{3 p l^2}{4 t^2} = 60,000 \text{ psi } -(OK)$$

Deflection

$$y = \frac{15}{96} \frac{p l^4}{E t^3} = .0017 \text{ in } -(OK)$$

C. Vertical Gap Bridge

As the back-up ring expands the vertical gap between segments must also be bridged to prevent failure of the actuator bladder. This bridge must also be capable of resisting 5000 psi.

Bridge Height = $h = 4 \text{ in.}$

Bridge Material is Inconel 718.

Shear

$$\tau_{\text{yield}} = \frac{p \cdot l}{2t} = \frac{5000(.92)}{2(.188)} = 12234 \text{ psi } -(OK)$$

$$\tau_{\text{bending}} = \frac{Mc}{I} = \frac{3}{4} \frac{p l^2}{t^2} = \frac{3}{4} \frac{(5000)(.92^2)}{(.188)^2} = 89803 \text{ psi } -(OK)$$

D. Leaf Spring Requirements

The leaf spring provides the force necessary to return the back-up ring segment to its stowed position when the actuator bladder is deflated. It is desirable to have this return force very high in order to overcome friction in the links at the bottom of the segment and in order to be less affected by the drilling mud. The leaf spring is required to deflect one inch without yielding.

$$l = 12 \text{ in}$$

$$y = \text{deflection} = 1 \text{ in.}$$

$$W = \text{deflection force (LBS)}$$

$$t = \text{thickness (in)}$$

$$w = \text{width} = 1 \text{ in.}$$

Material is Inconel 718

$$\sigma_{\text{yield}} = 150,000 \text{ psi}$$

$$\sigma_{\text{ULT}} = 180,000 \text{ psi}$$

$$\sigma = \frac{Mc}{I} = \frac{W l c}{I} \quad c = t/2$$

$$y = \frac{1}{3} \frac{W l^3}{EI}$$

$$y = \frac{\sigma l^2}{3cE}; \quad c = t/2 \quad \text{therefore} \quad t = \frac{2\sigma l^2}{3yE}$$

Use $\sigma = 120,000 \text{ psi}$

$$t = \frac{2(120,000)(12^2)}{3(1)(30 \times 10^6)} = .384 \text{ in.}$$

$$W = \frac{\sigma I}{l c} = \frac{\sigma w t^2}{6l} = \frac{(120,000)(1)(.384^2)}{6(12)} = 245 \text{ LBS}$$

E. Bladder Molded Shape

The bladder, when unpressurized, must assume a convoluted shape in order to reduce to an outside diameter of 6.25 inches maximum. It must, however, be able to expand to 7.88 inch diameter minimum.

$$\sin 11.25^\circ = \frac{r_1}{2.9 - r_1} ; r_1 = \frac{2.9 \sin 11.25^\circ}{1 + \sin 11.25^\circ}$$

$$r_1 = .473$$

$$c_1 = \left(\frac{90 + 11.25}{360} \right) (2\pi) (.473) = .837$$

$$\sin 11.25^\circ = \frac{r_2}{1.94 + r_2} ; r_2 = \frac{1.94 \sin 11.25^\circ}{1 - \sin 11.25^\circ}$$

$$r_2 = .470$$

$$c_2 = \left(\frac{180 - 2(11.25)}{360} \right) (2\pi) (.470) = 1.293$$

$$b = 2.90 - .473 - .473 \sin 11.25^\circ = 2.335$$

$$c = (1.94 + .470) \cos 22.5^\circ = 2.227$$

$$d = c + .470 \sin 11.25^\circ = 2.319$$

$$a = \frac{b-d}{\cos 11.25^\circ} = .0166$$

One complete cycle then is equal to $2(.837) + 1.293 + 2(.0166) = 3.00$ which gives for the expanded diameter of the outside of the bladder $\frac{8(3.00)}{\pi} + 2(.125) = 7.89$ which is .01 more than required.

F. Metal Fabric Wire Diameter

The metal fabric will be designed to span a gap of .03 under a pressure of 5000 psi. The fabric will be woven of Inconel 718 wire

$$\sigma_{\text{yield}} = 150,000 \text{ psi}$$

$$\tau_{\text{ult.}} = 180,000 \text{ psi}$$

Assume 6 MIL wire

$$\tau_{\text{Shear}} = \frac{p l d}{2 \pi \frac{d^2}{4}} = \frac{2 p l}{\pi d}$$

$$\tau_{\text{Shear}} = \frac{2 (5000) (.03)}{\pi (.006)} = 15900 \text{ psi --(OK)}$$

$$\sigma_{\text{Bending}} = \frac{M c}{I}$$

$$M_{\text{max}} = \frac{1}{24} p d l^2$$

$$I = \frac{1}{4} \pi (d/2)^4$$

$$c = d/2$$

$$\sigma_{\text{Bending}} = \frac{(\frac{1}{12} p \frac{d}{2} l^2) (\frac{d}{2})}{\frac{1}{4} \pi (d/2)^4} = \frac{4 p l^2}{3 \pi d^2}$$

$$\sigma_{\text{Bending}} = \frac{4 (5000) (.03)^2}{3 \pi (.006)^2} = 53,000 \text{ psi --(OK)}$$

This calculation was made only to determine if the wire size is approximately correct. The small diameter of the wire and small gap probably reduces the accuracy of the calculation to that of an approximation at best. The optimum diameter should be determined experimentally.

APPENDIX B

APPLICATION		REVISION			
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED
		A	Corrections and changes to Table I and II.	1 Jun 79	<i>[Signature]</i>

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ARE: FRACTIONS DECIMALS ANGLES $\pm .XX \pm \pm$ $.XXX \pm$	CONTRACT NO.			1555 PLACENTIA AVENUE NEWPORT BEACH CALIFORNIA 92660	
	APPROVALS	DATE		Procedure for Preparation of Fluoro- elastomer Compound, GEM 255	
DRAWN R. Wallstrom <i>RW</i>	8 Nov 78				
CHECKED					
MATERIAL			SIZE A	CODE IDENT NO. 1F668	DRAWING NO. 10590
FINISH					
DO NOT SCALE DRAWING			SCALE	SHEET 1 OF 9	

1. SCOPE

This procedure establishes the formulation, mixing methodology and steps for preparing the GEM 255 rubber compound intended for use as Geothermal Packer seal elements.

