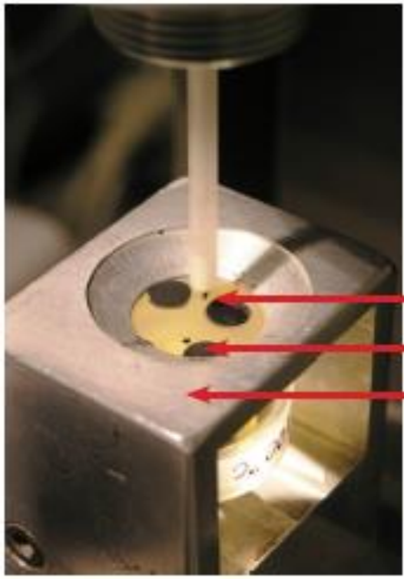
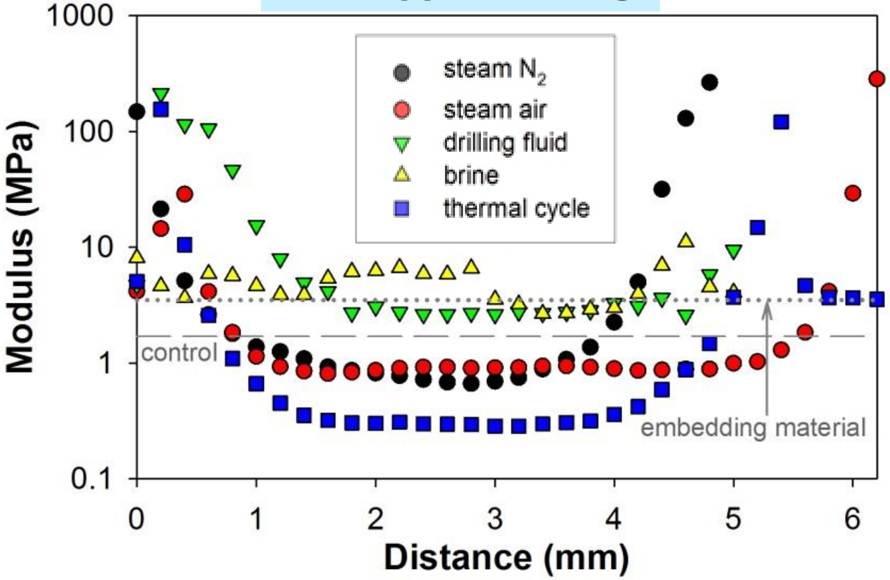


FKM type I O-ring



SNL-developed state-of-the-art modulus profiling apparatus (left) and modulus-distance relation of Type I FKM O-ring (right) after exposure to different environments

Elastomeric Material Evaluation and Development

Project Officer: Joshua Mengers

Total Project Funding: $800K

May 11-14, 2015

Principal Investigators: Dr. Toshifumi Sugama (BNL) and Dr. Erica Redline (SNL)

Co-PIs: Dr. Tatiana Pyatina (BNL), and Dr. James McElhanon and Dr. Douglas Blankenship (SNL)

Presenter Name: Dr. Toshifumi Sugama

Brookhaven National Laboratory and Sandia National Laboratories

Relevance/Impact of Research

Objectives: In FY 14, the objective of this BNL-SNL joint project was to accomplish the baseline studies and material characterization of existing high-temperature and performance commercial elastomeric materials for use as wellbore-, casing-, and fracturing pip packers, pumping systems, drilling tool components, etc. under both conventional hydrothermal and EGS well environments, including drilling fluid at 300^{o}C. In FY 15, the focus centers on conducting second round of simulated well environmental exposure tests for advanced and state-of-the art materials selected based upon information obtained in FY 14 study.

Impact: Compared with that of conventional materials, the elastomeric materials to be developed will extend their service-life cycles up to 300^{o}C,and will afford the following benefits:

- Potential deployment of down-hole drilling and pumping tools and annular isolation packers to higher temperature environment than currently available (up to 200^{o}C);
- Lifecycle extension of elastomer-depending tools and systems;
- Reduction of drilling- and fracturing-operation and tool maintenance costs;
- Reduction of operation and maintenance costs at geothermal power plants because of the elimination of time-consuming and expensive repairing and replacing expenditures.

High-temperature elastomeric polymers to be evaluated

Elastomeric polymers and maximum service temperature

(O-ring relative cost comparison based on EPDM)

- **Ethylene propylene diene monomer (EPDM), 180°C (356°F)** (A)
- **Fluorocarbon (FKM), 200°-250°C (392°-482°F)**
  - Type 1. Coplymer consisting of Vinylidene fluoride (VDF) and hexafluoropropylene(HFP), 200°C (392°F) (Ax2.5)
  - Type 2. Terpolymer consisting of VDF, HFP, and tetrafluoroethylene (TFE), 225°C (437°F) (A x2.6)
  - Type 3. Tetrapolymer consisting of VDF, HFP, TFE, and perfluoromethylvinylehter (PMVE), 250°C (482°F) (Ax2.8)
- **Perfluorocarbon (FFKM), 327°C (620°F)** (A x13.8)
- **Tetrafluoroethylene propylene (FEPM), 260°C (500°F)** (A x5.7)
- **Fluorosilicone (FSR), 225°C(437°F)** (A x 6.3)

Five different testing environments

1. 5 cycle steam-cooling fatigue in N_2 [One cycle:300°C steam for 24 hrs- 25 °C (cooling rate of 50°C/hr)] under pressure of 1200 psi

