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Evaluation of Elastomers for Geothermal Well Applications

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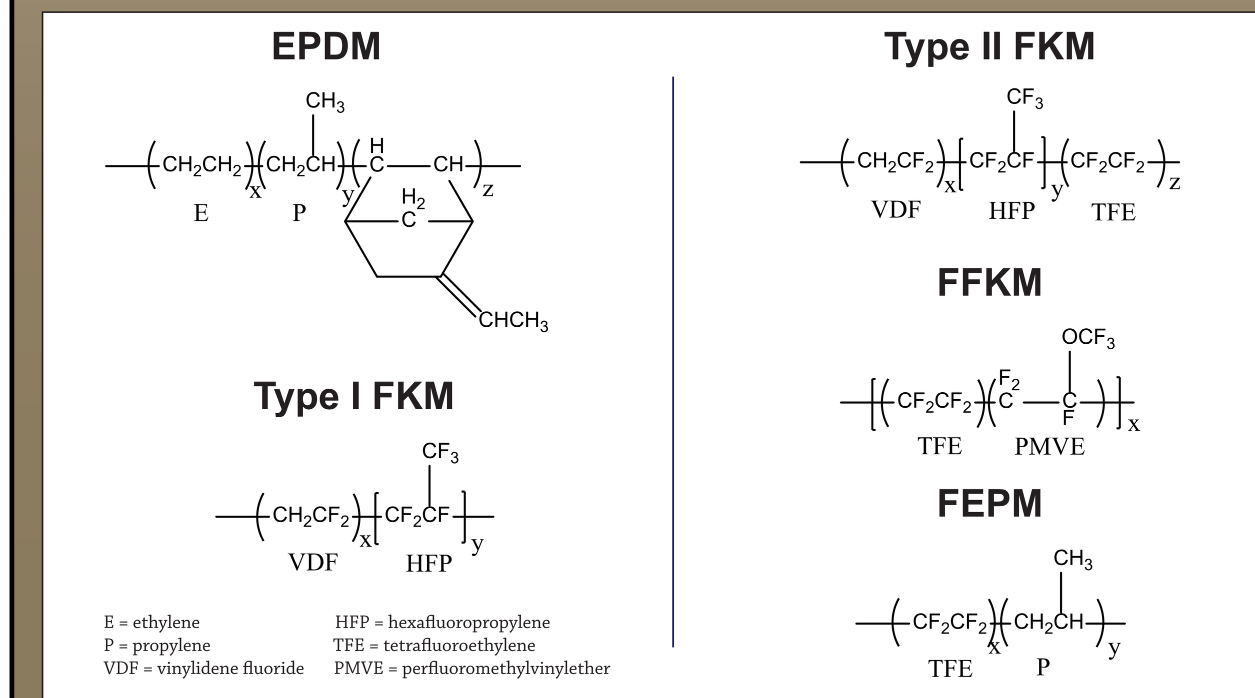
1. INTRODUCTION

The emphasis on sustainable energy has brought with it challenges associated with materials performance. In particular, geothermal wells push the boundaries of elastomer stability due to harsh environmental conditions, where temperatures around 300°C and pressures of 5000 psi or greater are not uncommon. Additionally, well brines and drilling fluids subject these materials to very severe chemical environments, which also impacts elastomer degradation and stability. The aim of this study is to understand how commercially available elastomers perform under geothermal well-like conditions and make recommendations to the community based on these results. This poster highlights the degradation chemistry and mechanical performance of several elastomers after aging in several different environments.

2. MATERIALS



E = ethylene
P = propylene
VDF = vinylidene fluoride
HFP = hexafluoropropylene
TFE = tetrafluoroethylene
PMVE = perfluoromethylvinylether

3. EXPERIMENTAL METHODS

Aging in Steam, N_2

5 cycles of steam/cooling in N_2.
One cycle = 300°C steam for 24 hrs, quench to 25 °C at 1200 psi.

Aging in Steam, Air

5 cycles of steam/cooling in air.
One cycle = 300°C steam for 24 hrs, quench to 25 °C at 1200 psi.

