Degradation of different elastomeric polymers in simulated geothermal environments at 300°C

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Abstract

This study evaluates the degradation of six different elastomeric polymers used for O-rings: EPDM, FEPM, type I- and II-FKM, FFKM, and FSR, in five different simulated geothermal environments at 300°C: 1) non-aerated steam/cooling cycles, 2) aerated steam/cooling cycles, 3) water-based drilling fluid, 4) CO₂-rich geo-brine fluid, and, 5) heat-cool water quenching cycles. The factors assessed included the extent of oxidation, changes in thermal behavior, micro-defects, permeation of ionic species from the test environments into the O-rings, silicate-related scale-deposition, and changes in the O-rings' inverse tensile compliance.

The reliability of the O-ring to maintain its integrity depended on the elastomeric polymer composition and the exposure environment. FSR disintegrated while EPDM was oxidized only to some degree in all the environments, FKM withstood heat-water quenching but underwent chemical degradation, FEPM survived in all the environments with the exception of heat-water quenching where it underwent severe oxidation-induced degradation, and FFKM displayed outstanding compatibility with all the tested environments. The paper discusses the degradation mechanisms of the polymers under the aforementioned conditions.

Keywords: Elastomer, FKM, FFKM, EPDM, FEPM, thermal degradation, chemical degradation

1. Introduction

Elastomeric materials used as non-metallic pump bearings in geothermal environments offer several advantages over metallic bearings. Firstly, they can be lubricated with water instead of oil, abating environmental issues. Secondly, they possess high resilience and stiffness, absorbing impact- or shock-loads without permanent deformation. Thirdly, these materials have low

friction and excellent corrosion-resistance. Finally, their original dimensions are readily restored after localized deflections caused by passing mineral particles.

Fluoroelastomers are of particular interest because of their thermal resistance, demonstrated both in laboratory and field studies [1-3]. However, for geothermal applications such as submerged pumps, a combination of thermal and chemical stability of elastomers is necessary. Several studies have focused on chemical degradation of FKM in aggressive aqueous environments [1, 4-6]. They revealed de-crosslinking, formation of carbonyl groups followed by backbone cleavage, [6] and reactions with metal cations such as Na^+ , Fe^{2+} , Mg^{2+} , and Ca^{2+} present in geo-fluid, with the formation of polyfluorocarboxylate complexes with scale deposition on the surface [4]. Such sensitivity to the chemical environment compromised the thermal stability and mechanical properties of the elastomer.

On the other hand, there are many different-types of commercial fluorocarbon-based elastomeric materials that can withstand temperatures above 200°C [7-10]; among them are type II FKM terpolymers, consisting of polyvinylidene fluoride (VDF), hexafluoropropylene (HFP), and tetrafluoroethylene (TFE), the type III FKM tetrapolymer, comprising VDF, HFP, TFE, and perfluoromethylvinylether (PMVE), the FEPM copolymer consisting of TFE and propylene (P), the fluorosilicone copolymer (FSR) composed of polysiloxane (PS) and trifluoropropylpolysiloxane (TFPPS), and the perfluorocarbon copolymer (FFKM) that includes TFE and PMVE. Further, some geothermal wells have down-hole temperatures over 250°C in addition to harsh chemical environments containing highly concentrated corrosive $\text{CO}_2(\text{g})$ - and $\text{H}_2\text{S}(\text{g})$ -derived acids. Drilling tool components, such as O-rings, gaskets, seals, and packers, are exposed not only to environments containing these corrosive gasses, but also encounter water-based drilling fluids, which contain organic compounds, in the down-hole well reservoir [11].

To the best of authors' knowledge there are no general publications with systematic analyses of degradation and stability of different elastomers under the geothermal environments. The present study focused on investigating and evaluating the stability and degradation of O-rings made with fluorocarbon-based elastomeric polymers, such as types I and II FKM, FEP, FFKM, and FSR polymers and the ethylene propylene diene monomer (EPDM) polymer, after direct exposure (without compression) to five different simulated geothermal environments at 300°C: 1) drilling fluid, 2) CO₂-rich reservoir brine fluid, 3) aerated steam/cooling cycles, 4) non-aerated (under N₂ environment) steam/cooling cycles, and, 5) heating in air/water quenching thermal shock. The elastomers were investigated for: the extent of oxidation, identification of oxidation derivatives, chemical structure-transformation, thermal stability, morphological alteration, micro-defects, permeation-depth profile of the ionic species through the O-ring, and changes in mechanical properties. Obtaining information on these factors was accomplished using ATR-FTIR, TGA, micro-energy dispersive X-ray spectroscopy, and modulus profile testing, in conjunction with visual observations of the changes in the O-ring's appearance.