2. 5 cycle steam-cooling fatigue in air (One cycle: same as that of No. 1 test) under same pressure

3. 300°C-7day drilling fluid at pH 9-10

Major chemical ingredients	Percent
Water	74 to 83
Barite	15 to 10
Ca-Bentonite	7 to 5
Caustic soda	0.3
Soda ash	1
Polyanionic cellulose (PAC)	1.2 to 0.3
Xanthan gum	0.5 to 0.3
Starch	1-0.5

4. 300°C-7day CO_2-rich brine at pH 4-5

Major Components	Percent
Chorine	13.5
Sodium	6
Calcium	2
Potassium	1.5
Magnesium	0.9
Minor Components	**PPM**
Carbon dioxide	15,000
Iron (ferrous)	1000
Manganese	930
Lithium	410
Zinc	370
Boron	330
Silicon	250
Barium	130
Dihydrogen sulfide	70

5. 5 cycle thermal shock (One cycle: 300°C-24hr -heat and 25°C water quenching)

Accomplishments, Results and Progress

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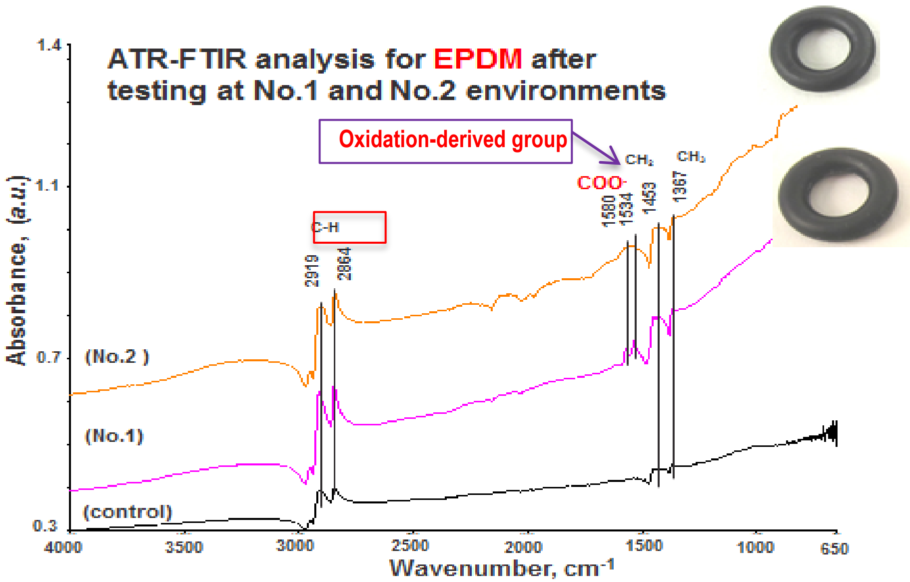
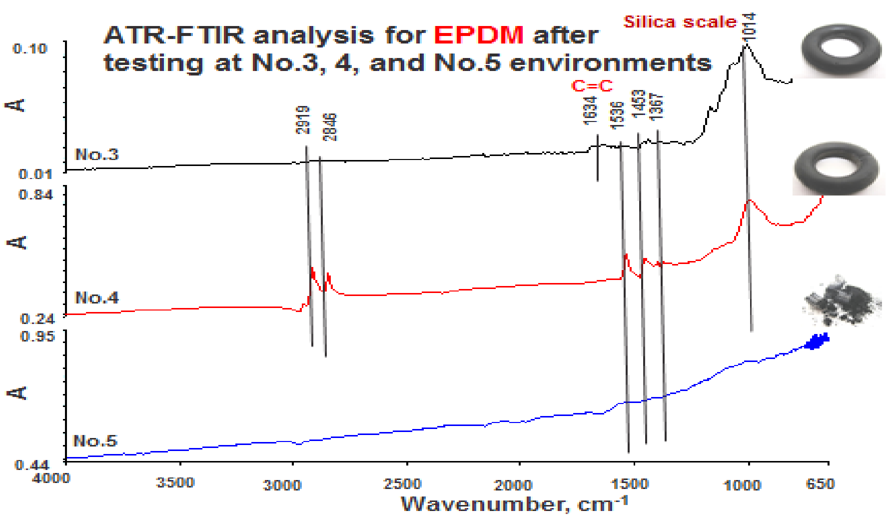
Original Planned Milestone/ Technical Accomplishment	Actual Milestone/Technical Accomplishment	Date Completed
Task 1. Collection of commercial elastomeric materials	Completed.	March 2014
Task 2. Short-term brine and drilling fluid exposure, and 5-cycle heat or steam-cooling fatigue tests	Completed.	June 2014
Task 3. Post-test analyses	Completed.	September 2014
Task 4. Deliver report to DOE and geothermal industries	Completed T. Sugama ,T. Pyatina (BNL), and E. Redline, J. McElhanon, D. Blankenship (SNL), “Evaluation of the performance of O-rings made with different elastomeric polymers in simulated geothermal environments at 300ºC,” BNL-SNL annual technical report.	November 2014
Task 5. Evaluation of upgraded EPDM-, FEPM-, and FFKM-based O-rings	As of March 2015, 60 % completed.	
Task 6. Evaluation of elastomeric composites related to packers and pump bearings	As of March 2015, 30 % completed.	
Task 7. Post-test analyses		
Task 8. Deliver report to DOE and geothermal industries		

