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Material Compatibility of Elastomers Used in the Salt Waste Processing Facility (SWPF)

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DISCLAIMER

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Savannah River National Laboratory®

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EXECUTIVE SUMMARY

After discovery of failed Viton™ B Fluoroelastomer gaskets at the Salt Waste Processing Facility (SWPF) in early calendar 2021, a short-term (27 day) compatibility test was conducted between SWPF process solutions including Average Salt Simulant, 1 mM nitric acid, 10 mM boric acid, Caustic-Side Solvent Extraction (CSSX) solvent, and Next Generation Solvent (NGS) and the following four polymers: Viton™ B, Viton™ Extreme™ ETP-600S, expanded polytetrafluoroethylene (ePTFE), and Garlock® Blue-Gard® 3700. To the aqueous solutions, 20 mg/L of the following organics were added to represent impurities: Dibutyl phosphate, n-butanol, 2-butanone, ethyl acetate, 4-*sec*butyl phenol, and N-(3,7-dimethyloctyl) amine. The 1 mM nitric acid, 10 mM boric acid, NGS, and CSSX solvent exposure tests were performed at 35 °C, with NGS, CSSX, and Average Salt Simulant Solution tests also performed at ambient temperature. The physical characteristics of the polymeric gaskets, their surface chemistry and the chemistry of the solutions were monitored.

The gasket material behavior is summarized. Viton™ B Fluoroelastomer showed low swelling (less than 2%) with the test solutions due to the presence of a surface treatment or barrier layer, presumed talc (magnesium silicate hydroxide). However, if the talc layer was removed, Viton™ B is susceptible to fast caustic hydrolysis as noted in the literature (expect significant swelling). The talc surface treatment is generally applied by gasket manufacturers to reduce friction during gasket installation and to prevent sticking between materials, not for chemical protection. It is possible that a combination of over-torquing the gaskets and breaking of the protective talc layer led to gasket degradation in the facility. The degree to which each factor contributed to the failure cannot be determined based on the data available at this time. It is noted that reliance on a surface treatment for chemical resistance is less desirable than having sufficient inherent resistance. Fourier Transform Hydrogen Nuclear Magnetic Resonance (FT-HNMR) indicated that Viton™ B did not absorb 2-butanone, dibutyl phosphate, and *sec*butylphenol in 1 mM nitric acid and in10 mM boric acid.

The ETP-600S Fluoroelastomer gained weight and volume during testing (swelling less than 5%), with some hardness loss in Average salt simulant, 10 mM boric acid and 1 mM nitric acid solutions. This was expected based on the literature and information provided by the polymer manufacturer (The Chemours Company). The free volume available in this polymer explains the rate of mass gain in such a short period (27 days of contact) and it should be considered for long-term performance of this gasket. The extent of the swelling in Average salt simulant, in 1mM nitric acid, and in 10 mM borica was less than 5% which is considered as "little effect" by the manufacturer (The Chemours Company). Longer-term exposures are recommended to better assess this behavior. The ETP-600S did better when exposed to CSSX or NGS solvent with a volume swelling of 2% or less. FT-HNMR showed that ETP-600 did not absorb 2-butanone, dibutyl phosphate, and *sec*butylphenol in1 mM nitric acid and in 10 mM boric acid.

The Garlock® Blue-Gard® 3700 material gained significant mass and volume in Average salt solution, NGS and CSSX solvent, but it showed resistance against 1 mM nitric acid and 10 mM boric acid. The material density gradually dropped from 1.62 to 1.49 g/mL in 27 days. Garlock® Blue-Gard® 3700 is a composite material (fiber-reinforced rubber) where the fibers (Aramid fibers) provide strong mechanical properties to the composite and in applications where it is compressed between two metallic flanges, it can be resilient to the SWPF process solutions. FT-HNMR indicated Garlock® leached methyl acetate in Average Salt Solution and acetone in 1 mM nitric acid and in 10 mM boric acid.

The ePTFE polymer only gained mass and volume in NGS and CSSX solvents because of its high porosity at the polymer surface. ePTFE is chemically compatible with all the SWPF liquids. However, the radiation resistance of ePTFE is known to be lower than that of most other polymers. This aspect may be reviewed in more detail if other sealing options do not show adequate compatibility. However, ePTFE is not recommended for high gamma radiation fields due to polymer scission and the production of F_2 (or HF in the presence of water) gas.

It is recommended that the compatibility test continue for an additional two months to verify the uptick in mass gained in Viton™ B, determine the steady state mass gained by ETP-600, and test the more superior sealing material Kalrez® that just arrived. Another material that is cheaper and with outstanding chemical resistance is peroxide-cured Viton® GF-600S that has nearly all the properties of Kalrez® at a lower cost.

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LIST OF ABBREVIATIONS

CSSX	Caustic-Side Solvent Extraction
DOE	Department of Energy
ePTFE	Expanded Polytetrafluoroethylene
ETP	Viton™ Extreme™ ETP-600S
gm	gram
FTIR	Fourier Transform Infrared Spectroscopy
FT-HNMR	Fourier Transform Hydrogen Nuclear Magnetic Resonance
HFP	Hexafluoro propylene
MCU	Modular Caustic-Side Solvent Extraction Unit
mL	milliliter
mM	millimolar
NGS	Next Generation Solvent
PTFE	Polytetrafluoroethylene
PVDF	Poly(vinylidene fluoride)
PVME	Perfluoro(methyl vinyl ether)
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request

1.0 Introduction

Near the beginning of calendar year 2021, Salt Waste Processing Facility (SWPF) processed nearly a million gallons of initially diluted, and subsequently undiluted, supernatant. Higher than usual levels of Isopar L were detected in the Decontaminated Salt Solution (DSS). After shutting down the process and inspecting the DSS coalescers, personnel discovered the coalescers media appeared deformed and at least one had extruded out of the sealing surfaces. The gasket material was removed and sent to the Savannah River National Laboratory to possibly determine the cause of gasket degradation. A memorandum[1] was issued documenting the results that could not rule out assembly error of the coalescer. For example, over torquing the gaskets beyond their recommended degree of compression. may have been a potential failure mode. SRNL recommended performing a quick compatibility test between the different process solutions used at SWPF and four different polymeric materials (the fifth one-Kalrez®- arrived at the end of this test).[2]

The materials identified for testing included Viton™ B Fluoroelastomer (current SWPF gasket material – the gasket that failed in 2021), Viton™ Extreme™ ETP-600S (a modifier Fluoroelastomer with improved caustic resistance), Garlock® Blue-Gard® 3700 (compressed non-asbestos fiber composite), and expanded Polytetrafluoroethylene (ePTFE). The Viton™ Extreme™ ETP-600S Fluoroelastomer was selected mainly due to improved caustic resistance compared to standard FKM Fluoroelastomer types. The Garlock® Blue-Gard® 3700 material was selected due to previous use in the MCU facility. The ePTFE material was mainly selected for chemical inertness and to serve as baseline for comparison. The ePTFE-type material is the standard material used by the fabricator of the DSS coalescers, however, the SWPF contract at the time prohibited the use of Teflon in general.

The compatibility test was intended to determine short-term potential chemical and/or physical changes within a period of contact time with the liquids.[3] No specific acceptance criteria for compatibility were established. For simplicity, it was assumed that no significant physical and/or chemical changes is an indication of compatibility. Other properties such as long-term compression set resistance, compressive stress relaxation (CSR) and other viscoelastic properties were not determined in this study. To ascertain long-term gasket performance, measurement of data meaningful to the application as well the use of apparatus (devices) that represents a legitimate model of the application must be used. In this case, only physical and chemical measurements were performed for expediency and to screen for early or significant degradation. Even though, no tensile testing (strain energy density) or compressive set testing or dynamic mechanical and rheological thermal analysis was done to detect changes, the basic element of compatibility is chemical stability. To that end, the use of Fourier Transform Infrared (FTIR) spectroscopy, Fourier Transform Hydrogen Nuclear Magnetic Resonance (FT-HNMR), and other spectroscopies along with basic physical dimensional measurements such as density, thickness, volume, and hardness measurement should provide sufficient evidence for compatibility. A chemical attack on the polymer backbone or at the cross-link points that can lead to a failure that can be detected by spectroscopic methods. This work focuses on the chemical stability of the polymeric materials identified above.

2.0 Experimental Methods

2.1 Compatibility Test

2.1.1 Objective

The authors sought to compare and evaluate four different elastomers with respect to five different liquids (some liquids were heated to 35 °C). This temperature was chosen to mimic the stripping temperature at the Salt Waste Processing Facility (SWPF).

Ideally, the elastic properties of a given material would remain unchanged after any amount of time in service. Obviously, exposure to working fluids and to higher than ambient temperatures cause some shift in mechanical properties. However, to be considered for long-term service, the change in properties should ideally reach desirable equilibrium values. In extreme environments, however, materials should ultimately be selected because of greatest stability in molecular integrity as well as viscoelastic behavior under compression, tension, or shear. The degree of mechanical property change for acceptability was not defined in this task.

2.2 Composition of the Liquids and Solutions Used and Quality Control

Personnel prepared two liters of the Caustic-Side Solvent Extraction (CSSX) and Next Generation Solvent extraction (NGS). The composition of CSSX is listed in Table 2-1 and NGS in Table 2-2.

Table 2-1. Components and Composition of CSSX
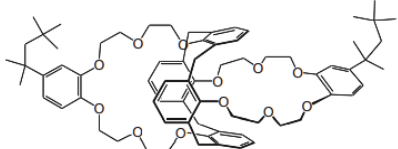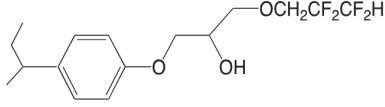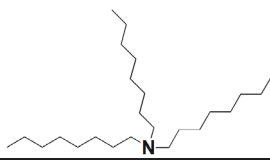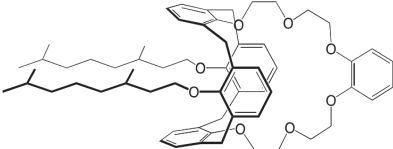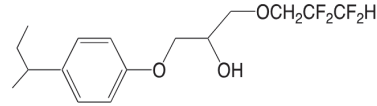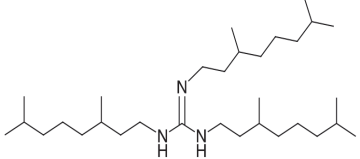
Component	Name	Chemical Name	Structure
Extractant	BOBCalixC6	Calix[4]arene-*bis*-(*t*-octylbenzo-crown-6) MW 1149.5 0.007 M	
Modifier	Cs-7SB	1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol MW 338.35 0.750 M	
Suppressor	TOA	Tri-*n*-octylamine MW 353.67 0.003 M	
Diluent	Isopar L	C_{12}-isoparaffinic hydrocarbon Balance	

Table 2-2 Components and Composition of NGS

Component	Name	Chemical Name	Structure
Extractant	MaxCalix	1,3-*alt*-25,27-bis(3,7-dimethyloctyl-1-oxy)calix[4]arene-benzocrown-6 MW 955.36 0.0500 M	
Modifier	Cs-7SB	1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol MW 338.35 0.500 M	
Suppressor	TiDG	*N,N',N''*-tri(3,7-dimethyloctyl)guanidine MW 479.89 (516.35 for HCl salt 0.003 M	
Diluent	Isopar L	C_{12}-isoparaffinic hydrocarbon Balance	

Two liters of Average SRS Simulant were prepared with the target composition provided in Table 2-3 following the recipe reported by Walker.[4] This simulant was developed to represent an average SRS supernatant liquid waste and this solution composition has been used in the past for solvent extraction performance evaluations (CSSX and NGS).[5] The simulant contains 5.6 M Na^+ and 1.9 M free OH^-, with nitrate and nitrite anions being the next most concentrated anions present. Cesium nitrate and other lesser components were not added.