2. Experimental procedures

2.1. Materials

Elastomers with the following chemistries were tested: 1) a hydrocarbon-based polymer (poly(ethylene-*co*-propylene-*co*-5-ethylidene-2-norbornene, EPDM) and a copolymer of hydrocarbon and a fluorocarbon monomers (poly[tetrafluoroethylene (TFE)-*co*- propylene (P) copolymer, FEP); 2) *co*- and terpolymers of fluorocarbons and hydrocarbon monomers with hydrogen, partially substituted by fluorine (hydrogen in α -position) (poly[vinylidene fluoride (VDF)-*co*- hexafluoropropylene (HFP), type I FKM] and poly[vinylidene fluoride (VDF)-*co*- hexafluoropropylene (HFP)-*co*- tetrafluoroethylene (TFE), type II FKM]); 3) fluorocarbon *co*-

polymer (poly[tetrafluoroethylene (TFE)-*co*- perfluoromethylvinylether (PMVE), FFKM) and 4) a fluorosilicone elastomer (poly[siloxane (PS)-*co*- trifluoropropylpolysiloxane (TFPPS), FSR).

Figure 1 shows their chemical structures. The μ EDX measurements demonstrated that the tested O-rings were not pure elastomers but composite materials. Table 1 gives their compositions expressed in atomic percent of oxides (the total amount of measured oxides set at 100%).

Table 1. Composition of tested O-rings determined by μ EDX measurements and expressed in atomic percent of oxides.

Elastomer	ZnO	CaO	SO ₃	PbO	BaO	NiO	TiO ₂	Fe ₂ O ₃	Cr ₂ O ₃	SiO ₂	Co ₂ O ₃	CeO ₂
EPDM	67	21	12	-	-	-	-	-	-	-	-	-
FEPM	7.0	38	18	-	-	-	1.0	2.0	-	33	-	-
Type I FKM	-	12	-	83	4.3	0.55	0.15	-	-	-	-	-
Type II FKM	-	82	-	-	15	-	1.3	1.7	-	-	-	-
FFKM	-	-	26	-	-	62	-	-	12	-	-	-
FSR	-	3.6	-	-	-	1.7	-	1.8	2.7	76	9.3	4.9

EPDM

Type I FKM

FFKM

Type II FKM

FSR

Figure 1. Chemical structures of the elastomeric polymers used in the study.

2.2. Measurements

Five different exposure environments were employed in this work. The first, denoted as No. 1, consisted of five cycles of: 24 hr in non-aerated (N_2 (g) saturated) steam at 300°C followed by quenching to 25°C ; the No. 2 environment was five cycles of: 24 hr of aerated steam at 300°C

with quenching to 25°C; the third, No. 3, exposed the materials to water-based drilling fluid (pH 9-10) at 300°C for seven days; the fourth, No. 4, was immersion in CO₂-rich geo-brine fluid (pH 4-5) at 300°C for seven days; and, the fifth, No. 5 was a five cycle thermal shock where one cycle was 300°C air heating for 24 hrs in an oven and then placing the 300°C-heated samples directly into 25°C water. Compositions of the simulated drilling and geo-brine fluids are given in Tables 2 and 3 respectively; all the chemicals were provided by Sigma-Aldrich and deionized water was used for all the tests. Details of the first testing procedure were as follows. The O-rings were hung in the head space of an autoclave filled with D.I. water at 30% of the total volume and sealed. The air in the headspace was replaced with N₂, and the temperature was brought up to 300°C. After 24 hours the autoclave was cooled to room temperature at the rate of 50°C/hour. This steam/cooling process was repeated 5 times. The same procedure was used for No. 2 environment, except that the air remained in the head space of the autoclave so the steam was aerated. All the O-rings after the No. 3 and 4 exposures were physically cleaned with a D.I. water-soaked napkin to remove any non-adhering contaminants from their surfaces. All O-rings were dried in an oven at 90°C for 24 hours before conducting the post-test analyses.

Table 2. Composition of the simulated drilling fluid

<u>Major Component</u>	<u>Percent</u>
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

Table 3. Composition of the simulated geo-brine fluid

<u>Major Components</u>	<u>Compounds</u>	<u>Percent</u>
Cl^-	NaCl	13.5
Na^+	NaCl	6
Ca^{2+}	CaCl_2	2
K^+	KCl	1.5
Mg^{2+}	MgCl_2	0.9
<u>Minor Components</u>	<u>Compounds</u>	<u>PPM</u>
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

Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used to identify the oxidation derivatives that were incorporated into polymeric elastomers exposed to these environments and to assess the alterations in their chemical structures. To obtain information on thermal-, hydrothermal-, and chemical-stabilities and the extent of oxidation, Thermo Gravimetric Analysis (TGA) at the heating rate of 20°C/min in a N₂ flow was employed. A micro energy-dispersive X-ray spectrometer (μEDX) was used to explore whether these environments created micro-defects in O-rings, and to investigate the permeation depth of the ionic species from drilling and geo-brine fluids through O-rings. The μEDX analyses were performed on an area of 2.0 x 1.5 mm (3 mm²).

To characterize changes in the stiffness of the O-rings exposed to different environments, elastic modulus profiles of each aged specimen were taken using a home-built instrument. The machine operates by scanning the surface with a parabolic tip at user-defined intervals (in this case, 0.2 mm) and uses displacement from a known force applied to each point on a sample to calculate inverse tensile compliance, which is proportional to the tensile (elastic) modulus [12]. Sample preparation included cross-sectioning O-rings, embedding the materials in epoxy, and polishing with a polishing wheel to achieve a smooth surface.