EPDM



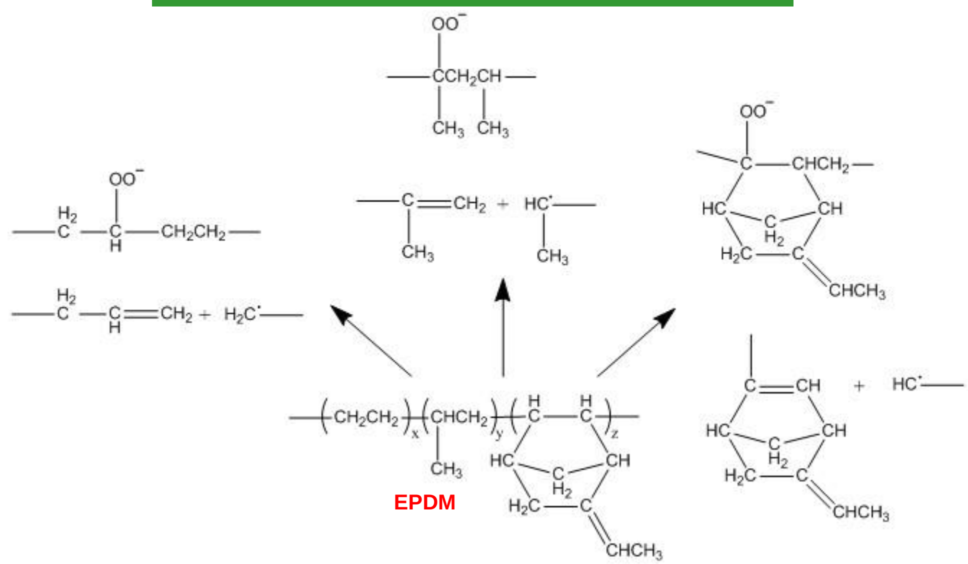


Thermogravimetryic (TG) and Derivative Thermogravimetric (DTG) Analyses

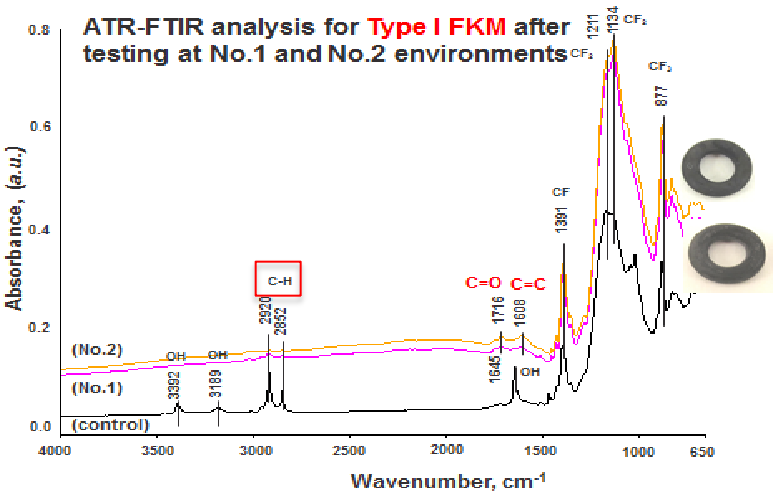
Testing environment	T_o, °C	$T_{max.}$, °C	*IDR**, %.min/°C
Control	118	476	2.86
No. 1	94	467	2.65
No. 2	44	458	2.45
No. 3	95	514	**3.62**
No. 4	117	474	2.72
No. 5	29	-**	-

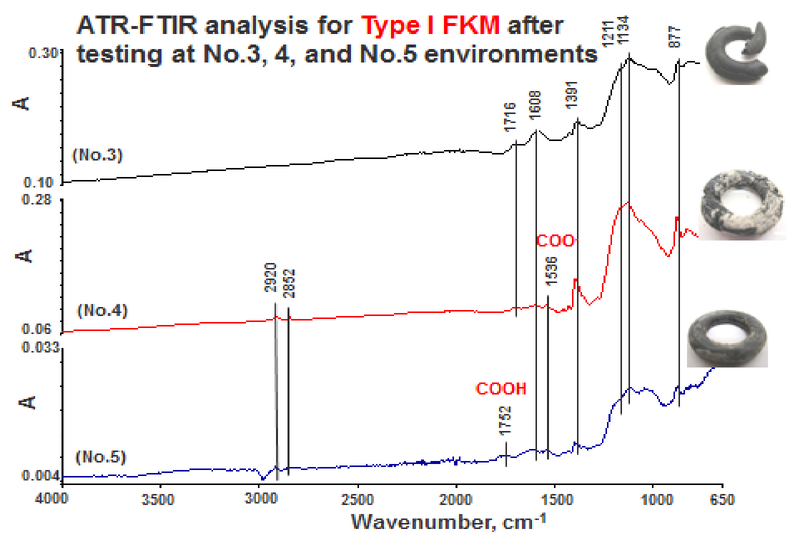
***Integrated decomposition rate, **not applicable**