2. APPLICABLE DOCUMENTS

The following documents form a part of this specification of the extent specified herein. Later issues of these documents may be used at the option of the supplier providing no degradation of the product ensues.

Federal

Q-A-51 Acetone, Technical

American Society for Testing and Materials

ASTM D2516	Nomenclature for Rubber-Grade Carbon Blacks
ASTM D15	Compound and Sample Preparation for Physical Testing of Rubber Products
ASTM D412	Tension Testing of Vulcanized Rubber
ASTM D2240	Indentation Hardness of Rubber and Plastics By Means of a Durometer, Test for

3. REQUIREMENTS

3.1 Material. All materials for the preparation of these rubber compounds shall be formulated and processed to meet the requirements of this procedure. All materials shall be homogeneous, clean and suitable for the purpose intended.

- 3.2 Processing. The compounds shall be prepared according to this procedure.
- 3.3 Mechanical Properties. The compounded rubber shall have properties according to this procedure.
- 3.4 Workmanship. Each batch of rubber shall be prepared, handled and stored to minimize contamination. Contamination is herein defined as the presence of any material in the compound which is visible to the unaided eye. Contaminated rubber may be removed from the compound if it does not exceed 1% by weight of the compound at the time of removal. If the contaminated rubber exceeds 1% by weight, the compound must be discarded.

4. QUALITY ASSURANCE PROVISIONS

- 4.1 Acceptance. The supplier of materials under this procedure shall certify that each batch conforms to all requirements of the procedure. Certification shall include the actual results of all laboratory tests used to determine conformance. A batch is defined herein as the quantity of homogeneous material compounded on a rubber mill at one time.
- 4.2 Rejection. A batch of material which does not meet the requirements of one or more tests under this procedure may be retested once. Failure to meet the requirements with the second testing shall be cause for rejection of the material. Criteria for rejection are established by Table I, Table II and paragraph 3.4.

4.3 Test Methods. Qualification and acceptance testing of the material to the requirements of this procedure shall be in accordance with the following.

4.3.1 Tensile Strength and Elongation. The tensile strength and ultimate elongation shall be determined in accordance with ASTM D412 using Die "C" for the specimens. Results shall conform to the requirements of Table II.

4.3.2 Hardness. The hardness shall be determined in accordance with ASTM D2240. Results shall conform to the requirements of Table II.

4.4 Mixing. This compound shall be formulated according to the recipes and tolerances given in Table I.

TABLE I
FORMULATION GEM 255

Item	Seq. No.	Component Description	phr	Tolerances
a	1	VT-R-4590 (DuPont)	100	+2%
b	2	Austin Black (Cities Service)	10	+1%
c	2	Statex M-568 (N-568) (Cities Service)	25	+2%
d	2	Maglite K (C. P. Hall)	3	±.5%
e	2	Diak #7 (DuPont)	1.5	±.5%
f	2	Luperco 130 XL (Ram Chemicals)	1.5	±.5%

NOTE: The tolerances show the degree of accuracy required for weighing each individual component and the required material balance for the total compound (+5%). This latter value includes losses due to removal of

contaminated material. Adjustments to the tolerances may be warranted as more experience is accumulated.

The compound shall be mixed on a two-roll rubber mill precleaned with solvent such as acetone. All parts of the equipment which would come in contact with the compound during the mixing operation shall be cleaned. The floor adjacent to the mill shall be swept to remove contaminants.

4.5 Mixing Procedure

4.5.1 Premix

4.5.1.1 Alternately sprinkle in item f into d and mix until well dispersed.

4.5.1.2 Add b to e until mixture is dry; breakup lumps until mixture is powdered. If all of b is used up before mixture is dry, add c until dry state is reached.

4.5.1.3 Add d and f to b and e sprinkling one into the other, mixing until well dispersed.

4.5.1.4 Take half of the remaining b and c and sprinkle into the above mixture of d + f + b and e.

4.5.1.5 Take last half of b and c and alternately sprinkle into mixture form in 4.5.1.4., above, and mix until well dispersed.

4.5.2 Final Mix. Add mixture formed in 4.5.1.5. to the bulk rubber (component a in Table I) while it is banded on mill.

4.6 Curing Procedures

4.6.1 Test Sheets

- 4.6.1.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.1.2 Remove stock from mill when approximate thickness of 100 mils is attained.
- 4.6.1.3 Cut out a 5.75" by 5.75" square from stock making sure to mark mill mixing direction.
- 4.6.1.4 Put sample into a preheated 75 mil ASTM sheet mold such that mill direction is identifiable.
- 4.6.1.5 Place loaded mold into heat platens at 350⁰F for 15 minutes at 20 tons force. After one minute at force, "bump" sample 3 times by releasing pressure to almost zero and then repressurizing to 20 tons.
- 4.6.1.6 After step 4.6.1.5, remove sample from mold and follow post-curing procedure.

4.6.2 Packer Seals

- 4.6.2.1 Freshen stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.2.2 For a 2.75 inch OD packer seal, the following procedure is used. Place loaded mold onto heat platens at 300⁰F for 30 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of pressure change from 50 tons to just above zero, then repressuring to 50 tons.

4.6.2.3 Raise cure temperature to 350°F. Upon reaching 350°F cure for 30 additional minutes.

4.6.2.4 After 4.6.2.3, remove sample from mold and follow post-curing procedure.

4.6.3 O-Rings

4.6.3.2 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.

4.6.3.2 For a compression mold which makes 4 each 2-329 O-rings the following procedure is used. Place loaded mold into heat platens at 300°F for 30 minutes at 50 tons pressure. After one minute subject sample to a "bump" procedure consisting of 3 cycles of pressure change from 50 tons to just above zero, then repressuring to 50 tons.

