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ADDENDUM TO MATERIAL SELECTION GUIDELINES FOR GEOTHERMAL ENERGY UTILIZATION SYSTEMS

Part I: Extension of the Field Experience Data Base
Part II: Proceedings of the Geothermal Engineering and Materials (GEM) Program Conference (San Diego, CA, 6–8 October 1982)

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PITFALLS OF ELASTOMER COMPATIBILITY TESTING

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ABSTRACT

An extensive compatibility test program was conducted starting with 34 compounds and six 190C fluids. Both immersion tests and simulation tests were conducted for time periods ranging from 46 hours to over six months. Deficiencies in both types of tests were determined. Immersion tests, while useful for reducing the number of candidate compounds, can easily lead to incorrect conclusions. It is essential that simulation tests be conducted before a final elastomer is selected for use in a critical design.

INTRODUCTION

In early 1980, Brookhaven National Laboratory sponsored an extensive test program to determine the best elastomers for use in geothermal binary power-plant applications. The program, now complete, met its objectives. In addition, much was learned concerning the idiosyncrasies of such compatibility testing. The purpose of this paper is to discuss main observations and conclusions regarding elastomer testing in hostile environments.

TEST PROGRAM APPROACH

The program plan is shown in Figure 1. The program started with the short-term testing of a large number of elastomers, and ended with the long-term testing of only a few believed to be the best.

Equipment and elastomeric parts manufacturers were contacted to find the best currently available high-temperature elastomers for the binary power plant application. Tensile specimens of 34 such compounds were immersion tested for five days (120 hours) in six 190C (375F) fluids of interest: isobutane, brine, ASTM No. 1 oil, ASTM No. 3 oil, Pacer DHT-185M synthetic oil, and Chevron Cylinder Grade 460X oil. The best eight were selected based upon the least change in weight, volume, ultimate tensile strength and elongation, and hardness.

These eight were then simultaneously tested a) by immersion in five 190C (375F) fluids for six months and b) as O-rings for 46 hours at 190C, 230C, and 265C (375F, 450F, 510F) (accelerated ageing) in three fluids and at a differential pressure of 21 MPa (3000 psi).

Based upon these O-ring tests, four compounds were selected for testing as O-rings for approximately six months in three fluids at 204C (400F) and 21 MPa differential pressure.

IMMERSION TEST PITFALLS

Tensile specimens of each compound were tested in autoclaves generally at the vapor pressure of the fluid. Such tests are economical, but can lead to incorrect conclusions.

Mechanical Property Changes

In the immersion testing; weight, volume, ultimate tensile properties, and hardness are measured before and after ageing the elastomer in the heated fluid of interest. If these properties don't change, one would assume that the elastomer is immune to that fluid and would be an excellent choice for the application.

However, changes are likely to occur -- so the obvious thing to do is to select those that change the least. This is not always valid because the properties that can be measured in immersion tests are not necessarily those required for a good seal material.

Table I shows the percentage changes for eight compounds after immersion for 120 hours in 190C ASTM No. 1 oil. (These eight were selected from the 34 tested as the most promising for one or more of the six fluids of interest.)

The only easy polymer to delete is EPDM (which the immersion tests indicated was good in brine and isobutane). These eight compounds were then tested as O-rings with ASTM No. 1 oil at a 21 MPa (3000 psi) differential pressure for 46 hours; tests were conducted at 190C, 230C, and 265C (375F, 450F, and 510F).

The EPDMs were ranked the best of the eight. The EPDMs did swell about 10%, but remained circular in cross section. All others exhibited various degrees of permanent set -- the worst being almost square in cross section. In addition, the AFLAS and Kalrez compounds extruded slightly.

Later in the 6-month long O-ring tests, the EPDM O-ring did experience very slow nibbling. (More

about this later.) However, they are still ranked best or nearly so.

Immersion tests submit the specimens to the thermochemical effects of a hot fluid environment. With experience, one can sort through the large quantity of data and narrow the list candidates.

However, as the above illustration shows, immersion tests alone are insufficient for selecting the correct elastomer for a hostile environment. Simulation tests which produce the mechanical effects as well as the thermochemical effects are essential.

Test Duration

Immersion tests usually are conducted for less than five days. Results from the two and six-month tests showed that even five days can be insufficient for long-term applications.