Table 2-3. Target SRS Average Simulant Composition.

Component	Molarity Target
Na^+	5.60
K^+	0.015
OH^-	1.91
NO_3^-	2.14
NO_2^-	0.52
AlO_2^-	0.31
CO_3^{2-}	0.16
SO_4^{2-}	0.15
Cl^-	0.025
F^-	0.032
PO_4^{3-}	0.01
$C_2O_4^{2-}$	0.008

Personnel also prepared 1 mM nitric acid by diluting 14.7 M nitric with the appropriate amount of Double-Distilled and Deionized water (DD-DI). 10 mM boric acid was prepared by adding the appropriate amount of boric acid to DD-DI water.

To the Average Salt Simulant, the 1 mM nitric acid, and the 10 mM boric acid approximately 20 mg/L of organic impurities were added (see Table 2-4). The impurities represent degradation

products of the Modifier (CS-7SB), the tributyl phosphate, and typical organic composition of Savannah River Site (SRS) supernatant (laboratory returns and other tank processes). No impurities were added to the NGS and CSSX liquids.

Table 2-4. Target impurities added at 20 mg/L each.

Component	Mol. Weight (g/mol)	Density (g/mL)	Solubility (g/L)
n-butanol	74.12	0.81	73
dibutyl phosphate	210.21	1.06	18
sodium formate	68.01	1.92	438
ethyl acetate	88.11	0.902	83
N-(3,7-dimethyloctyl) amine	157.3	Not available	Not available
4-secbutylphenol	150.24	0.988	100
2-butanone	72.11	0.805	290

N, N'-di(2,7-dimethyloctyl) urea was not available for the testing, but we expect that there should be no impact due to its large molecular size (>125 cm^3/mol).

Testing of samples containing Average Salt Simulant were conducted at ambient temperature. Samples containing the NGS and CSSX solvents were conducted at ambient temperature and at 35 °C (cesium stripping from CSSX and NGS solvent is performed at 35 °C). Samples containing 1 mM nitric acid and/or 10 mM boric acid were conducted at 35 °C. Ambient temperatures were at 23 °C (measured and recorded daily) for the duration of the testing.

The following four gasket polymers were tested: Viton™ B Fluoroelastomer (a peroxide crosslinked terpolymer of vinylidene fluoride (VF2), hexafluoropropylene (HFP), and tetrafluoroethylene(TFE) [a], Viton™ Extreme™ ETP-600S (a peroxide crosslinked Fluoroelastomer comprised of TFE-PVME-Ethylene), Expanded PTFE (ePTFE, polymer capable of crystallization with a network of nodes and fibrils that create lots of empty space and making the polymer air permeable), and Garlock® Blue Gard 3700 (a compressed non-asbestos gasket comprised of synthetic fibers such as aramid fibers such as Kevlar® and an ethylene-propylene-diene monomer (EPDM) rubber binder) used by the Modular Caustic-Side Solvent Extraction unit (MCU). Other gasket materials such as Grafoil™ flexible graphite may also be acceptable for the intended service but were not tested in this study.

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[a] TFE (-CF2-CF2-)= Tetrafluoroethylene, PVME (CF-O-CF3)= fluorinated poly vinyl methyl ether, and HFP (-CF-CF3) =Hexafluoropropylene
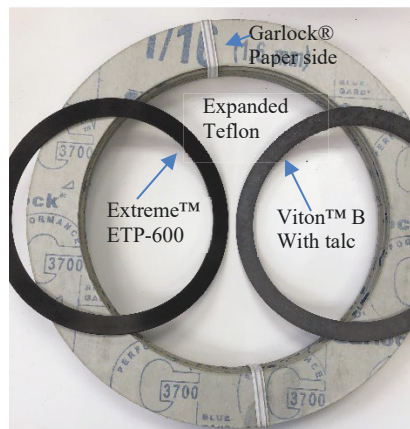
Figure 1. A picture of the gasket material tested

The initial physical dimensions and hardness of the gaskets were measured and recorded. The initial hardness data (from 10 measurements and following ASTM D2240) is shown in Table 2-5.

Table 2-5. The initial hardness (Shore M units) of the polymers tested

Gasket	ETP	Viton™ B	ePTFE	Garlock®
Average Hardness (Shore M)	91.8	84.3	87.6	99.6
Standard Deviation (Shore M)	0.3	0.6	0.6	0.2

It is noted that Shore Durometer hardness scale A is typically used for most elastomers, with a +/- 5 point tolerance for manufacturing purposes. However, Shore/Durometer Scale M is often used for testing thinner materials (below 0.24 inch thick) and O-rings due to curvature. The Shore/Durometer hardness test is more applicable for the elastomers than the ePTFE and the Garlock® gasket materials. However, the test was primarily used in this testing for evaluating changes due to immersion.

2.3 Quality Assurance

Quality assurance requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. The work was performed with functional classification of General Service under the applicable TTQAP, Technical Task and Quality Assurance Plan.[5] Completed R&D Directions are stored in ELN experiment A2869-0071-44.

2.4 Polymer-Solution Batch Contact Testing

A single gasket piece of each type weighing approximately 0.9 to 1.6 grams was placed in 60 mL of solution contained in a glass vial with Teflon cap. The glass vials were place incubators for the 35 °C incubators (Innova). The ambient temperature samples were placed in a shaker. The Innova incubated shaker ovens agitated the samples at a rate of 120 rpm. The oven display temperature was manually monitored and recorded periodically throughout testing and was checked with a calibrated M &TE thermocouple at test completion and confirmed to be within 1 °C of the target value. Testing began on August 20, 2021. The gasket pieces were removed twice a week for

analysis. A total of seven sampling events took places in 27 days. In a typical testing, the polymer was removed from the liquid, the excess liquid on it removed, weighted in air and under DD-DI water, hardness measured with a digital Centaur Shore M unit, and finally, the thickness of the piece was measured with a caliper ruler. For samples that contacted aqueous solutions (like 1 mM boric acid, 10 mM nitric acid, and/or Average Salt Simulant), the gasket piece was dipped for about 3 minutes in double-deionized and distilled water (DD-DI) and then wiped dry with Kim wipes. For gasket pieces that contacted Next Generation Solvent (NGS) and/or Caustic-Side Solvent Extraction (CSSX), were dipped in dichloromethane for one minute (to remove excess liquid layer) and then wipe dried with Kim wipes prior to measurements (hardness, density, volume, and weight).

Limitations of this work include solutions may not mimic actual process conditions. For example, the materials are exposed to milligrams of impurities while in the process they may see grams of impurities. Similarly, the contact time in this work is only 27 days while at the process will be several months or even years (recall Fick's diffusion is proportional to the square root of contact time).

3.0 Results and Discussion

The data is presented with the net weight of the polymer on the ordinate and the net volume of the polymer on the coordinate. The slope represents density while the 'width" of the data along the coordinate represent the net swelling of the polymer. The letters "A" and " B" represent duplicate of the same conditions with the same oven while the number "25" and "35" represent the temperature of the oven. In the chart title, the percent hardness loss or gained is listed after 27 days of batch contact as well as the volume gained.
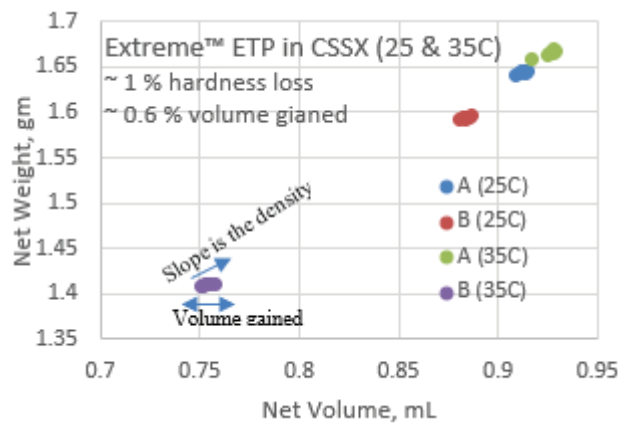
Figure 2. An example of the data presented here

3.1 Viton™ B

3.1.1 Compatibility in Average Salt Simulant

No significant physical changes (swelling or shrinkage) were observed in the Viton™ B pieces immersed in the salt simulant containing impurities as noted in Figure 3A and 3B for the length of time of this experiment. The volume gained (<1%) is much less than the volume gained in Fuel C (3%) listed in Reference 6 that the vendor considers not significant. No significant changes in the

hardness of the sample were detected. The weight gained data (as shown in Figure 3A and 3B) appears to indicate an initial loading with an associated plateau and possibly another increase in weight trending before the experiment was terminated. The initial sigmoidal-shaped load is typically associated with polymer surfaces containing a polydisperse-diameter pores system. Typically, these pores form when the polymer is molded on surfaces containing "antistick" agents. However, a more likely explanation is that the Viton™ B gasket surface is covered with a talc, magnesium silicates, powder to prevent it from sticking to another gasket and to reduce friction during gasket installation. This talc layer may act like a barrier to mass transfer to the gasket, and it delays or slows down the interaction of the gasket with any exterior liquids. If the talc (magnesium silicates) powder is compatible with the contacting liquid or it is not physically removed it can perform as a mass transfer barrier. However, a closer look of the data in 3B seems to indicate a re-initiation of mass gain by the sample (at the last sampling point or at the 27th day), which coincides with the removal of the talc as noted by its relatively weaker FTIR peak (see Figure 3C). The sample was also "sticky" to stainless steel surfaces (but not to the thin nitrile gloves we wore). Steel surfaces have polar and hydrogen bonding components (chromium oxide and hydroxides) just like the Nitrile Butadiene Rubber (NBR) that can form attractive forces with Viton™ B (via dispersive force attraction). However, we believe that a solvent component absorbed on the Viton™ B surface that gave the surface a strong hydrogen bonding component that preferentially sticks to steel surfaces (or that the surface of Viton™ B re-oriented exposing its hydrogens [from its vynilidene group or VF_2] and they hydrogen bonded with the steel surface). Caustic is expected to attack VF_2 group (Ref.6). Reference 6 indicates this polymer should swell below 10% in 30% NaOH. Once the talc layer is removed expect Viton™ B to swell.
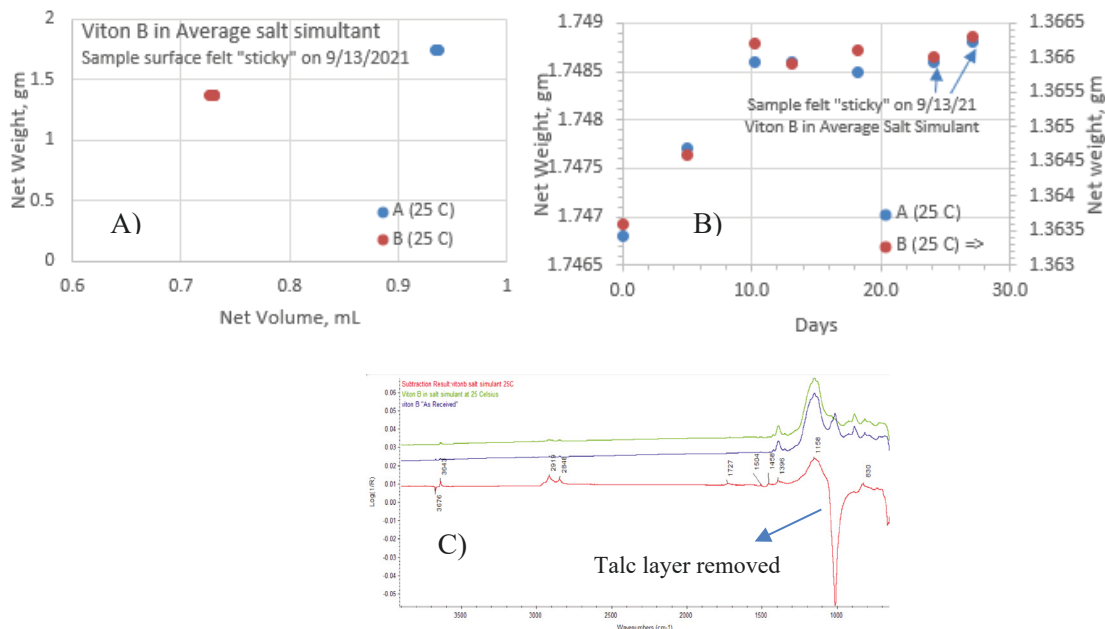