4.6.3.3 Raise cure temperature to 350°F. Upon reaching 350°F continue curing for another 15 minutes.

4.6.3.4 After 4.6.3.3, remove sample from mold and follow post-curing procedure.

4.7 Post Curing Procedure

4.7.1 Immediately upon removing cured sample from mold, place sample into 350°F preheated, nitrogen atmosphere oven chamber and continue temperature environment as follows:

<u>Period</u>	<u>Chamber Temp.</u>
1st hour	350°F
1 - 2 hours	400°F
2 - 3 hours	450°F
3 - 20.5 hours	500°F

4.7.2. Remove hot sample from chamber to cool.

4.7.3 Upon cooling, the sample is ready for intended application.

4.8 Properties. Properties of the resultant compounds shall conform to the values and tolerances shown in Table II.

TABLE II
TYPICAL PROPERTIES OF COMPOUND GEM 255

Property Units	Median Value/Tolerance*	
	Virgin	Chem. Aged**
Ultimate tensile strength @ RT, psi	1760 + 440	1270 + 320
Ultimate elongation at break, @ RT, %	180 + 45	180 + 45
Shore A hardness @ 260°C	79 $\pm$ 5	79 $\pm$ 5
Extrusion resistance @ 260°C, psia	9.1 + 4	5.0 + 3

*Median values have been selected based on test data and tolerances have been selected arbitrarily. It is recommended that these selected values be reviewed and adjusted after more experience is generated.

**Chemical Effects Test Procedure TP10582

4.9 Packaging. When cooled to ambient room temperature (hand test) the rubber shall be cut into appropriate size slabs, wrapped in plastic film and boxed. The box shall be closed to prevent contamination during subsequent handling and storage.

4.10 Marking. The box shall be identified in a clear manner with the following information:

Compound Number

Date of Compounding

Supplier's Name or Other Identification

"STORE IN A COOL, DRY PLACE"

APPENDIX C

APPLICATION			REVISION		
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ARE: FRACTIONS DECIMALS ANGLES ± .XX ± ± .XXX ±	CONTRACT NO.		'GARDE, INC. 1555 PLACENTIA AVENUE NEWPORT BEACH CALIFORNIA 92660
	APPROVALS	DATE	
	DRAWN R. Sedwick	11 JUN 78	
	CHECKED		
MATERIAL			Procedure for Preparation of EPDM/Fluoro- elastomer Blend Compound GEM 266
FINISH			
DO NOT SCALE DRAWING	SIZE A	CODE IDENT NO. 1F668	DRAWING NO. 10668
SCALE		SHEET 1 OF 7	

1. SCOPE

This procedure establishes the formulation, mixing methodology and steps for preparing GEM 266 rubber compounds intended for use as geothermal packer seal elements.

2. APPLICABLE DOCUMENTS

The following documents form a part of this specification to the extent specified herein. Later issues of these documents may be used at the option of the supplier providing no degradation of the product ensues.

Federal

Q-A-51 Acetone, Technical

American Society for Testing and Materials

ASTM D2516	Nomenclature for Rubber-Grade Carbon Blacks
ASTM D15	Compound and Sample Preparation for Physical Testing of Rubber Products
ASTM D412	Tension Testing of Vulcanized Rubber
ASTM D2240	Indentation Hardness of Rubber and Plastics By Means of a Durometer, Test for

3. REQUIREMENTS

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- 3.2 Processing. The compounds shall be prepared according to this procedure.
- 3.3 Mechanical Properties. The compounded rubber shall have properties according to this procedure.
- 3.4 Workmanship. Each batch of rubber shall be prepared, handled and stored to minimize contamination. Contamination is herein defined as the presence of any material in the compound which is visible to the unaided eye. Contaminated rubber may be removed from the compound

if it does not exceed 1% by weight of the compound at the time of removal. If the contaminated rubber exceeds 1% by weight, the compound must be discarded.

4. QUALITY ASSURANCE PROVISIONS

- 4.1 Acceptance. The supplier of materials under this procedure shall certify that each batch conforms to all requirements of the procedure. Certification shall include the actual results of all laboratory tests used to determine conformance. A batch is defined herein as the quantity of homogeneous material compounded on a rubber mill at one time.
- 4.2 Rejection. A batch of material which does not meet the requirements of one or more tests under this procedure may be retested once. Failure to meet the requirements with the second testing shall be cause for rejection of the material. Criteria for rejection are established by Table I, Table III and paragraph 3.4.
- 4.3 Test Methods. Qualification and acceptance testing of the material to the requirements of this procedure shall be in accordance with the following:
- 4.3.1 Tensile Strength and Elongation. The tensile strength and ultimate elongation shall be determined in accordance with ASTM D412 using Die "C" for the specimens. Results shall conform to the requirements of Table II.
- 4.3.2 Hardness. The hardness shall be determined in accordance with ASTM D2240. Results shall conform to the requirements of Table II.
- 4.4 Mixing. This compound shall be formulated according to the recipes and tolerances given in Table I.

TABLE I
FORMULATION OF GEM 266 COMPOUND

Item	Seq. No.	Component Description	phr	Tolerances
a	1	Nordel 1660 (DuPont)	50	$\pm 2\%$
b	2	VT-R-4590 (DuPont)	50	$\pm 2\%$
c	3	Hypalon 20 (DuPont)	2.5	$\pm .5\%$
d	5	Austin Black (Cities Service)	7.5	$\pm 1\%$
e	5	Maglite K (C. P. Hall)	2.5	$\pm .5\%$
f	4	Statex 160 (N110)(Cities Service)	52.5	$\pm 2\%$
g	5	Diak #7 (DuPont)	3.0	$\pm .5\%$
h	5	Luperco 130XL (Ram Chemicals)	1.5	$\pm .5\%$
i	5	Cyanox 2246 (American Cyanamid Co.)	.25	$\pm .5\%$
j	5	Thermoguard S (M & T Chemicals Inc.)	2.5	$\pm .5\%$

NOTE: The tolerances show the degree of accuracy required for weighing each individual component and the required material balance for the total compound ($\pm 5\%$). This latter value includes losses due to removal of contaminated material. Adjustments to the tolerances may be warranted as more experience is accumulated.