The five-day tests gave no indication that any of the eight compounds were becoming brittle in any of the oils. (Table I for instance.) However, at two months, Precision Fluoroelastomer 16959 was brittle after immersion in both ASTM No. 1 oil and Chevron Cylinder Grade 460X oil. After six months, L'Garde Viton 501 and Vernay Laboratory VL1503M3 in Chevron Cylinder Grade 460X oil joined the brittle group. In addition, the ultimate elongations of the Precision and Vernay fluoroelastomers in Pacer DHT-185M oil had decreased 58% -- indicating they too might be heading for the brittle column.

Figure 2 shows average ultimate elongation changes for three polymers (2 compounds each in three oils). The loss in elasticity for the fluoroelastomers is clear -- but only after 2 months or more of testing. The EPDM and AFLAS compounds look all right.

Therefore, short-term immersion tests may lead to erroneous conclusions also.

Rarely does one have the luxury of testing for the duration of the product's desired life. Accelerated ageing tests may be the solution. Arrhenius observed that reaction rates increased with increasing temperature.

The problem with accelerated ageing is that new reactions may start at some higher temperature. (As an analogy, accelerated ageing of ice above 0°C would give invalid results.) Therefore, accelerated ageing might result in dismissing a candidate that could outperform others at a lower temperature. It is important then to stay within the reactivity continuum and not transcend thresholds to new reactions.

Correct Test Fluid

The tests in oil also showed that immersion testing should be conducted in the fluid of interest -- not in a "similar" fluid.

In reviewing the short-term immersion test data, it appeared that ASTM No. 1 oil, Chevron Cylinder Grade 460X oil and Pacer DHT-185M oil had about the same affect on the elastomers. (An exception noted was that the Pacer oil affected EPDM compounds less.) The longer term immersion tests showed that Pacer oil generally affected all elastomers least (of the three oils) and Chevron Cylinder Grade 460X oil affected them generally the most. Once observing this, another review of the short-term data supported this conclusion.

The relative rankings of elastomers can change from oil to oil also. A dramatic example of this was with Kalrez 1018 which tends to be a superior compound in oil immersion tests. In the Pacer and ASTM No. 1 oils, it was superior; it could almost be considered immune to these 190C (375F) fluids. After two months in Chevron Cylinder oil, however, it absorbed the oil gaining weight and volume, developed numerous longitudinal cracks resulting in reduced ultimate strength and elongation, and lost 20% of its hardness.

Charts showing performance of polymers or specific compounds in generic type fluids can provide valuable guidance. For hostile environments, however, it is essential to test the compounds in the specific fluids of interest -- and as noted earlier, it is important to use immersion tests strictly for screening, and simulation tests for making the final decision. Field tests should be used for confirmation.

ACCELERATED AGEING O-RING TEST PITFALLS

Although the immersion tests were all conducted at 190C (375F), the O-ring tests were conducted at 190C, 230C, and 265C (375F, 450F, 510F) for 46 hours to simulate 190C (375F) for approximately 2 days, 1 month and 1 year, respectively, at a 21 MPa (3000 psi) differential pressure. In general, and as expected, damage such as permanent set, nibbling, extrusion (and of course failure) increased with temperature. (Also as expected, there was no indication that thresholds to new reactions were transcended over this temperature range.)

Two fluoroelastomers and two EPDMs were then tested in three of the fluids at 204C (400F) for six months. Failures occurred in less time predicted by the short-term accelerated O-ring tests and the Arrhenius equation. Inspection of the O-rings after testing, showed that nibbling or extrusion was more common in the long-term tests.

For instance, the EPDMs tested with isobutane and ASTM No. 1 oil for 46 hours showed no visible signs of damage except for the Parker EPDM E692-75 in 265C (510F) isobutane; a large section had been nibbled away. In the long-term tests, both EPDMs showed some degree of nibbling. In isobutane, it was enough to cause catastrophic failure. In 204C (400F) ASTM No. 1 oil for 209 days (6.8 months), there was moderate nibbling and no failures. (In the latter tests, L'Garde Viton 501 and Vernay Fluoroelastomer VL1503M3 both experienced slight nibbling, severe permanent set and no failures. The Vernay compound was brittle as was seen in the long-term immersion tests.)

Based upon all the O-ring test data, mechanical damage (such as permanent set, nibbling and extrusion) does increase with temperature. However, this is somewhat "proportional" to the thermochemical degradation produced by accelerated ageing. In addition, there can be mechanical damage that is time dependent only. (Nibbling is visualized as rubber entering the gap, tearing off because of tension or shear, and being replaced by new rubber to continue the process.)