Figure 3. Density of Viton™ B (A), the kinetics of mass gained (B), and the surface chemistry of aged Viton™ B by FTIR (C)

3.1.2 Compatibility in 1 mM Nitric Acid

A more noticeable swelling of about 1% (and weight gain) of Viton™ B is detected with dilute nitric acid (as shown in Figure 4A and 4B). The volume gained after 27 days is much less than

the 3% volume gained listed by the vendor for this polymer in Fuel C. The talc film was not visually observed, and probably dissolved away, and consequently the Viton™ B gasket adsorbed and retained weight and increased in volume. But the rate of loading appeared to slow down before the experiment was terminated as shown in Figure 4B. This is likely due to initial loading associated with filling empty voids near the surface of the gasket. There are no chemical groups in Viton™ B that can be oxidized by dilute nitric acid and there are no hydrogen bonding groups in the chemical microstructure of Viton™ B. All Viton™ types have excellent resistance to nitric acid within temperature and concentration limits.
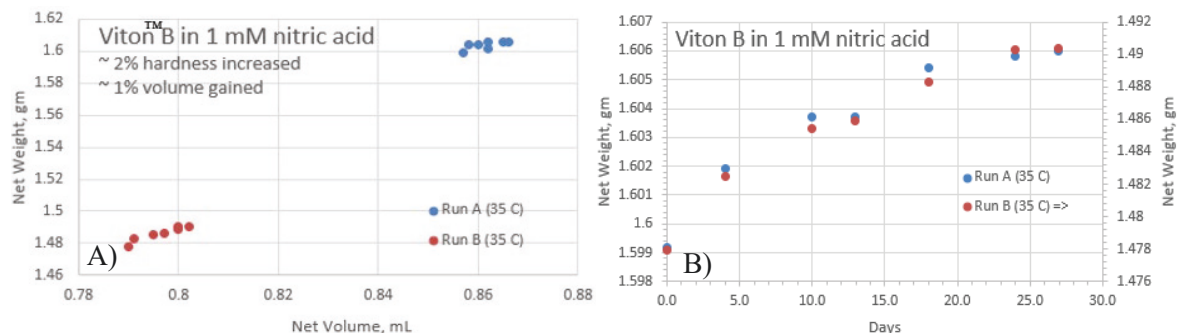
Figure 4.   The density (A), the rate of loading (B), loading as function of square root of time (C), and the logarithm of time (D) of Viton™ B in 1 mM nitric acid.

3.1.3 Compatibility with 10 mM Boric Acid

No significant weight gain or volume increase (~ 0.5%) was detected in Viton™ B that contacted 10 mM boric acid containing impurities as shown in Figures 5A and 5B. The volume gained is much lower than the 3% volume gained listed in Reference 6. This is expected since boric acid contains hydrogen bonding capable groups (hydroxyls) and Viton™ B has no hydrogen accepting or donating groups in its chemical structure. However, the rate of mass gained in Figure 5B appeared not to have reached steady state by the end of the testing. The loading data can be linearized by plotting it as a function of the square of time (Figure 5C) as an indication that the loading process is mass transfer controlled (diffusion through a hydrodynamic boundary layer that formed under laminar conditions) from the solution to the polymer piece and it is adequate for predictions.[7] However, plotting the natural logarithm of this data (Figure 5D) revealed the loading process does not strictly follow Fick's law of diffusion[8] (for example, the slope in Figure 5D does not equal 0.5) indicating significant chemical interaction between the polymer and solute.
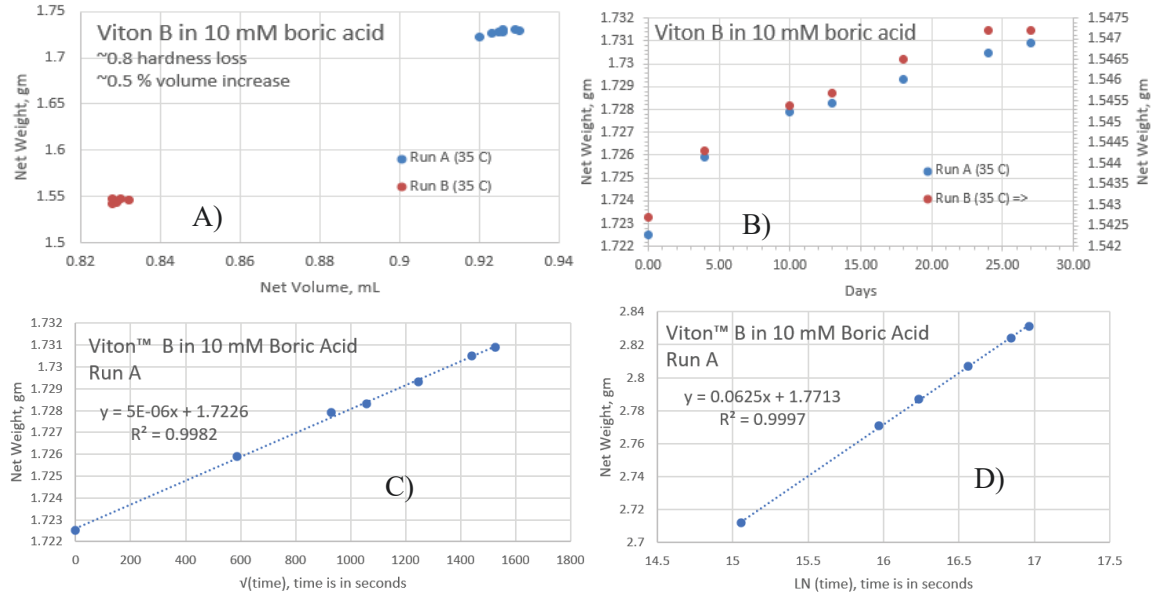
Figure 5. The density (A), kinetics of loading (B), loading as a function of square root of time (C), and as function of the logarithm of time (D) of Viton™ B in 10 mM boric acid

3.1.4 Compatibility with Next Generation Solvent Extraction (NGS) Solvent

No significant weight and/or volume change (<1%) was detected in Viton™ B pieces that contacted NGS liquid within the time period of this experiment as shown in Figures 6A, 6B, and 6C. This result is expected since Viton™ B is a fluorinated elastomer and the only organic component in NGS with fluoride is the Modifier (CS-7SB) with a relatively large molecular volume (~ 211 cm^3/mol) that may not fit into the free volume of Viton™ B. However, there appears to be an uptick in mass gain at the end of the experiment (see Figure 6A and 6B) due to the loss of the talc overlayer. Alternatively, the diffusion timescale could be long compared to the time of this experiment.
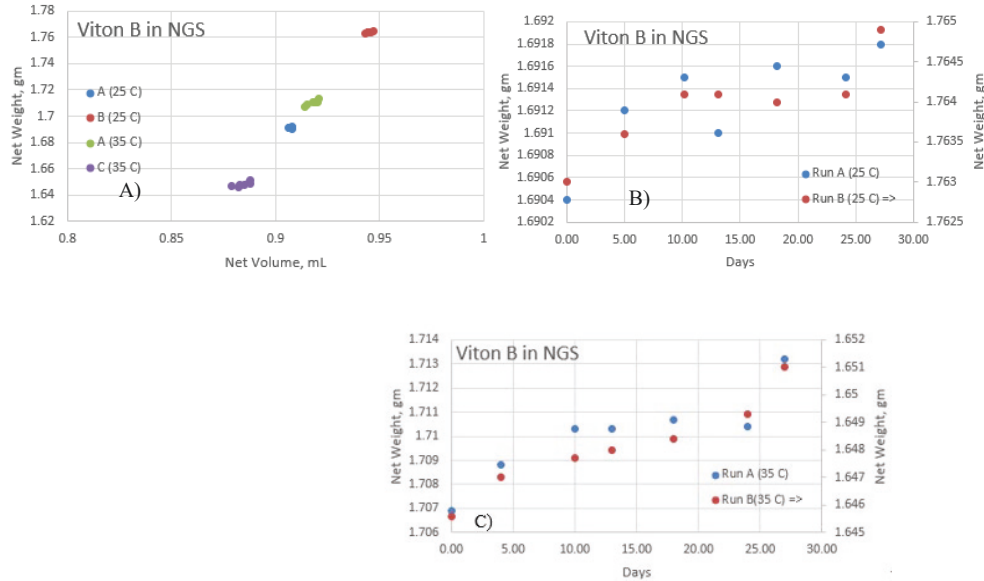
Figure 6. Density (A) and rate of mass gained at 25 °C (B), and at 35 °C (C) of Viton™ B in NGS solvent

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3.1.5 Compatibility with Caustic-Side Solvent Extraction (CSSX) Solvent

Similar to the results observed when Viton™ B was contacted with NGS, there was no significant change to the weight and/or volume of Viton™ B when exposed to CSSX (as shown in Figure 7A and 7B). This is again expected since the only differences between NGS and CSSX are the extractant used and differences in the Modifier concentrations. However, a noticeable uptick in mass gained is seen at the end of the experiment in Figures 7B and 7C due to the loss of the talc overlayer and it may indicate that the polymer has not reached steady state in loading materials.
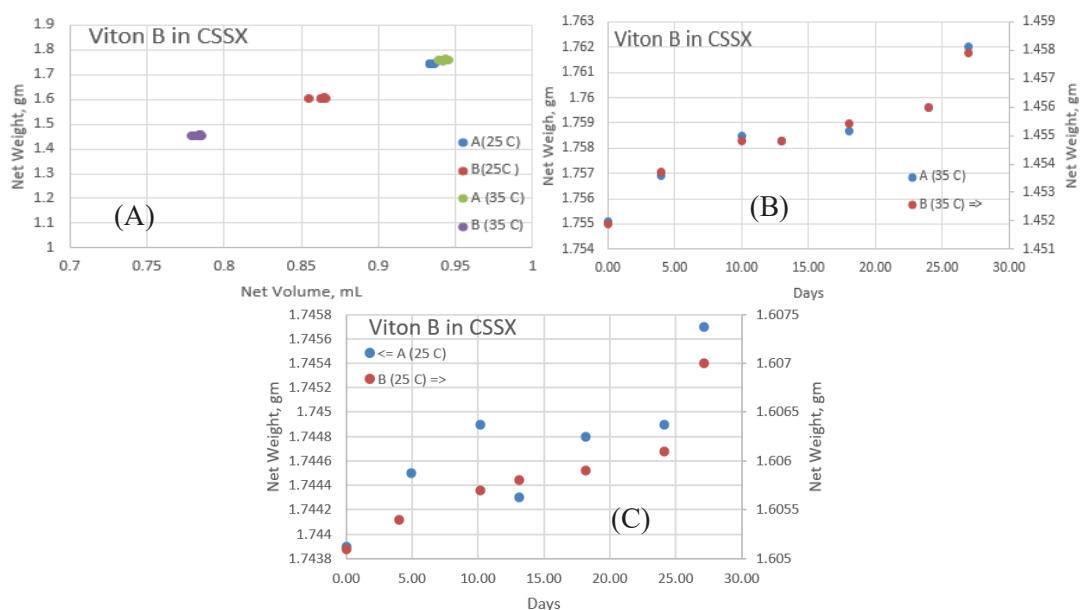
Figure 7. The density (A) and rate of loading (B and C) of Viton™ B in CSSX solvent