3. Results and discussion

3.1. Elastomers with hydrocarbon chains (EPDM and FEPM)

Figures 2 and 3 illustrate the ATR-FTIR absorption spectra in the region between 4000 to 650 cm^{-1} and the appearance of EPDM and FEPM O-rings exposed to environments No. 1 through 5. The spectra for the controls encompassed the following hydrocarbon bands: those at 2919 cm^{-1} (EPDM) or 2920 cm^{-1} (FEPM) and 2846 cm^{-1} (EPDM) or 2852 cm^{-1} (FEPM) were due to the C-H asymmetric ($V_{\text{as C-H}}$), and symmetric ($V_{\text{s C-H}}$) stretching vibrations, respectively, and those at 1453 (EPDM) or 1465-1442 cm^{-1} (FEPM) and 1367 cm^{-1} (EPDM) or 1388 cm^{-1} (FEPM) were from $-\text{CH}_2-$ scissoring (δ_{CH_2}) and $-\text{CH}_3$ asymmetric bending (δ_{asCH_3}) vibrations [13,14]. Additionally, the FEPM control spectrum showed the following bands from fluorocarbon bonds: CF (V_{CF}) at 1326 cm^{-1} , and CF_2 asymmetric and symmetric stretching vibrations ($V_{\text{as CF}_2}$ and $V_{\text{s CF}_2}$) at 1168 cm^{-1} and in the region of 1089-1014 cm^{-1} respectively. The band at 1688 cm^{-1} on the FEPM spectrum may be due to water.

As is evident in photos, the O-rings exposed to steam/cooling cycles of non-aerated and aerated testing (Figures 2 and 3 (b) and (c)) and to drilling and geo-brine fluids ((d) and (e)) displayed excellent integrity.

Although the appearance of the O-rings exposed to the first four environments did not change, the ATR-FTIR measurements showed new bands assigned to carboxylate, $\text{COO}-$, asymmetric ($V_{\text{as COO-}}$) stretching vibration [15-17] in the region of 1580-1534 cm^{-1} (EPDM) and at 1564 cm^{-1} (FEPM). Also, the spectra showed stretching vibration bands ($V_{\text{C=C}}$) at 1634 cm^{-1} (EPDM) [18] and 1650 cm^{-1} (FEPM) after exposure to aerated steam/cooling, drilling (both EPDM and FEPM) and geo-brine (FEPM) fluids. Thus the EPDM and FEPM O-rings appeared to undergo some oxidation with the formation of oxidation derivatives in these environments. Nevertheless, the CH bands at 2919/2920 and 2846/2852 cm^{-1} (EPDM/FEPM) and strong absorption bands of all TFE- and propylene-associated groups in FEPM were still present in the spectra of these O-rings.

The spectra of drilling- and geo-brine treated EPDM O-rings also had a prominent band at 1014 cm^{-1} perhaps due to the precipitation of a silicate (bentonite or other)-related scale layer [19,20]. This band was absent from spectra of FEPM O-rings exposed to drilling and geo-brine fluids, suggesting that although the surface of the O-rings was oxidized, it seemed to resist the deposition of silicate scales.

On the other hand, the O-rings exposed to thermal cycles degraded completely (FEPM) or partially (EPDM) and their spectra showed almost complete disappearance of C-H- and CH_2 -related bands, demonstrating the rupture of the backbone hydrocarbon chains. The intensities of CF- and CF_2 -associated bands in FEPM spectrum considerably decreased and bands of oxidation-induced derivatives appeared at 1690 cm^{-1} ($\text{C}=\text{O}$) and 1538 cm^{-1} (COO^-). In the case of EPDM the polymer degraded down to volatile derivatives that escaped the samples leaving behind non-volatile residuals.

Figure 2. ATR-FTIR absorption spectra and appearance of EPDM O-rings before (a) control, and after: (b) No. 1 non-aerated (N_2), (c) No. 2 aerated steam/cooling cycles, (d) No. 3 drilling fluid, (e) No. 4 geo-brine fluid, (f) No. 5 thermal shock tests.

The results demonstrated that elastomers with hydrocarbon chains may have a great stability in hydrothermal and harsh chemical environments but are vulnerable to the hot dry air

heating/water quenching. These results are in agreement with reference [18], which suggests degradation involving oxygen incorporation and chain scission, followed by reactions with the free radicals and deposition of derivatives of each polymeric section of the poly(ethylene-*co*-propylene-*co*-5-ethylidene-2-norbornene) EPDM terpolymer structure (Figure 4). Similarly, in the case of the FEPM, degradation in the thermal shock tests may be initiated at Poly-P unit while the CF and CF₂ bonds in the Poly TFE survive (Figure 5) [21-23].