Therefore, accelerated ageing (increased temperature) simulation tests can result in less mechanical damage than will be seen at the operating temperature. Perhaps mechanical damage can be accelerated more realistically by higher pressure, but it would take considerable work to develop such a relationship. Accelerated aged simulation tests are still the most valuable tool for expediently evaluating long-term elastomer-fluid compatibility.

SUMMARY CONCLUSIONS

Immersion tests provide a lot of data economically. However, results must be interpreted with caution using analysis and experience.

1. Based upon the results of EPDM compounds in oil, screening out polymer systems based on immersion test data alone may be a mistake -- unless perhaps all compounds within the group become brittle. It is essential that simulation testing be conducted for accurate evaluation for hostile environments.

2. For long-term applications, immersion testing must be conducted over a long time period or at some limited but increased temperature. Careful judgement must be exercised to avoid extrapolating short-term data which can be extremely erroneous.

3. Immersion testing should be conducted in the exact fluid of interest. Compatibility data from similar fluids can provide guidance, but the exact fluid is essential for critical applications.

Simulation testing is essential for accurate evaluation of elastomers for hostile environments. It is superior to immersion testing (although more expensive) in that it provides the mechanical (stresses) damage mechanisms as well as thermochemical effects. If long-term simulation tests aren't practical, carefully executed increased temperature (accelerated aged) simulation tests are recommended even though mechanical damage may be less severe than in actual use.

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BIBLIOGRAPHY

Friese, G. J., "Elastomer Compatibility With Brine, Isobutane, and Oils", 1981 Annual Meeting, Geothermal Resources Council, 25-29 October 1981, Houston, Texas.

Friese, G.J., Performance of Elastomers in Hot Brine, Isobutane and Oils, L'Garde, Inc. Publication Number LTR-81-GF-102, September 1981.