Aging in Drilling Fluid:

300°C, 7 days, ~1200 psi submerged in a drilling fluid mimic with pH 9-10.
Drilling fluid composition:

Major Components	Percent
Water	74-83
Barite	10-15
Bentonite	5-7
Caustic soda	0.3
Soda ash	1
Polyanionic cellulose	0.3-1.2
Xanthan gum	0.3-0.5
Starch	0.5-1

Aging in Brine:

300°C, 7 days, ~1200 psi submerged in a brine with pH 4-5.
Brine composition:

Major Components	Compounds	Percent
Cl^-	NaCl	13.5
Na^+	NaCl	6
Ca^{2+}	$CaCl_2$	2
K^+	KCl	1.5
Mg^{2+}	$MgCl_2$	0.9
Minor Components	-	**PPM**
CO_2	$NaHCo_3$	15,000
Fe^{2+}	$FeCl_2$	1000
Mn^{2+}	$MnCl_2$	930
Li^+	LiCl	410
Zn^{2+}	$ZnCl_2$	370
B^{3+}	H_3BO_3	330
Si^{4+}	Na_2SiO_3	250
Ba^{2+}	$BaCl_2$	130
H_2S	H_2SO_4	70

Thermal Cycle Aging:

24 hours at 300°C with water quenching to 25°C and hold for 5 hours - repeated five times.

Thermogravimetric Analysis (TGA):

Sample sizes ranged from approximately 10 - 50 mg. Ramp 20°C/min to 700°C on a TA Instruments TGA Q50 V20.10.

Fourier Transform Infrared Spectroscopy (FTIR):

Attenuated Total Reflection FTIR was used to identify any potential chemical changes in the elastomers after exposure to the different aging environments.

Modulus Profile Testing:

Modulus profiles were taken using a home-built instrument. The machine operates by scanning the surface with a parabolic tip at user-defined intervals (0.2 mm) and using displacement from a known force applied to each point on sample to calculate modulus. Samples are cross-sectioned and embedded in epoxy prior to running the experiment.

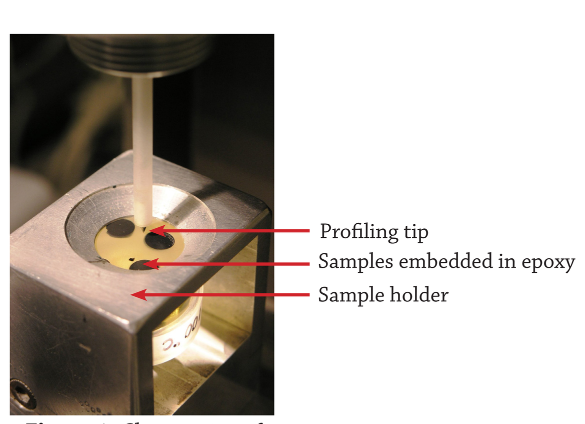
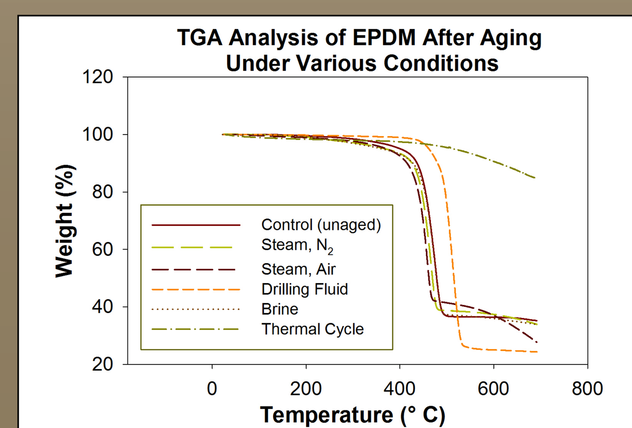


Figure 1. *Close-up view of modulus profiler set-up.*

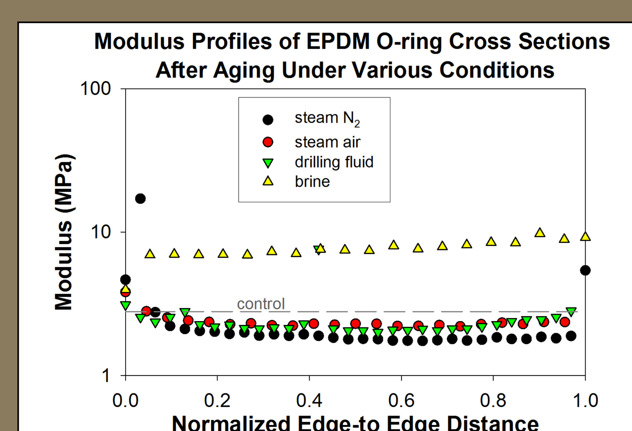
Figure 2. *Top: top-down, Bottom: side view of cross-sectioned o-rings embedded in epoxy.*