The compound shall be mixed on a two-roll rubber mill precleaned with solvent such as acetone. All parts of the equipment which could come in contact with the compound during the mixing operation shall be cleaned. The floor adjacent to the mill shall be swept to remove contaminants.

4.5 Mixing Procedure

4.5.1 Premix

4.5.1.1 Add d to g until mixture is dry; break lumps until mixture is powdered. If all of d is used before mixture is dry, add f until dry state is reached.

- 4.5.1.2 Combine e and h, then add i, then j, then d and g sprinkling one into the other, mixing until well dispersed after the addition of each component.

4.5.2 Final Mix

- 4.5.2.1 Combine items a, b and c on mill and run several minutes to make the banded rubber warm and pliable.
- 4.5.2.2 Slowly add f then the mixture resulting from 4.5.1.2. As each component of combination of components is added to the mill, frequent cross-cutting of the rubber should be accomplished for uniform mixing.

4.6 Curing Procedures

4.6.1 Test Sheets

- 4.6.1.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.1.2 Remove stock from mill when approximate thickness of 100 mils is attained.
- 4.6.1.3 Cut out a 5.75" by 5.75" square from sheet making sure to mark mill mixing direction.
- 4.6.1.4 Put sample into a preheated 75 mil ASTM sheet mold, such that mill direction is identifiable.
- 4.6.1.5 Place loaded mold into heat platens at 350°F for 60 minutes at 20 tons force. After one minute at force "bump" sample 3 times by releasing force to almost zero and then reapplying it to 20 tons.
- 4.6.1.6 After step 4.6.1.5, remove sample from mold and follow post-curing procedures.

4.6.2 Packer Seals

6 of 7

- 4.6.2.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.2.2 For a 2.75 inch OD packer seal, the following procedure is used. Place loaded mold into heat platens at 350⁰F for 90 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of force change from 50 tons to just above zero, then repressuring to 50 tons.
- 4.6.2.3 After 4.6.2.2, remove sample from mold and follow post-curing procedure.

4.6.3 O-Rings

- 4.6.3.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.3.2 For a compression mold which makes 4 each 2-329 O-rings the following procedure is used. Place loaded mold into heat platens at 350⁰F for 60 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of force change from 50 tons to just above zero, then repressuring to 50 tons.
- 4.6.3.3 After 4.6.3.2, remove sample from mold and follow post-curing procedure.

4.7 Post-Curing Procedure

- 4.7.1 Immediately upon removing cured sample from mold, place sample into 350⁰F preheated, nitrogen atmosphere oven chamber and continue temperature environment as follows:

<u>Period</u>	<u>Chamber Temp.</u>
1st hour	400 ⁰ F
1 - hours	450 ⁰ F
2 - 3 hours	500 ⁰ F
3 - 8.0 hours	550 ⁰ F

After 8 hours cool to at least 300⁰F in nitrogen oven.

4.7.2 Upon cooling the sample is ready for intended application.

4.8 Properties. Properties of the compound shall conform to the values and tolerances shown in Table II.

TABLE II
TYPICAL PROPERTIES OF COMPOUND GEM 266

Property, Units	Median Value/Tolerance*	
	Virgin	Chem Aged**
Ultimate Tensile Strength @ RT, psi	1280 + 320	1220 + 305
Ultimate Elongation at Break, @ RT, %	150 + 38	130 + 33
Shore A Hardness @ 260°C	88 ± 6	89 ± 6
Extrusion Resistance @ 260°C, psia	14 + 5	14 + 5

* Median Values have been selected based on test data and tolerances have been selected arbitrarily. It is recommended that these selected values be reviewed and adjusted after more experience is generated.

** Chemical Effects Test Procedure TP10582

4.9 Packaging. When cooled to ambient room temperature (hand test) the rubber shall be cut into appropriate size slabs, wrapped in plastic film and boxed. The box shall be closed to prevent contamination during subsequent handling and storage.

4.10 Marking. The box shall be identified in a clear manner with the following information:

Compound Number

Date of Compounding

Supplier's Name or Other Identification

"STORE IN A COOL, DRY PLACE"

APPENDIX D

APPLICATION		REVISION			
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED
		A	Corrections and changes to Tables I and II	1 Jun 79	

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ARE: FRACTIONS DECIMALS ANGLES $\pm .XX \pm \pm$ $.XXX \pm$	CONTRACT NO.		1555 PLACENTIA AVENUE NEWPORT BEACH CALIFORNIA 92660
	APPROVALS	DATE	
	DRAWN R. Wallstrom	DATE 6/1/79	
	CHECKED		
MATERIAL			Procedure for preparation of EPDM compound GEM 267
FINISH	SIZE A	CODE IDENT NO. 1F668	DRAWING NO. 10589
DO NOT SCALE DRAWING	SCALE		SHEET 1 OF 8

1. SCOPE

This procedure establishes the formulation, mixing methodology and steps for preparing GEM 267 rubber compounds intended for use as geothermal packer seal elements.

2. APPLICABLE DOCUMENTS

The following documents form a part of this specification to the extent specified herein. Later issues of these documents may be used at the option of the supplier providing no degradation of the product ensues.

Federal

Q-A-51

Acetone, Technical

American Society for Testing and Materials

ASTM D2516

Nomenclature for Rubber-Grade Carbon Blacks

ASTM D15

Compound and Sample Preparation for Physical Testing of Rubber Products.

ASTM D412

Tension Testing of Vulcanized Rubber

ASTM D2240

Indentation Hardness of Rubber and Plastics By Means of a Durometer, Test for

3. REQUIREMENTS

3.1 Material. All materials used for the preparation of these rubber compounds shall be formulated and processed to meet the requirements of this procedure. All materials shall be homogeneous, clean and suitable for the purpose intended.