Degradation Mechanism of EPDM



Type I FKM

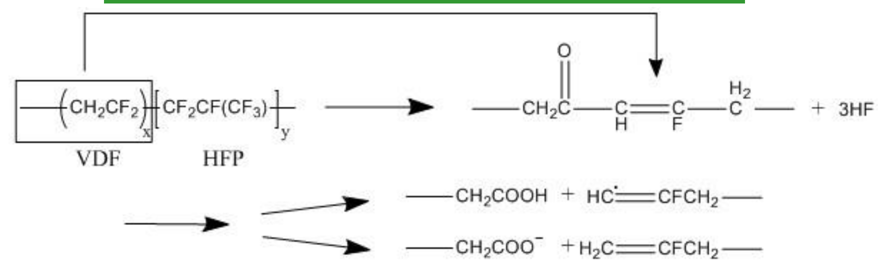




TG and DTG Analyses

Testing environment	T_o, ° C	$T_{max.1}$, ° C	MLR*, %.min/° C	$T_{max.2}$, ° C	MLR, %.min/° C	IDR, %.min/°C
Control	300	478	3.52	-	-	3.52
No. 1	74	425	1.10	533	0.04	1.14
No. 2	50	462	1.13	539	0.28	1.42
No. 3	197	455	1.83	-	-	1.83
No. 4	68	469	1.82	169	0.03	1.85
No. 5	286	479	2.21	-	-	2.21

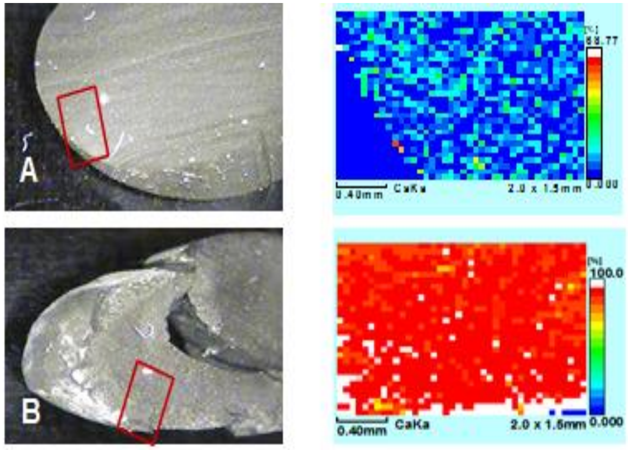
Degradation Mechanism of Type I FKM



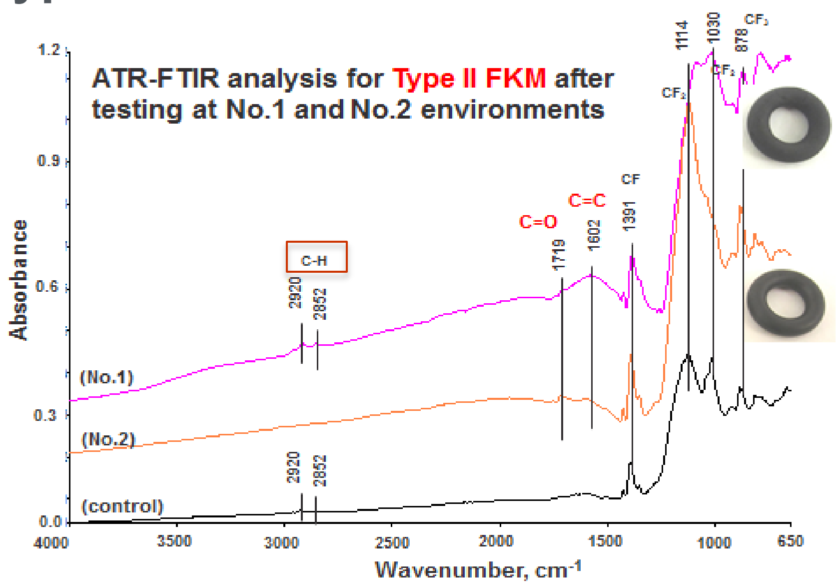
EDX mapping of Ca coupled with micro-structure images for cross-sectional area

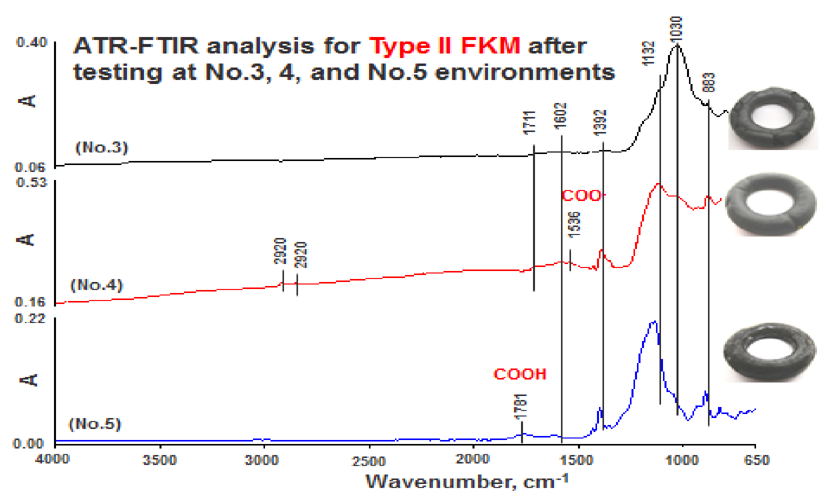
A: control

B: After exposure in drilling fluid



Type II FKM





TG and DTG Analyses

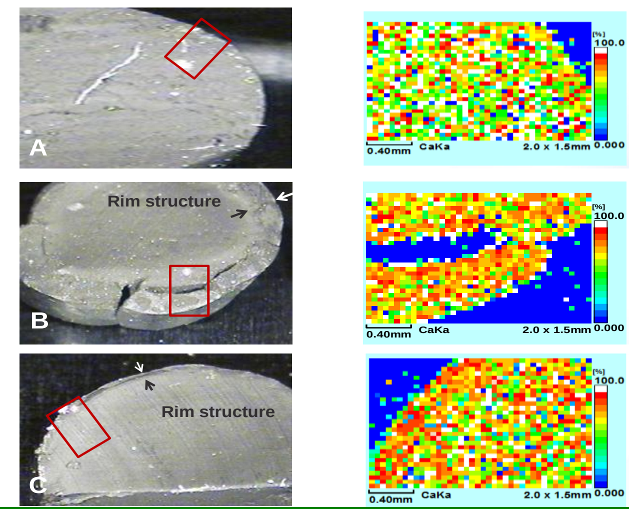
Testing environment	T_o, °C	T_{max}, °C	IDR, %.min/°C
Control	228	497	3.39
No. 1	65	484	2.27
No. 2	53	484	1.85
No. 3	54	465	1.09
No. 4	107	469	1.85
No. 5	241	492	2.93