4. RESULTS & DISCUSSION

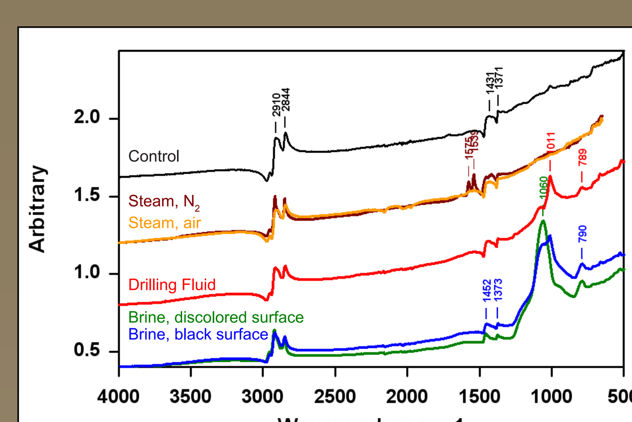
EPDM



- Good thermal stability under all aging conditions except thermal shock.
- Unexpectedly, thermal stability improved after aging in drilling fluid.

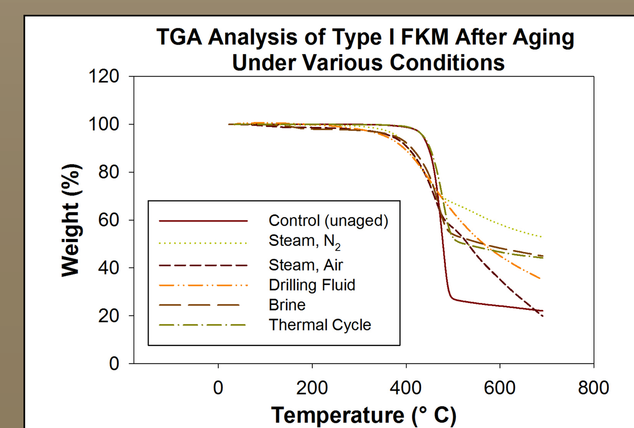


- Edge hardening with steam, N_2.
- Slight decrease in modulus under all aging conditions except brine.
- Modulus increased after brine exposure.

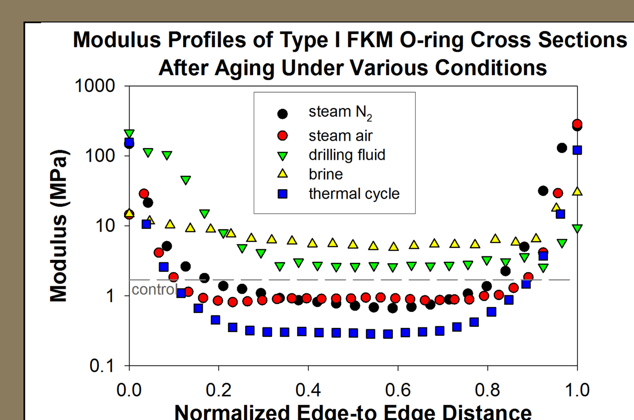


- Hydrocarbons at: 2910 and 2844 cm^{-1} (C-H asymmetric and symmetric stretching), 1431 (CH_2 scissoring), 1371 (CH_3 asymmetric bending).
- Steam in air and N_2 both showed bands from 1530 - 1580 cm^{-1}, indicating COO^- formation.
- Drilling fluid and brine had evidence of COO^- and C=C formation indicating some degradation.
- Peaks at 1050 and 1011 likely due to scale formation on surface.
- Thermal shock (not shown) had an absence of C-H peaks, indicating degradation of the hydrocarbon chain backbones.

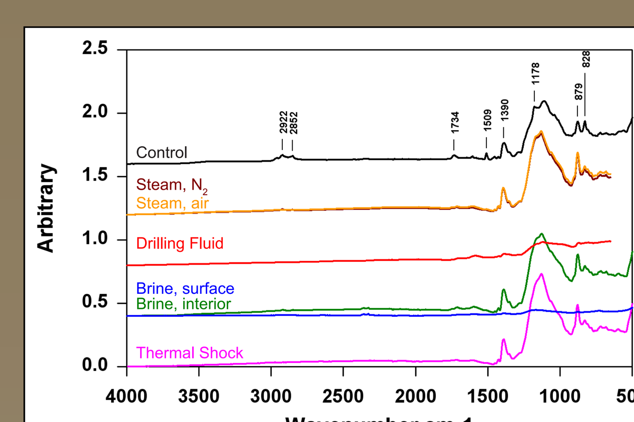
Type I FKM



- Poor thermal stability under all aging conditions except thermal shock.
- Worst thermal stability for: steam tests (N_2 and air), drilling fluid and brine.