3.2 Processing. The compounds shall be prepared according to this procedure.

3.3 Mechanical Properties. The compounded rubber shall have properties according to this procedure.

- 3.4 Workmanship. Each batch of rubber shall be prepared, handled and stored to minimize contamination. Contamination is herein defined as the presence of any material in the compound which is visible to the unaided eye. Contaminated rubber may be removed from the compound if it does not exceed 1% by weight of the compound at the time of removal. If the contaminated rubber exceeds 1% by weight, the compound must be discarded.

4. QUALITY ASSURANCE PROVISIONS

- 4.1 Acceptance. The supplier of materials under this procedure shall certify that each batch conforms to all requirements of the procedure. Certification shall include the actual results of all laboratory tests used to determine conformance. A batch is defined herein as the quantity of homogeneous material compounded on a rubber mill at one time.
- 4.2 Rejection. A batch of material which does not meet the requirements of one or more tests under this procedure may be retested once. Failure to meet the requirements with the second testing shall be cause for rejection of the material. Criteria for rejection are established by Table I, Table III and paragraph 3.4.
- 4.3 Test Methods. Qualification and acceptance testing of the material to the requirements of this procedure shall be in accordance with the following:
- 4.3.1 Tensile Strength and Elongation. The tensile strength and ultimate elongation shall be determined in accordance with ASTM D412 using Die "C" for the specimens. Results shall conform to the requirements of Table II.
- 4.3.2 Hardness. The hardness shall be determined in accordance with ASTM D2240. Results shall conform to the requirements of Table II.
- 4.4 Mixing. This compound shall be formulated according to the recipes and tolerances given in Table I.

TABLE I.
FORMULATION OF GEM 267 COMPOUND

Item	Seq. No.	Component Description	phr	Tolerances
a	1	Nordel 1660 (DuPont)	100	$\pm 2\%$
b	2	Statex 160 (N110) (Cities Service)	75	$\pm 2\%$
c	2	Cyanox 2246 (American Cyanamid Co.)	0.5	$\pm .5\%$
d	4	Di-Cup R (Harwick Chemical Corp.)	3.5	$\pm .5\%$
e	1	Hypalon 20 (DuPont)	5.0	$\pm 1\%$
f	2	Thermoguard S (M & T Chemicals Inc.)	5.0	$\pm 1\%$
g	3	Polybutadiene, #6081 (Polysciences, Inc.)	20	$\pm 1\%$

NOTE: The tolerances show the degree of accuracy required for weighing each individual component and the required material balance for the total compound ($\pm 5\%$). This latter value includes losses due to removal of contaminated material. Adjustments to the tolerances may be warranted as more experience is accumulated.

The compound shall be mixed on a two-roll rubber mill precleaned with solvent such as acetone. All parts of the equipment which could come in contact with the compound during the mixing operation shall be cleaned. The floor adjacent to the mill shall be swept to remove contaminants.

4.5 Mixing Procedure.

4.5.1. Premix

- 4.5.1.1 Combine enough of item b with item g to make a dry mix and set aside for later addition. Mix thoroughly by heating g & b to 125⁰F and maintaining while mixing.
- 4.5.1.2 Combine c and f making sure they are thoroughly mixed, then carefully mix into it 1/3 of b, sprinkling in a little at a time, while adding the balance of b.

4.5.2 Final Mix

- 4.5.2.1 Combine items a and e on mill and run several minutes to make the banded rubber warm and pliable.
- 4.5.2.2 Slowly add mixture resulting from 4.5.1.2. As each component or combination of components is added to the mill, frequent cutting of the rubber should be accomplished to encourage uniform mixing.
- 4.5.2.3 In sequence add items g and d with frequent cross-cutting.

4.6 Curing Procedures

4.6.1 Test Sheets

- 4.6.1.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.1.2 Remove stock from mill when approximate thickness of 100 mils is attained.
- 4.6.1.3 Cut out a 5.75" by 5.75" square from sheet making sure to mark mill mixing direction.
- 4.6.1.4 Put sample into a preheated 75 mil ASTM sheet mold, such that mill direction is identifiable.
- 4.6.1.5 Place loaded mold into heat platens at 350⁰F for 60 minutes at 20 tons force. After one minute at force "bump" sample 3 times by releasing force to almost zero and then reapplying it to 20 tons.

4.6.1.6 After step 4.6.1.5, remove sample from mold and follow post-curing procedures.

4.6.2. Packer Seals

4.6.2.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.

4.6.2.2 For a 2.75 inch OD packer seal, the following procedure is used. Place loaded mold into heat platens at 350°F for 90 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of force change from 50 tons to just above zero, then repressuring to 50 tons.

4.6.2.3 After 4.6.2.2, remove sample from mold and follow post-curing procedure.

4.6.3. O-Rings

4.6.3.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.

4.6.3.2 For a compression mold which makes 4 each 2-329 O-rings the following procedure is used. Place loaded mold into heat platens at 350°F for 60 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of force change from 50 tons to just above zero, then repressuring to 50 tons.

4.6.3.3 After 4.6.3.2, remove sample from mold and follow post-curing procedure.

4.7 Post Curing Procedure

4.7.1 Immediately upon removing cured sample from mold, place sample into 350°F preheated, nitrogen atmosphere oven chamber and continue temperature environment as follows:

<u>Period</u>	<u>Chamber Temp</u>
1st hour	400°F
1 - 2 hours	450°F
2 - 3 hours	500°F
3 - 8.0 hours	550°F

After 8 hours cool to at least 300°F in nitrogen oven.

4.7.2 Upon cooling the sample is ready for intended application.

4.8 Properties. Properties of the compound shall conform to the values and tolerances shown in Table II on the following page.

TABLE II
TYPICAL PROPERTIES OF COMPOUND GEM 267

Property, Units	Median Value/Tolerance*	
	Virgin	Chem Aged**
Ultimate Tensile Strength @ RT, psi	1290 + 325	1240 + 310
Ultimate Elongation at Break, @ RT, %	110 + 28	120 + 30
Shore A Hardness @ 260°C	90 ± 6	90 ± 6
Extrusion Resistance @ 260°C, psia	14 + 4	14 + 4

*Median values have been selected based on test data and tolerances have been selected arbitrarily. It is recommended that these selected values be reviewed and adjusted after more experience is generated.