To support the above information and evaluate changes in the thermal stability of the elastomers after the exposures to the aggressive environments, the thermal degradation of the O-rings was evaluated at temperatures of up to 700°C. The following information was collected: 1) the onset temperature of weight loss (T_o), 2) the maximum decomposition rate and its temperature (T_{max} , DR_{max}), and 3) the percentage of the integrated decomposition rate during the entire thermal decomposition (IDR). Table 4 summarizes the information on decomposition temperatures and percent of the integrated decomposition rate for the tested O-rings. Material changes due to oxidation caused a decrease in the on-set temperature of weight loss for all EPDM and FEPM samples. Only the thermal behavior of the EPDM sample exposed to the geo-brine fluid was similar to the control, suggesting minor sensitivity of EPDM to that environment. FEPM O-rings demonstrated the fewest changes in thermal behavior after exposure to the drilling and geo-brine fluids. In agreement with the ATR-FTIR, data both EPDM and FEPM samples exposed to the thermal shock environment had the lowest decomposition onset temperatures of only 29°C (EPDM) and 27°C (FEPM) (versus 118 and 152°C for the controls). The TGA of these samples showed a low rate of mass loss up to 700°C, typical of oxidized carbonaceous compounds. The reduction in the percent of the integrated decomposition rate loss was likely caused by the formation of oxidation derivatives along with the scission of hydrocarbon backbone chains.

According to the literature, [14] these derivatives convert into carbonaceous by-products that lead to the decrease of the integrated decomposition rate.

Figure 3. ATR-FTIR absorption spectra and appearance of FEPM O-rings before (a) control, and after: (b) No. 1 non-aerated (N_2), (c) No. 2 aerated steam/cooling cycles, (d) No. 3 drilling fluid, (e) No. 4 geo-brine fluid, (f) No. 5 thermal shock tests.

For O-rings made of both EPDM and FEPM there is a general agreement between the FT-IR and TGA measurements, showing major changes in the thermal-shock exposed samples and limited alterations in the samples exposed to geo-brine, drilling fluids and steam environments.

Figure 4. Hypothetical degradation mechanisms of EPDM terpolymer.

Figure 5. Hypothetical degradation mechanism of FEPM copolymer.

Since the carboxylate, --COO^- , group was among the several derivatives formed by the oxidation of the hydrocarbon bonds in elastomeric polymers, there was a possibility for the --COO^- group to react with Na, K, Mg, and Ca counter mono- and di-valent cations present in No. 3 and No. 4 environments (drilling and geo-brine fluids). This reaction would engender the formation of $\text{COO}^- \text{ } ^+\text{M}$ (M = metal cation) carboxylate salts. To obtain information on the depth of O-ring oxidation and metal cation penetration as a result of reaction with the carboxylate anion, metal measurements in EPDM O-ring cross-sections were carried out by μEDX elemental mapping analysis coupled with micro-imaging.

The Ca mapping image of the EPDM samples after drilling and geo-brine fluids closely resembled that of the control. There was no additional calcium in the body of the O-rings in comparison with the control. This result implies that the reaction between carboxyl anion detected in the O-ring by ATR-FTIR analysis and calcium from drilling and geo-brine fluids was minimal, if any. In fact, the O-ring calcium content slightly decreased in brine, which was probably due to the calcium reacting with the anions in this fluid and leaching out of the O-ring. On the other hand, zinc content increased, possibly due to the cation of this metal reacting with the carboxylic acid anion oxidation derivatives in the O-ring (data not shown).

Of particular interest in any O-ring application are changes in elasticity, which could negatively impact sealing force (e.g. edge and/or overall hardening or softening). To evaluate such changes after O-ring exposure to different environments an elastic modulus (inverse tensile compliance) was measured on O-ring cross-sections. Figure 6 summarizes results of these measurements for control O-rings and O-rings exposed to the five test environments. The figures show some important discrepancies between modulus measurements at different edges. For the most part these were due to the flaking of the strongly degraded material at edges and, in some cases, due to the uneven scale deposition. Despite these discrepancies the modulus measurements allow the deduction of general tendencies of changes in elastic properties of treated O-rings. An increase in modulus values after a treatment indicates material stiffening while decreased values correspond to material softening.

Both EPDM and FEPM did not exhibit any dramatic changes in the modulus of O-ring bodies after exposure to the test environments except the thermal shock tests where the O-rings were completely or partially degraded. With the exception of geo-brine treatment, all other environments slightly softened the EPDM O-rings (Figure 6a). This softening effect was the strongest after the exposure to the aerated steam/cooling environment. The geo-brine exposure hardened the core of the O-ring. As μ EDX measurements showed, the hardening of the material in the geo-brine fluid is not related to the calcium permeation. Reactions with zinc cations from the brine and loss of sulfur cannot be excluded as contributing factors to this hardening.

The control FEPM O-ring modulus was more than 4 times higher than for EPDM (14 MPa vs. 2.8 MPa). Some edge softening of FEPM O-ring occurred after the exposures to the geo-brine and steam environments. Unlike for EPDM there was no FEPM hardening in geo-brine fluid.

In agreement with other test results EPDM and FEPM demonstrated good resistance to all test environments except thermal shock.