3.1.6 FTIR Analysis of the surface of Viton™ B

An examination of the FTIR data (Figure 8) of the surface of the Viton™ B that contacted the different liquids after 27 days revealed no chemical degradation. However, the talc peak at 1020 cm^{-1} diminished significantly in the NGS and Average Salt Simulant indicating the talc layer may have been removed or dissolved and it coincides with the upward gain of mass and volume of Viton™ B at the 27th day of sampling. Please note that the talc removal might have also occurred during sample handling in addition sloughing off on its own. Either way, relying on the talc to protect the Viton™ B is not a solid approach, but more of an artifact or lucky break for the Viton™ B.
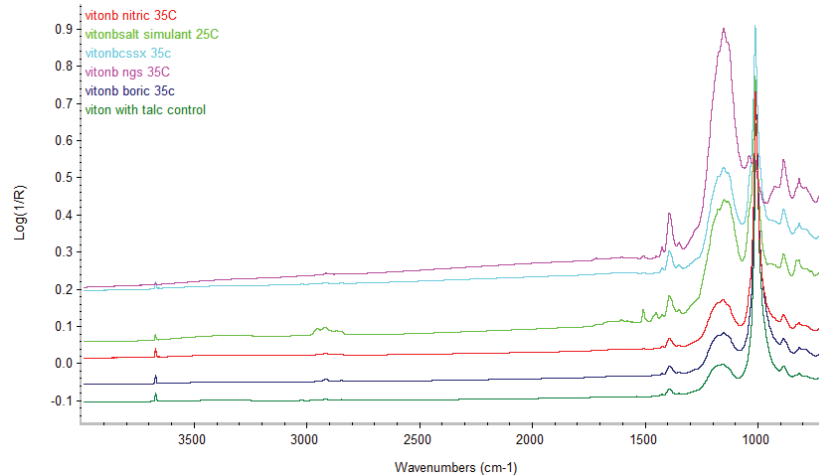
Figure 8. FTIR of the surface of Viton™ B after 27 days in contact with NGS, CSSX, Average Salt Simulant, 1 mM nitric acid, and 10 mM boric acid

3.2 Viton™ Extreme™ ETP-600S

3.2.1 Compatibility in Average Salt Simulant

There is evidence of significant volume gain (~ 4.5%) and hardness loss (~ 4%) of ETP-600S when in contact with average salt simulant with impurities for 27 days as shown in Figure 8A. But the volume gained is less than the 5% value listed by the vendor for this polymer exposed to methanol for 7 days (see Reference 6 where the vendor considers 5% or less swelling an acceptable rating and methanol is used for its small molecular size). The data suggest that the interaction did not reach steady state when the experiment was terminated after 27 days as shown in Figure 8B. This interaction was not expected. A potential explanation is that this is filling of void spaces in the surface with pore channels that permit easy liquid entry. However, the elastomer would have to be a foam-like structure to support that volume change. Another possibility is that the "free space" in the ETP-600S compound is large enough for a small solute to fit in (for example volume increase of the sample is proportional to the molar volume of the solute). The rate of loading in Figure 9B does not strictly follows Fick's diffusion law (nonlinear when the log of net weight is plotted versus the log of time) but the loading behavior can explain by diffusion through a hydrodynamic boundary layer which is expected under laminar conditions.

Figure 9. Density and rate of loading on Extreme™ ETP-600S in contact with Average Salt Simulant

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3.2.2 Compatibility in 10 mM Boric Acid

Viton™ Extreme™ ETP-600S appears to increase in mass and volume (4%) in boric acid (see Figure 10A, and 10B). Again, it is less than the 5% listed in Reference 6. The gain indicates the f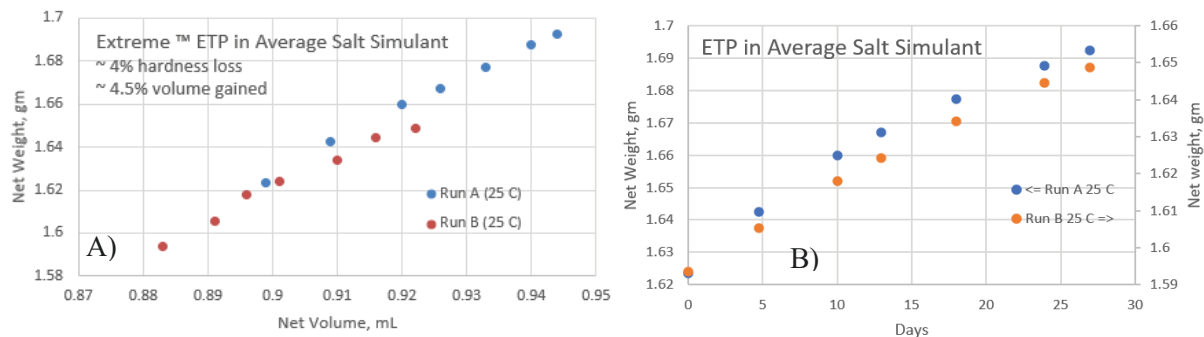ree volume space in this elastomer is large enough for the borates to enter it and possibly interact, via hydrogen bonding or dipolar interaction, possibly with the oxygen in the PVME part of this elastomer. More data is needed to determine the equilibrium swelling of Extreme™ ETP-600 in 10 mM boric acid containing impurities. The loading data can be linearized by plotting it as a function of the square of time (Figure 10C) as expected for diffusion through a hydrodynamic boundary layer and it is adequate for predicting loading.[7] However, plotting the natural logarithm of this data (Figure 10D) revealed the loading process does not strictly follow Fick's law of diffusion[8] (i.e. slope in Figure 10D does not equal 0.5) indicating significant chemical interaction between the polymer and solute.
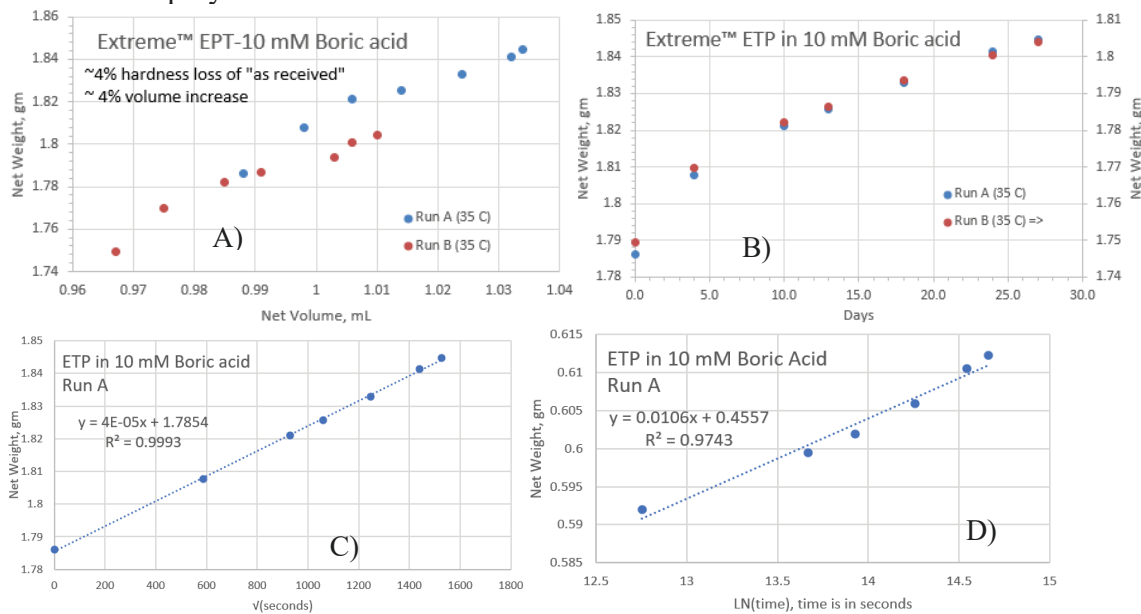
Figure 10. The density (A), kinetics of loading (B), loading as a function of square root of time (C), and as function of the logarithm of time (D) of ETP-600S in 10 mM boric acid

3.2.3 Compatibility in 1 mM Nitric Acid

The mass and volume of Extreme™ ETP-600S in 1 mM nitric acid was still linear with time in the last day of sampling indicating that the sample did not reach equilibrium with 1 mM nitric acid (see Figure 11A and 11B). The 3.5% volume gained after 27 days is less than the 5% gained listed by the vendor for this polymer (Reference 6). Longer-term testing is needed to better evaluate long-term stability. It is surprising that this polymer loads more liquid than Viton™ B, at least based on the data for these specific fluids.
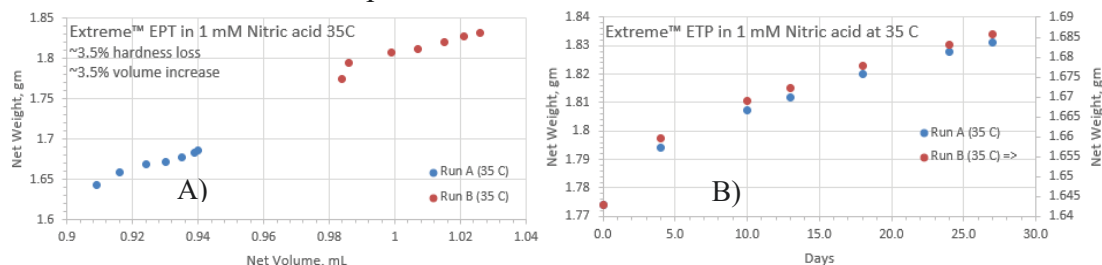
Figure 11. Density and mass gain of Extreme™ ETP-600S in 1mM nitric acid.