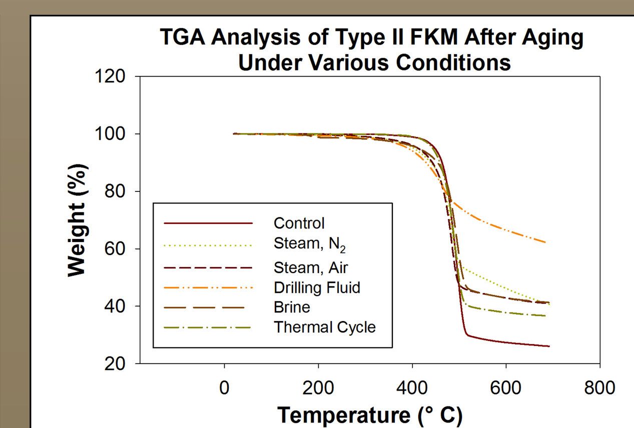


- Edge hardening under all conditions.
- Decrease in internal modulus after steam tests and thermal cycle aging.
- Internal modulus increase after brine and drilling fluid exposure.

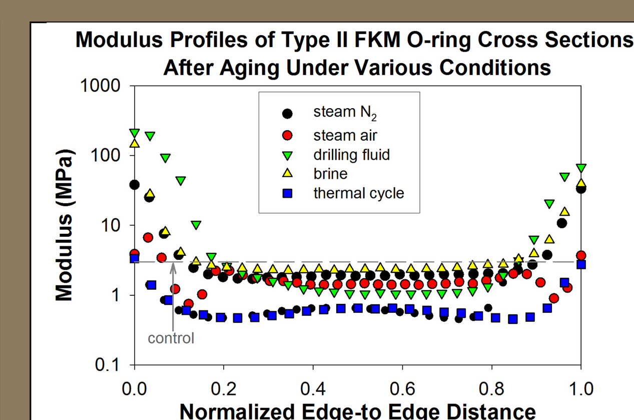


- VDF hydrocarbons at: 2922 and 2852 cm^{-1}.
- Fluorocarbons at: 1390 (C-F), 1178 (CF_2, asymmetric), 1134 (CF_2 symmetric), 879 cm^{-1} (CF_3).
- Steam/N_2 had decrease in C-H intensity + formation of bands at 1716 (C=O) and 1608 cm^{-1} (C=C), indicating oxidation of VDF group. Steam/air had no C-H, thus more degradation than Steam/N_2.
- Brine/drilling showed presence of C=C, C=O and COO^- (1536 cm^{-1}) and were severely degraded.
- Type I FKM was more resistant to thermal shock, but had degradation products relating to C=C, C=O and COOH.

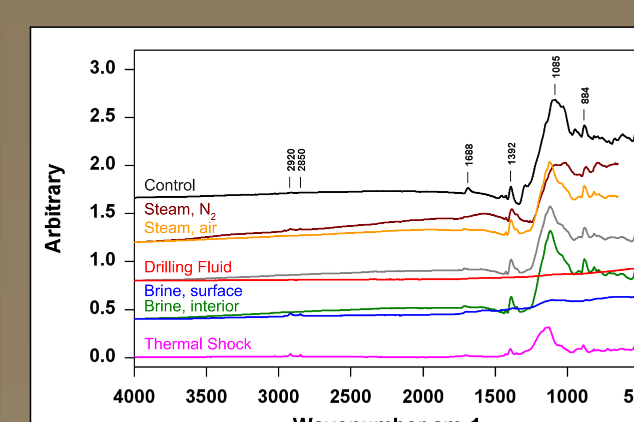
Type II FKM



- Poor thermal stability under all aging conditions except thermal shock.
- Thermal stability improved relative to Type I FKM.

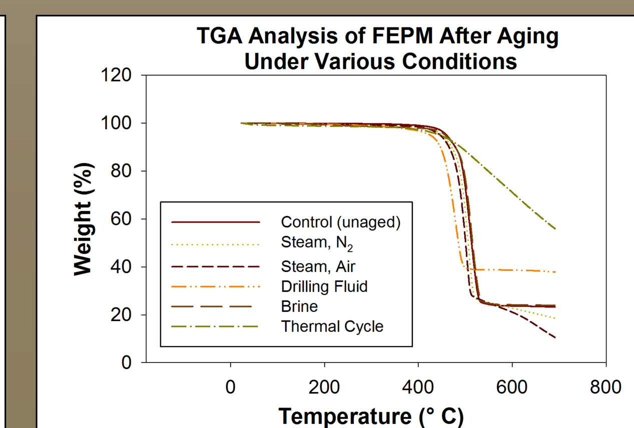


- Edge hardening for steam/N_2, drilling fluid and brine.
- "W" shaped curves for steam/air and thermal cycle.
- Decrease in internal modulus after most tests. Thermal cycle had largest decline.