Table 4. The temperatures of the onset of the weight loss (T_o), of the maximum decomposition rate (T_{max}), maximum Decomposition Rate (DR_{max}) and Integrated Decomposition Rate (IDR) values for O-rings before and after exposure in different environments.

Testing environment	T_o , °C	T_{max} , °C	DR_{max} , %/min	IDR , weight %
EPDM				
Control	118	476	30	61
No. 1 non-aerated steam	94	467	33	55
No. 2 aerated steam	44	458	36	28
No. 3 drilling fluid	95	514	37	73
No. 4 geo-brine fluid	117	474	29	58
No. 5 thermal shock	29	-	-	-
FEPM				
Control	152	514	37	75
No. 1 non-aerated steam	54	506	45	66
No. 2 aerated steam	47	502	45	46
No. 3 drilling fluid	114	480	29	60
No. 4 geo-brine fluid	95	513	38	75
No. 5 thermal shock	27	507	3.4	16
Type I FKM				

Control	300	478	26	70
No. 1 non-aerated steam	74	425 (533)*	6.2	32
No. 2 aerated steam	50	462 (539)*	11	46
No. 3 drilling fluid	197	455	6.0	29
No. 4 geo-brine fluid	68	469 (169)*	14	44
No. 5 thermal shock	286	479	20	44
Type II FKM				
Control	228	497	48	70
No. 1 non-aerated steam	65	484	21	42
No. 2 aerated steam/	53	484	26	60
No. 3 drilling fluid	54	465	5.9	20
No. 4 geo-brine fluid	107	469	23	54
No. 5 thermal shock	241	492	28	59
FFKM				
Control	354	478	39	71
No. 1 non-aerated steam	273	483	37	59
No. 2 aerated steam	162	478	38	72
No. 3 drilling fluid	229	494	38	72
No. 4 geo-brine fluid	141	478	35	73
No. 5 thermal shock	372	487	44	73
FSR				
Control	168	522	18	52
No. 1 non-aerated steam	51	-	-	-

No. 2 aerated steam	-	-	-	-
No. 3 drilling fluid	40	422	0.14	2.3
No. 4 geo-brine fluid	41	563	-	-
No. 5 thermal shock	49	498	-	-

* - temperature of the second decomposition peak

3.2. Elastomers with fluorocarbon and hydrocarbon bonds (FKM I and FKM II)

Types I and II FKM elastomers have fluorocarbon bonds in both the hexafluoropropylene (HFP) and the vinylidene fluoride (VDF) monomers as well as hydrocarbon bonds in the VDF monomer. Type II FKM has an additional monomer with only fluorocarbon bonds, tetrafluoroethylene (TFE) (Figure 1). As a result, the ATR-FTIR spectra of the control FKM I and FKM II O-rings encompassed similar bands, with a higher proportion of fluorocarbon bonds in FKM type II (Figures 7 and 8). All of the bands except for the three at 3392, 3189, and 1645 cm^{-1} ascribed to water (not shown for FKM Type II), were related to three different fluorocarbon groups [1, 24, 25] and C-H stretching. These bands included for Type I (Type II) FKM: CF (V_{CF}) at 1391 (1391) cm^{-1} , CF_2 asymmetric ($V_{as\text{ }CF_2}$) at 1211 (1114) cm^{-1} , and CF_2 symmetric ($V_{s\text{ }CF_2}$) at 1134 (1030) cm^{-1} , and CF_3 at 877 (878) cm^{-1} ; the absorption bands at 2920 and 2852 cm^{-1} were the C-H ($V_{as\text{ }C-H}$) and ($V_{s\text{ }C-H}$) stretching modes in VDF. The intensity of $V_{as\text{ }C-H}$ and $V_{s\text{ }C-H}$ bands was nearly 10 times lower in Type II than in Type I FKM (0.0349 vs. 0.342), which is consistent with the lower proportion of poly-VDF to other poly-fluorocarbons in Type II in comparison with Type I FKM.

After the exposure to non-aerated and aerated steam environments there were two major changes in the spectra of both types of FKM, type I (type II), namely, strong intensity decline or

disappearance of C-H bands and emergence of two new bands at 1716 (1719) and 1608 (1602) cm^{-1} attributed to the C=O ($V_{C=O}$) [24] and C=C ($V_{C=C}$) stretching, respectively, due to the oxidation of the VDF monomer. The C-H bands completely disappeared from the spectrum of type I FKM after the aerated steam/cooling tests suggesting higher sensitivity of the elastomer to aerated than to non-aerated conditions.

The drilling and geo-brine fluids visibly degraded FKM type I and damaged FKM type II O-rings. The FKM type I O-rings had multiple cracks, partial tears, breakage, surface spalling, and sever deposition of scales (Figure 7d and 7e). The type II FKM O-rings were significantly less damaged (Figure 8d and 8e); however, the spectra analyses showed that all O-rings were oxidized and the oxidation derivatives contained C=O (1716 (1711) cm^{-1}), C=C (1608 (1602) cm^{-1}) and COO⁻ (1536 (1536) cm^{-1}) groups for type I (type II) FKM. The C-H related bands completely disappeared from the spectra of O-rings exposed to the drilling fluid (Figures 7d and 8d).