3.2.4 Compatibility in Next Generation Solvent (NGS) Solvent

At 35 °C, Extreme™ ETP-600S appeared to gain more mass than at ambient temperature (see Figure 11A and 11B). However, the volume gained (1%) is less than the 5% volume gained in methanol (see Reference 6). This is consistent with polymer chains vibrating and making more space available for a thermodynamically favored solute to enter and sit in the Viton® Extreme™ ETP-600 space. Diffusion rates are also likely greater at higher temperatures.
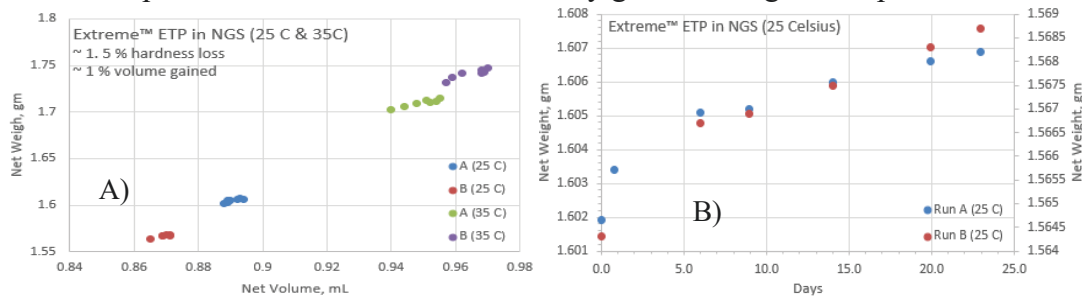
Figure 12. Density and mass gained by Extreme™ ETP-600S in NGS solvent

3.2.5 Compatibility in Caustic-Side Solvent Extraction (CSSX)

Just like in NGS, Viton™ Extreme™ ETP-600S similarly absorbed CSSX but to a lesser extent (see Figure 13A and 13B). The volume gained after 27 days (0.6 %) is negligible compare to the 5 % volume gained in methanol for this polymer (see Reference 6). The rate of loading stays the same throughout the testing indicating, the material did not reach steady state conditions.
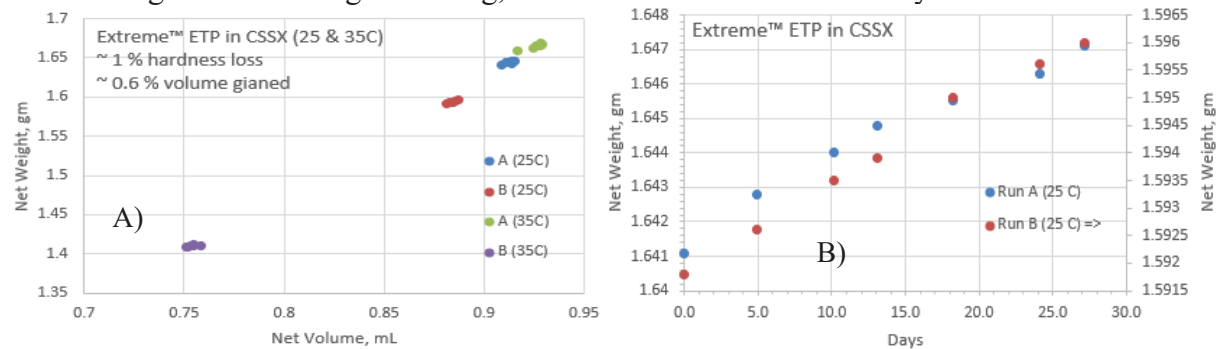
Figure 13. Density and mass gained by Extreme™ ETP-600S in CSSX solvent.

FTIR examination of the surface of the Viton™ Extreme™ ETP-600S pieces that contacted the solutions is shown in Figure 14. Examination of the FTIR revealed no remarkable changes other than changes in polymer chain orientation driven by contacting these liquids. But no chemical reaction or degradation is observed.
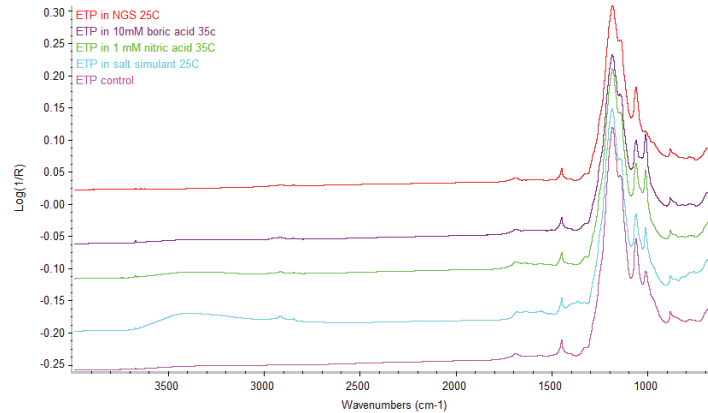
Figure 14. FTIR of the surface of Extreme™ ETP-600S in NGS, CSSX, Average Salt Simulant, 1 mM nitric acid and 10 mM boric acid

3.3 Garlock® Blue Gard® 3700

3.3.1 Compatibility in 1 mM nitric acid

The initial jump in the data shown in Figure 15A and 15B is due to the swelling of the paper coating the vendor placed on one side of the gasket. The gasket was stable in this solution despite a 7% volume swelling and 3% hardness loss. This gasket is a compressed fiber, non-asbestos type of gasket, much different in construction and composition than the Viton B and Extreme ETP-600S Fluoroelastomers and ePTFE fluoropolymer.
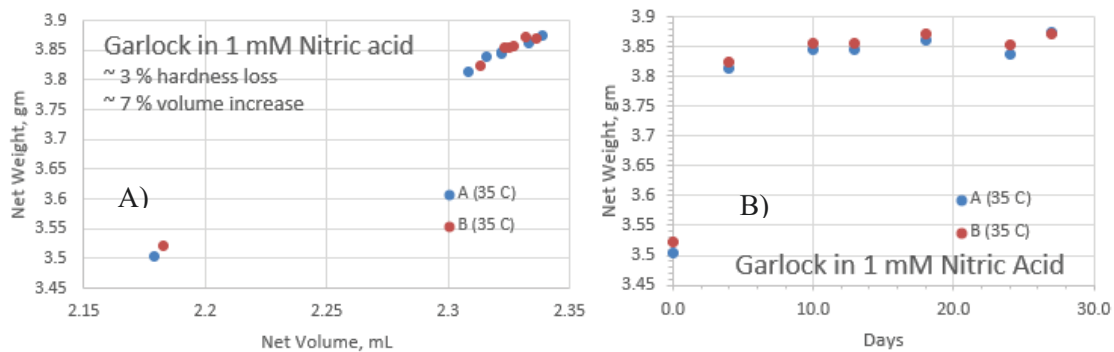
Figure 15. Density and weight gained versus time by Garlock® Blue-Gard® 3700 in 1 mM nitric acid

3.3.2 Compatibility in 10 mM boric acid

The only noticeable change is the gap between the second data point and the first data point in Figure 16A and 16B that is due to the paper coating the vendor applied to one side of the gasket. After the paper coating saturated, there was not further, or relatively minor, physical changes (about 7% swelling).
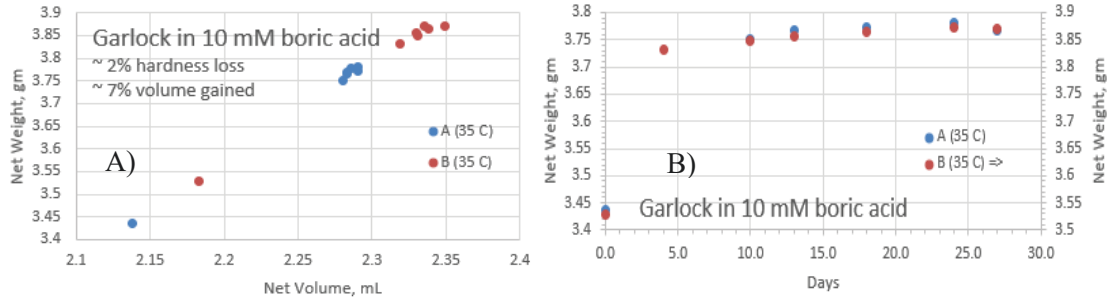
Figure 16. Density and weight gained with time by Garlock® Blue-Gard® 3700 in 10 mM boric acid

3.3.3 Compatibility in Average Salt Simulant

No remarkable changes are observed other than the large gap between the second and the first data point (Figure 17A and 17B) due to the paper coating placed on one side of the gasket by the vendor. However, the Garlock® weight continue to trend up by the end of the test (Figure 17B).
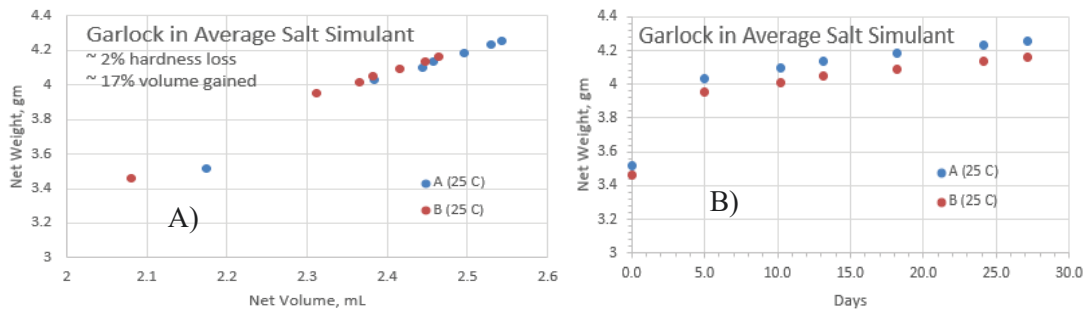
Figure 17. Density and weight gained with time by Garlock® Blue-Gard® 3700 in Average Salt Simulant

3.3.4 Compatibility in NGS Solvent

In addition to the expected saturation of the paper coating on one side of the Garlock® gasket, the gasket slowly gained mass and volume (see Figure 18A and 18B). A noticeable drop in hardness (6.5%) was recorded at the end of this test (the gasket had a softer surface) as shown in Figure 18C. The density gradually dropped from 1.62 to 1.48 g/mL in 27 days.
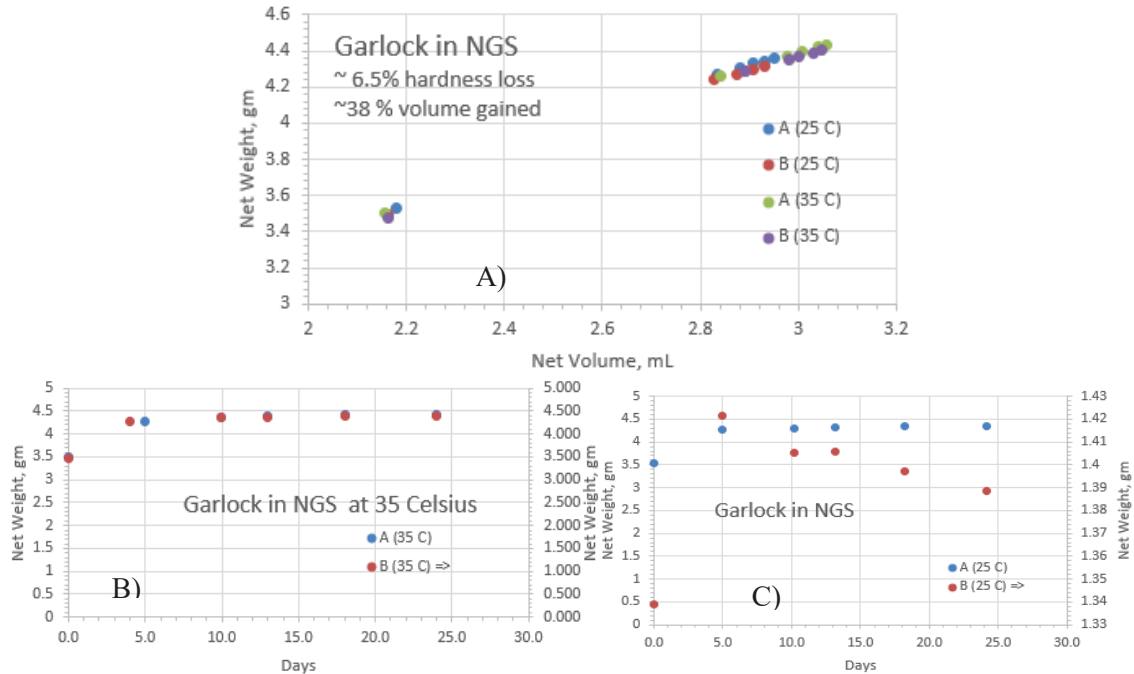
Figure 18. The density and weight gained by Garlock® Blue-Gard® 3700 in NGS solvent