**Chemical Effects Test Procedure TP10582

4.9 Packaging. When cooled to ambient room temperature (hand test) the rubber shall be cut into appropriate size slabs, wrapped in plastic film and boxed. The box shall be closed to prevent contamination during subsequent handling and storage.

4.10 Marking. The box shall be identified in a clear manner with the following information:

Compound Number

Date of Compounding

Supplier's Name or Other Identification

"STORE IN A COOL, DRY PLACE"

APPENDIX E

APPLICATION		REVISION			
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ARE: FRACTIONS DECIMALS ANGLES ± .XX ± ± .XXX ±	CONTRACT NO.					
	APPROVALS	DATE				
	MATERIAL	DRAWN R. Sedwick <i>[Signature]</i> 11 JUN 79		Procedure for preparation of EPDM/Fluoroelastomer Blend Compound GEM 275		
	FINISH	CHECKED				
DO NOT SCALE DRAWING			SIZE A	CODE IDENT NO. 1F668	DRAWING NO. 10669	
			SCALE		SHEET 1 OF 8	

1. SCOPE

This procedure establishes the formulation, mixing methodology and steps for preparing GEM 275 rubber compounds intended for use as geothermal packer seal elements.

2. APPLICABLE DOCUMENTS

The following documents form a part of this specification to the extent specified herein. Later issues of these documents may be used at the option of the supplier providing no degradation of the product ensues.

Federal

Q-A-51

Acetone, Technical

American Society for Testing and Materials

ASTM D2516

Nomenclature for Rubber-Grade Carbon Blacks

ASTM D15

Compound and Sample Preparation for Physical Testing of Rubber Products.

ASTM D412

Tension Testing of Vulcanized Rubber

ASTM D2240

Indentation Hardness of Rubber and Plastics By Means of a Durometer, Test for

3. REQUIREMENTS

3.1 Material. All materials used for the preparation of these rubber compounds shall be formulated and processed to meet the requirements of this procedure. All materials shall be homogeneous, clean and suitable for the purpose intended.

3.2 Processing. The compounds shall be prepared according to this procedure.

3.3 Mechanical Properties. The compounded rubber shall have properties according to this procedure.

- 3.4 Workmanship. Each batch of rubber shall be prepared, handled and stored to minimize contamination. Contamination is herein defined as the presence of any material in the compound which is visible to the unaided eye. Contaminated rubber may be removed from the compound if it does not exceed 1% by weight of the compound at the time of removal. If the contaminated rubber exceeds 1% by weight, the compound must be discarded.

4. QUALITY ASSURANCE PROVISIONS

- 4.1 Acceptance. The supplier of materials under this procedure shall certify that each batch conforms to all requirements of the procedure. Certification shall include the actual results of all laboratory tests used to determine conformance. A batch is defined herein as the quantity of homogeneous material compounded on a rubber mill at one time.
- 4.2 Rejection. A batch of material which does not meet the requirements of one or more tests under this procedure may be retested once. Failure to meet the requirements with the second testing shall be cause for rejection of the material. Criteria for rejection are established by Table I, Table II and paragraph 3.4.
- 4.3 Test Methods. Qualification and acceptance testing of the material to the requirements of this procedure shall be in accordance with the following:
- 4.3.1 Tensile Strength and Elongation. The tensile strength and ultimate elongation shall be determined in accordance with ASTM D412 using Die "C" for the specimens. Results shall conform to the requirements of Table II.
- 4.3.2 Hardness. The hardness shall be determined in accordance with ASTM D2240. Results shall conform to the requirements of Table II.
- 4.4 Mixing. This compound shall be formulated according to the recipes and tolerances given in Table I.

TABLE I.
FORMULATION OF GEM 275 COMPOUND

Item	Seq. No.	Component Description	phr	Tolerances
a	1	Nordel 1660 (DuPont)	50	<u>+2%</u>
b	2	VT-R-4590 (DuPont)	50	<u>+2%</u>
c	3	Hypalon 20 (DuPont)	2.5	<u>±.5%</u>
d	6	Austin Black (Cities Service)	7.5	<u>+1%</u>
e	6	Maglite K (C. P. Hall)	2.5	<u>±.5%</u>
f	4	Statex 160 (N110) (Cities Service)	52.5	<u>+2%</u>
g	6	Diak #7 (DuPont)	3.0	<u>±.5%</u>
h	6	Luperco 130XL (Ram Chemicals)	1.5	<u>±.5%</u>
i	6	Cyanox 2246 (American Cyanamid Co.)	.25	<u>±.5%</u>
j	6	Thermoguard S (M&T Chemicals Inc.)	2.5	<u>±.5%</u>
k	5	Polybutadiene, #6081 (Polysciences Inc.)	20	<u>+1%</u>

NOTE: The tolerances show the degree of accuracy required for weighing each individual component and the required material balance for the total compound (+5%). This latter value includes losses due to removal of contaminated material. Adjustments to the tolerances may be warranted as more experience is accumulated.

The compound shall be mixed on a two-roll rubber mill precleaned with solvent such as acetone. All parts of the equipment which could come in contact with the compound during the mixing operation shall be cleaned. The floor adjacent to the mill shall be swept to remove contaminants.

4.5 Mixing Procedure.

4.5.1 Premix

- 4.5.1.1 Add d to g until mixture is dry; break lumps until mixture is powdered. If all of d is used before mixture is dry, add f until dry state is reached.
- 4.5.1.2 Heat f & k to 125°F, then mix thoroughly, while still hot, to make a dry mix.
- 4.5.1.3 Combine e & h, then add i, then j, then d & g sprinkling one into the other, mixing until well dispersed after the addition of each component.