For both types I and II FKM, the appearance of the thermal-shock exposed O-rings was far better than the appearance of the O-rings exposed to drilling and geo-brine fluids (Figure 7f and 8f).). However, three oxidation derivatives , C=C, COO⁻, and COOH at 1752 cm^{-1} for FKM type I and at 1781 cm^{-1} for FKM Type II were evident in these samples along with declined intensity of C-H bands.

The TGA data of Type I and II FKM samples confirmed their poor resistance to the drilling and geo-brine fluids as these samples had significantly lower maximum decomposition rates and total weight loss than the control samples (Table 4). On the other hand, their resistance to the thermal shock tests was considerably better than for elastomers with the hydrocarbon chains, such as

EPDM and FEPM. These data in conjunction with previous studies [4, 6, 26, 28, 29] suggest that the poly-VDF is the first to be oxidized in the structure of the tested FKM elastomers. As a result of this oxidation, derivatives containing C=O and COO⁻ groups and hydrofluoric acid form.

The μ EDX mapping of Type I FKM O-rings exposed to the drilling and geo-brine fluids showed Ca permeation through the entire tested area (Figure 9). The amount of the calcium reacted with the O-ring was significantly higher after the exposure to the drilling fluid (white and red colors) than after the geo-brine fluid (green and yellow colors). Since there was no calcium permeation into the body of the EPDM O-ring, where, according to ATR-FTIR measurements, carboxyl presence was more important than in the FKM material, it is reasonable to assume that strong calcium permeation into the type I FKM O-ring was due to the calcium reaction with hydrofluoric acid accumulated in the degraded elastomer. The difference in the metal content of these O-rings may also play a role in calcium permeation (Table 1).

Figure 10 shows the μ EDX maps of Ca for the cross-sectional area marked with a red rectangle from the edge to the core of type II FKM O-rings before and after exposure to the No. 3 (drilling) and No. 4 (geo-brine) environments. The Ca mapping image of the control O-ring showed that the material already contained Ca, as indicated by the uniform distribution of white- and red-colors throughout the cross-sectional area. For the O-ring exposed to the drilling fluid (No. 3 environment), the morphological image revealed a rim-like layer at the subsurface. Additionally, micro-cracks were observed in the interfacial regions between the rim layer and the rest of the O-ring body, demonstrating that the formation of this rim resulted in structural damage. The Ca mapping image of this defect-laden area revealed a relatively high concentration of Ca, represented by the dense red-color, down to a depth of at least 0.4 mm from the surface. The O-ring exposed to geo-brine (No. 4 environment) also showed a rim layer in the subsurface.

However, this layer was thinner than for No. 3 drilling fluid environment, and there were no micro-defects. Correspondingly, the dense red-color is evident in a superficial layer of around 0.2 mm. Thus, the extent of Ca penetration in No. 3 (drilling fluid) appeared to be much higher than in No. 4 (geo-brine fluid), suggesting a higher extent of oxidation. This result is in agreement with the results of the ATR-FTIR and TGA analyses. Similarly to type I FKM, the calcium permeation was likely a result of the reaction between calcium ions from the fluids and hydrofluoric acid in the body of the degraded O-rings. Additionally, the creation of the oxidized outer layer is likely caused by the diffusion limited oxidation (DLO). DLO occurs when the diffusion rate of oxygen into the material is slower than the oxidation reactions, thereby limiting those reactions to the outermost edges of the material.

Figure 6. Modulus for cross-sectional areas before and after exposures in test environments for (a) EPDM; (b) FEPM; (c) Type I FKM; (d) Type II FKM; (e) FFKM

Figure 7. ATR-FTIR absorption spectra and appearance for Type I FKM O-rings before (a) control, and after: (b) No. 1 non-aerated (N_2), (c) No. 2 aerated steam/cooling cycles, (d) No. 3 drilling fluid, (e) No. 4 geo-brine fluid, (f) No. 5 thermal shock tests.

Figure 8. ATR-FTIR absorption spectra and appearance for Type II FKM O-rings before (a) control, and after: (b) No. 1 non-aerated (N_2), (c) No. 2 aerated steam/cooling cycles, (d) No. 3 drilling fluid, (e) No. 4 geo-brine fluid, (f) No. 5 thermal shock tests.

The modulus of the control sample for type I FKM was lower than for EPDM suggesting a softer material (1.7 MPa vs. 2.8 MPa for EPDM) while type II FKM had modulus similar to EPDM

(3.0 MPa). The bodies of the O-rings made with both FKM types softened and the edges hardened in steam and heat environments (Figures 6c and d). The softening was the most severe after the thermal shock where the modulus lost almost 80% of its value. The aggressive fluids and non-aerated steam had the strongest effect on the edge hardening. According to the results of μ EDX measurements, formation of calcium salts (possibly calcium fluoride) could have contributed to the O-ring-edge hardening in the drilling and geo-brine fluids. For the type II FKM, the sudden drop in modulus at about 0.8 mm distance from the left edge corresponds to the rim structure that damaged the material integrity. In general, in agreement with TGA measurements, the changes in the modulus were less dramatic for type II FKM than for type I. The calcium originally present in type II FKM could have counteracted the effect of hydrofluoric acid and oxidation derivatives released during the degradation of the elastomer through formation of CaF_2 and calcium-bound carboxylates. The modulus measurements confirmed that apart from the thermal shock environment, the FKM elastomers were less resistant to the tests conditions than EPDM.