3.3.5 Compatibility in CSSX Solvent

As seen before with the NGS solvent, the Garlock® gasket, after its paper coating swelled, did not increase in mass or volume with time but the density dropped gradually from 1.61 to 1.49 g/mL indicating swelling has occurred in this polymer.
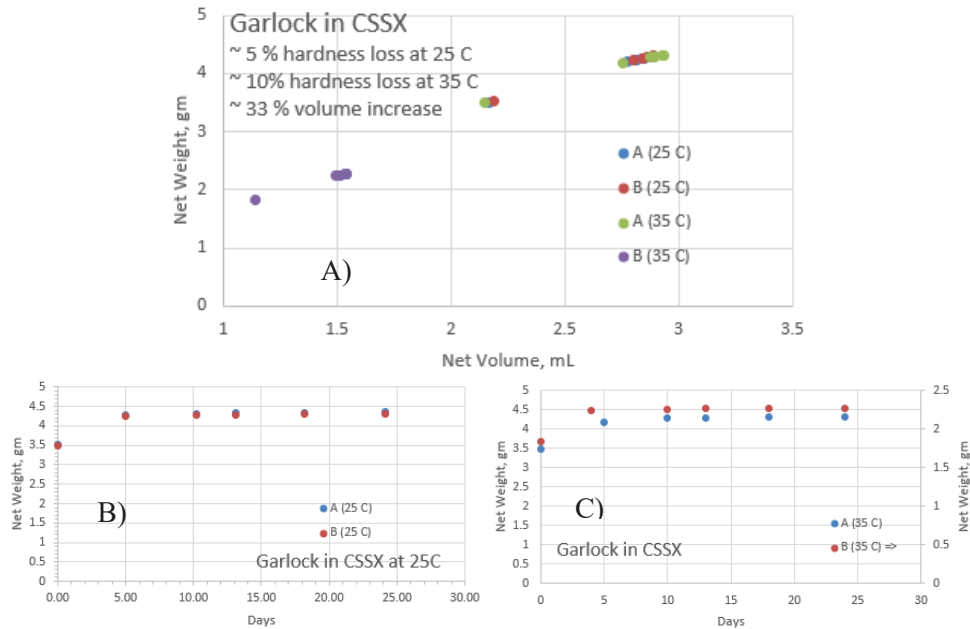
Figure 19. Density and mass gained by Garlock® Blue-Gard® 3700 in CSSX

An FTIR surface analysis of the Garlock® gaskets that contacted the liquids showed that an initial surface species containing either nitrates or borates (possibly sorption from the air or intentionally

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put on by the vendor) was not present when Garlock® was in contact with Average Salt Simulant, NGS, and CSSX solvent exposing the underneath aramid fibers and the EPDM rubber (see Figure 20). This exposure did not have any serious effect on the surface chemistry of Garlock® with these liquids.
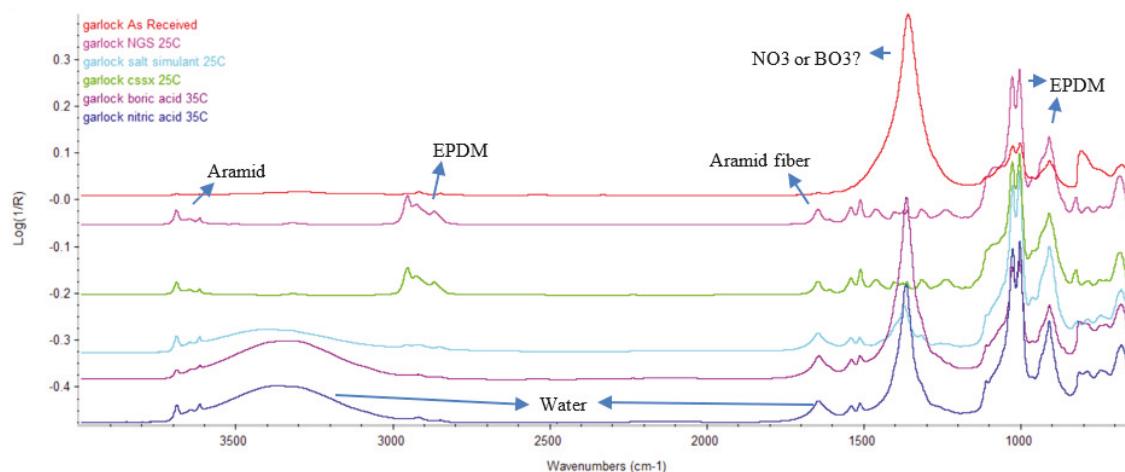
Figure 20. The FTIR spectra of the surface of Garlock® Blue-Gard® 3700 after contact in Average salt simulant, 1 mM nitric acid, 10 mM boric acid, NGS and CSSX solvent

3.4 Expanded PTFE Compatibility

The data obtained from the contact between the expanded Teflon and the liquids are shown in Appendix A (Figures 24 to 29). The data clearly shows that Teflon is chemically compatible with the liquids tested here. A noticeable initial pick up in weight and volume was observed in NGS and CSSX solvent and it is mostly due to the porous space at the surface of the expanded Teflon. Once the surface was loaded, all physical data reached steady state and a quick FTIR analysis of the aged Teflon showed no evidence of chemical reaction or incompatibility. As already known, the low resistance of Teflon PTFE to gamma irradiation generally prevents or limits it use in radiation service. Recall that under gamma irradiation undergoes chain scission (depolymerization with amorphous region degrading faster than the crystalline regions) and giving off F_2 gas (and HF in the presence of water).[6]

3.5 Hydrogen Nuclear Magnetic Resonance (HNMR) Analysis of the aged Aqueous solutions

The H-NMR (solvent suppression) of the Average Salt Simulant that contacted the four gaskets studied in this work is shown in Figure 21. The poor signal to noise is due to the low number scans taken as time was expiring in the program. An organic impurity can phase separate from the aqueous solution by residing at the aqueous-air interface or partition into the gas phase or is absorbed by the walls of the vial or by the polymeric material. A control aqueous sample with no polymeric material in it was used to determine if the absence of an impurity in the samples containing polymeric material is due to adsorption of the polymer. Review of Figure 21 suggest that the solution did not chemically change to a large extent, but the ETP-600S, ePTFE, and Viton™ B compounds did leach a low molecular weight and soluble organic possibly containing silicon grease (at -0.03 ppm). In addition, the formate anion (peak at 8.25 ppm) is lower intensity in the solution that contacted ePTFE sample. Assuming, that the only interaction between the

polymers and the solutions is adsorption and leaching (but not chemical reactions), ePTFE appears to absorb formate (a very dipole molecule) which is contrariant to the common theory of "like dissolves like". It does appear that ETP absorbed more organic impurities (such as dibutyl phosphate and *sec*butyl phenol) than the other gaskets based on the lower peak heights around 0.5 to 1.5 ppm region relative to the control Average Salt Solution spectrum. The effect is possibly due to the ethylene monomer in the ETP polymer. Garlock® Blue-Gard® 3700 appeared to have leached methyl acetate (3.4 and 2.0 ppm). No 2-butanone or amine are seen in these liquids.
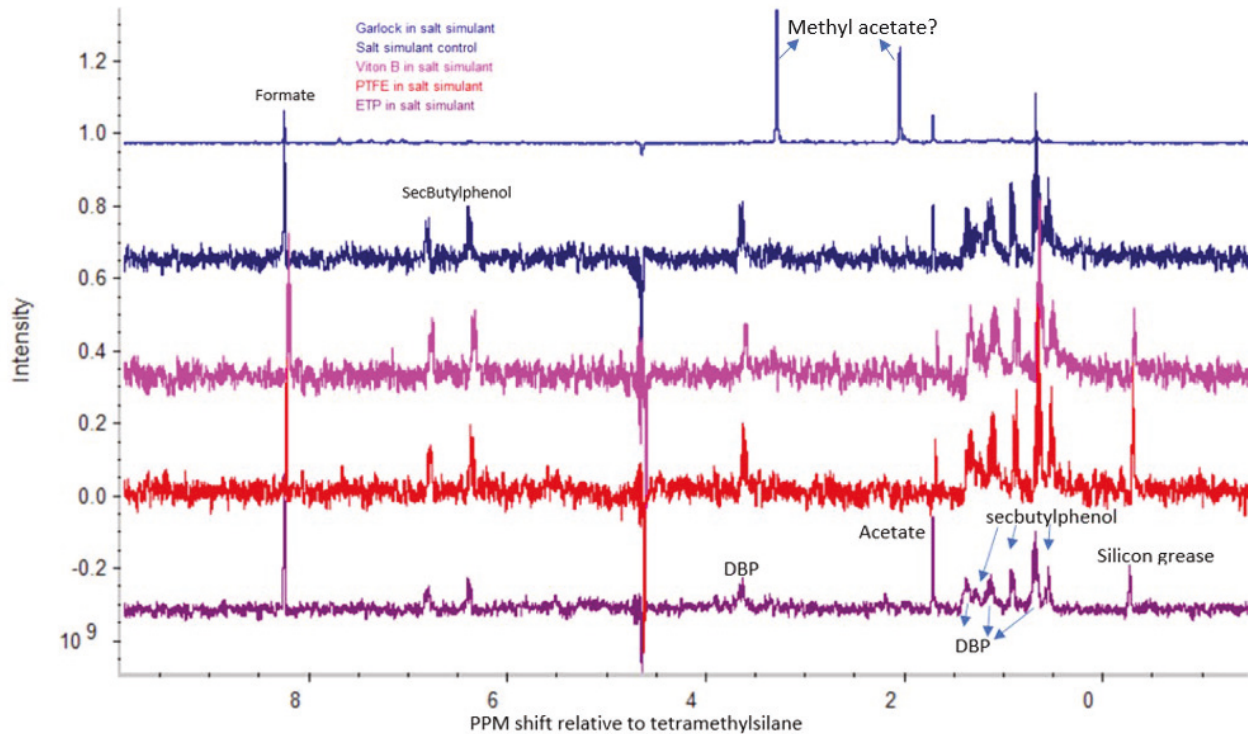
Figure 21. H-NMR (solvent suppression) of the Average salt simulant that contacted the gasket materials

On the other hand, the organic impurities had a more profound impact in the 1 mM nitric acid as shown in Figure 22. The figure clearly shows that ETP, ePTFE, and Viton B adsorbed the formate while the ETP and Viton B leached unsaturated organics, possibly highly substituted rings (multiple peaks at 7 ppm possibly due to phthalates or dihydrobenzoic acid) and the same time they leached a compound like 2-butanone (peaks at 2.5, 2.1, and 0.9). No ethyl acetate or amine are seen in these liquids. Garlock® leached Acetone.
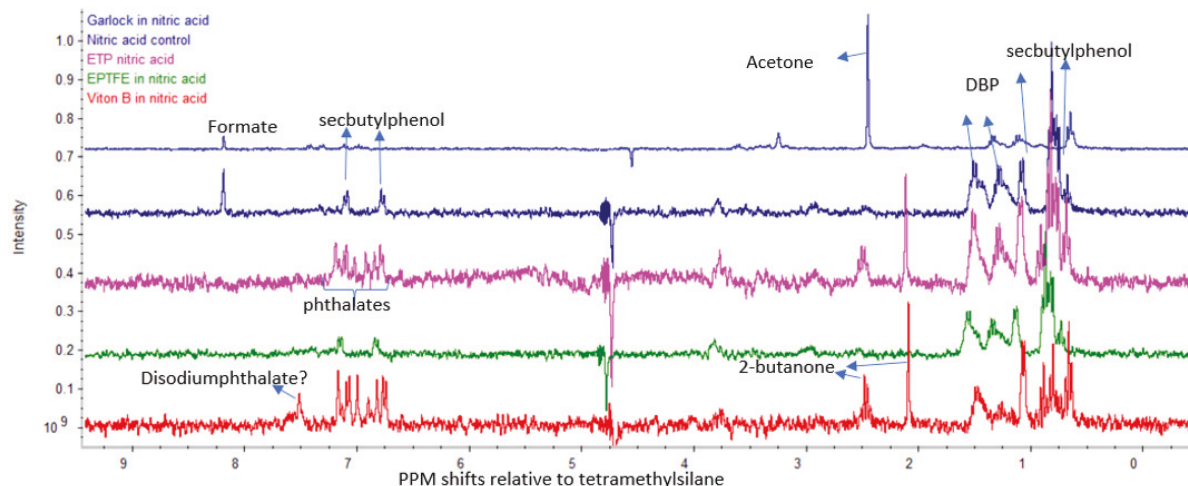
Figure 22. HNMR (solvent suppression) of 1 mM nitric acid that contacted the gasket materials

Finally, ETP and Viton B appeared to have adsorbed the formate in 10 mM boric acid and they also leached or not absorbed 2-butanone which is not observed in the 1 mM nitric acid solution (possibly due to evaporation during storage before sampling). There is also the presence of unsaturated groups in the solution (6.88 and 7.17 ppm) possibly due to modified *sec*butylphenol leached by the ePTFE and ETP. No ethyl acetate or amines are seen in these solutions (possibly due to adsorption). Garlock® appeared to have leached acetone.