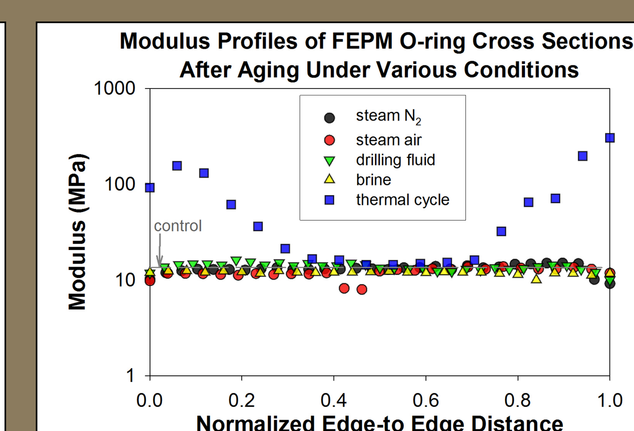


- VDF hydrocarbons at: 2920 and 2850 cm^{-1} less intense vs. FKM Type I (i.e. less VDF than Type I).
- Fluorocarbons at: 1392 (C-F), 1114 (CF_2, asymmetric), 1085 (CF_2 symmetric), 884 cm^{-1} (CF_3)
- Band at 1688 cm^{-1} may be due to water.
- Steam/N_2 had loss of C-H bands + formation of bands associated with C=O and C=C.
- Drilling fluid, brine and thermal shock samples showed presence of C=C, C=O, COOH and COO^- (1536 cm^{-1}) indicating oxidative degradation.

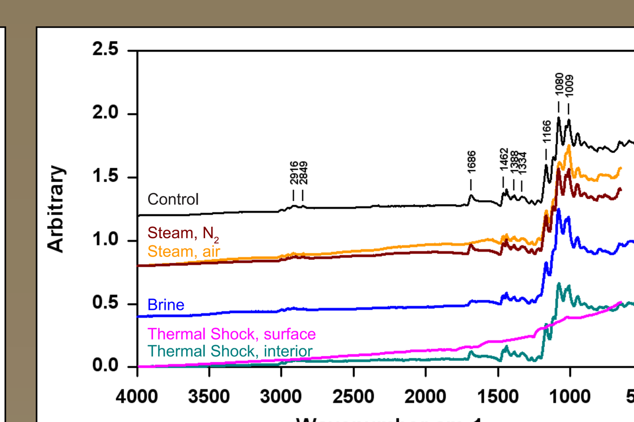
FEPM



- Good thermal stability under all aging conditions except thermal shock.
- Behavior similar to EPDM, except in drilling fluid.

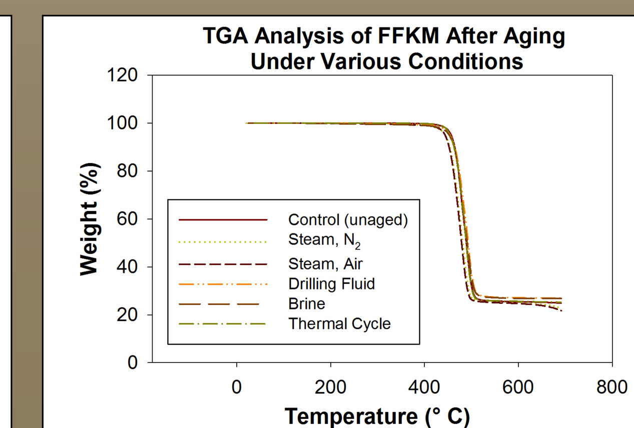


- Edge hardening after thermal cycle test.
- No change in modulus for all other aging conditions.