EDX mapping of Ca coupled with micro-structure images for cross-sectional area

A: control

B: After exposure in drilling fluid

C: After exposure in brine



HF trapping scheme by CaO pigment present in O-ring

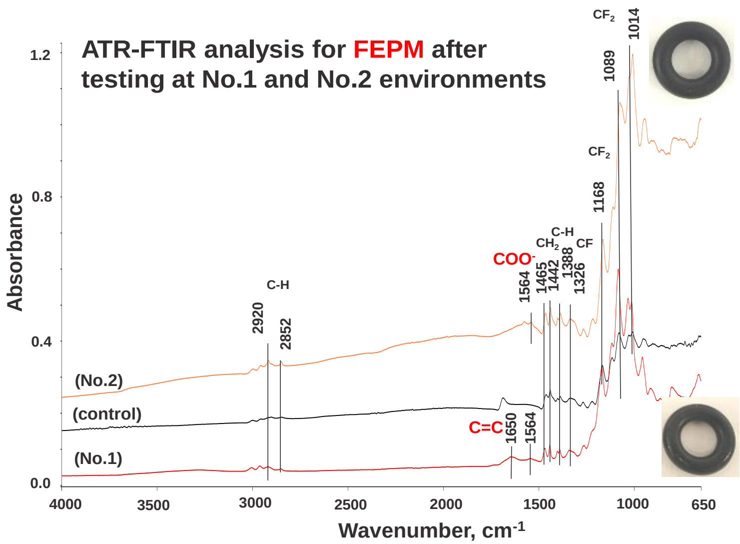
$$(\text{-CH}_2\text{CF}_2\text{-})_x[\text{-CF}_2\text{CF(CF}_3\text{)-}]_y \longrightarrow \text{-CH}_2\text{-C(=O)-CH=CF-CH}_2\text{-} + 3\text{HF}$$

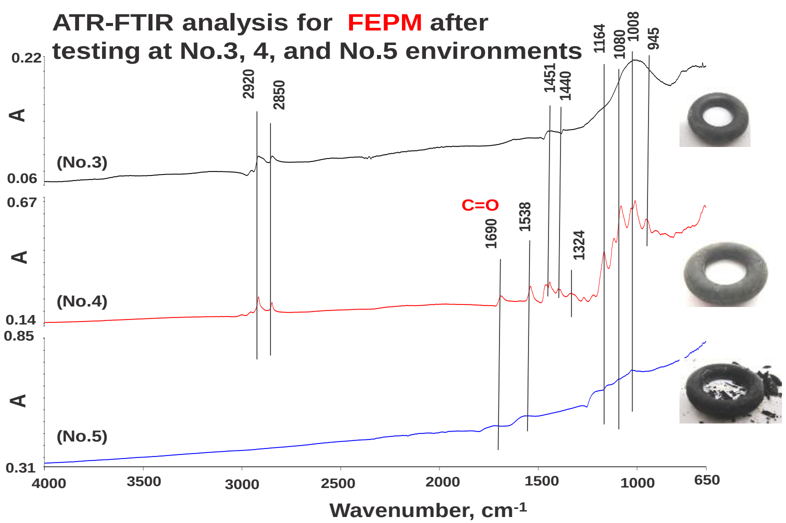
Poly-VDF Poly-HFP

$$2\text{HF} + \text{CaO} \longrightarrow \text{CaF}_2 + \text{H}_2\text{O}$$

Accomplishments, Results and Progress

FEPM

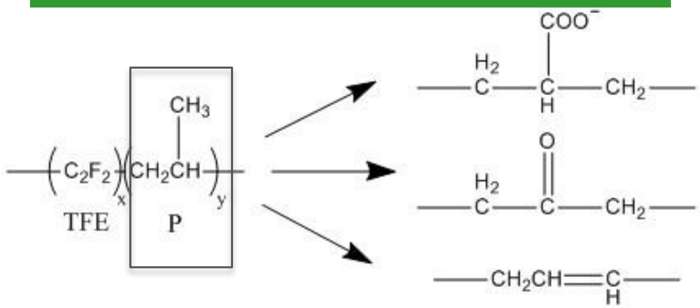




TG and DTG Analyses

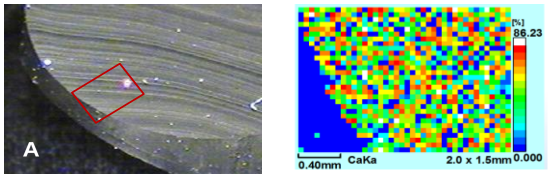
Testing environment	T_o, °C	T_{max}, °C	IDR, %.min/°C
Control	152	514	3.64
No. 1	54	506	3.35
No. 2	47	502	3.25
No. 3	114	480	2.83
No. 4	95	513	3.66
No. 5	27	507	0.65