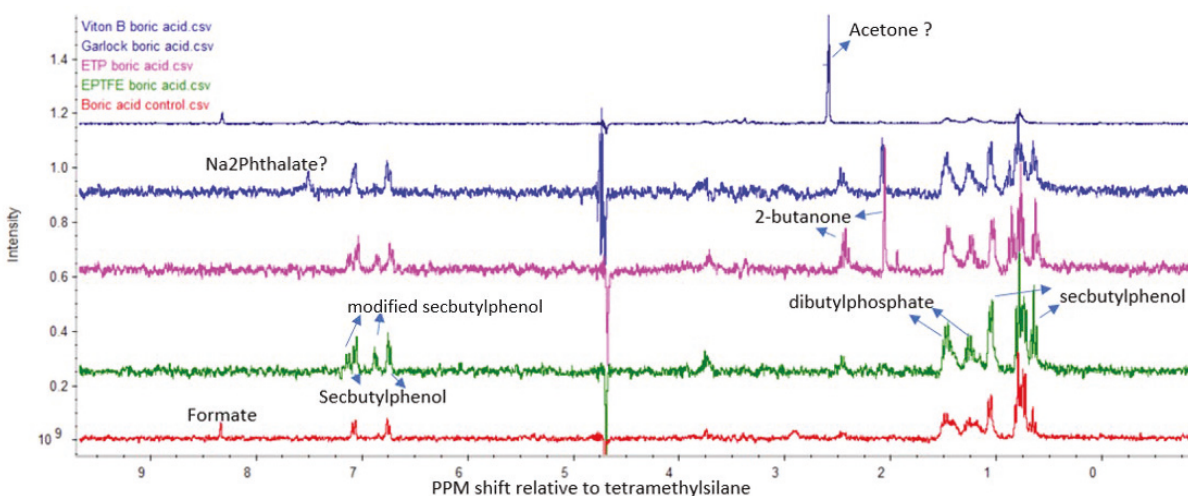**Figure 23. H-NMR (solvent suppression) of 10 mM boric acid that contacted the gasket materials**

3.6 Polymer Swelling in the Process Solutions

For a better discrimination of which polymeric material changes the least in the process solutions, Tables 3-1 to 3-7 list the percent volume change (swelling) of each polymeric material at a given solution. In Average salt simulant (see Table 3-1), Garlock® swelled the most while among the Fluoroelastomers like Viton™ B changed the least, as explained before, due to the talc overlayer. Once the talc overlayer is removed, the data indicates Viton™ B will swell. ETP-600S modestly swelled (5%) at a level slightly higher than reported in the literature (Reference 6). As expected, ePTFE volume change was due to liquid filling its pore spaces.

Table 3-1. Material volume percent change in Average salt simulant

Days	Viton™ B	ETP-600S	Garlock®	ePTFE
0	0.0	0.0	0.0	0.0
5	-0.2	1.0	10.3	1.5
11	-0.2	1.9	13.0	0.9
13	0.1	2.5	13.7	-0.1
19	0.1	3.4	15.4	0.2
24	0.0	4.1	17.0	0.2
27	0.1	4.7	17.7	0.3

In 10 mM boric acid (see Table 3-2), Viton™ B swelled at a lower rate than ETP-600S due to the talc overlayer on Viton™ B. Garlock® swelled the most and ePTFE was inert to dilute boric acid.

Table 3-2. Material volume percent change in 10 mM boric acid

Days	Viton™ B	ETP-600S	Garlock®	ePTFE
0	0.0	0.0	0.0	0.0
5	0.2	0.9	6.4	0.1
11	0.3	1.8	6.8	0.1
13	0.4	2.6	6.8	-0.1
19	0.8	3.7	7.1	-0.2
24	0.3	4.2	7.4	-0.3
27	0.6	4.6	6.9	-0.2

In 1 mM nitric acid, Viton™ B swelled slower than ETP-600S consistently with the results observed in the other process solutions (see Table 3-3). Consistent with the other process solutions, Garlock® swelled the most and ePTFE was inert to dilute nitric acid.

Table 3-3. Material volume percent change in 1 mM nitric acid

Days	Viton™ B	ETP-600S	Garlock®	ePTFE
0	0.0	0.0	0.0	0.0
5	0.4	0.5	5.9	0.1
11	0.5	1.6	6.5	0.5
13	0.5	2.3	6.6	0.3
19	1.2	3.0	7.0	-0.2
24	0.9	3.5	6.4	-0.1
27	1.2	3.8	7.1	-0.3

In the case of the NGS solvent, Viton™ B swelled slower than ETP-600S at 25 ºC (see Table 3-4) and 35 ºC (see Table 3-5) again due to the talc overlayer on Viton™ B. Significant volume change was observed in Garlock® possibly due to its rubbery EPDM component interacting with Isopar™ L and the Modifier (CS-7SB) components of NGS. Similarly, a noticeable swelling was observed in ePTFE. This is possibly due to the NGS liquid filling the empty pores in ePTFE.   Similarly swelling rate behavior was observed when the polymeric materials contacted CSSX solvent with more swelling observed at 35 ºC (see Table 3-6) than at 25 ºC (see Table 3-7).

Overall, based on the rate and extent of swelling in SWPF process solutions, the polymeric materials can be ranked as follows:

Viton™ B (due to talc overlayer) < ePTFE (due to porosity) < ETP-600S < Garlock®.

Table 3-4. Material volume percent change in NGS at 25 ºC

Days	Viton™ B	ETP-600S	Garlock®	ePTFE
0	0.0	0.0	0.0	0.0
5	0.1	0.3	30.4	0.3
11	-0.1	0.3	32.6	0.3
13	0.1	0.5	33.5	0.5
19	0.2	0.6	34.4	0.6
24	0.1	0.6	35.4	0.6
27	0.2	0.6	36.1	0.6

Table 3-5. Material volume percent change in NGS at 35 ºC

Days	Viton™ B	ETP-600S	Garlock®	ePTFE
0	0.0	0.0	0.0	0.0
5	-0.1	0.3	32.7	0.3
11	0.3	0.7	37.9	0.7
13	0.4	1.2	39.1	1.2
19	0.6	1.4	40.6	1.4
24	0.6	1.2	41.4	1.2
27	0.7	1.5	41.8	1.5

Table 3-6. Material volume percent change in CSSX at 25 ºC

Days	Viton™ B	ETP-600S	Garlock®	ePTFE
0	0.0	0.0	0.0	0.0
5	0.2	0.3	28.0	0.3
11	-0.5	0.2	29.6	0.2
13	0.1	0.3	30.3	0.3
19	0.1	0.6	31.4	0.6
24	0.1	0.7	31.8	0.7
27	0.1	0.7	32.4	0.7

Table 3-7. Material volume percent change in CSSX at 35 ºC

Days	Viton™ B	ETP-600S	Garlock®	ePTFE
0	0.0	0.0	0.0	0.0
5	-0.2	0.4	29.6	0.4
11	-0.2	0.7	33.3	0.7
13	0.1	0.7	34.5	0.7
19	0.3	1.1	35.7	1.1
24	0.4	0.8	36.0	0.8
27	0.3	1.1	36.5	1.1

4.0 Conclusions

Five different SWPF process solutions were contacted with four different polymeric materials that include two Fluoroelastomers (Viton™ B and Viton™ Extreme™ ETP-600S), Garlock® Blue-Gard® 3700 (a composite of rubber and polymeric fibers), and Expanded PTFE. Physical and chemical measurements were conducted on both the polymeric material and the process liquids as a function of contact time.

Analysis of the measurements revealed that Viton™ B with a talc film swelled slower than the other polymeric materials but the rate trended upwards when the talc film was no longer visible on Viton™ B (expect higher swelling with contact time). The noticeable swelling of Viton™ Extreme™ ETP-600S which was higher in the process aqueous solution than in the organic solvents (NGS and CSSX) was within the range published in the literature (< 5% a limit reported as insignificant in Reference 6) but the swelling rate was nonzero at the end of test (higher swelling is expected at longer contact time). The contradictory results (ETP-600S swelling more than Viton™ B) observed in this work is an artifact due to the talc overlayer on Viton™ B.

The composite material Garlock® Blue-Gard® 3700 swelled the faster and the most in this test and it leached residual solvent such as acetone to the process liquids as revealed by FT-HNMR.

The chemically inert Expanded PTFE swelled (volume and weight gain) due to its porous structure and the swelling was much higher at 35 ºC in the NGS and CSSX solvents.

There was no evidence of chemical reactions between the polymeric materials and process liquids used in this work.

5.0 Recommendations and Path Forward

Based on the data obtained to date, SRNL recommends that the compatibility test continue for an additional two months to verify the uptake in Viton™ B in absence of the talc layer. If Viton™ B is to be used in applications with incompatible liquid media, it is recommended that it is deployed with a talc layer since it appears to be protective. However, reliance on surface treatments for chemical resistance of gaskets is tenuous and not the primary intent of the treatment (anti-friction). Therefore, the talc overlayer is not a good nor reliable engineering design option. The next step is to thermodynamically model the interactions[9] seen in this study (and adjust parameters to fit reality) although, kinetic barriers not accounted for can defeat any thermodynamic prediction. Future work should include Viton™ B without a talc overlayer.

The expanded PTFE material was primarily tested as a baseline for comparison, but it showed overall more chemical resistance as expected. This material was initially recommended for the coalescer application by the vendor, but it is acknowledged that the ePTFE material has lower resistance to ionizing radiation. Use of this material for improved chemical resistance may be feasible within a periodic replacement period, if such an approach is viable. Periodic gasket replacement is obviously not preferred from an operational perspective.

Additional tests can be performed with Kalrez® (the material arrived on September 21, 2021) if additional options are needed. Based on the vendor's literature, Kalrez® has superior chemical resistance relative to Viton™ B and Viton™ ETP-600S as it contains the ethylene group (-CH$_2$-CH$_2$-) in its chemical microstructure. Another possible material for future analysis is the Viton® GF-600S. This material would be potentially cheaper and more available than Kalrez® FFKM and generally provides better chemical resistance than Viton™ A or B types. Finally, Grafoil® Flexible Graphite should also be considered although it might be susceptible to nitric acid solutions.