4.5.2 Final Mix

- 4.5.2.1 Combine items a, b & c on mill and run several minutes to make the banded rubber warm and pliable.
- 4.5.2.2 Slowly add f & k, then the mixture resulting from 4.5.1.3. As each component or combination of components is added to the mill, frequent cross-cutting of the rubber should be accomplished for uniform mixing.

4.6 Curing Procedures

4.6.1 Tests Sheets

- 4.6.1.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.1.2 Remove stock from mill when approximate thickness of 100 mils is attained.
- 4.6.1.3 Cut out a 5.75" by 5.75" square from sheet making sure to mark mill mixing direction.
- 4.6.1.4 Put sample into a preheated 75 mil ASTM sheet mold, such that mill direction is identifiable.
- 4.6.1.5 Place loaded mold into heat platens at 350°F for 60 minutes at 20 tons force. After one minute at force "bump" sample 3 times by releasing force to almost zero and then reapplying it to 20 tons.

4.6.1.6 After step 4.6.1.5, remove sample from mold and follow post-curing procedures.

4.6.2. Packer Seals

4.6.2.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.

4.6.2.2 For a 2.75 inch OD packer seal, the following procedure is used. Place loaded mold into heat platens at 350°F for 90 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of force change from 50 tons to just above zero, then repressuring to 50 tons.

4.6.2.3 After 4.6.2.2, remove sample from mold and follow post-curing procedure.

4.6.3. O-Rings

4.6.3.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.

4.6.3.2 For a compression mold which makes 4 each 2-329 O-rings the following procedure is used. Place loaded mold into heat platens at 350°F for 60 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of force change from 50 tons to just above zero, then repressuring to 50 tons.

4.6.3.3 After 4.6.3.2, remove sample from mold and follow post-curing procedure.

4.7 Post Curing Procedure

4.7.1 Immediately upon removing cured sample from mold, place sample into 350°F preheated, nitrogen atmosphere oven chamber and continue temperature environment as follows:

<u>Period</u>	<u>Chamber Temp</u>
1st hour	400°F
1 - 2 hours	450°F
2 - 3 hours	500°F
3 - 8.0 hours	550°F

After 8 hours cool to at least 300°F in nitrogen oven.

4.7.2 Upon cooling the sample is ready for intended application.

4.8 Properties. Properties of the compound shall conform to the values and tolerances shown in Table II on the following page.

TABLE II.
TYPICAL PROPERTIES OF COMPOUND GEM 275

Property, units	Median Value/Tolerance*	
	Virgin	Chem Aged**
Ultimate Tensile Strength @ RT, psi	1390 + 350	1280 + 320
Ultimate elongation at break, @ RT, %	60 + 15	30 + 8
Shore A Hardness @ 260°C	98 ± 6	96 ± 6
Extrusion Resistance @ 260°C, psia	14 + 5	14 + 5

* Median values have been selected based on test data and tolerances have been selected arbitrarily. It is recommended that these selected values be reviewed and adjusted after more experience is generated.

** Chemical Effects Test Procedure TP 10582

4.9 Packaging. When cooled to ambient room temperature (hand test) the rubber shall be cut into appropriate size slabs, wrapped in plastic film and boxed. The box shall be closed to prevent contamination during subsequent handling and storage.

4.10 Marking. The box shall be identified in a clear manner with the following information:

Compound Number

Date of Compounding

Supplier's Name or Other Identification

"STORE IN A COOL, DRY PLACE"

APPENDIX F

APPLICATION		REVISION			
NEXT ASSY	USED ON	LTR	DESCRIPTION	DATE	APPROVED

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ARE: FRACTIONS DECIMALS ANGLES $\pm .XX \pm \pm$ $.XXX \pm$	CONTRACT NO.		1555 PLACENTIA AVENUE NEWPORT BEACH CALIFORNIA 92660
	APPROVALS	DATE	
	DRAWN R. Sedwick	11 JUN 79	
	CHECKED		
MATERIAL			Procedure for preparation of Propylene-TFE Compound GEM 291
FINISH			SIZE A CODE IDENT NO. 1F668 DRAWING NO. 10670
DO NOT SCALE DRAWING			SCALE SHEET 1 OF 8

1. SCOPE

This procedure establishes the formulation, mixing methodology and steps for preparing the GEM 291 rubber compound intended for use as Geothermal Packer seal elements.

2. APPLICABLE DOCUMENTS

The following documents form a part of this specification of the extent specified herein. Later issues of these documents may be used at the option of the supplier providing no degradation of the product ensues.

Federal

Q-A-51 Acetone, Technical

American Society for Testing and Materials

ASTM D2516 Nomenclature for Rubber-Grade Carbon Blacks

ASTM D15 Compound and Sample Preparation for Physical
Testing of Rubber Products

ASTM D412 Tension Testing of Vulcanized Rubber

ASTM D2240 Indentation Hardness of Rubber and Plastics
By Means of a Durometer, Test for

3. REQUIREMENTS

3.1 Material. All materials for the preparation of these rubber compounds shall be formulated and processed to meet the requirements of this procedure. All materials shall be homogeneous, clean and suitable for the purpose intended.

- 3.2 Processing. The compounds shall be prepared according to this procedure.
- 3.3 Mechanical Properties. The compounded rubber shall have properties according to this procedure.
- 3.4 Workmanship. Each batch of rubber shall be prepared, handled and stored to minimize contamination. Contamination is herein defined as the presence of any material in the compound which is visible to the unaided eye. Contaminated rubber may be removed from the compound if it does not exceed 1% by weight of the compound at the time of removal. If the contaminated rubber exceeds 1% by weight, the compound must be discarded.