Figure 9. EDX mapping of Ca coupled with micro-structure images for cross-sectional area of type I FKM before (a) and after exposure in (b) No. 3 drilling fluid, and (c) No. 4 geo-brine fluid.

Figure 10. EDX mapping of Ca coupled with micro-structure images for cross-sectional area of type II FKM before (a), after exposure in (b) No. 3 drilling fluid, and (c) No. 4 geo-brine fluid.

3.3. Elastomers with fluorocarbon bonds (FFKM)

The FFKM elastomer does not have any hydrocarbon bonds. Figure 11 shows the ATR-FTIR spectra in the range between 1700 and 650 cm^{-1} , where the most changes took place, and the appearance of FFKM O-rings after exposure to the five environments. The spectrum of the control FFKM, poly(TFE-*co*-PMVE) copolymer structure contained five representative bands at

1287, 1177, 1140, 1095, and 879 cm^{-1} . The contributors to these bands were as follows: CF (V_{CF}) at 1287 cm^{-1} , and CF_2 ($V_{as\ CF2}$) at 1177, and CF_2 ($V_{s\ CF2}$) at 1095 cm^{-1} , CF_3 (V_{CF3}) at 879 cm^{-1} , and C-O-C asymmetric ($V_{as\ C-O-C}$) and symmetric stretching ($V_{s\ C-O-C}$), at 1140 and 1005 cm^{-1} , respectively, as shoulder bands. As is seen in the photographs, the O-rings did not change visually after exposure to the test environments with the exception of scale deposition in the geo-brine fluid (Figure 11(e)). Although shifts in some bands were visible, in general, the spectral features were similar to those of the control, and unlike for other O-rings, it was very difficult to identify the presence of oxidation derivatives. A pronounced band that appeared at 1014 cm^{-1} after the exposure to geo-brine fluid was assigned to the silicate scale. A new band between 1500 cm^{-1} and 1600 cm^{-1} was not identified; it could be a result of sample contamination in the oven.

The TGA data showed that there was a slight decrease in the temperatures of the decomposition onset for the FFKM O-rings after exposure to No.1-4 environments (Table 4); however, the total weight loss and the decomposition temperature ranges did not change significantly. In agreement with the ATR-FTIR data, the results suggest only a mild effect of the aggressive environments on the FFKM elastomer and its high resistance to the thermal shock tests.

The FFKM O-rings exposed to aggressive fluids were also analyzed for calcium permeation using μEDX . Figure 12 shows calcium measurements in the control and geo-brine exposed O-rings where silicate scale deposition was observed. The control FFKM O-ring was Ca-free. Similarly, there was no calcium in the O-ring body after No. 3 (not shown) and No. 4 environments (Figure 12b), highlighting that Ca ions did not migrate into the material. As expected, there were no micro-defects in these O-rings. One interesting observation was the deposition of some Ca-based scales on the surface of the O-ring exposed to No. 4 (geo-brine

fluid), suggesting that the surface of the FFKM copolymer might have undergone a physicochemical modification during the exposure to this environment.

Figure 11. ATR-FTIR absorption spectra and appearance for FFKM O-rings before (a) control, and after: (b) No. 1 non-aerated (N_2), (c) No. 2 aerated steam/cooling cycles, (d) No. 3 drilling fluid, (e) No. 4 geo-brine fluid, (f) No. 5 thermal shock tests.

Since ATR-FTIR measurements suggested silicate bonds in the scale, deposition of some calcium-silicates is likely. Such scale deposition should be addressed as a potential drawback of FFKM. Although the elastomer possesses an outstanding stability in all environments, scale may accumulate at longer exposure times.

Figure 12. EDX mapping of Ca coupled with micro-structure images for a cross-sectional area of FFKM before (a) and after exposure in (b) No. 4 geo-brine fluid.

Figure 6(e) shows modulus measurements for the FFKM O-rings exposed to the five different environments. The control O-ring had a modulus almost twice as high as EPDM; however, it was almost three times lower than that of FEPM (5.1 MPa for FFKM, 2.8 MPa for EPDM and 14 MPa for FEPM). The changes in the modulus were very small after all the tests for FFKM O-rings, strongly confirming its excellent resistance to aggressive environments. The higher modulus after the exposure in the geo-brine fluid at some parts of the elastomer could be a result of the scale deposition, which was also observed in the micro-EDX tests. The FFKM O-rings with fluorocarbon bonds showed the best performance among the tested elastomers in all aggressive environments.