6.0 References

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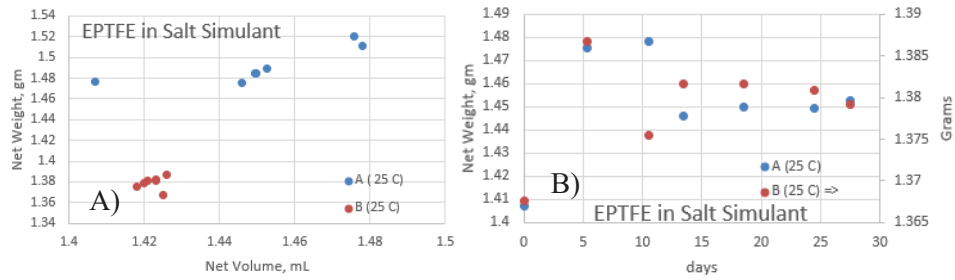
Appendix A. Expanded PTFE

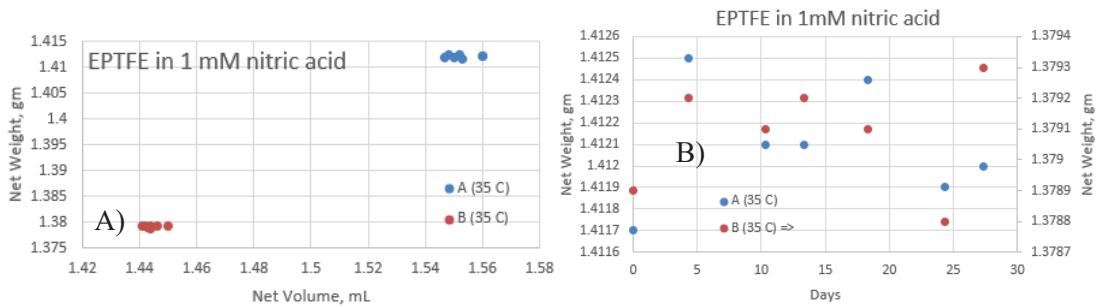**Figure 24. Density (A) and rate of mass gain (B) of ePTFE in Average Salt Simulant**

Figure 25. Density (A) and rate of mass gain (B) of ePTFE in 1 mM Nitric Acid
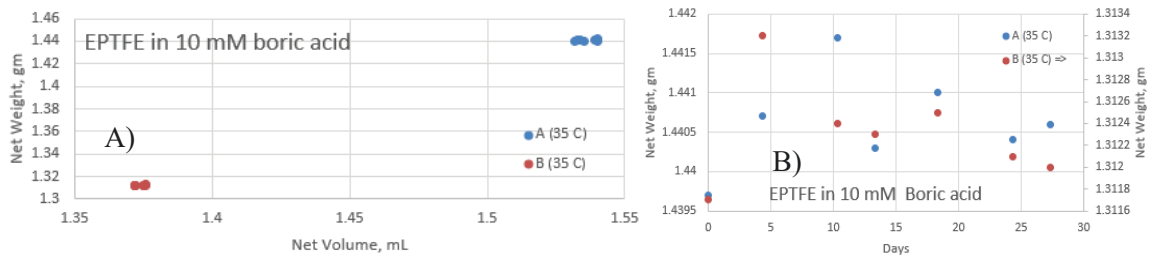

Figure 26. Density (A) and rate of mass gain (B) of ePTFE in 10 mM boric acid
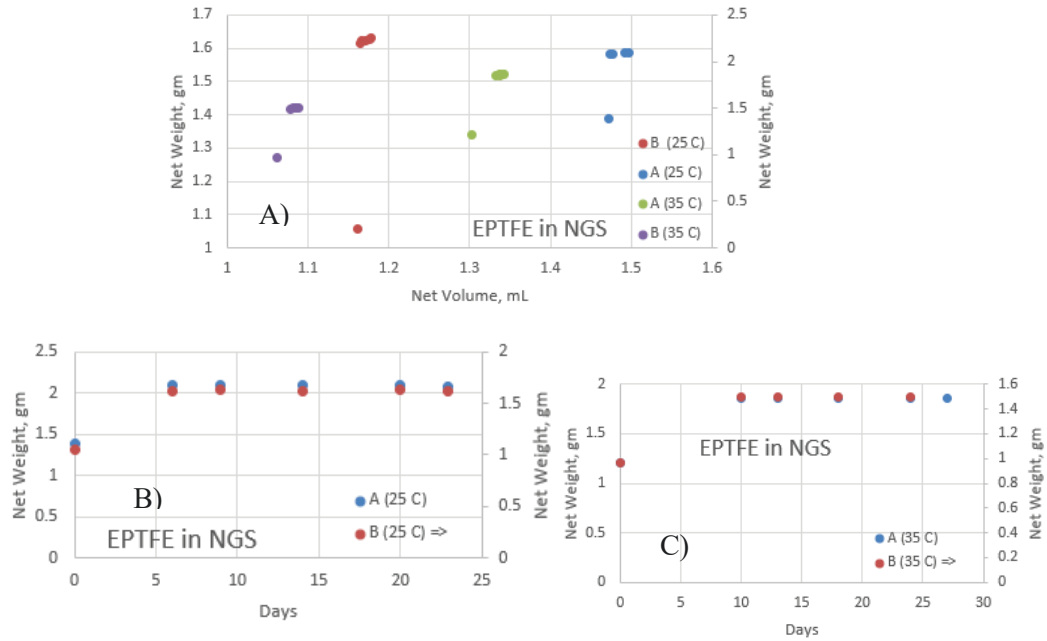
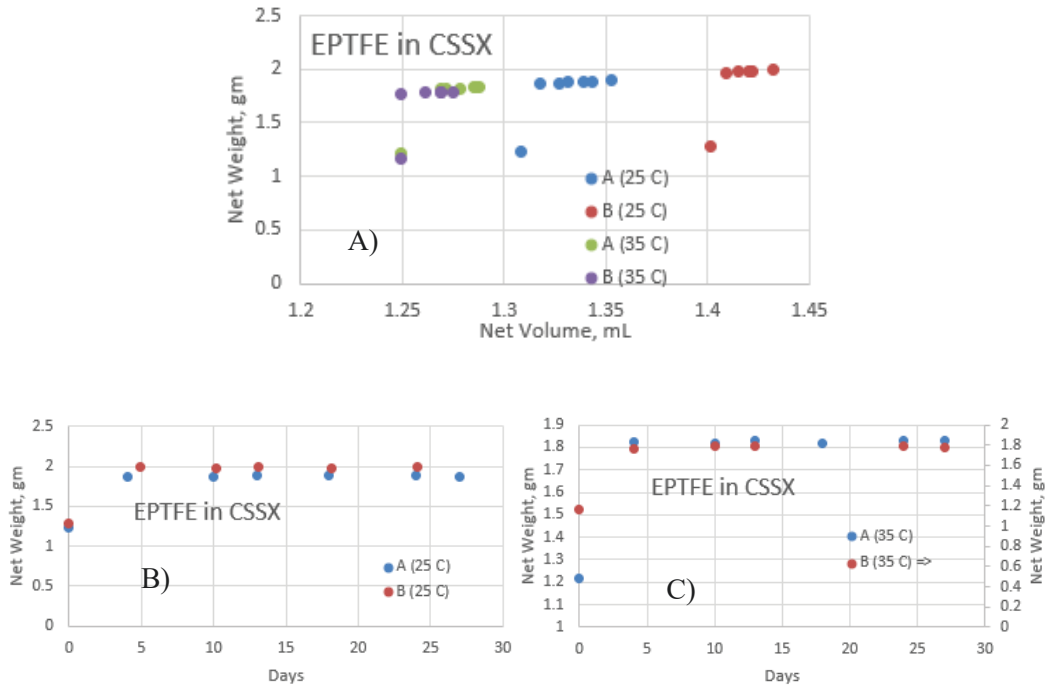**Figure 27. Density (A) and mass gain (B, C) of ePTFE in NGS solvent**

Figure 28. Density (A) and mass gain (B, C) of ePTFE in CSSX solvent
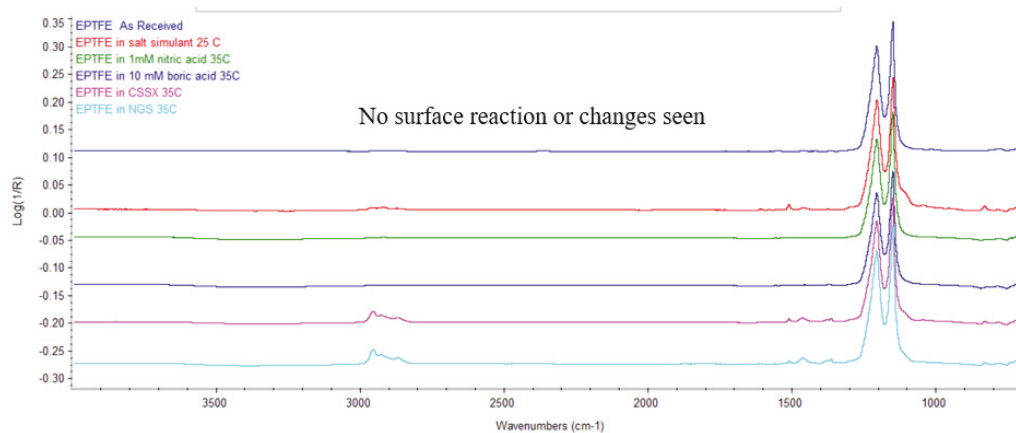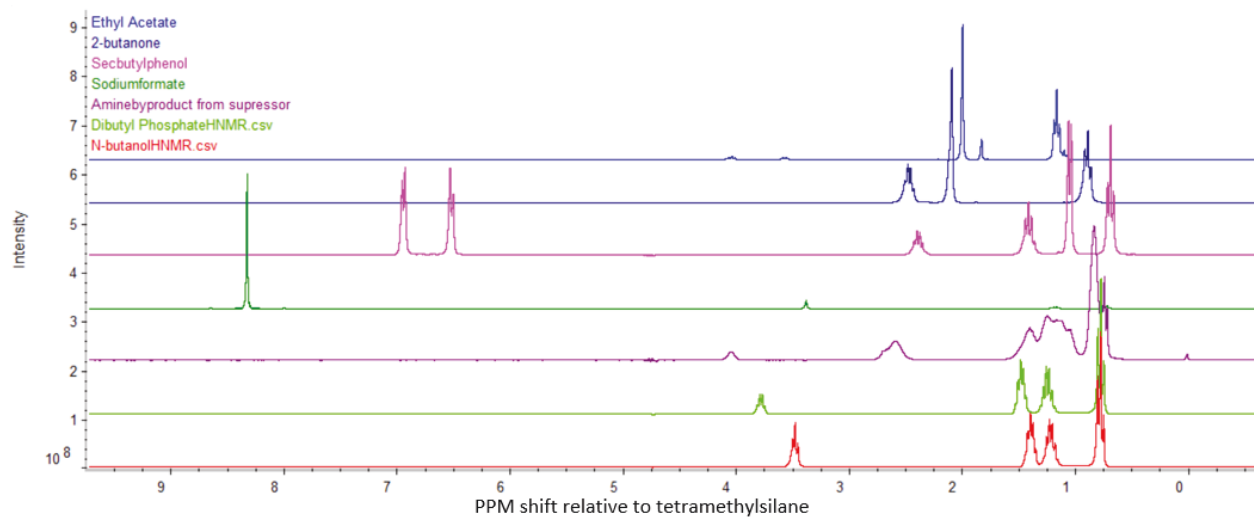
Figure 29. FTIR of the surface of ePTFE after contacting 1 mM nitric acid, 10 mM boric acid, Average Salt Simulant, NGS and CSSX solvent

Appendix B H-NMR of the Impurities Added in this Work

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