Degradation Mechanism of FEPM

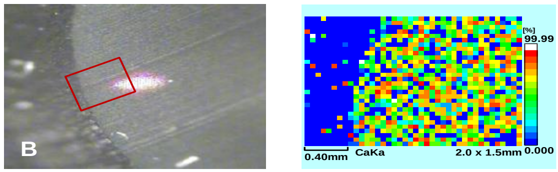


EDX mapping of Ca coupled with micro-structure images for cross-sectional area

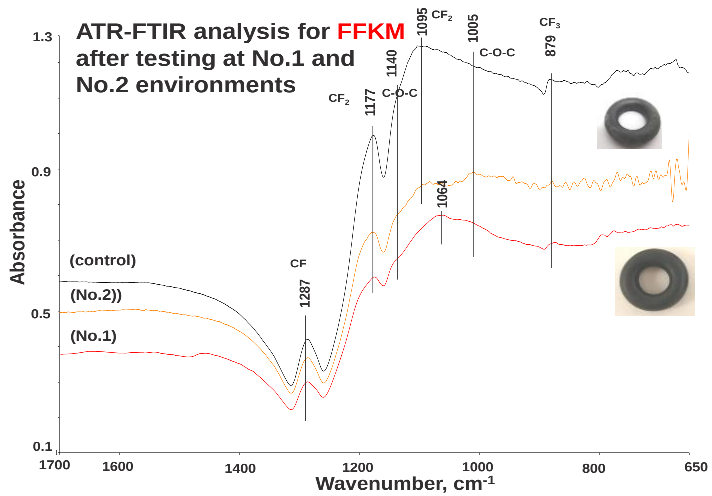
A: control

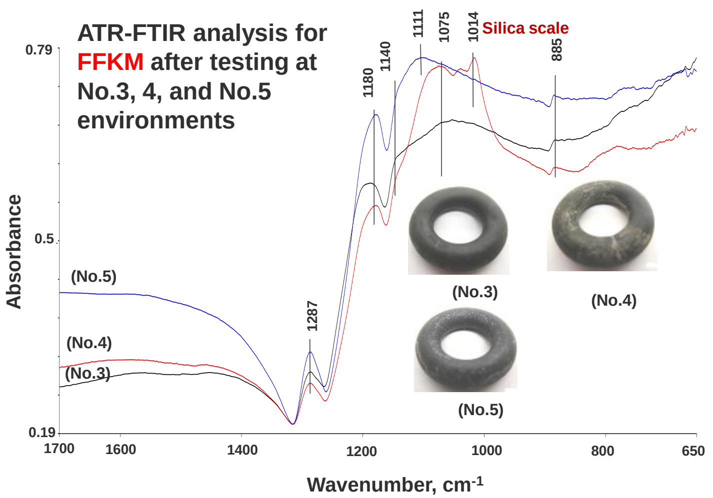


B: After exposure in drilling fluid



FFKM





TG and DTG Analyses

Testing environment	T_o, ° C	T_{max}, ° C	*IDR*, %.min/°C
Control	354	478	3.58
No. 1	273	483	3.58
No. 2	162	478	3.59
No. 3	229	494	3.53
No. 4	141	478	3.52
No. 5	372	487	3.66

FFKM chemical structure

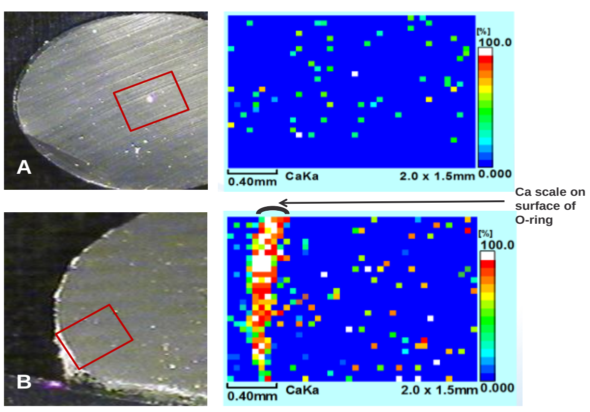
$(-C_2F_4-)_x\ [-CF_2-(CFOCF_3)-]_y$

Poly-TFE　　Poly-PMVE

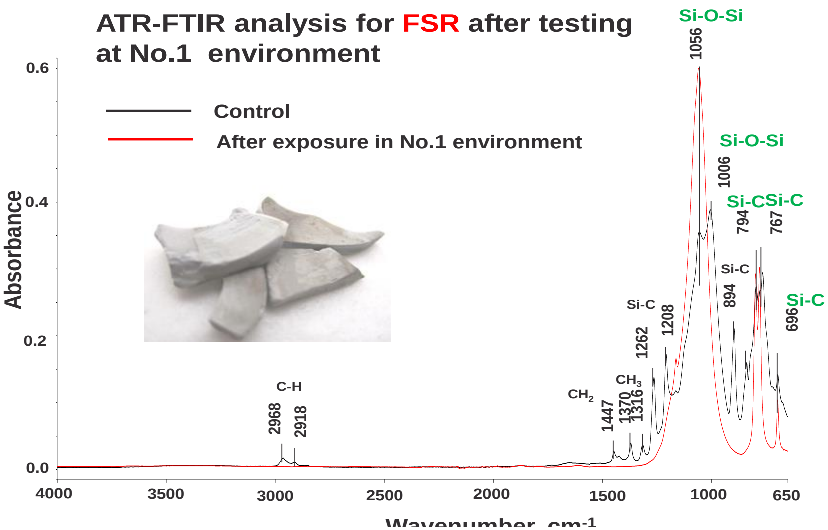
EDX mapping of Ca coupled with micro-structure images for cross-sectional area