3.4. Elastomers with fluorosilicone chemistry (FSR)

The tested FSR elastomer had a polysiloxane backbone chain with the side chains containing fluorocarbon and hydrocarbon groups (Figure 1). Correspondingly, the ATR-FTIR spectrum of the control FSR copolymer encompassed eleven major bands: $V_{as\ CH}$ and $V_{s\ CH}$ at 2968 and 2918 cm^{-1} , δ_{CH_2} at 1447 cm^{-1} , δ_{CH_3} at 1370 cm^{-1} , Si-C bending vibration (δ_{Si-C}) at 1262 and 894 cm^{-1} , Si-C stretching mode (V_{Si-C}) at 794, 767, and 696 cm^{-1} , and Si-O-Si stretching ($V_{Si-O-Si}$) at 1056 and 1006 cm^{-1} [30-35]. Additionally, the δ_{S-C} band at 894 cm^{-1} was likely overlapped by the V_{CF_3} band. Figure 13 shows the ATR-FTIR spectra after exposure to the five environments and the appearance of the FSR O-ring after the No. 1 environment.

A dramatic change in spectral features was observed from the sample exposed to aggressive environments: most of the bands, except for an intensive $V_{Si-O-Si}$ signal and several V_{Si-C} -related bands were eliminated, and no oxidation derivatives formed. This is the result of severe

hydrothermal degradation of FSR. In fact, the O-ring was disintegrated. Several investigators have studied the mechanism of hydrothermal degradation for silicon rubber [36-39]. They reported that three linkages within the FSR structure, Si-CH₃, -CH₂, and -O, were vulnerable to rupture. Such bond breakages led to the generation of silanol, Si-OH, groups at the rupture sites and then subsequent condensation reactions between silanols created new oxygen-bridged Si-O-Si linkages. Assuming a similar degradation mechanism may occur in FSR, the reason for disappearance of the majority of hydrocarbon-related bands could be the breaking off of -CH₃ and -CH₂ groups. Furthermore, the development of an intensive Si-O-Si signal is likely associated with an increased number of new Si-O-Si linkages. These new Si-O-Si linkages formed by condensation reactions may be created during the step in which O-rings are heated at 90°C before ATR-FTIR analysis. On the other hand, since the V_{Si-C} -related bands were directly related to the Si-C bond in Si-CH₃ groups, some Si-CH₃ may still be present as the end groups. If this hypothesis is reasonable, the degradation mechanism of FSR in all hydrothermal geothermal environments at 300°C can be postulated (Figure 14).

Figure 13. ATR-FTIR absorption spectra and appearance for FSR O-rings (a) control, and after: (b) No. 1 non-aerated (N_2), (c) No. 2 aerated steam/cooling cycles, (d) No. 3 drilling fluid, (e) No. 4 geo-brine fluid, (f) No. 5 thermal shock tests.

Figure 14. Proposed hydrothermal degradation mechanism of FSR

Among all the tested elastomeric polymers, the “as-received” FSR was identified as the O-ring possessing the highest T_{max} value of 522°C (Table 4). However, its undesirable vulnerability to all hydrothermal environments suggested that it would be very difficult to use this elastomer in geothermal fields. Thus, no further study was conducted with FSR.

4. Conclusions

Tests of O-rings made with different types of elastomers in 300°C steam, heat, and chemically aggressive environments (drilling and geo-brine fluids) demonstrated that the elastomer with fluorocarbon bonds performed the best under all conditions. Elastomers with hydrocarbons in their back bone chain showed a good resistance to chemically aggressive fluids but a poor performance when exposed to dry heat, while the elastomers with fluorocarbon and hydrocarbon bonds with α hydrogen with respect to fluorocarbons performed poorly in all but high heat environments; the fluorsilicone-based elastomer degraded in all tests.

Degradation of the elastomers with hydrocarbons in their backbone (EPDM and FEPM) went through chain scissions and oxygen incorporation with the formation of carboxylate ions. However, there was no any calcium permeation into the elastomers from aggressive fluids, implying that there was not any significant reaction between the oxidative derivatives and the cations from the fluids. The elastomers with α hydrogen with respect to fluorocarbon groups (FKM, types I and II) degraded with the formation of carboxylate ions and hydrofluoric acid. In contact with aggressive fluids containing calcium, reactions between calcium and degradation derivatives caused calcium permeation into the elastomer body, resulting in the material hardening at the edges. An increase in the proportion of fluorocarbon bonds increased thermal resistance of elastomeric materials. Excluding α hydrogen from the structure of the fluorocarbon-based polymer improved general material performance in all tests. The FFKM elastomer, having only fluorocarbon bonds, was resistant to all test environments with only some calcium silicate scale deposition in geo-brine fluid at 300°C. The data suggest that the FSR elastomer with the fluorsilicone back bone and hydrocarbon and fluoro-hydrocarbon side chains degraded through

the breakage of silicon-carbon and hydrocarbon bonds, formation of silanol groups, and condensation reactions of silanols creating new oxygen-bridged Si-O-Si linkages.

The tested O-rings were composite materials that included various additives, which likely affected their performance in the tested environments. The seven day exposures of tested elastomers do not provide sufficient data to draw conclusions on their long-term performance. Further long-term exposures of select elastomers will be done in experiments in actual geothermal wells.

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