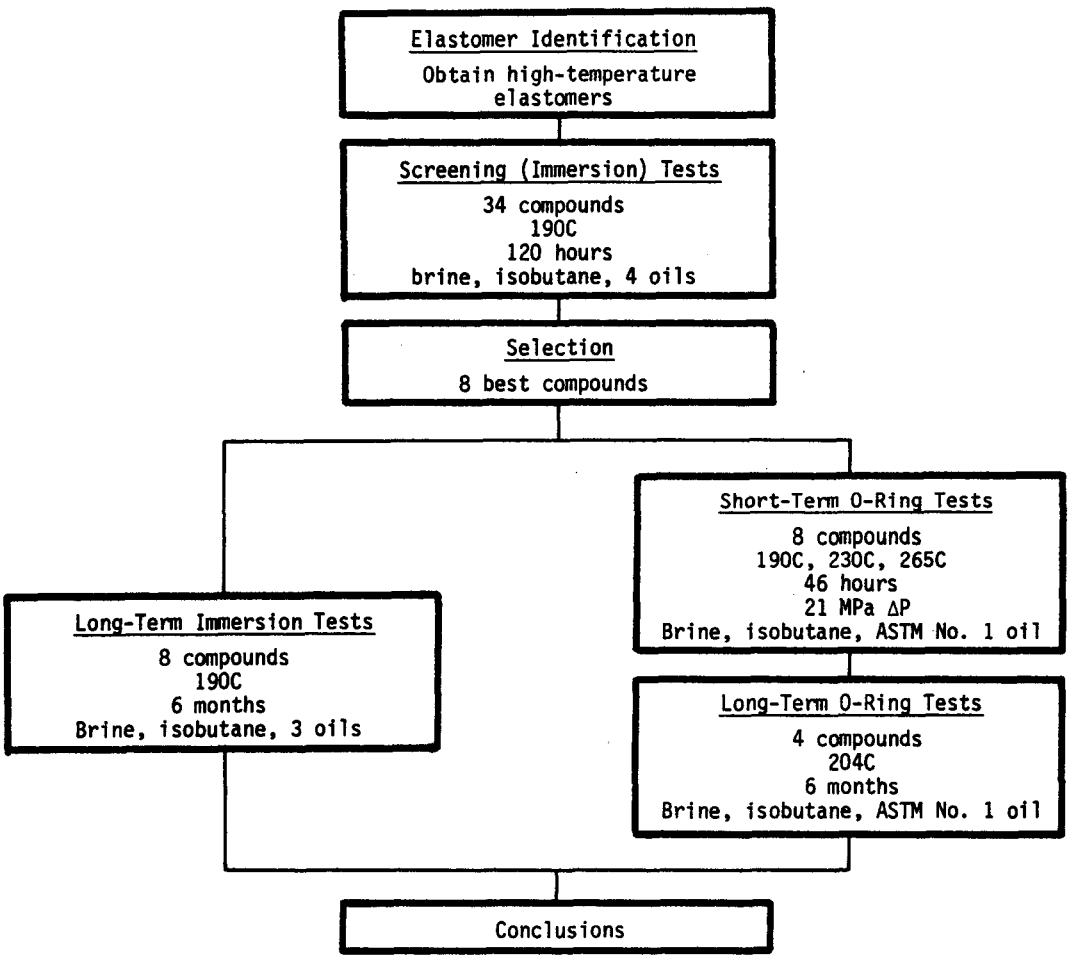

FIGURE 1. PROGRAM APPROACH

TABLE I. EFFECT OF 190C ASTM NO. 1 OIL FOR 120 HOURS

Compound	Wt. Chg. (%)	Swell (%)	Ult. Stress (%)	Ult. Elong. (%)	Hardness (%)
EPDM:					
L'Garde Y267	+58	+69	-48	-7	-19
Parker E692-75	+44	+61	-38	-21	-17
Fluoroelastomers:					
L'Garde 501	-1	+0	+7	+3	+6
Precision 16959	-1	+0	-11	-12	+3
Vernay VL1503M3	-0	+0	-1	+0	+4
AFLAS					
L'Garde 291	+2	+4	-11	+19	-4
Seals Eastern 7170X14	-0	+2	-18	-1	+1
Perfluoroelastomer					
DuPont Kalrez 1018	-1	+1	+1	-10	+6

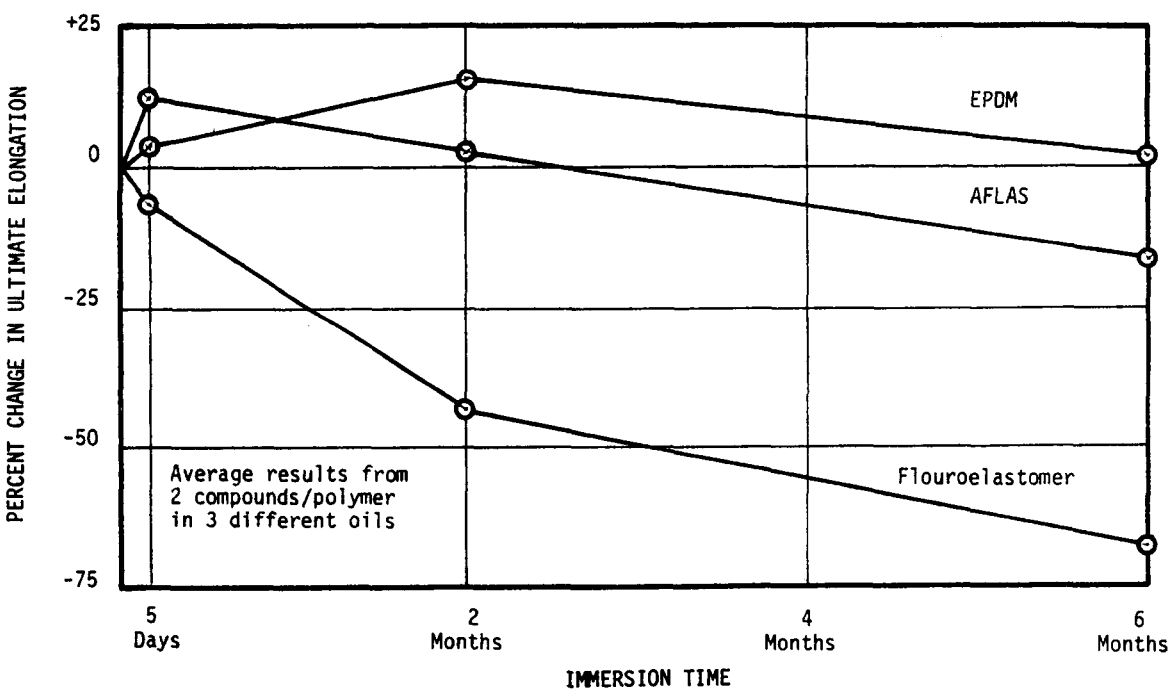

FIGURE 2. FLUOROELASTOMER COMPOUNDS BECOMING BRITTLE IN OIL