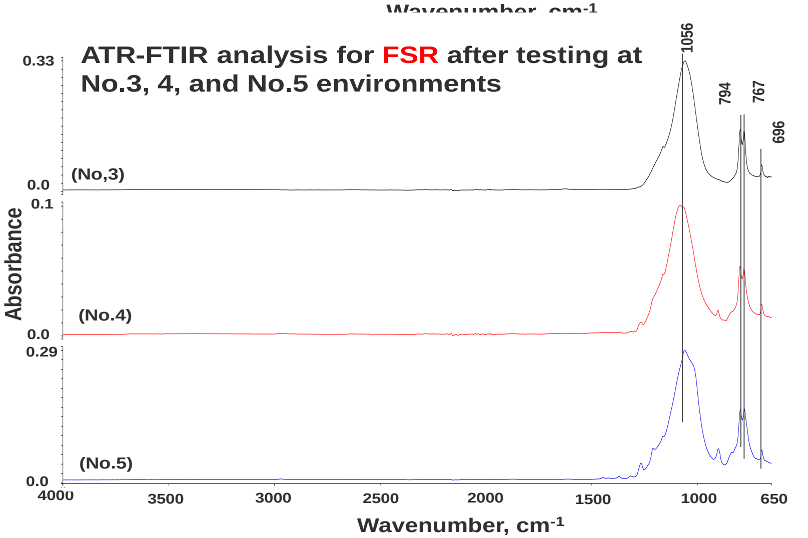
A: control

B: After exposure in brine



FSR

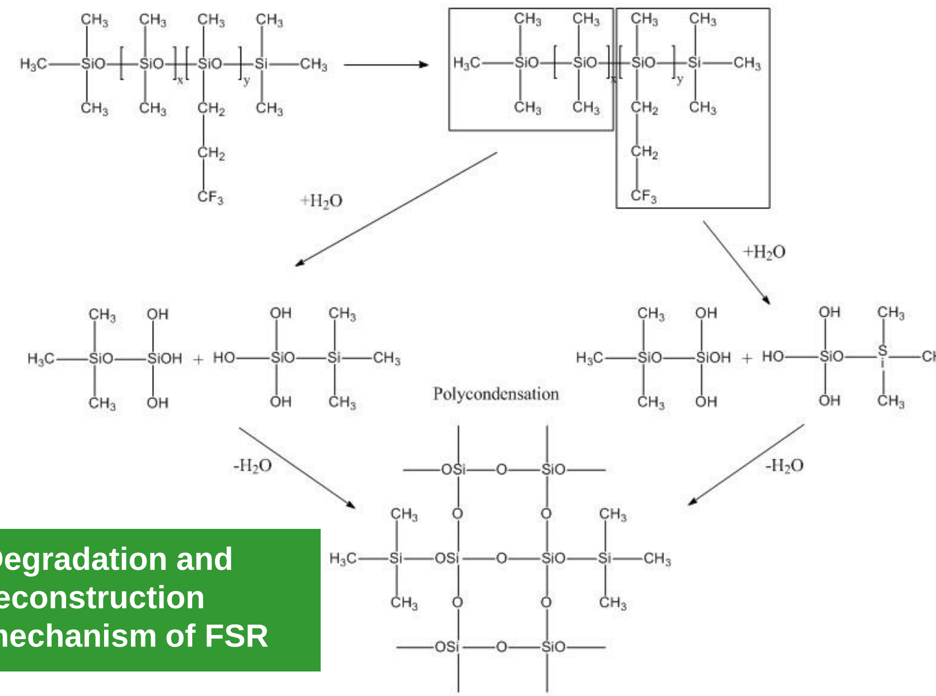




Thermogravimetry (TG) and Derivative Thermogravimetry (DTG) Analyses

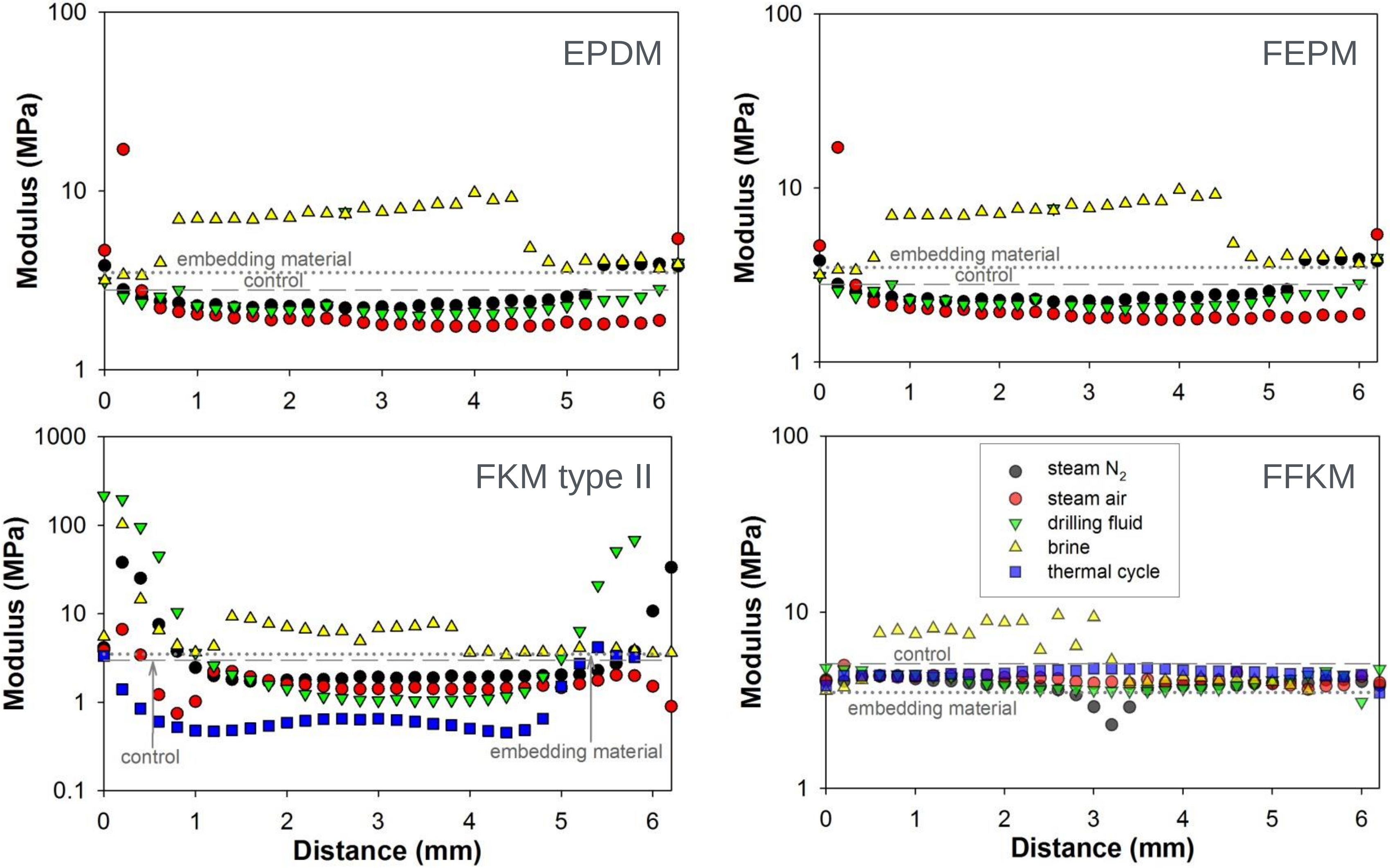
Testing environment	T_o, °C	T_{max}, °C	IDR, %.min/°C
Control	168	522	2.43
No. 1	51	-	-
No. 2	-*	-	-
No. 3	40	422	0.009
No. 4	41	563	0.30
No. 5	49	498	0.91

* Untested



Degradation and reconstruction mechanism of FSR

Cross-sectional modulus profiles of different O-rings after exposure in five different environments



Ranking of stability, with one being the best, of different polymer O-rings for each environment and comparison of their raw material costs based upon EPDM as the benchmark.

Elastomeric polymer (raw material cost factor based on EPDM)	Non-aerated steam-cooling	Aerated steam-cooling	Drilling fluid	CO_2-rich geo-brine fluid	Heat-quenching thermal shock
EPDM (1)	2	3	2	3	4
Type I FKM (1x2.5)	4	5	5	5	3
Type II FKM (1x2.6)	3	4	4	4	2
FEPM (1x5.6)	2	2	3	2	4
FFKM (1x13.8)	1	1	1	1	1
FSR (1x6.3)	5	6	6	6	5

Future Directions

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Milestone or Go/No-Go	Status & Expected Completion Date
Task 1. Continue evaluation and characterization of advanced, economic elastomeric materials	May. 2016
Task 2. Conduct field exposure test for screened materials at Ormat power plant site.	Jun. 2016
Task 3. Post-field test analyses	Sep. 2016
Task 4. Deliver annual report covering all information obtained in FY2016 to DOE and prepare peer-reviewed journal article	Dec. 2016
Go/no-go decision	

Summary

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

	FY2014 (Oct. 2013-Sep. 2014)	FY2015 (Oct. 2014- Mar. 2015)