4. QUALITY ASSURANCE PROVISIONS

- 4.1 Acceptance. The supplier of materials under this procedure shall certify that each batch conforms to all requirements of the procedure. Certification shall include the actual results of all laboratory tests used to determine conformance. A batch is defined herein as the quantity of homogeneous material compounded on a rubber mill at one time.
- 4.2 Rejection. A batch of material which does not meet the requirements of one or more tests under this procedure may be re-tested once. Failure to meet the requirements with the second testing shall be cause for rejection of the material. Criteria for rejection are established by Table I, Table II and paragraph 3.4.
- 4.3 Test Methods. Qualification and acceptance testing of the material to the requirements of this procedure shall be in accordance with the following:

4.3.1 Tensile Strength and Elongation. The tensile strength and ultimate elongation shall be determined in accordance with ASTM D412 using Die "C" for the specimens. Results shall conform to the requirements of Table II.

4.3.2 Hardness. The hardness shall be determined in accordance with ASTM D2240. Results shall conform to the requirements of Table II.

4.4 Mixing. This compound shall be formulated according to the recipes and tolerances given in Table I.

TABLE I
FORMULATION GEM 291

Item	Seq. No.	Component Description	phr	Tolerances
a	1	AFLAS 100 (Asahi Glass)	100	±2%
b	2	Statex 160 (N110) (Cities Service)	50	±2%
c	3	Maglite K (C.P. Hall)	3.0	±.5%
d	3	Luperco 130 XL (RAM Chemicals)	5.0	±1%
e	3	Diak #7 (DuPont)	5.0	±1%
f	4	Polybutadiene, #6081 (Polysciences, Inc.)	5.0	±1%

NOTE: The tolerances show the degree of accuracy required for weighing each individual component and the required material balance for the total compound (±5%). This latter value includes losses due to removal of contaminated material. Adjustments to the tolerances may be warranted as more experience is accumulated.

The compound shall be mixed on a two-roll rubber mill precleaned with solvent such as acetone. All parts of the equipment which

would come in contact with the compound during the mixing operation shall be cleaned. The floor adjacent to the mill shall be swept to remove contaminants.

4.5 Mixing Procedure

4.5.1 Premix

- 4.5.1.1 Add b to e until mixture is dry; break lumps until mixture is powdered.
- 4.5.1.2 Heat b and f to 125°F, then mix thoroughly, while still hot, enough b to f to make a dry mix.
- 4.5.1.3 Combine c and d, then add b + e sprinkling one into the other, mixing until well dispersed after the addition of each component.

4.5.2 Final Mix

- 4.5.2.1 Add b, then mixture resulting from 4.5.1.3, then b + f to banded rubber on mill. As each component is added to the mill, frequent cross-cutting of the rubber should be accomplished for uniform mixing.

4.6 Curing Procedures

4.6.1 Test Sheets

- 4.6.1.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.1.2 Remove stock from mill when approximate thickness of 100 mils is attained.
- 4.6.1.3 Cut out a 5.75" by 5.75" square from stock making sure to mark mill mixing direction.
- 4.6.1.4 Put sample into a preheated 75 mil ASTM sheet mold such that mill direction is identifiable.
- 4.6.1.5 Place loaded mold into heat platens at 350°F for 20 minutes at 20 tons force. After one minute at

force, "bump" sample 3 times by releasing pressure to almost zero and then repressurizing to 20 tons.

- 4.6.1.6 After step 4.6.1.5, remove sample from mold and follow post-curing procedure.

4.6.2 Packer Seals

- 4.6.2.1 Freshen stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.2.2 For a 2.75 inch OD packer seal, the following procedure is used. Place loaded mold onto heat platens at 250°F for 30 minutes at 50 tons force. After one minute subject sample to a "bump" procedure consisting of 3 cycles of pressure change from 50 tons to just above zero, then repressuring to 50 tons.
- 4.6.2.3 Raise cure temperature to 350°F. Upon reaching 350°F cure for 60 additional minutes.
- 4.6.2.4 After 4.6.2.3, remove sample from mold and follow post-curing procedure.

4.6.3 O-Rings

- 4.6.3.1 Freshen basic stock by banding on mill for several minutes until stock is warm and pliable.
- 4.6.3.2 For a compression mold which makes 4 each 2-329 O-rings the following procedure is used. Place loaded mold into heat platens at 250°F for 30 minutes at 50 tons pressure. After one minute subject sample to a "bump" procedure consisting of 3 cycles of pressure change from 50 tons to just above zero, then repressuring to 50 tons.
- 4.6.3.3 Raise cure temperature to 350°F. Upon reaching 350°F continue curing for another 20 minutes.

4.6.3.4 After 4.6.3.3, remove sample from mold and follow post-curing procedure.

4.7 Post Curing Procedure

4.7.1 Immediately upon removing cured sample from mold, place sample into 350°F preheated, nitrogen atmosphere oven chamber and continue temperature environment as follows:

<u>Period</u>	<u>Chamber Temp.</u>
1st 4½ hours	350°F
4½ - 5 hours	400°F
5 - 5½ hours	450°F
5½ - 8 hours	500°F

After 8 hours cool to at least 300°F in nitrogen oven.

4.7.2 Upon cooling, the sample is ready for intended application.

4.8 Properties. Properties of the resultant compounds shall conform to the values and tolerances shown in Table II on the following page.

TABLE II
TYPICAL PROPERTIES OF COMPOUND GEM 291

Property, Units	Median Value/Tolerance*	
	Virgin	Chem Aged**
Ultimate Tensile Strength @ RT, psi	1870 + 470	1730 + 430
Ultimate Elongation at Break, @ RT, %	110 + 28	130 + 33
Shore A Hardness @ 260°C	95 ± 6	95 ± 6
Extrusion Resistance @ 260°C, psia	14 + 5	12 + 5

*Median values have been selected based on test data and tolerances have been selected arbitrarily. It is recommended that these selected values be reviewed and adjusted after more experience is generated.

**Chemical Effects Test Procedure TP10582.

4.9 Packaging. When cooled to ambient room temperature (hand test) the rubber shall be cut into appropriate size slabs, wrapped in plastic film and boxed. The box shall be closed to prevent contamination during subsequent handling and storage.

4.10 Marking. The box shall be identified in a clear manner with the following information:

Compound Number
Date of Compounding
Supplier's Name or Other Identification
"STORE IN A COOL, DRY PLACE"