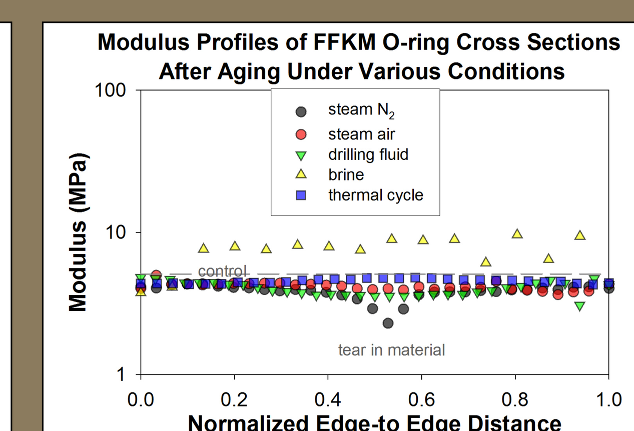


- Hydrocarbons at: 2916 and 2849 cm^{-1} (C-H stretching), 1465 - 1442 (CH_2 scissoring), 1388 cm^{-1} (C-H bending).
- Fluorocarbons at: 1362 (C-F), 1166 and 1009-1090 cm^{-1} (CF_2).
- Band at 1688 cm^{-1} may be due to water.
- Steam/N_2 had formation of band at 1564 cm^{-1}(COO^-).
- Steam/air incorporated C=C (1650 cm^{-1}).
- Drilling fluid and brine added bands associated with C=O and C=C groups.
- Loss of C-H bands after thermal shock + appearance of C=O (1690 cm^{-1}) and COO- (1538 cm^{-1}).

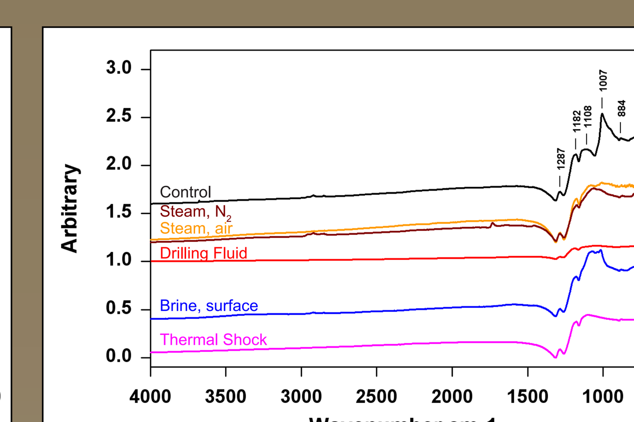
FFKM



- Best thermal stability under all aging conditions of all materials tested.
- FFKM is also the most expensive of all elastomers in this study.



- No change in modulus after thermal cycle testing.
- Slight decrease after steam/air and drilling fluid.
- Slight increase after brine exposure.



- Fluorocarbons at: 1287 (C-F), 1182 (CF_2 asymmetric), 1108 (CF_2 symmetric), 884 cm^{-1} (CF_3).
- C-O-C band at 1140 (shoulder) and 1007 cm^{-1}.
- No noticeable changes in the spectra were observed under the aging conditions, except for drilling fluid
- The band at 1014 cm^{-1} that appears in the drilling fluid spectrum was assigned to silicate scale formation on the surface of the O-ring.
- Unlike the other materials, no bands associated with oxidative degradation were observed for FFKM.

5. CONCLUSIONS

EPDM is a low-cost alternative to fluoropolymers for geothermal well applications under all conditions but thermal shock. Additionally, the material has an unexpected improvement in thermal resistance in drilling fluid. However, products associated with oxidative degradation were observed for all tests. This material is the lowest cost of all materials in the study.

Type I FKM showed edge hardening and evidence of oxidative degradation in all of the conditions studied. The edge hardening and resulting flaking behavior could cause a reduction in the sealing force, making this material unsuitable for o-ring applications under the conditions studied. However, the material may be adequate for use at lower use temperatures.

Type II FKM was also observed to have edge hardening and oxidative degradation in all of the conditions studied, but to a lesser extent than Type I FKM. This is likely due to less VDF in Type II, as VDF undergoes preferential degradation to the other polymer segments. As with Type I FKM, this polymer may be adequate for use at lower temperatures.

FEPM performed similarly to EPDM. FEPM remained relatively stable after steam tests and aging in drilling fluid and brine. Oxidative degradation products were noted under all aging conditions, and the thermal shock sample had additional evidence of degradation associated of the propylene group (loss of C-H bands in FTIR spectrum).

FFKM remained the most stable under all aging conditions in this study, as evidenced by a lack of change in modulus, thermal stability, and FTIR spectra. However, the scale formation observed in the brine could lead to mechanical instability after further aging. While this is the best choice of all materials studied, it is also the most expensive.

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