Target/Milestone	• Complete short-term exposure tests for O-rings made with six different elastomeric polymers in five different environments at 300ºC and post-test analyses. • Deriver annual report describing the details of all experimental works performed in FY14 to DOE and geothermal industries.	•Evaluate integrity of advanced EPDM-, FEPM-, and FFKM-based O-rings in 300ºC various harsh environments. •Evaluate stability of EPDM-, Type II and III FKM-, and FEPM-based elastomeric composites related to packers and pump bearings in 300ºC various harsh environments.
Results	• FY14 annual report including the results below was completed. • The relative strengths and weaknesses of these O-rings, as well as their chemical compatibility, depended on the environments and elastomer structure. • Lowest cost EPDM possessed a relatively good resistance to all employed environments, except for thermal shock. • FFKM displayed outstanding resistance to these harsh environments .However, one major concern may be its extremely high cost. • For integrity and stability in conjunction with economical aspect, FEPM was attractive, despite some degradation after thermal shock. • Ideal cost effective and high-performance elastomeric materials are to possess those properties bridging the gap between high cost FFKM and FEPM or EPDM.	•As of March, ASTM tensile and elongation tests of O-rings after exposure testing was completed. Other post-test analyses are currently underway. •As of March, the exposure test of dumbbell-shaped samples made with four different packer-related elastomeric polymer composites in six different environments at 300ºC was completed. ASTM tensile, modulus, and elongation tests for exposed samples are currently being undertaken.